

Characterization of Biomass Residues Aiming Energy and by-Products Generation

Sibele Augusta F. Leite^a, Brenno S. Leite^{b*}, Camila S. Carriço^c, Ana Teresa P. Dell'Isola^b, José Vicente H. Dangelo^a

^a Department of Chemical Systems Engineering, School of Chemical Engineering, University of Campinas, Av. Albert Einstein 500, Campinas, SP CEP 13.083-852, Brazil.

^b Institute of Science and Technology, University of Viçosa (Universidade Federal de Viçosa- Campus Florestal), Rodovia LMG 818, km 6, CEP: 35.690-000, Florestal-MG, Brazil.

^c Chemistry Department, University of Minas Gerais (UFMG), Av. Antonio Carlos, 6627, CEP 31270-901, Belo Horizonte, MG, Brazil

brennoleite@ufv.br

Rice husk and banana pseudostem are potential residues to be used as feedstock in biorefineries in order to obtain products and energy from biomass. This work presents some of their important properties and characteristics in order to provide a discussion of their use and adequacy for different process such as combustion, biodigestion, pyrolysis or to produce materials such as biosilica, biopolyol and lignocellulosic fiber. Rice husk (RH) and banana pseudostem (BP) were characterized through physicochemical analyses determining the following parameters: organic carbon (TOC), nitrogen (TNK), proximate analyses, FT-IR spectroscopy, thermogravimetric analyses (TG) and higher heating value (HHV). They were also submitted to biosilica extraction and liquefaction to obtain biopolyol. The chemical characteristics and the thermal behavior presented by the semi-dried samples indicate that there is a great potential of these residues to be used in combustion and pyrolysis processes. Also, the high C / N ratio turns RH and BP suitable co-substrates to be used in anaerobic digestion. Biosilica extraction was possible in both residues, but RH showed a higher result (12.7%) compared to the BP (2.1%). The liquefaction of the residues presented high yield ($\approx 70\%$) and biopolyols presented hydroxyl number compatible with the production of polyurethane foams.

1. Introduction

Brazil occupies a prominent position in global agribusiness, producing more than 300 different products for domestic consumption and also exporting them for 200 countries. In 2013 exportations reached nearly 100 billion dollars and the main exported products were coffee, sugar/ alcohol, meat and soybeans. However, other products like banana and rice should be highlighted in the Brazilian agribusiness. Brazil's climate and soil are favorable throughout the whole national territory allowing it to occupy the fifth position worldwide in banana production capacity, responsible for 7% of the total production, corresponding to more than 7 million tons. Brazil also occupies the ninth position in rice production worldwide and is the largest producer in South America. In 2015 rice production reached 12 million tons and in the last decade productivity has increased 20% (InformaEconomics FNP, 2015).

The growing scenario of these activities contributes to increase the generation of agricultural waste which should be used more efficiently in order to minimize environmental impacts. It is estimated that 1 ton of rice husk is generated for every 4 tons of gathered rice (Rambo et al., 2011) and about 3 tons of banana pseudostem is generated for each ton of banana produced (Souza et al., 2010). In banana production, pseudopseudostem is the largest amount of residue; the plant bears fruit only once before it dies. These residues are traditionally left on the ground where they can serve as organic fertilizer, although this kind of usage does not add any value to them (Tock et al., 2010).

Rice husk and banana pseudostem are lignocellulosic residues combining cellulose, hemicelluloses and lignin. They are potential residues to be used as feedstock in biorefineries that integrate conversion processes

and unit operations in order to produce products and energy from biomass. This concept is analogous to a petroleum refinery, which produces multiples fuels and products from petroleum. However, a biorefinery has the advantage of using renewable raw materials (Cherubini, 2010). The use of these residues in biorefineries implies the necessity to know and understand some of their physicochemical properties. Hence, the objective of this work was to characterize the rice husk (*Oryza sativa*) and the banana pseudostem (*Musa sp*), in order to compare their properties and investigate their potential to produce energy and by-products with higher commercial values. These residues were characterized by physicochemical analyses determining the following parameters: organic carbon, nitrogen (TNK), proximate analyses, FT-IR spectroscopy, thermogravimetric analyses (TG), higher heating value (HHV). They were also submitted to silica extraction and biopolyol synthesis.

2. Experimental

2.1 Sampling

Rice husk and banana pseudostem samples were collected during a period of four months, at Minas Gerais State, Brazil. Five samples were taken during this period collecting around 500 g of each residue each time. Then they were pre-dried at 65 °C using an oven-dry, for two days to eliminate extrinsic moisture and to obtain samples in the same operative conditions and capable of being handled. They were cut in a knife mill (Marconi – MA280) to get fibers of 0.5 – 1.0 mm length for storage and future physicochemical analyses, which were performed in duplicate.

2.2 Chemical Analyses

2.2.1 Organic Carbon (TOC)

Total organic carbon (TOC) was determined following the Walkley-Black method, which is based on the oxidation of the organic carbon by the dichromate ion and sulfuric acid for 30 minutes, at 150 °C. The organic carbon content was calculated by back-titration with ammonium iron (II) sulfate hexahydrate (Silva, 2009).

2.2.2 Total Kjeldhal Nitrogen (TKN)

The TKN content was measured according to the American Public Health Association standard methods (APHA, 1998). After acid digestion, organic nitrogen of many organic materials is converted to ammonium. Samples were distilled with the Kjeldahl analyser (TE-0364, by Tecnal) in alkaline medium and absorbed in boric acid. Ammonia content was determined by titration with a standard standard hydrochloric acid.

2.2.3 Proximate Analysis

Moisture content was determined as the loss of mass after drying at 105 °C in an oven for 2 h and the ash content was determined as the residue after combustion in a muffle furnace at 710 °C for 1 h. Volatile matter (VM) was determined as the mass fraction released when 1.0 g of sample was heated in a muffle furnace at 850 °C for 7 min. The percentage of fixed carbon (FC) was the fraction that remained after subtracting the ash and the VM content (Rendeiro and Nogueira, 2008).

2.2.4 Determination of chemical groups by FT-IR (Fourier Transform Infrared) Spectroscopy

Functional groups from biosilica and polyols were identified by FT-IR spectra, obtained from a Perkin Elmer FT-IR Spectrometer Frontier, with Universal ATR Sampling Accessory. The measurements were carried out within the mid-infrared area (4000 to 500 cm^{-1}). Samples were directly spread on the surface of the ATR crystal (germanium) and analysed in transmission mode. The resolution was set to 4 cm^{-1} , 16 scans were recorded and then corrected against the spectrum with ambient air as background. The spectra were treated by software Perkin Elmer Spectrum V 10.03.06.0100.

2.2.5 Thermogravimetric analysis (TG)

Thermogravimetric analysis curves were performed in a Thermogravimetric Analyser Model TGA 250, by TA Instruments using a heating rate of 10 °C min^{-1} , with air and nitrogen (with a fixed flow rate of 20 $\text{cm}^3 \text{min}^{-1}$) in the temperature range from 25 to 700 °C. Samples (10.00 ± 0.5 mg) were placed on a platinum pan. The TG curve obtained has shown that some significant thermal effects occurred in the samples. The TG instrument was calibrated using calcium oxalate monohydrate.

2.2.6 Higher Heating Value (HHV)

Combustion was carried out in a calorimeter (IKA C200) to obtain the higher heating value, according to ASTM E 711 (Rambo et al., 2015). Samples were weighted (200 ± 0.2 mg) directly into the crucible and

inserted into the vessel. A cotton thread was attached to the platinum ignition wire and placed in contact with the sample. The vessel was filled with oxygen (99.95%) at 30 bar. The calorimeter system was previously calibrated using combusting tablets made of certified benzoic acid supplied by IKA®.

2.3 By-products

2.3.1 Biosilica content

The biomass was mashed into small pieces (< 0.1mm) and then leached with a solution of concentrated hydrochloric and nitric acids (3:1) followed by a treatment with a solution of concentrated sulfuric acid and hydrogen peroxide 30% (2:1). The remaining solution was then filtered and the solid phase collected was dried at 100 °C, for 2 hours and then calcined in a muffle furnace at 600 °C, for 4 h (Chakraverty et al., 1988).

2.3.2 Biopolyol Synthesis

Liquefaction was carried out in a vertical autoclave (Primatec autoclaves) at 120°C under vapor pressure (1.94 atm), during 0.5 and 1.5 hours. About 5 grams of RH and BP were added in erlenmeyers with the solvent (crude glycerol) and catalyst (sulfuric acid 95%). It was used an amount of 7 wt% of catalyst and a mass ratio biomass/ solvent of 5:1. The resulting reaction mixture was filtered in order to separate the residue and filtrate. The residue was dried in an oven, at 105°C, for 24 hours to obtain the liquefaction yield (Eq (1)):

$$\text{Liquefaction yield (\%)} = \left(\frac{\text{Biomass weight} - \text{Residue weight}}{\text{Biomass weight}} \right) \times 100 \quad (1)$$

The liquid obtained from filtration was also dried at 85°C to obtain the polyol. The polyols' hydroxyl number were determinate according to ASTM D4274 standard (Carriço et al., 2016).

3. Results and Discussion

The conversion of biomass aims the transformation of carbonaceous solid materials into fuels and chemicals. The decomposition of the biomass is dependent on physicochemical properties. Proximate analysis (moisture, ash, volatile matter and fixed carbon content) initially is convenient to evaluate the potential of using the biomass as a fuel, since they direct influence the higher heating value (combustion heat). The chemical composition is an important information about the biomass as well: the higher the content of carbon and hydrogen the better is expected to be the combustion heat (García et al., 2014). The results for proximate analysis, HHV, TOC and TKN are shown in Table 1.

According to the proximate analysis RH and BP have low moisture content, 6.45 wt% and 7.47 wt% respectively. The results were comparable to vegetal coal (5.29 wt%) and were below 10 wt%, which was expected for pre-dried biomass and is favourable for combustion processes. High moisture content may have an undesirable impact over the quality and efficiency of the combustion, since evaporation is an endothermic process (García et al. 2012). Ash content was 12.15 wt% for RH and 4.54 wt% for BP. It represents the inorganic part of the fuel after the complete combustion and may indicate the presence of silica species. In biomass residues, ash is expected to be in the range from 5 to 20 wt%. Higher values may affect biomass energy conversion, since they create high thermal resistance because of the generation of slag deposits (Fernandes et al., 2013). The biomass analysed also presented high carbon content. The Volatile Matter (VM) and Fixed Carbon (FC) were 74.08 wt% and 13.77 wt% for RH and 88.92 wt% and 6.54 wt% for BP, respectively. Comparing to vegetal coal, the values indicate that the biomass residues have higher VM/FC ratio. This implies in a higher reactivity since volatile matter makes ignition easier at low temperatures (García et al. 2012).

Rice husk and banana pseudostem presented attractive HHV, from 11.5 to 13.7 MJ/kg (HHV for vegetal coal is 21.25 MJ/kg). These results are in accordance to the proximate analysis that indicates high levels of organic matter (high carbon content) and low moisture and ash content. In addition, data obtained by the Walkley–Black method pointed out that carbon is the main component in RH (50.5 wt%) and in BP (64.9 wt%). Carbon is expected to contribute positively, by increasing the HHV (García et al., 2014). Results obtained for nitrogen content (0.38 wt% RH and 0.47 wt% BP) are considered satisfactory since they imply in low concentration of nitrogen oxides and toxic gases generated during the thermochemical conversion process, which would otherwise cause undesirable environmental impacts (Fernandes et al., 2013).

Table 1: Results for Proximate Analysis, Organic Carbon (TOC), Total Kjeldhal Nitrogen (TKN) and Higher Heating Value (HHV).

	Proximate Analysis (wt%)				TOC (wt%)	TKN (wt%)	HHV (J/g)
	Moisture	Ash	VM	FC			
Rice Husk	6.45 ± 0.23	12.75 ± 0.08	74.08 ± 0.63	13.77	50.5±2.7	0.38 ± 0.02	13,745.04
Banana Pseudostem	7.67 ±0.34	4.54 ± 0.30	88.92 ± 0.56	6.54	64.90 ± 3.20	0.47 ±0.03	11,497.93
Vegetal Coal ¹	5.29	5.9	26	68.10	79.34 ²	0.65 ¹	29,712

¹ García et al., 2012 ; ² Results from Ultimate analysis performed with Perkin-Elmer CNH 2400.

Considering the parameters evaluated in the proximate analysis and the carbon content RH and BP are suitable to be used in fast pyrolysis. Even though RH proprieties may compromise the process yield and fuel quality, because of its high ash content (Bridgwater, 2012). The high TOC content and the low nitrogen content may also contribute to transform BP and RH into interesting alternatives to be used as co-substrates for the anaerobic digestion of animal manure. They can provide suitable carbon(C)/nitrogen(N) ratio (around 20) for the mixture and this is important to avoid the release of high quantities of ammonia, which may be inhibitory for the methanogens (Wu et al., 2010). The quantity of the biomass added to the biodigester should be calculated in order to avoid compromising process quality. In general, animal manure and sewage sludge are treated through wet anaerobic digestion, which consists of an organic feedstock with solid content below 15 wt%(Kothari et al., 2014). Hence, considering the low content of moisture in the RH and BP, 6.45 and 7.67 wt% respectively, they could be used in small portion as co-substrates in biodigestion process.

In order to corroborate the results of the physicochemical analysis and to evaluate the thermal stability of the samples, Thermogravimetric Analyses (TG) and their derivatives (DTG) were performed under oxidant and inert atmosphere. Figure 1 presents TG/DTG curves for BP and RH under oxidant atmosphere. For both biomasses, the first stage of decomposition occurs at temperatures between 50-100 °C and it is attributed mainly to water and volatile compounds losses. According to TG/DTG curves, RH presents thermal stability until 200 °C and above this temperature mass losses are higher. The second stage, from 220 to 350 °C, corresponds to the degradation of organic matter, including mostly hemicellulose and cellulose. The third stage, which is between 400-500 °C, corresponds mostly to the degradation of the lignin (Moliner et al., 2014). Banana pseudostem presents similar behavior, although decomposition of organic matter starts at 150 °C. The residue that remains above 500 °C may be considered ash (Fernandes et al., 2013). From Figure 1, it can be observed that mass loss due to readily oxidisable organic matter (cellulose / hemicellulose) occurs on the second stage and accounts to about 60 wt% for BP and 50 wt% for RH. These results and the residues remained are consistent with TOC and ash content (Table 1). They are also coherent with the literature that shows that RH has more lignin content compared to BP (Rambo et al., 2015). Under inert atmosphere, the samples showed one event less than under the oxidizing one (Figure 2). After water losses (below 100 °C), degradation of organic matter occurred approximately from 200 to 500 °C, where the peak/shoulders indicates that more than one reaction is being involved at the same time (Moliner et al., 2014). It corresponds to the reactions of lignocellulosic pyrolysis: depolymerization, decarboxylation and cracking (Fernandes et al., 2013).

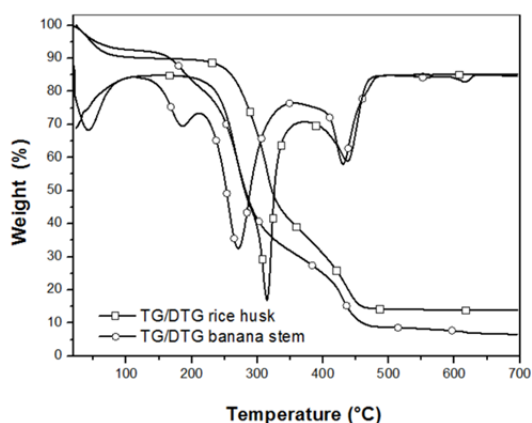


Figure 1: TG/DTG curves from rice husk (□) and banana pseudostem (○) under oxidant atmosphere.

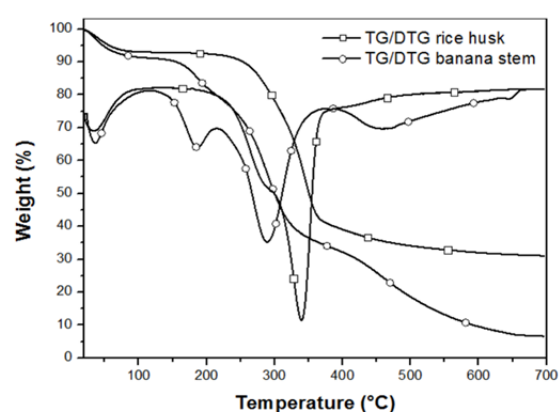


Figure 2: TG/DTG curves from rice husk (□) and banana pseudostem (○) under inert atmosphere.

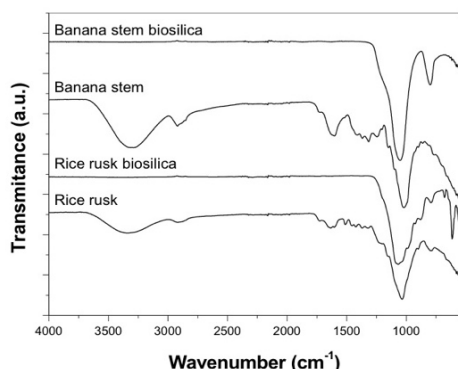


Figure 3: FT-IR spectral analysis of the biomass/biosilica samples

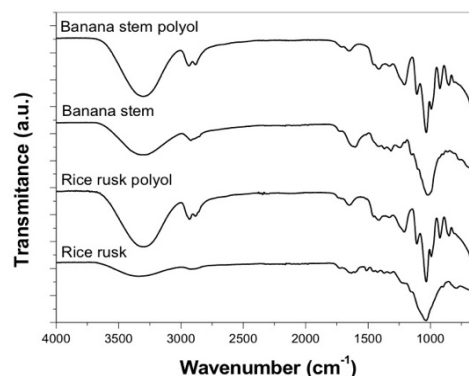


Figure 4: FT-IR spectral analysis of the biomass/biopolyol samples

Besides the usage for energy generation, biomass can be used for obtaining new materials as well. According to the thermal stability results in the TG / DTG curves, when indicating the fibers of these residues, it should be considered their application at lower temperatures, below 150 °C for BP and 200 °C for RH, since above these temperatures, the mass loss due to decomposition is high.

In this work, the biosilica extracted from RH and BP was investigated. The first evidence of the existence of biosilica in these materials was the ash content obtained from the proximate analysis (12.75 wt% for RH and 4.54 wt% for banana pseudopseudostem). Ultimately, biosilica was extracted to be quantified: RH presented 12.7 ± 0.4 wt% and BP 2.1 ± 1.0 wt%. The presence of silica groups was confirmed by FT-IR characterization (Figure 3). Spectra indicate the presence of the group siloxane (Si-O-Si) that is a typically strong with a prominent band around 1030 cm^{-1} . The band around 1030 cm^{-1} was enlarged due to the increase of the inorganic content during extraction process. The spectra also show peaks around 800 cm^{-1} which may be attributed to the presence of amorphous silica (O-Si-O) (Smidt et al., 2002).

Another promising application of lignocellulosic biomass is to prepare biopolyols, a precursor of polyurethanes production. In this work RH and BP liquefaction was efficient, presenting yields around 70% (Table 2). The biopolyols obtained in this study showed hydroxyl number between 296 and $534 \text{ mg KOH g}^{-1}$, which is adequate to produce rigid foams (Vilar, 2002). From Table 2, it can be observed the liquefaction yield was lesser for RH and this result may be linked to its higher lignin content. Lignin is the major barrier to use lignocellulosic biomass in bioconversion processes. Furthermore Carriço et al. (2016) showed in their work the hydroxyl number of polyol decreases as the lignin content increases. Results from Table 2 show that it is possible to enhance the liquefaction yield and tailor biopolyol properties by choosing reaction's conditions and the biomass. Infrared spectra of biomass and biopolyols are showed in Figure 4 and indicate the main changes in the chemical structure by the liquefaction process. The band at 3306 cm^{-1} , corresponding to the bonds of the aromatic and aliphatic OH groups, which is more expressive in polyols spectra, confirms the efficiency of the liquefaction. In 2938 and 2888 cm^{-1} , which refers to the stretching of the methyl and methylene groups, is less intense in the biomass than in the polyols and can be explained due to the liquefaction process: it decomposes the macromolecules of the fiber into smaller molecules and increasing the amount of these groups (Wang et al., 2009).

Table 2: Results from the best liquefaction yield and the respectively hydroxyl number for rice husk (RH) and banana pseudostem (BP)

	Parameters reaction			Liquefaction yield (wt%)	Hydroxyl number (mg KOH g^{-1})
	Catalyst (wt%)	Time (h)	Solvent/biomass (wt%)		
RH	7	0.5	5:1	65.8	296
RH	7	1.5	5:1	60.5	376
BP	7	0.5	5:1	79.5	484
BP	7	1.5	5:1	73.7	534

4. Conclusions

Physicochemical characterization and HHV from rice husk and banana pseudostem are compatible with the ones from vegetal coal. The low moisture content for the predried raw materials and the temperature range in which the organic matter degradation occurs are important parameters to be considered in applications of fast pyrolysis processes. The high C/N ratio makes them suitable co-substrates for the use in a biodigestion process. These wastes may also be used for the production of compounds such as biosilica, lignocellulosic fibers and biopolyol synthesis. This work shows these agricultural residues present a great potential to be used as renewable feedstock in biorefineries.

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