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Thermal characterization of lignocellulosic residue from different sugarcanes

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Abstract Bagasse samples from four different sugarcane were directly collected as the residues of milling in a processing plant. The samples were dried at 105 °C, compressed to small granules and then their TG/DTA and DSC curves in synthetic air were recorded. Similar thermogravimetric curves were obtained for the different samples and they exhibited four mass loss steps. However, the analysis of the exotherm DSC peaks showed that the oxidation of the organic matter resulted different enthalpy values (ΔH/kJ g^{-1}).

Keywords Sugar-cane bagasse · Lignocellulosic residue · Thermal analysis

Introduction

Sugar-cane bagasse has been historically used as fuel in plants since the end of last century when it started to substitute firewood in high-pressure boilers. With the technological progresses of sugarcane agroindustry in Brazil, bagasse started to be more valued as a source of energy, responsible for the necessities of the own plant, and later, started to be marketed for other plants or industries.

Nowadays, most of the plants sells the spare bagasse at a variable of price between 2.0 and 7.0 US$/t depending on the location of the plant in relation to potential buyers [1]. The market, in general, pays for ton of bagasse, in nature, the same price for ton of sugarcane. That is equal to join onto the bagasse an initial commercial value proportional to ¼ of the cost of the surplus material.

One of the fundamental characteristics of bagasse is its energy content, which depends on the amount of humidity (50%) and the residual sugar content. Since the residual sugar content is usually low, humidity is considered as a main limiting factor of calorific power. In São Paulo State practically all the agroindustry are energetically self-sufficient because of the large amount of generated bagasse [2].

The geographical location of plants and the maximum production period are positive points that reinforce the viability of investments in energetic cogeneration. Processing plants are located in an area of larger consumption of the country and the harvest period coincides with the drought, saving the reservoirs of hydroelectric power stations.

Already in those first months of 2008, preliminary results allowed to compose an idea of the Internal Offer of Energy—OIE. Such results indicate that the total energy requirement in Brazil (OIE) reached 238.3 million equivalent tons of petroleum (tep) in 2007, 5.4% larger than the amount in 2006, and equivalent to approximately 2% of the world energy. In relation to 2006, the demand for renewable energy in Brazil grew in all the sources. For the first time, the participation of "hydro energy and electricity" were supplemented by "energy derived from sugarcane" in the Head Office Brazilian Energetic (MEB) [3].

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One of the largest problems is to quantify and to qualify the production of alternative electric power starting from bagasse, seeking for a more rational use, taking into account the market value, economical cost, accounting, environmental and for the development of new technologies, sources or energy forms.

Experimental

Sampling and collection of the sample

Sugarcane bagasse samples were collected at Santa Cruz Processing Plant, located in the area of Araraquara city, São Paulo State, Brazil, during the whole harvest period (May to November of 2007). The samples were collected by a horizontal probe according to Consecana normative N-025 [4], disintegrated and soon after crushed, were conditioned in plastic sacks properly identified and stored in refrigerator for subsequent analyses. Four main sugarcane samples were used in São Paulo State, Brazil depending on factors such as soil characteristic, abundance, physico-chemical characteristics and quantity of total recoverable sugar, which may influence, in addition to the amount of alcohol and sugar, the quality of sugarcane bagasse that will be applied for energy generation. In this study, the criteria used to select the varieties of cane were their abundance in the Araraquara city region and their different characteristics (see in Table 1).

Extraction of proto-lignin

Sugar-cane bagasse samples, about ~5 g, were firstly water extracted with portions of 200 mL of distilled water to eliminate soluble solids and then they were placed in a Schott bottle. After the addition of 140 mL of chloroform and 70 mL of methanol was they were heated for 4 h at 60 °C, then filtered and the residue was placed in an oven for 4 h at 105 °C.

Table 1 Varieties of the sugarcane collected at Santa Cruz Processing Plant, located in the area of Araraquara city, São Paulo State, Brazil

Sample	Variety	Characteristics
1	SP81-3250	Rich in sugar and productive
2	RB855113	Size and density
3	RB855156	Precocious
4	RB867515	Rustic and tall

Symbolism example: RB = Brazil Republic; 85 = year in which the specie was spread (19th century); 5113 = number code attributed to variety; SP = São Paulo State; 81 = year in which the specie was spread (20th century)

The resulting samples were placed under round-bottomed flask with 20 mL of HCl and 180 mL of dioxane [5]. The mixtures were kept under reflux for 40 min, filtered and then about ~5 g of sodium bicarbonate was added. The resulting solutions were subjected to a route-steam up to the volume had been reduced to approximately 10 mL, then more 400 mL of distilled water and ~5 g of anhydrous sodium sulfate was added. The solutions were finally heated at 60 °C until the total precipitation of the proto-lignin.

Thermogravimetric analysis (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC)

Among thermoanalytical techniques thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) were used. The sugarcane samples were dried at 105 °C [6], crushed with a pestle and sifted to form into smaller granules. Simultaneous TG/DTA curves were obtained using sample masses around 2.50 mg from four sugarcane samples. Sample holder, made of α-alumina and reference material (also α-alumina) was used. As further experimental settings 20 °C min^{-1} heating rate in the 30–600 °C temperature range and synthetic air, flow rate of 50 mL min^{-1} was applied.

DSC curves were obtained using around 2 mg initial sample masses, prepared as it was described above. All the DSC curves were obtained using aluminum crucible with perforated lid ($\phi = 1$ mm) and an empty aluminum crucible at the reference side. 50 mL min^{-1} of synthetic air and nitrogen purging was maintained in the 30–600 °C temperature range at a heating rate of 20 °C min^{-1}.

Infrared spectra (FTIR)

Bagasse and proto-lignin samples were analyzed in a "NICOLET" (I model Impact 400 SX-FT) FTIR spectrophotometer in the 4,000–400 cm^{-1} wavenumber interval with a spectral resolution of 4 cm^{-1} in KBr pellets.

Results and discussions

Thermogravimetric analysis (TG) and differential thermal analysis (DTA)

Figure 1a presents the thermogravimetric curves (TG) obtained for all the four sugarcane bagasse samples. In agreement with the DTA and DSC curves (Figs. 1b and 2a, respectively) four mass loss steps were observed.

The first mass loss from 25 to 145 °C was attributed to the removal of the humidity present in the sample, possibly

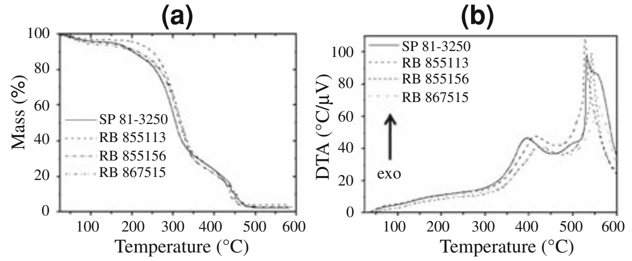

Fig. 1 **a** TG curves for sugarcane bagasse **b** DTA curves for sugarcane bagasse—(both at $\beta = 20$ °C min^{-1} and flow = 50 mL min^{-1})

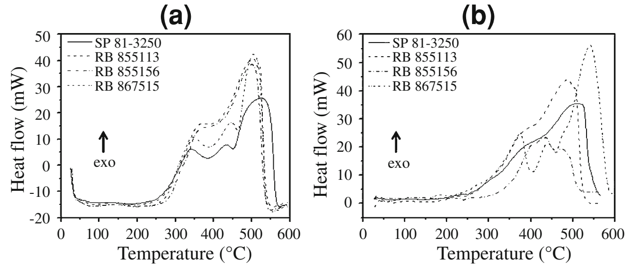

Fig. 2 **a** DSC curves obtained for the bagasse **b** DSC curves obtained for the lignin (both at $\beta = 20$ °C min^{-1} and flow = 50 mL min^{-1})

absorbed from atmosphere; it because of the relative humidity of the air was in order of 85% in that period. Mass variation for this step varied from 4.5 to 6.4%. The lowest and the highest values were observed for SP 81-3250 and RB 867515 samples, respectively.

The organic matter decomposed in different steps: 1—for varieties SP 81-3250 and RB 867515 it was observed that the thermal decomposition happened in four significant steps, which can be associated mainly to the thermal decomposition of sucrose, hemicelluloses, celluloses and lignin. 2—for samples RB 855113 and RB 855156 one can observe that the same thermal decomposition takes place in three significantly different steps. The mass loss due to the drought organic matter at the end of thermal decomposition varied from 90.8 to 97.7% in the 120–550 °C temperature interval.

Figure 1b presents the results for differential thermal analysis for all the sugar-cane varieties. DTA curves showed only two significant exothermic events. The first one, about 400–450 °C, and the second one in approximately 500–550 °C, are in agreement with the mass losses observed in the TG curves.

Differential scanning calorimetry (DSC) curves for sugarcane bagasse and proto-lignin

DSC curves of the sugarcane bagasse (Fig. 2a) obtained under synthetic air atmosphere, show a wide exothermal peak, with two maxima at ~364 and 502 °C, for RB 855113 and RB 855156 samples, while RB 867515 and SP 81-3250 present three peak maxima at 345, 440 and 504 °C. The peak at 504 °C for RB 867515 is sharp and coincident with the maxima of RB 855113 and RB 855156. The DSC curve obtained for RB 867515 is in agreement with the TG curve obtained under similar conditions. For SP 81-3250, the exothermic peak at 526 °C appears with similar shape and intensity compared to RB 867515.

The enthalpy of oxidation (ΔH_{ox}) calculated from exothermic peaks for RB 867515, RB855156 and RB 855113 were 11.1, 11.8, 10.9 kJ/g respectively. For SP 81-3250, the corresponding ΔH_{ox} values were found as 8.6 kJ/g, which is 29.6% lower compared to the other varieties.

The proto-lignin samples were submitted to DSC analyses in the same conditions used to sugar-cane bagasse. In the DSC curves (see Fig. 2b) a wide exothermal peak with two maxima at ~380 and 500 °C for SP 81-3250; ~380 and 485 °C for RB 855113 and ~430 and 475 °C for RB 855156 can be observed. The RB 867515 exhibits three maxima at ~370, 440 and 540 °C. The peak at 475 °C for RB 855156 is sharp and coincident with the maximum of RB 855113. For SP 81-3250, the exothermic peak at 500 °C has a less intensity, in comparison to the other samples.

The intermediate values of oxidation enthalpy (ΔH_{ox}) were calculated for SP 81-3250 and RB 855113, 7.2 and 8.4 kJ/g, respectively, while the same for ΔH_{ox} for RB 855156 was the lowest, 3.3 kJ/g. The RB 867515 sample exhibited the highest enthalpy value of oxidation, as 9.0 kJ/g.

Infrared spectra (FTIR) for sugarcane bagasse and proto-lignin

The infrared absorption spectra recorded between 4,000 and 400 cm^{-1} for the sugarcane bagasse and proto-lignin samples can be seen in Fig. 3a and b.

The wide band between 3,500 and 3,000 cm^{-1} for all of the samples are due to OH stretching vibrations of alcohols and phenols and bands in the 2,920–2,925 cm^{-1} range regarding the C–H vibrations aliphatic groups (methyl and methylene) [7]. This band has less intensity for RB 855156 in the spectrum of lignin when compared with other samples.

The bands in 1740, 1620, 1450 and 1510 cm^{-1} correspond to the C=C stretching of the aromatic ring of lignin in bagasse and show more intense bands for RB 855113 and RB 855156. This kind of bands are present in all proto-lignin samples, however the intensities of the first bands are larger in the spectra of proto-lignin originating from SP 81-3250 and RB 867515.

Bands in 1,460 cm^{-1} are representative for the stretching of –CH–, $–CH_2–$ and $–CH_3$ radicals in lignin [8].

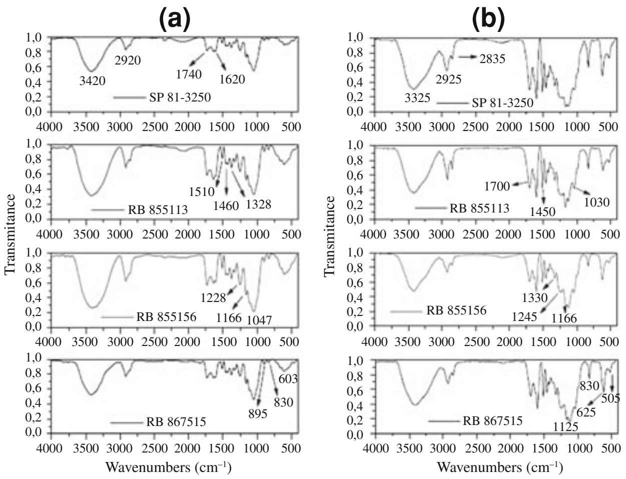

Fig. 3 Infrared spectrum for: **a** sugarcane bagasse; **b** lignin

In the FTIR spectra the bands appearing between 1,328 and 1,245 cm^{-1} are for the vibration of the syringyl and guaiacyl units for all of the sugar-cane varieties. Bands in 1,166 cm^{-1} are vibration C–H in the plan due to guaiacyl and syringyl units.

For RB 855113 and RB 855156 samples the bands around 1,030 cm^{-1} are due to C–H and C–O deformations; decrease of intensity of this band in the RB 855156 sample is an evidence for the degradation in the lignin structure.

Finally, the band at 830 cm^{-1} shows the vibrations of C–H out of the plan of hydroxyphenyl unit and are present in all varieties. However, it show low intensity for the proto-lignin from RB 855156. This band also indicates the presence of cellulose [9].

Conclusions

The results obtained from TG/DTA analysis showed four mass loss steps and were similar for all sugar-cane varieties. The first one corresponds to the humidity loss; the others are representative for the oxidative thermal degradation of the organic matter, which is mainly sucrose, hemicellulose, cellulose and lignin. The DSC curves from bagasse in oxidative atmosphere suggest that RB 855156 and RB 867515 may be advantageously used for energy production. The proto-lignin from RB 867515 presented high ability to generate energy. DSC curves like IR curves of proto-lignin showed a fingerprint of the extracted proto-lignin from each sugarcane variety.

Infrared spectra presented characteristic bands for hemicellulose, cellulose and lignin. The FTIR spectra for Proto-lignin showed the efficiency of extraction method using dioxane-HCl in agreement with DSC curves.

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