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Multivariate analysis of coconut residues by near infrared spectroscopy

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ABSTRACT

Near infrared (NIR) spectroscopy was used to determine the content of Klason lignin, acid-soluble lignin, total lignin, extractives, ash, acid-insoluble residue, glucose, xylose, rhamnose, galactose, arabinose, mannose and total sugars in coconut residues. The samples were analyzed at several processing stages: wet unground (WU), dried unground (DU) and dried and sieved (DS). Partial least squares models were built, and the models for the analytes exhibited $R^2 > 0.80$, with the exceptions of rhamnose, arabinose, galactose, mannose and ash from all fractions, and the lignin content from the WU fraction, which were predicted poorly ($R^2 < 0.70$). There were some significant differences between the models for the main lignocellulosic components at the various stages of biomass. These results proved that NIR spectroscopy is useful for analysis at biorefineries, and it can be used as a faster and more economical alternative to the standard methods.

1. Introduction

Brazil generates a substantial amount of lignocellulose agricultural waste [1], which includes coconut biomass. Coconut (*Cocos nucifera L.*) is grown in approximately 93 countries [2], with a world production of 60.7 million tons in an area of 11.8 million hectares [3]. Brazil is ranked fourth in the world in coconut production, producing 2.8 million tons of coconuts in an area of 287 thousand hectares [4].

However, coconut production is an important contributor to the nation's pollution problems because 80–85% of the coconut's raw weight is treated as solid waste residue in the form of husks [5], resulting in an annual production of approximately 2.3 million tons of coconut husks in the country.

Coconut husk is the mesocarp, composed of coir fibers [6]. The world production of coir fibers ranges between 5 and 6 million tons per year. However, less than 10% of coir fiber is commercialized [7], and most of the husks are abandoned in nature, wasting natural resources and causing environmental pollution [8].

Coconut husk is attractive because of its high proportions of well-defined polymeric structures of cellulose (35.00–47.00%), hemicellulose (15.00–28.00%) and lignin (16.00–45.00%); its low amounts of ash (2.70–10.00%); and, depending on the coconut variety, its high extractives content, ranging from 3.40% to 30.00% [9–13]. Efforts have been made to enhance the value of this residue as a precursor for biorefinery technologies. As a result, coconut husks have been considered a renewable resource in lignocellulosic biorefining for the production of biofuels [13,14], polymer composites [6,8,15], adsorbents [7] and chemicals [2].

The yields of these processes depend on the chemical composition of the coconut samples [16]. The biomass composition can be determined by traditional methods [17], although they are frequently time-consuming and expensive. Therefore, accurate and robust methods of analysis are of great value, particularly if integrated online in a biorefinery. In this context, NIR spectroscopy is fast, simple to apply, and non-destructive, so it is a suitable alternative to the existing reference methods. However, the applications of NIR spectroscopy are almost entirely dependent on chemometric tools. Partial least squares regression (PLS) can be directly applied to the NIR spectra, resulting in calibration models to predict the properties of interest [18].

Studies using NIR spectroscopy, coupled with chemometric tools, have shown the utility of NIR spectroscopy for the characterization of different biomasses. However, these models were developed for samples that have undergone extensive biomass preparation, including cutting, drying, comminution, sieving and removing extractives. As a result, significant amounts of time and money are spent on these analyses [16].

In this study, NIR spectra and chemometric methods were applied to minimally processed (wet unground (WU) and dried unground (DU)) coconut samples, as well as to dried and sieved

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Table 1
Descriptive statistics for the chemical constituents (%) of 28 samples of coconut husks.

Statistic parameters/constituents[a]	Median value	Minimum value	Maximum value	Mean value	Standard deviation	Coefficient of variation
TL	25.130	17.001	35.807	24.802	4.305	17.305
KL	23.830	16.003	34.504	23.405	4.034	17.204
ASL	1.370	0.702	2.102	1.421	0.407	28.207
AIR	24.178	16.252	34.955	24.002	4.066	17.005
Extrac	20.175	1.404	41.601	20.467	11.451	55.708
Ash	1.070	0.336	3.099	1.404	0.969	68.601
Glu	25.005	17.642	32.406	24.938	3.233	12.964
Xyl	11.220	6.400	16.516	11.464	0.536	4.676
Arab	2.390	1.828	4.302	3.043	0.606	19.702
Gal	1.041	0.591	1.669	1.054	0.581	55.167
Rha	0.293	0.281	0.515	0.389	0.060	15.800
Man	0.505	0.362	2.033	0.752	0.403	53.001
TS	40.614	28.797	50.998	40.825	3.868	9.476

[a] TL: total lignin; KL: Klason lignin; ASL: acid-soluble lignin; AIR: acid-insoluble residue; Extrac: extractives; Glu: glucose; Xyl: xylose; Arab: arabinose; Gal: galactose; Rha: rhamnose; Man: manose; TS: total sugars.

(DS) biomasses, in order to determine their chemical compositions with respect to extractives (Extrac), ash, acid-soluble lignin (ASL), Klason lignin (KL), acid-insoluble residue (AIR), total lignin (TL), glucose (Glu), xylose (Xyl), galactose (Gal), mannose (Man), arabinose (Arab), rhamnose (Rha) and total sugars (TS). The quality of the final models was evaluated by determining the figures of merit.

2. Material and methods

2.1. Samples

Twenty-eight samples of coconut residues were analyzed with respect to the DS fraction, and 26 samples were analyzed with respect to the DU and WU fractions. All of the samples were collected during the period of 2010–2012 in Brazil; most of them originated from the North and Northeast regions, whereas the others came from the Southeast. Approximately 500 g of each biomass was collected during different processing stages (WU and DU). The WU and DU fractions were initially separated and stored in a freezer.

An additional 500 g of each biomass was cut into small pieces (20 mm sieve aperture), dried at 105 °C (until they reached a constant weight), ground using a Romer micro mill (Romer Labs, São Paulo, Brazil) and sieved for 20 min (180–850 μm). This biomass fraction was designated as DS (dried and sieved), and it was the fraction used for the reference analysis.

2.2. Reference analyses of biomasses

The reference analyses were carried out using standard NREL methods [19,20]. The moisture level was determined as the loss of mass after drying at 105 °C in an oven overnight, and the ash content was determined as the residue after the combustion of a sample with known dry-matter content. The muffle furnace Naber therm L-240H1SN was used at a temperature of 575 °C for 4 h.

Each fraction of the sample was then extracted with 95% ethanol using accelerated solvent extraction in a Dionex ASE 200 system (Thermo Fisher Scientific, Waltham, MA, USA), and these extractive-free materials were used for subsequent analyses. The extracted samples were then subjected to a two-stage acid hydrolysis, with 72% sulfuric acid (3 mL) in a water bath in the first step, followed by hydrolysis in an autoclave for 1 h at 120 °C with an acid concentration of 4%.

The ASL extract consisted of low-molecular-weight lignin solubilized in the acidic hydrolysis solution. The ASL concentration was measured in the diluted hydrolyzate (with a low-concentration acid solution) by UV spectroscopy in a Shimadzu UV-1700 spectrometer (Shimadzu, Kyoto, Japan) measuring the absorbance at 240 nm. The AIR, i.e., the dried solid residues (at 105 °C overnight) after the acid hydrolysis, was ashed to determine the acid-insoluble ash (AIA). The difference between the AIR and AIA levels gave the KL content. Finally, the TL content was calculated as the sum of the soluble and insoluble lignin during the acid hydrolysis, ASL and KL, respectively.

Structural carbohydrates were hydrolyzed into monomeric sugars, releasing monosaccharides into the acid hydrolysis solution (arabinose (Arab), galactose (Gal), rhamnose (Rham), glucose (Glu), xylose (Xyl) and mannose (Man)). They were quantified by high-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD) using an ED 40 electrochemical detector, along with a CarboPac-PA 10 column and precolumn. Standard monomeric sugar solutions were hydrolyzed concurrently during the secondary hydrolysis step, and this degradation was used to account for the loss of carbohydrates during the acid hydrolysis.

All of the analyses were performed in duplicate, with a standard deviation between duplicates of less than 1% for all parameters. All of the results were presented as percentages (%).

2.3. Visible–near infrared spectroscopy

A FOSS XDS instrument (FOSS, Hillerød, Denmark), equipped with the associated rapid content analyzer (RCA) module and a diffuse reflectance detector, was utilized to record the near-infrared spectra. The spectra (1100–2500 nm) were obtained in 0.5 nm increments and were generated by averaging 32 successive scans. WU and DU samples were scanned in a large rectangular cell because of their heterogeneous particles and larger particle sizes, and the DS samples were scanned in a small circular cell because of their small particle sizes. Each sample was analyzed in triplicate, and the average spectrum was used for further data treatment. One small circular cell with a ceramic standard as reference material was used over the scanning window to register the blank spectrum.

2.4. Multivariate data analysis

Statistical and multivariate data analyses were conducted using the UNSCRAMBLER 10.3 software package (Camo Software, Oslo, Norway), and one PLS routine from the PLS-toolbox 6.7 was used to calculate the figures of merit (Eigenvector Research, Wenatchee, WA, USA) for Matlab 7.2 software (MathWorks, South Natick, MA, USA).

PLS-1 (one dependent variable) was used for constituent quantification [21]. The original data set was randomly divided into two