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Characterization of sugarcane and coconut fibers by thermal analysis and FTIR

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Abstract Pyrolysis of sugarcane bagasse and coconut fiber was studied by thermal analysis in order to characterize their thermal behavior and to identify their constituents by the aid of their thermogravimetric curves and to determine their heat capacity by means of DSC. The Fourier Transform Infrared Spectrum (FTIR) was used to determine the main constituents present in both residues. The thermal degradation of sugarcane bagasse and coconut fiber presents two mass loss steps attributed to the release of humidity and to the decomposition of organic material (hemicellulose, cellulose and lignin). It was expected that the results of DSC analysis were almost the same for both types of biomasses.

Keywords Biomass · FTIR · Thermal analysis · Pyrolysis

Introduction

There are several different ways in which the abundance of energy surrounding us can be stored, converted and amplified for our use. Energy sources will play an important role in the future life of the World. The energy sources have been split into three categories: fossil fuels, renewable sources and nuclear sources [1]. The cost of producing energy from fossil fuel usually exceeds the cost of biomass fuels. Besides, the burning of fossil fuels causes green house gas emission which has remarkable effect to the environment [2]. The use of biomass as energy source is of interest due to the following envisaged benefits: (i) biomass is a renewable, potentially sustainable and relatively environmentally benign source of energy; (ii) a huge array of diverse materials, frequently stereo chemically defined are available from the biomass giving the user many new structural features to exploit [3]; (iii) increased use of biomass would extend the lifetime of diminishing crude oil supplies; (iv) biomass fuels have negligible sulfur content and therefore, do not contribute to sulfur dioxide emissions that cause acid rain; (v) the combustion of biomass produces less ash than coal combustion and the ash produced can be used as a soil additive in fields, etc.; (vi) the combustion of agricultural and forestry residues and municipal solid wastes (MSW) for energy production is an effective use of waste products that reduces the significant problem of waste disposal, particularly in municipal areas; (vii) biomass provides a clean, renewable energy source that could improve our environment, economy and energy securities [4, 5] and (viii) use of biomass could be a way to prevent more carbon dioxide production in the atmosphere as it does not increase the atmospheric carbon dioxide level. Biomasses are known to grow is a sustained way through the fixation and release of CO_2, mitigating global warming problems. In fact, the amount of CO_2 produced during the combustion of the fuels is the same amount absorbed during the gromassh of the plants. This is particularly the case of energy crops and agricultural residues [6].

The biomass can be defined as a hydrocarbon, which consists mainly of carbon, hydrogen, oxygen and nitrogen. Some types of biomass present significant proportions of inorganic species. The concentration of ashes generated for this inorganic goes since <1% in softwoods until 15% in herbaceous biomass and agro-industrial residues [7]. Biomass is the fourth largest energy source in the world after

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coal, petroleum and natural gas, providing about 14% of the world's primary energy consumption. Renewable biomass is being considered as an important energy resource all over the world. Biomass is used to meet a variety of energy needs, including generating electricity, fueling vehicles and providing process heat for industries [8, 9]. Among all the renewable energy sources biomass is unique as it effectively stores solar energy. It is the only renewable source of carbon that can be converted into convenient solid, liquid and gaseous fuels through different conversion processes [10].

Sugarcane bagasse, an abundant agricultural lignocellulosic byproduct is a fibrous residue of cane stalks left over after crushing and extraction process of the juice from sugarcane. About 54 million dry tons of bagasse is produced annually throughout the world [11]. Is a complex material being the main product of the sugarcane industry and generated in large quantities during the processing of sugarcane in sugar mill. Bagasse offers the advantage of being a cheap, plentiful and low polluting fuel. On the average, bagasse contains about 45–50% moisture, 43–52% fiber, and 2–6% soluble solids. The typical composition of bagasse fiber is about of 26.6–54.3% cellulose, 22.3–29.7% hemicellulose and 14.3–24.45% lignin [12]. Bagasse has a net calorific value of around 8,000 kJ/kg, with a moisture content of around 50 mass% and ash content in the range of 4–5 mass%. It is therefore utilized as a fuel in boilers in the sugar mills to generate steam and electricity [13]. Bagasse is characterized as a low-density fiber and by its wide particle size distribution (<100 μm to larger than 10 cm). Is used primarily in the sugar mill to cover the own energy requirement of the sugar production process [12]. Burning of bagasse in cogeneration process for meeting internal energy needs and is inefficient and wasteful. There has been a significant interest in converting this residue into higher energy dense products by means of pyrolysis, carbonization, liquefaction, gasification and combustion. This study is focused on the pyrolysis of bagasse and coconut fiber.

The coconut fiber is a short fiber; a little flexible and hard when compared to the others fibers. Their hardness is associated mainly to the presence of lignin, which is also responsible for the yellowish color and for the brown color to the mature coconut [14]. Coconut is a common and abundant fruit. The fiber is the inner part which covers the shell containing of the nut. This fibrous part is generated as a waste in the processing of coconut fruit. The composition of the fiber is about 5% of water soluble; 3% of pectin and related compounds; 0.3% of hemicellulose; 46% of lignin and 2% of ash [15]. Thus, coconut fiber is classified as a lignocellulosic material.

In Brazil annually about 1.5 billion coconuts (*Cocos nucifera*) are produced [16]. Coconut fibers (coir) can be extracted from either mature or immature fruits (for example, they are sold in Brazil though obtained from green fruits used for their water, which is one of the popular refreshments and has therapeutic properties).

Between the more than a hundred products made directly or indirectly of coconut fiber can to be outstanding: cords, carpets, plant pots, brushes, brooms, automotive upholstery, painting of civil construction, plates of fiber-resin, plates of fiber-cement between others due to the good water retention property [14].

Pyrolysis which according to its physical-chemical substance belongs among thermic processes, is one of the ways that may lead to transformation of certain kinds of biomaterials into a more refined form of energy [17]. The basic thermochemical process is for converting biomass to a more useful fuel. The pyrolysis method has been used for commercial production of a wide range of fuels, solvents, chemicals and other products from biomass feed stocks. Pyrolysis produces energy fuels with high fuel-to-feed ratios making in the most efficient process for biomass conversion and the method most capable of competing with and eventually replacing non-renewable fossil fuel resources [1]. Conventional pyrolysis consists of the slow, irreversible thermal decomposition of the organic components in biomass. Slow pyrolysis has traditionally been used for the production of charcoal. Fast pyrolysis is characterized by high heating rates and rapid quenching of the liquid products to terminate the secondary conversion of the products [7].

Depending on the pyrolysis temperature, the char fraction contains ashed inorganic materials in different degrees, any unconverted organic solid and carbonaceous residues produced from thermal decomposition of the organic components. The liquid fraction is a complex mixture of water and organic chemicals. For highly cellulosic biomass feed stocks the liquid fraction usually contains acids, alcohols, aldehydes, ketones, esters, heterocyclic derivatives and phenolic compounds. The liquid products of pyrolysis are complex mixtures of oxygenated aliphatic and aromatic compounds. The tars contain native resins, intermediate carbohydrates, phenols, aromatics, aldehydes, their condensation products and other derivatives. Pyroligeneous acids can consist of 50% CH_3OH, C_3H_6O (acetone), phenols and water. CH_3OH can be produced by pyrolysis of biomass. CH_3OH arises from the methoxyl groups of uronic acid and from the breakdown of methyl esters and/or ethers from decomposition of pectin-like plant materials. Acetic acids come from the acetyl groups of hemicelluloses. The pyrolysis gas mainly contains CO_2, CO, CH_4, H_2, C_2H_6, C_2H_4, minor amounts of higher gaseous organics and water vapors [7].

The production of electricity in large scale from biomass (and this include, obviously sugarcane bagasse and coconut fiber) having a large interest consequently is a topic which has been studied in the recent years. This interest focused the attention of several factors: (i) production of electricity from biomass, which has a practically closed carbon cycle and with low or almost zero amount of SO_x emission; besides, the amount of residual ash is lower than the generated amount when mineral coal is used; (ii) the increase of the energy produced by bio-resources may lead to save some crude oil and other fossil energy bearers.

The objective of this paper is to characterize sugarcane bagasse and coconut fiber samples, to determine calorimetric properties of the sugarcane bagasse and coconut fiber through DSC analysis, to monitor the decomposition products of pyrolysis and to obtain the related kinetics parameters.

Experimental

The biomass residues used in the study were:

- Sugarcane bagasse originating from Campinas' region in Brazil and
- Coconut fiber originating from Rio de Janeiro state, Brazil

For their characterization thermoanalytical techniques (TG/DTG, DTA and DSC) and Fourier Transform Infrared Spectroscopy (FTIR) were used.

The treatment of raw material covered two steps: in the first one is the drying of the sugarcane bagasse on the sun (Fig. 1a). The second was the grinding of the sun-dried material (Fig. 1b) in a mill. Coconut fiber was received air-dry (Fig. 1c). The coconut fiber was also ground in a mill. Both the milling processes (sugarcane bagasse and coconut fiber) were conducted in a knife granulator mill, with granulometry of 2 mm, provided by Embrapa in Rio de Janeiro.

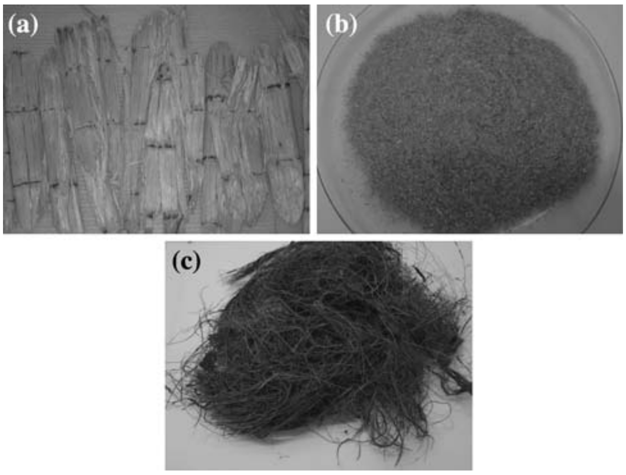

Fig. 1 **a** Dry sugarcane bagasse, **b** ground sugarcane bagasse, **c** dry coconut Fiber

The thermal degradation of sugarcane bagasse and coconut fiber were studied between 303 and 1,073 K under nitrogen flow in a TA model SDT 2960 Simultaneous DTA-TGA analyzer by using of 283 K min^{-1} heating rate and 120 mL min^{-1} gas flow. The sample masses were approximately 10 mg.

The specific heat determinations have been done by using TA DSC 2010 Differential Scanning Calorimeter, TA Instruments in nitrogen atmosphere applying 283 K min^{-1} heating rate until 673 K.

The FTIR analysis was carried out in a *Spectrum One FTIR Spectrometer* (PerkinElmer). It was used in the Attenuated Total Reflectance Method (ATD) with application of noise's attenuating (*Automatic Smooth*).

Results and discussion

Thermal analysis

As it can be seen in Fig. 2 the TG curve of the sugarcane bagasse presented three mass loss steps. The first one up to 373 K is attributed to the moisture elimination accompanied by 7.7% of mass loss. The second step occurring between 473 and 523 K and representative for the release of many organic extractives e.g. fats, waxes, alkaloids, terpenes, glycosides, etc. The resulted mass change is around 25%. The third step appearing in the 523–653 K temperature range is attributed to the decomposition of lignin, hemicellulose and cellulose. Is important to emphasize that the thermal degradation of hemicellulose and cellulose takes place in very near temperatures around under 603 K (see DTG curves in Fig. 2), depending of the nature of the heteropolymers presents in the biomass. In such case is not possible to detect separated peaks for these compounds. The residue of pyrolysis process accomplishes 15% of initial mass and consists of inorganic compounds in the form of oxides. Table 1 shows the results of X-ray fluorescence analysis of the ashes.

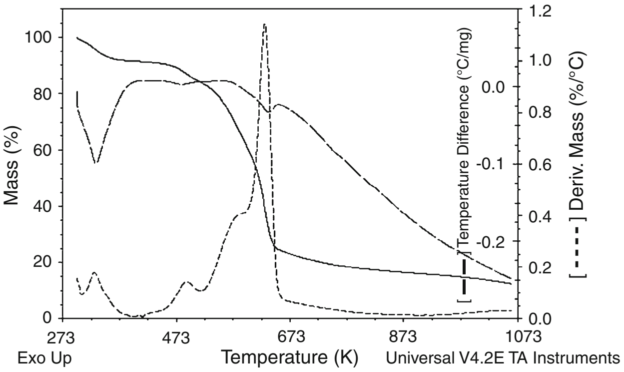

Fig. 2 TG, DTG and DTA of sugarcane bagasse

Table 1 XRF analysis of ashes of sugarcane bagasse

Elements	Concentration in ashes of sugarcane bagasse/%
K_2O	60.9
CaO	28.9
ScO_2	2.9
SO	2.6
MnO_2	2.2
Fe_2O_3	1.7
CuO	0.8

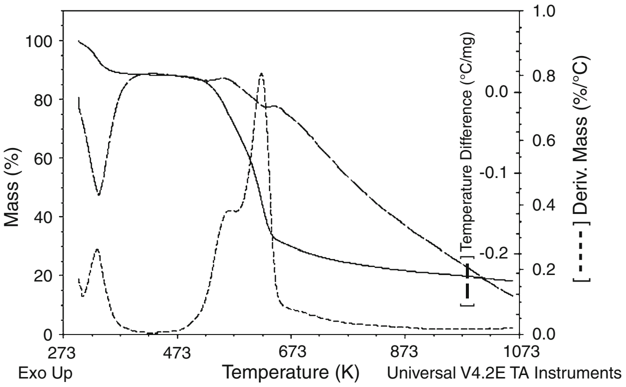

Fig. 3 TG, DTG and DTA of coconut fiber

Table 2 XRF analysis of ashes of coconut fiber

Elements	Concentration in ashes of coconut fiber/%
K_2O	71.5
CaO	12.8
Cl_2O	11.2
Fe_2O_3	1.5
SO	1.2
ScO_2	0.8
CuO	0.3
ZnO	0.2
BrO	0.2
RbO_2	0.2

For the coconut fiber (see Fig. 3) the TG curve shows two stages of decomposition: the first stage around 323 K corresponds to moisture elimination. The second one between 523 and 643 K is attributed to decomposition of organic materials which is the superposition of two parallel processes (see DTG curve of Fig. 3). In this step, the mass loss caused by organic species presents in the raw material: lignin, hemicellulose and cellulose. The residues is about 20% of initial sample mass and its composition is shown in Table 2.

Table 3 Specific heat capacity of sugarcane bagasse

T/K	C_P sugarcane bagasse/J g^{-1} K^{-1}
423.08	2.24485
448.03	2.524433
462.96	2.610374
	Mean = 2.459886

Table 4 Specific heat capacity of coconut fiber

T/K	C_P coconut fiber/J g^{-1} K^{-1}
458.06	3.240422
462.96	3.206149
468.08	3.215612
	Mean = 3.220728

The specific heat capacities of sugarcane bagasse and coconut fiber were determined by DSC ant the relevant rata at three different temperatures as well as their average are given in Tables 3 and 4.

FTIR spectroscopy studies

This technique was used for structural characterization of the sugarcane bagasse and the coconut fiber.

The absorption spectrum on the infrared region of the sugarcane bagasse, can be observed in the Fig. 4. The main characteristics are attributed to the presence of lignin, hemicellulose and cellulose, characteristic of natural fibers. In general, the IR spectra for the native and the chemically modified fibers are representative in the 3,200–3,600 cm^{-1} range. The large band is attributed to the axial deformation of the O–H group. For the sugarcane bagasse used in the study this peak appeared at 3,330 cm^{-1}. At 2,888 cm^{-1} the observed absorption band is related to the axial deformation of C–H group. The peak at 1,721 cm^{-1} is

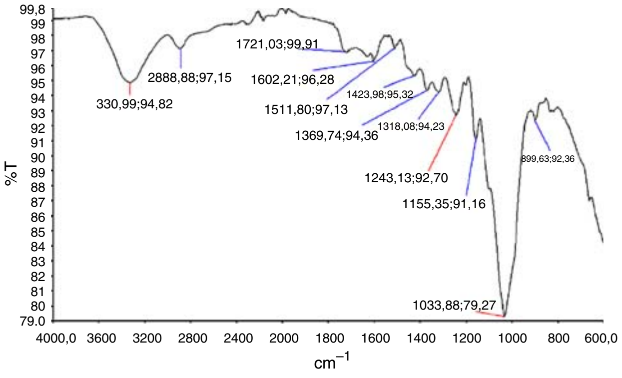

Fig. 4 FTIR of sugarcane bagasse

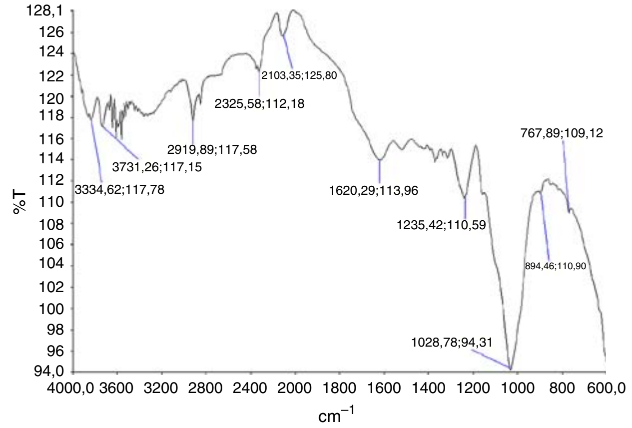

Fig. 5 FTIR of coconut fiber

characteristic of the carbonyl band (C=O) of the hemicellulose in the sugarcane bagasse. The band at 1,423 cm^{-1} is representative for the symmetric deformation of CH$_2$ group of cellulose, while the band at 1,243 cm^{-1} refers to the C–O–C in cellulose chain. The band at 1,155 cm^{-1} is in connection with the asymmetric deformation of C–O–C of the cellulose and hemicellulose.

The absorption spectrum for the coconut fiber presents some similarities with the one of the sugarcane bagasse (see Fig. 5). At 2,919 cm^{-1} the band is related to the axial deformation of C–H group, while the one at 2,103 cm^{-1} is related to the C=C stretching vibrations. The carbonyl group of the hemicelluloses gives signal at 1,620 cm^{-1}, while the band at 1,235 cm^{-1} is associated to the presence of C–O–C in cellulose chain. The strong absorption band at 1,028 cm^{-1} is related to the C–OH stretching vibration.

Conclusions

By using thermoanalytical and FTIR technique the sugarcane bagasse and the coconut fiber could be characterized well. By the comparison of the results recorded under the same experimental conditions one can conclude that sugarcane bagasse has higher thermal stability exhibiting 7.5, 25 and 42.5% of mass losses in the first, second and third mass loss stages, respectively. The coconut fiber looses about 10% humidity in the first decomposition stage and approximately 55% in the second stage. Some differences were found in the amount of residue: about 15% for the sugarcane bagasse and 20% residue was determined for the coconut fiber.

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