Biomass Conv. Bioref.
DOI 10.1007/s13399-015-0158-6

ORIGINAL ARTICLE

Genotype contribution to the chemical composition of banana rachis and implications for thermo/biochemical conversion

Mathias Florian Tiappi Deumaga · Thomas Happi Emaga · Raphael Tchokouassom · Caroline Vanderghem · Mario Aguedo · Sébastien Gillet · Nicolas Jacquet · S. Danthine · Deleu Magali · Aurore Richel

Received: 24 June 2014 / Revised: 25 January 2015 / Accepted: 27 January 2015

Abstract Chemical composition of banana rachis from three varieties (Grande naine, Pelipita, and CRBP969) was analyzed, and the genotype contribution to composition variability was investigated. Wet chemistry and instrumental analysis procedures (X-ray diffraction, ^{31}P NMR spectroscopy, and thermogravimetry) were used. Some significant differences were found among the three genotypes: GN-AAA genotype was found to be significantly the highest in ash fraction (30.16 %) and the lowest in acid insoluble lignin (6.58 %) at 95 % confidence level. It showed also the highest content in potassium (43.5 % in ash). Implication of compositional differences on valorization efficiency by biochemical or thermochemical pathways was investigated. For this purpose, correlation coefficients between compositional characteristics and yields in volatile compounds from pyrolysis and glucose yields from enzymatic saccharification were analyzed. Ash content was revealed to be the main drawback parameter for volatile yields from pyrolysis (r=−0.93), while for glucose yields during saccharification were limited mainly by the content in guaiacyl units of the lignin fraction (r=−0.98). However, a strong and positive correlation was established between the volatiles yield and the acid insoluble lignin content (r=0.98) Thus, according to these observations and based on their compositional significant differences, GN-AAA was the better candidate for bioconversion pathway while PPT-ABB and CRBP969-AAAB samples were shown to be better candidates for thermochemical conversion pathway. This work gives important preliminary information for considering banana rachis as an interesting feedstock candidate for biorefinery.

Keyword Banana rachis · Genotype · Biorefinery · Saccharification · Thermogravimetry

M. F. T. Deumaga (✉) · T. H. Emaga · C. Vanderghem · M. Aguedo · S. Gillet · D. Magali · A. Richel
Department of Chemistry and Bio-industries, ULg-Gembloux Agro-Bio Tech, Passage des Déportés N°2, 5030 Gembloux, Belgium
e-mail: mftiappi@student.ulg.ac.be

T. H. Emaga · R. Tchokouassom
African Research Centre on Bananas and Plantains (CARBAP), P.O. Box 832, Douala, Cameroon

N. Jacquet · S. Danthine
Department of Food Science and Formulation, ULg-Gembloux Agro-Bio Tech, Passage des Déportés N°2, 5030 Gembloux, Belgium

1 Introduction

The limits on the use of fossil resources for a sustainable economy and concerns on their environmental impact have caused a grown interest in research of alternative solutions. Thus, many lignocellulosic biomass feedstock including woody biomass, dedicated energy crops, and agricultural wastes have been investigated as reliable, non-edible, and eco-friendly resources. However, because of their different origins, challenges are focusing at investigating key factors (growth conditions, variety, tissue origin) that influence their chemical composition and structural features, as they might significantly affect their thermochemical or biochemical conversion ability [1–5]. Banana is a herbaceous tropical plant from the *Musaceae* family [6]. Edible varieties arose from hybridization of *Musa acuminata* (AA) and *Musa balbisiana* (BB) [7]. In spite of their great economic importance, mainly for some developing countries where they are intensively grown, banana and plantain generate large quantities of organic residues as leaves, pseudo-stems, corms, and rachis, representing about 80 % of the total fresh plant weight. For

Published online: 13 February 2015

the year 2012 in Cameroon, where banana is among the main agricultural resources, production reached 1.4 million tons [8] resulting in about 90,000 tons of dry residues. A few studies have been carried out for chemical composition analysis of different morphological parts of plants from the "Dwarf Cavendish" variety [9–12]. However to date, genotype contribution to their chemical composition has not yet been explored. Banana rachis (Fig. 1a, b) has been shown to have some interesting features as a lignocellulosic feedstock for biorefinery [12, 13]. In this study, the genotype contribution to chemical composition of banana rachis samples from three varieties of different genotypes was investigated. We also analyzed the implications of the chemical composition on thermochemical and biochemical conversion routes. This work will provide useful information for the setting of specific biorefinery processes for banana rachis residues.

2 Material and methods

2.1 Plant materials

Rachises from mature banana bunches were collected at the Banana Genetic Collection in *CARBAP*[1] research center, in Cameroon. Selected varieties for this study are described in Table 1. The banana plants from which they were harvested were grown in the same location with same environmental conditions and handling operations.

2.2 Chemical composition analysis

The collected samples were chopped, oven-dried at 60 °C until constant weight. They were further milled with a hammer miller (Model MFC CZ13, CULLATI) and sieved to particle sizes less than 1 mm before analysis. Ash content (total and residual) was determined by the TAPPI T211 om-02 method described by Ehrman et al. [14]. Soluble minerals from ash analysis were performed by the Analytical Chemistry Laboratory of Gembloux-Agro Bio-Tech (University of Liège, Belgium). Nitrogen content was determined by the standard Kjeldahl procedure (AOAC 984.13). A nitrogen-to-protein conversion factor (4.4) was used. NDF, ADF, and ADL were determined by the Goering and Van Soest procedure [15]. Extractives (water and ethanol) were quantified by the soxhlet method [16, 17]. For the determination of neutral sugars, a modified version of the classical Saeman's hydrolysis procedure [18] was used. It consisted in 1 h prehydrolysis at 30 °C with 72 % H_2SO_4, followed by dilution to 4 % H_2SO_4 and 1 h final hydrolysis at 121 °C (autoclave). Monosaccharides released where further quantified by gas chromatography equipped with a flame ionization detector (GC-FID, Hewlett-Packard Co.; column: HP1-methylsiloxane 30-m length/0.32-mm diameter/0.25-μm film thickness, Scientific Glass Engineering, S.G.E. Pty. Ltd., Melbourne, Australia). Acid insoluble lignin and acid soluble lignin (ASL) were determined by the method described by Sluiter et al. [19]. ASL which represents the low molecular weight lignin fraction was determined by UV absorption spectroscopy at 205-nm wavelength (λ=110 L mol^{-1} cm^{-1}).

[1] Centre Africain de Recherches sur Bananiers & Plantains

2.3 ^{31}P nuclear magnetic resonance (NMR) lignin analysis

A comparative ^{31}P NMR analysis of the lignin extracted by formic/acetic acid solvent extraction procedure [20] was carried out. The procedure described by Ragauskas et al. [21] allowed the quantification of hydroxyl groups from the aliphatic regions and from aromatic H, G, and S lignin units (*p*-hydroxyphenyl, guaiacyl, and syringyl). Spectra were acquired after derivatization with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphos-pholane (TMDP) in the presence of pyridine, with cyclohexanol as internal standard. $CDCl_3$ was used for the magnetic field lock, DMF as lignin solvent, and $Cr(acac)_3$ as relaxation agent. Exactly about 20 mg of each sample was analyzed with a Varian Unity 600-MHz instrument at 298 °K (1600 scans, 90° pulse, 1.049-s acquisition time, and 25-s relaxation delay). Internal standard peak was set at 144.8 ppm.

2.4 Thermo-gravimetric analysis (TGA)

TGA analyses were performed with a TGA/DSC1 instrument from Mettler-Toledo (Greifensee, Switzerland). The pyrolysis was conducted under a nitrogen flow of 20 ml/min. The experiments were conducted in triplicate using 70-μl alumina pans. The sample mass was precisely weighed around 10 mg, and the thermograms were obtained over a temperature range comprised between 40 and 600 °C at three different heating rates (10, 25, and 100 °C/min) as described by Hodgson et al. [1]. DTG proximate composition in terms of moisture (40–105 °C), volatiles (105–550 °C), and char and ashes (550–900 °C) was made. Kinetic analysis was performed according to the following Friedman's differential and iso-conversional equation [22], where consideration of reaction order is not necessary:

$$\ln\left(\frac{\mathrm{dx}}{\mathrm{dt}}\right) = \ln[Af(x)] - \frac{\mathrm{Ea}}{RT} \quad \text{with} \quad x = \frac{W}{\mathrm{Wi}} \tag{1}$$

where wi=initial weight, w=weight loss at time t, A=pre-exponential factor, Ea=activation energy, T=absolute temperature (°K) and R=gas constant. Activation energies (Ea) over the volatile's pyrolysis regions were calculated by plotting ln(dx/dt) against 1/*T* (°K) [3]. Well-reliable activation energies

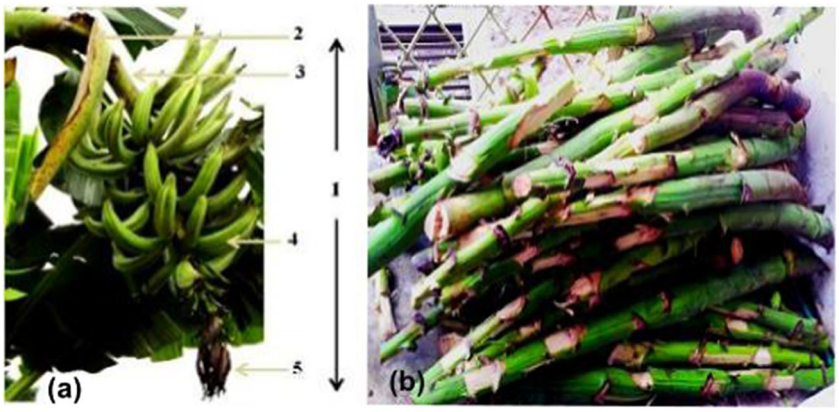

Fig. 1 **a** Morphology of banana inflorescence (picture by Tiappi F., 2011) *1* banana bunch, *2* floral peduncle, *3* rachis, *4* banana fingers, *5* male bud. **b** Bunch stalks released as waste from banana harvesting stations

were obtained as average of values with the multiple heating rate procedure.

2.5 X-ray diffraction analysis

The cristallinity index (CrI) of the three extractives-free samples was determined isothermally by X-ray diffraction using a D8 ADVANCE diffractometer (Bruker, Rheinstetten, Germany) (Cu Kα radiation source, λ=1.54178 Å at 40 kV and 30 mA) equipped with a Vantec (Bruker, Rheinstetten, Germany) detector, and a TTK450 low-temperature chamber and TCU 110 temperature control unit (Anton Paar, Graz, Austria) connected to a circulating water bath (Julabo, Sellbach, Germany). D-spacings were determined in the $1°<2\theta<13°$ and $15°<2\theta<27°$ ranges using the Bragg law. Only results from the latter range were considered since no particular observation was made in the first one. Diffrac Plus Evaluation 14.0.0.0 program (Bruker, Rheinstetten, Germany) was used to normalize and process the results. Crystallinity index was calculated from XRD data by the peak-height method described by Kurt et al. [23].

2.6 Water retention capacity

Water retention capacity was determined by a modified version of the method described by Femenia et al. [24]. About 0.25 g of samples was suspended in 10 ml of distilled water (instead of phosphate buffer) for 24 h at ambient temperature. The tubes were further centrifuged at 1500 g for 5 min (Beckman Coulter Allegra X-15R Centrifuge, Suarlée, Belgium). Liquid supernatant was carefully removed and humidity of remaining wet pellet was measured by oven drying at 105 °C. Water retention ratio was determined relatively to the dry weight mass of the samples.

2.7 Enzymatic digestibility

The enzymatic hydrolysis procedure used was described by Jacquet et al. [25]. An enzymatic mixture of cellulase from *Trichoderma reesei* (Celluclast 1.5 L, activity 30 FPU/ml) and cellobiase from *Aspergillus niger* (Novozym 188, activity 295 CBU/ml) both purchased from Sigma-Aldrich (St. Louis, MO, USA) was used. Enzyme loadings were 3 FPU/g and 7.37 CBU/g for cellulase and cellobiase, respectively. About exactly 200 mg of samples was suspended in citric acid buffer solution (0.05 M, pH 4.8) at a concentration of 4 g/l in 50-ml screw-capped Duran bottles. Samples were incubated in a water bath at 55 °C and continuously stirred at 400 rpm for 48 h. Samples conversion to glucose was measured by the DNS colorimetric method at 540 nm UV absorption wavelength.

2.8 Statistical analysis

The Tukey honestly significant difference (HSD) test, also known as a *t* test, was used for the compositional comparison of the three genotypes. Statistical differences were measured at 95 % confidence level ($P<0.05$). Statistical analyses were performed with Statgraphics Plus version 5.1 software.

Table 1 Botanical accession of the studied varieties

Variety	Analysis code	Species/genetic group	Subgroup	Origin	Fruit type
Grande naine	GN	AAA	Cavendish	Asia (China/Vietnam)	Dessert
Pelipita	PPT	ABB	Pelipita	Philippines	Cooking banana
CRBP969	CRBP969	AAAB	(hybrid plantain)	CARBAP (Cameroon)	Pseudo-plantain

3 Results and discussion

3.1 Variation in cell wall composition

Global chemical composition of the three rachis samples is given in Table 2. Results are expressed as chemical components in the lignocellulosic fraction (cellulose, hemicelluloses, and lignin) and non-lignocellulosic fractions (ash, proteins, along with solvent extractable compounds).

Concerning non-lignocellulosic components, GN-AAA was shown to have significantly the highest total ash content (30.16 %) while PPT-ABB and CRBP969-AAAB had similar ash contents (29.05 and 29.04 %, respectively). No statistical difference was observed for extractive and protein contents.

The ash contents observed for the three genotypes were higher than values reported by Cordeiro et al. [12] for banana rachis (26.8 % ash in rachis from "Dwarf Cavendish"). That difference with our samples might be related to specific mineral inputs during the growth phase. Also, ash contents in the three samples were far above ash content from other herbaceous feedstock: 1.7–2.8 % in Miscanthus [1, 26, 27] and 3.86 % in corn stover [28]. Elhassan et al. [29] reported that because of their fast growth rate, bananas absorb and accumulate in their cell wall important amounts of minerals (free and structural minerals). Oliveira, et al. (2007) also reported that the high ash content in the rachis can be probably due to their function in nutrient transport from the corm to the fruits.

Table 3 shows the results for ash elemental composition in potassium, silicon, phosphor, calcium, magnesium, and sodium for the three samples. Values obtained were generally higher than observations made by Cordeiro et al. [12] in banana rachis (K: 28 %, P: 1.7 %; Si: 1.2 %, Mg: 0.3 %). GN genotype was shown to be significantly high in potassium (43.5 %) but the lowest in silicon (2.96 %) and phosphorus (0.82 %) contents. CRBP969-AAAB sample was significantly the highest in silicon (4.08 %) and the lowest in magnesium (0.27 %) content. The sodium content was negligible for all the samples analyzed. Unquantified fraction of ashes stands for insoluble crystallized minerals. Potassium was shown to be the major mineral in ash for all the samples. In fact, potassium plays key role in enzyme systems activation, nutrient absorption, and also plant resistance system to diseases [30]. Potassium contents in the three samples analyzed were significantly different regarding their genotype. GN-AAA sample had the highest content (43.50 %), followed by PPT-ABB (42.14 %) and CRBP969-AAAB (40.86 %). Those results were in accordance with Sathiamoorthy and Jeyabaskaran [30] who established that the requirement of potassium is higher for triploids than tetraploids genotypes.

Contents in extractive compounds (Table 2) were shown to be similar in all the samples analyzed at 95 % confidence level. Values for water and ethanol extractives were similar with observations from Cordeiro et al. [12] in banana rachis residue (14.7 and 1.4 %, respectively). High content in water extractives is commonly observed in herbaceous and softwood biomass feedstock [31] and sometimes can be a serious

Table 2 Global chemical composition (%*w*/*w* of dry matter) for the three banana varieties

	GN-AAA	PPT-ABB	CRBP969-AAAB
Non-lignocellulosic fraction			
Total ash	30.16±0.10a	29.05±0.13b	29.04±0.20b
Water extractives[a]	13.01±1.90a	13.53±0.07a	14.61±1.53a
Ethanol extractives[a]	0.63±0.20a	0.61±0.11a	0.86±0.02a
Proteins	4.88±0.05a	4.92±0.09a	4.70±0.00a
Lignocellulosic fraction			
Cellulose	36.28±0.45a	37.38±0.64a	37.11±1.37a
Hemicelluloses	17.78±2.97a	20.70±2.22a	19.51±3.76a
Acid insoluble lignins (AIL)[b]	6.58±0.03a	7.45±0.04b	7.31±0.02c
Acid soluble lignins (ASL)	2.06±0.01a	2.03±0.10a	2.17±0.02a
H/L[c] ratio	10.98±1.29a	7.42±0.25a	8.80±1.30a
Relative composition (%) of the neutral sugars in extractives free material			
Glucose	71.86±0.97a	70.02±0.51a	63.86±0.31b
Xylose	15.76±0.63a	16.00±0.29a	16.14±0.04a
Arabinose	6.84±0.17a	6.62±0.08a	7.38±0.27a
Mannose	2.53±0.06a	2.19±0.02b	1.67±0.02c
Galactose	2.52±0.07a	2.64±0.02ab	2.84±0.05b
Rhamnose	0.48±0.04a	0.63±0.00b	0.65±0.00b
Physical properties of crude samples			
Water retention capacity (%*w*/*w*)	12.87±0.48a	12.00±0.26a	11.66±0.41a
Crystallinity index (%)	55.73±0.72a	52.71±0.34a	55.59±1.18a

Values with the same letter are not significantly different at 95 % according to the Tukey's HSD test

[a] Values corrected from extracted ash and proteins

[b] Corrected for residual ash

[c] Holocelluloses (cellulose and hemicelluloses)/lignin (acid insoluble lignin)

Table 3 Soluble mineral content (%*w*/*w* in ash) for the three banana samples

	GN-AAA	PPT-ABB	CRBP969-AAAB
Potassium	43.50±0.75a	42.14±0.08ab	40.86±0.11b
Silicon	2.96±0.33a	3.04±0.22a	4.08±0.14b
Phosphorus	0.82±0.01a	1.16±0.00b	1.16±0.01b
Calcium	0.7±0.02a	0.65±0.02a	0.76±0.01a
Magnesium	0.55±0.01a	0.52±0.00a	0.27±0.01b

Values with the same letter are not significantly different at 95 % according to Tukey's HSD test

Table 4 Global composition of water extractives (%*w*/*w* water extractives)

	GN-AAA	PPT-ABB	CRBP969-AAAB
Ash	63.57±0.01a	61.55±0.08b	61.32±0.27c
Proteins	6.17±0.05a	6.77±0.11b	5.68±0.10c
Free sugars	1.25±0.94a	3.52±0.22b	0.19±0.06a
Others[a]	28.96±1.11a	28.00±0.21a	32.82±0.23b

Values with the same letter are not significantly different at 95 % according to the Tukey's HSD test

[a] Stands for uronic acids and tannins

drawback for biochemical conversions. Table 4 gives the composition of water-extracted compounds. Minerals from crude ash are shown to be the main extracted components. This observation shows that most of the minerals are non-structural thus easily extractable during pretreatment operations. PPT genotype extract had significantly the highest free sugar content (3.52 %), while CRBP969 was the lowest (0.19 %) among the three samples. Cordeiro et al. [12] reported that free sugar content in water extracts was related to starch hydrolyzed during water extraction.

Concerning the lignocellulosic fractions, cellulose and hemicellulose contents were statistically similar for the three genotypes analyzed at 95 % confidence level. Values of cellulose ranged from 36.28 to 37.38 % and were higher than the observation by Cordeiro et al. [12] for "Dwarf Cavendish" rachis. However, cellulose contents were in the range of Miscanthus [27] and wheat straw [32]. Hemicellulose contents ranged from 17.78 % in GN-AAA to 20.70 % PPT-ABB. Medic et al. [28] observed similar content of hemicelluloses in corn stover (17.6 %) Glucose was the most abundant monosaccharide in all the samples, followed by xylose and arabinose (Table 2). CRBP969-AAAB was significantly the lowest in glucose-relative content (63.86 %), while GN-AAA and PPT-ABB were similar (71.86 and 70.02 %). For the lignin content, the acid insoluble lignin fractions in the three samples were statistically different: PPT-ABB was shown to be the highest (7.45 %), followed by CRBP969-AAAB (7.31 %) while GN-AAA was the lowest (6.58 %). This observation implies that the content in acid insoluble lignin increased with abundance of the balbisiana gene over acuminata. Table 5 shows results of quantification of *p*-hydroxyphenyl, guaiacyl, and syringyl units from extracted lignin by ^{31}P NMR. The H/G/S ratio for GN was 40/31/29 which represented the highest ratio in hydroxyphenyl and the lowest in guaiacyl units, while CRBP969 (25/45/30) had the lowest ratio of *p*-hydroxyphenyl units and the highest in guaiacyl. Syringyl unit proportion was similar for GN, CRBP969, and PPT (37/33/30) Table 6.

Table 6 Degradation compounds from thermogravimetric analysis (%*w*/*w*) and mean activation energy Ea (Kj mol^{-1})

	Moisture	Volatiles	Char	Ea[a]
GN-AAA	2.89±0.33a	65.23±0.39a	28.38±0.06a	61.55±6.92a
PPT-AAB	2.55±0.00a	68.16±0.46b	24.63±0.94b	58.91±5.77a
CRBP969-AAAB	2.33±0.01a	67.14±0.11b	26.50±0.05ab	65.65±6.22a

[a] Calculated for the volatile's degradation phase

3.2 Implications for thermochemical biorefinery

Ash and lignin contents are among the principal factors influencing most thermochemical conversion reactions [33, 34]. Table 7 gives correlation coefficients (*r*) established between yields in volatile compounds from pyrolysis and principal samples characteristics. Quantification of degradation compounds from thermogravimetric pyrolysis is given in Table 6. Total ash content in crude samples from the three genotypes was negatively correlated ($r=-0.93$) with the yield in volatiles, and this was consistent with observations made by Donnison et al. [1] and Monti et al. [33]. As illustration in Table 6, the significantly higher ash content observed for the GN genotype resulted in a lower yield in volatiles (65.23 %) and the highest yield in char (28.38 %). High ash content in biomass is also known a serious drawback since it may lead to the fouling and corrosion of equipments during thermochemical conversion [35, 36, 33]. Concerning the influence of the lignin fraction, a positive correlation ($r=0.98$) was found between the AIL content and the volatiles yield. This observation was consistent with the negative correlation ($r=-0.99$) found between the H/L ratio and the volatiles yield. Yang et al. [37] analyzed pyrolysis of cellulose, hemicelluloses, and lignin. They found that lignin pyrolysis was overall exothermic and resulted in higher volatiles yield, mainly H_2 and CH_4. He associated this behavior with the abundance of aromatic ring structures and methoxyl groups. This hypothesis is

Table 5 Phenolic, aliphatic, and carboxylic hydroxyl group contents in lignins (mmol g$^{-1)}$ analyzed by quantitative ^{31}P NMR analysis and H/G/S distribution

	Aliphatic OH	H	G	S	Total carboxylic	Total phenolics	H/G/S ratio
GN-AAA	0.318	0.029	0.022	0.021	0.084	0.077	40/31/29
PPT-AAB	0.311	0.022	0.020	0.018	0.074	0.065	37/33/30
CRBP969-AAAB	0.314	0.018	0.033	0.022	0.070	0.080	25/45/30

Table 7 Correlation coefficient (r) between activation energy, volatiles yield, and saccharification yield and different sample characteristics

	Volatiles yield	Saccharification yield
Total ash (crude sample)	−0.93	0.74
Acid insoluble lignin (AIL)	0.98	−0.63
Holocelluloses/AIL (H/L ratio)	−0.99	0.42
p-Hydroxyphenyl unit content (H)	−0.35	0.99
Guaiacyl unit content (G)	0.29	−0.98
Syringyl unit content (S)	0.94	−0.74
Cristallinity index (CrI)	−0.79	−0.17
Water retention potential	−0.45	0.89

confirmed by the positive correlation (r=0.94) we found between the Syringyl unit contents and the volatiles yield as it is characteristic of methyl-rich lignin residues.

3.3 Implication for biochemical biorefinery

Recalcitrance of biomass to bioconversion is known to be notably affected by particle size, lignin content, crystallinity index, and water retention values, as they influence enzyme accessibility to biomass cell wall [2, 38, 39]. Results from enzymatic hydrolysis to glucose of the three samples are presented in Fig. 2 and results from water retention capacity and crystallinity index determination are given in Table 2. GN exhibited the highest conversion percentage to glucose after 48 h (23.85 %), followed by PPT and CRBP969 with 21.54 and 16.56 %, respectively. Moreover, it is well established that guaiacyl-rich lignin fractions have a more branched structure, a higher degree of polymerization and are more condensed, thus leading to greater resistance during enzymatic hydrolysis [40, 41]. This was consistent with our results as we found a strong and negative correlation (r=−0.99) between conversion yields and guaiacyl unit contents of lignin samples. Also, water retention capacity (Table 2) was found to be correlated positively (r=0.89) with enzymatic digestibility of the samples.

Considering all these observation and from a relative appraisal, GN-AAA sample was shown to be the best potential candidate for bioconversion because of its low lignin content in guaiacyl units, its greater water retention capacity, and larger H/L ratio. On the other hand, PPT-ABB and CRBP969-AAAB were relatively the best candidates for thermochemical conversions mainly because of their lower H/L ratio and the abundance of syringylic units in their lignin fractions.

4 Conclusion

The genotype contribution to chemical composition of banana rachis residues was investigated. A strong influence on chemical composition variability was established thus conditioning their valorization through thermochemical pathway (yields in volatiles) and also for bioconversion pathway (yields in glucose). The GN-AAA genotype was found to be significantly the highest ash content (30.16 %) and the lowest in AIL content (6.58 %) at 95 % confidence interval. Its ash fraction was also shown to be the richest in potassium (43.5 %). A negative correlation (r=−0.93) was established between the ash content and the yield in volatile compounds produced during thermogravimetric pyrolysis. During enzymatic bioconversion assay, GN-AAA sample exhibited the highest conversion rate to glucose (23.85 %) attributed to the lowest content in guaiacyl units of its lignin fraction and its greater water retention capacity. Thus GN-AAA was the better feedstock for bioconversion pathway. The PPT-ABB sample was significantly the

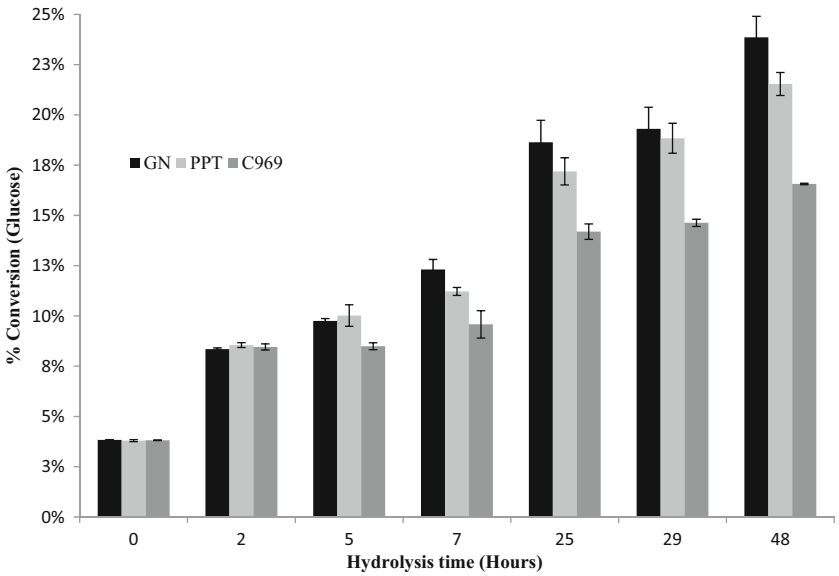

Fig. 2 Enzymatic conversion yields (48 h) of the three samples (extractives-free)

highest in AIL (7.45 %) and exhibited the highest yield in volatile compounds during thermogravimetric analysis. Strong positive correlations were established between the volatiles yield and the AIL content (r=0.98). CRBP969-AAAB exhibited the lowest enzymatic conversion rate to glucose (16.56 %) attributed to the higher content in guaiacyl units of its lignin fraction. Thus PPT-ABB and CRBP969-AAAB samples were better candidates for thermochemical conversion pathway.

Acknowledgments Financial support and scholarship for these studies (Project: Valorization of banana residues and contribution to local sustainable development) were provided by the Commission Universitaire pour le Développement (CUD) from Belgium. The authors are also grateful to the laboratory of post harvest technology, CARBAP-Cameroon and also to the research staff from the Industrial Chemistry and Biology laboratory and Analytical Chemistry Laboratory (GxABTech, ULg, Belgium).

Magali DELEU thanks the "Fond National de la Recherche Scientifique" from Belgium for her position as Research Associate.

References

1. Donnison IS, Hodgson EM, Nowakowski DJ, Shield I, Riche A, Bridgwater AV, Clifton-Brown JC (2011) Variation in Miscanthus chemical composition and implications for conversion by pyrolysis and thermo-chemical bio-refining for fuels and chemicals. Bioresour Technol 102(3):3411–3418. doi:10.1016/j.biortech.2010.10.017
2. Sharma-Shivappa RR, Xu J, Zhang X, Eubanks MW (2012) Gamagrass varieties as potential feedstock for fermentable sugar production. Bioresour Technol 116:540–544. doi:10.1016/j.biortech.2012.04.050
3. Fantozzi F, Slopiecka K, Bartocci P (2011) Thermogravimetric analysis and kinetic study of poplar wood pyrolysis. Paper presented at the Third International Conference on Applied Energy, Perugia, Italy, 16–18 May
4. Alexopoulou E, Sharma N, Papatheohari Y, Christou M, Piscioneri I, Panoutsou C, Pignatelli V (2008) Biomass yields for upland and lowland switchgrass varieties grown in the Mediterranean region. Biomass Bioenergy 32(10):926–933. doi:10.1016/j.biombioe.2008.01.015
5. García A, González Alriols M, Labidi J (2014) Evaluation of different lignocellulosic raw materials as potential alternative feedstocks in biorefinery processes. Ind Crop Prod 53:102–110. doi:10.1016/j.indcrop.2013.12.019
6. Lassois L, Busogoro JP, Jijakli H (2009) La banane : de son origine à sa commercialisation. Biotechnol Agron Soc Environ 13(4):575–586
7. Mohapatra D, Sabyasachi M, Namrata S (2010) Banana and its by-product utilization: an overview. J Sci Ind Res 69:323–329
8. FAOSTAT (2012) Bananas production in Cameroon. FAO. Accessed 12 August 2012
9. Belgacem MN, Cordeiro N, Torres IC, Moura JCVP (2004) Chemical composition and pulping of banana pseudo-stems. Ind Crop Prod 19(2):147–154. doi:10.1016/j.indcrop.2003.09.001
10. Happi ET, Andrianaivo RH, Wathelet B, Tchango JT, Paquot M (2007) Effects of the stage of maturation and varieties on the chemical composition of banana and plantain peels. Food Chem 103(2):590–600. doi:10.1016/j.foodchem.2006.09.006
11. Li K, Shiyu F, Zhan H, Zhan Y, Lucia LA (2010) Analysis of the chemical composition and morphological structure of banana pseudo-stem. Bioresources 5(2):576–585
12. Cordeiro N, Oliveira L, Evtuguin DV, Torres IC, Silvestre AJD (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 Crop Prod 26(2):163–172. doi:10.1016/j.indcrop.2007.03.002
13. Cordeiro N, Oliveira L, Evtuguin D, Silvestre AJD (2009) Structural characterization of stalk lignin from banana plant. Ind Crop Prod 29(1):86–95. doi:10.1016/j.indcrop.2008.04.012
14. Ehrman T (1994) Standard method for ash in biomass. Laboratory analytical procedure. National renewable energy laboratory
15. Goering HK, Van Soest PJ (1970) Forage Fiber Analyses (Apparatus, Reagents, Procedures, and some Applications). Agriculture Handbook N° 379
16. Ehrman T (1994) Standard method for the determination of extractives in biomass. Laboratory analytical procedure. National renewable energy laboratory_Ethanol project
17. Sluiter JB, Sluiter AD (2011) Summative mass closure. Laboratory analytical procedure_Review and integration. National renewable energy laboratory
18. Saeman JF, Bubl JL, Harris EE (1945) Quantitative saccharification of wood and cellulose. Ind Eng Chem 17:35–37
19. Sluiter JB, Ruiz RO, Scarlata CJ, Sluiter AD, Templeton DW (2010) Compositional analysis of lignocellulosic feedstocks. 1. Review and description of methods. J Agric Food Chem. doi:10.1021/jf1008023
20. Vanderghem C, Richel A, Jacquet N, Blecker C, Paquot M (2011) Impact of formic/acetic acid and ammonia pre-treatments on chemical structure and physico-chemical properties of Miscanthus x giganteus lignins. Polym Degrad Stab 96(10):1761–1770. doi:10.1016/j.polymdegradstab.2011.07.022
21. Ragauskas AJ, Pu Y, Cao S (2011) Application of quantitative 31P NMR in biomass lignin and biofuel precursors characterization. Energy Environ Sci 4(9):3154. doi:10.1039/c1ee01201k
22. Cardwell RD, Luner P (1976) Thermogravimetric analysis of pulps (part 2): kinetics for dynamic thermogravimetric analysis. Wood Sci Technol 10:16
23. Kurt SC, Terinte N, Roger I (2011) Overview on native cellulose and microcrystalline cellulose I structure studied by X-ray diffraction (WAXD): comparison between measurement techniques. Lenzinger Ber 89:118–131
24. Femenia A, Lefebvre AC, Thebaudin JY, Robertson JA, Bourgeois CM (1997) Physical and sensory properties of model foods supplemented with Cauliflower Fiber. J Food Sci 62(4):635–639
25. Jacquet N, Vanderghem C, Danthine S, Quievy N, Blecker C, Devaux J, Paquot M (2012) Influence of steam explosion on physicochemical properties and hydrolysis rate of pure cellulose fibers. Bioresour Technol 121:221–227. doi:10.1016/j.biortech.2012.06.073
26. Sun R, Tomkinson J (2002) Comparative study of lignins isolated by alkali and ultrasound-assisted alkali extractions from wheat straw. Ultrason Sonochem 9:85–93
27. de Vrije T, de Haas GG, Tan GB, Keijsers ERP, Claassen PAM (2002) Pretreatment of miscanthus for hydrogen production by *Thermotogaa elfi*. Int J Hydrog Energy 27:1381–1390
28. Medic D, Darr M, Shah A, Rahn S (2012) The effects of particle size, different corn Stover components, and gas residence time on torrefaction of corn stover. Energies 5(12):1199–1214. doi:10.3390/en5041199
29. Elhassan MAA, Asim FAS, Elsir A, Eldin MS Response of Dwarf Cavendish Banana to Potassium Sulfate in Sennar Area. In: Proceedings the 39th and 40th meetings of the national crop husbandry committe, Wad Medani (Sudan), 2006. (ARC), Wad Medani (Sudan), pp 157–165
30. Sathiamoorthy S, Jeyabaskaran KJ (2001) Potassium management of banana. Paper presented at the IPI PRII K in nutrient management for sustainable crop production in India, New Delhi, India

31. Shackford L (2003) A comparison of pulping and bleaching of kraft sofwood and Eucalyptus pulps. Paper presented at the 36th International Pulp and Paper Congress and Exhibition, Sao Paulo, Brazil
32. Sun Y, Cheng J (2002) Hydrolysis of lignocellulosic materials for ethanol production: a review. Bioresour Technol 83:1–11
33. Monti A, Di Virgilio N, Venturi G (2008) Mineral composition and ash content of six major energy crops. Biomass Bioenergy 32(3): 216–223. doi:10.1016/j.biombioe.2007.09.012
34. Suzuki T, Nakajima H, N-o I, Oda H, Miyake T (2011) Effect of mineral matters in biomass on the gasification rate of their chars. Biomass Convers Biorefinery 1(1):17–28. doi:10.1007/s13399-011-0006-2
35. Liu L, Ye XP, Womac AR, Sokhansanj S (2010) Variability of biomass chemical composition and rapid analysis using FT-NIR techniques. Carbohydr Polym 81(4):820–829. doi:10.1016/j.carbpol.2010.03.058
36. Oh H, Annamalai K, Sweeten JM (2011) Effects of ash fouling on heat transfer during combustion of cattle biomass in a small-scale boiler burner facility under unsteady transition conditions. Int J Energy Res 35:1236–1249. doi:10.1002/er.1768
37. Yang H, Yan R, Chen H, Lee DH, Zheng C (2007) Characteristics of hemicellulose, cellulose and lignin pyrolysis. Fuel 86(12–13):1781–1788. doi:10.1016/j.fuel.2006.12.013
38. Garcia-Aparicio M, Parawira W, Van Rensburg E, Diedericks D, Galbe M, Rosslander C, Zacchi G, Gorgens J (2011) Evaluation of steam-treated giant bamboo for production of fermentable sugars. Biotechnol Prog 27(3):641–649. doi:10.1002/btpr.580
39. Heiss-Blanquet S, Zheng D, Lopes Ferreira N, Lapierre C, Baumberger S (2011) Effect of pretreatment and enzymatic hydrolysis of wheat straw on cell wall composition, hydrophobicity and cellulase adsorption. Bioresour Technol 102(10):5938–5946. doi:10.1016/j.biortech.2011.03.011
40. Santos RB, Hart PW, Jameel H, H-m C (2013) Wood based lignin reactions important to the biorefinery and pulp paper industries. Bioresources 8(1):1456–1477
41. del Rio JC, Rencoret J, Gutierrez A, Nieto L, Jimenez-Barbero J, Martinez AT (2011) Structural characterization of guaiacyl-rich lignins in flax (Linum usitatissimum) fibers and shives. J Agric Food Chem 59(20):11088–11099. doi:10.1021/jf201222r