FTIR AND TGA/DTG CHARACTERIZATION OF SUGARCANE WASTE

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Abstract: Due to the huge sugarcane production in Brazil, there is also a significant amount of waste produced. The objective of this study is to characterize sugarcane residues (bagasse, leaf and husk) in terms of functional groups and thermal degradation by Fourier Transform Infrared Spectroscopy (FTIR) and Thermogravimetric Analysis (TGA/DTG). Comparing the results obtained from the leaf and bark with the bagasse, it is possible to notice similar behaviors in the thermal decomposition, differing by the number of lignocellulosic materials present in each residue. Functional groups were also similar in the three materials analyzed. These investigations are crucial since they add more trustworthy data for future research and potential biotechnological applications of the residues from sugarcane biomass.

Keywords: sugarcane; residues; lignocellulosic; FTIR; TG/DTG.

CARACTERIZAÇÃO POR FTIR E TG/DTG DO MATERIAL RESIDUAL DA CANA-DE-AÇÚCAR

Resumo: Devido à grande produção de cana-de-açúcar no Brasil, há também quantidade significativa de resíduos produzidos. O objetivo deste estudo é caracterizar os resíduos (bagaço, folha e casca) da cana-de-açúcar quanto aos grupos funcionais e degradação térmica por Espectroscopia de Infravermelho com Transformada de Fourier (FTIR) e Análise Termogravimétrica (TGA/DTG). Comparando os resultados obtidos da folha e da casca com o bagaço, é possível notar comportamentos semelhantes na decomposição térmica, diferenciando-se pela quantidade de materiais lignocelulósicos presentes em cada resíduo. Os grupos funcionais também foram semelhantes nos três materiais analisados. Tais investigações são cruciais, pois agregam dados mais confiáveis para futuras pesquisas e potenciais aplicações biotecnológicas dos resíduos da biomassa da cana-de-açúcar.

Palavras-chave: Cana-de-açúcar; resíduos; lignocelulósico; FTIR; TG/DTG.

1. INTRODUCTION

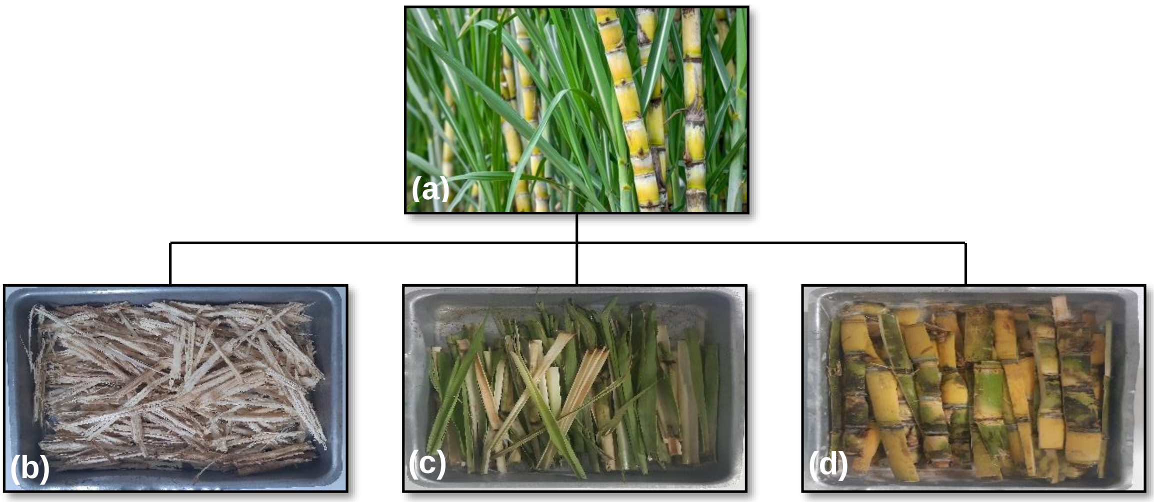
Sugarcane is an important product of Brazilian agriculture, with record harvest estimate for the year 2022 of approximately 259 million tons of biomass [1], therefore, the volume of residual material will also be quite expressive. It is possible to find in the literature possibilities of reuse of these residues, such as for the production of bio-oil, biochar, generation of electric energy and fuel [2,3,4,5].

According to Santos et al. [6], sugarcane comprises 30% of juice, which is already widely exploited both economically and with utilization studies, the remainder being composed of its residues; pomace, stem, bark and leaves; with emphasis on bagasse [7,8,9,10]. Such lignocellulosic materials are a complex structure of polymers containing cellulose, hemicellulose and lignin's [11], which when applied in a pyrolysis process can generate a large amount of compound with a large number of functional groups. Thus, the study by Fourier Transform Infrared Spectroscopy (FTIR) and Thermogravimetric Analysis (TG) is important to study the correlation of the thermal degradation of the residues with the chemical structure [12]. These residues are still little explored, with the exception of bagasse, in the literature. Therefore, the objective of this study is to characterize the residual materials of sugarcane (bagasse, leaf and bark) by FTIR-TG/DTG in order to expand the existing data with reliability for the production of future works.

2. METHODOLOGY

The waste used (bagasse, leaves and bark) (Figure 1) were purchased at the municipal market in Aracaju-SE. The materials were dried for about 24 h at 105 °C. After that, they were ground in a knife mill and reserved for further analysis. Moisture analysis was performed with an infrared balance (Shimadzu MOC63u).

Figure 1. (a) sugarcane plant; analyzed residues, (b) bagasse, (c) leaf and (d) bark.



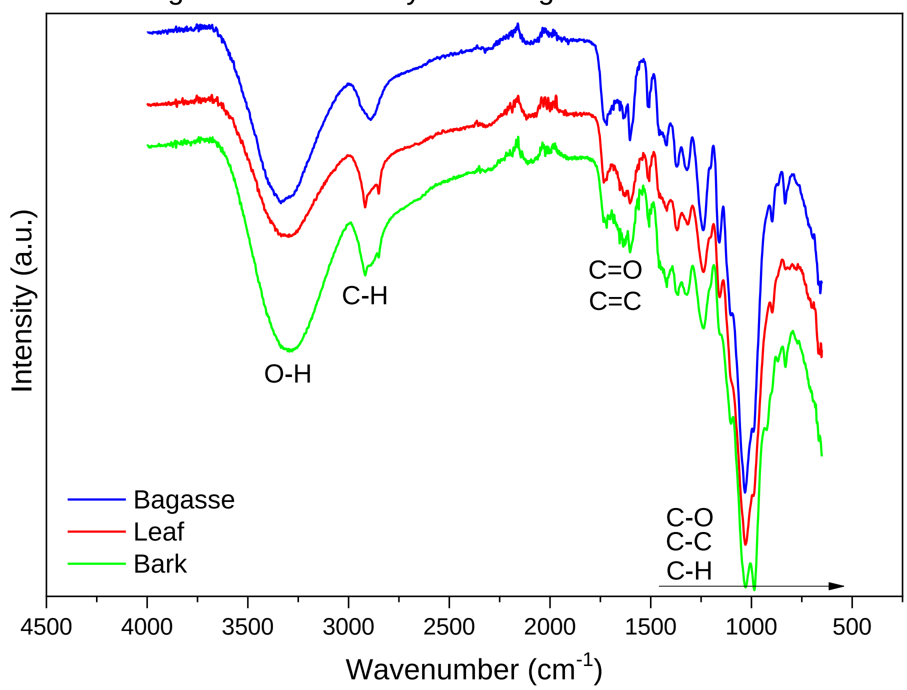
The characterization of the material was performed by Fourier Transform Infrared Spectrometry (FTIR) and thermogravimetric analysis (TGA). FTIR scans were performed at 25 °C in a Fourier transform infrared spectrometer (Agilent Cary 630). Each spectrum was collected in the wavelength range between 4000 and 500 cm^{-1} with 32 scans at a resolution of 4 cm^{-1}.

Thermogravimetric analyzes were performed in a Hitachi STA 7200 RV device. About 3 mg of samples were heated in platinum crucibles, from 25 °C to 600 °C at a constant rate of 10 °C/min in a 50 ml/min flow of nitrogen. All samples were analyzed under the same conditions: temperature range, atmosphere, and heating rate; to obtain answers with the correct conditions.

3. RESULTS AND DISCUSSION

In Figure 2 it is possible to observe the main functional groups observed in sugarcane residues. It is possible to verify that the residues presented similar peaks among themselves and, therefore, bands in the same spectrum. As the analyzes were carried out between the wavenumbers 4000 and 500 cm^{-1}, they present characteristics of the mid-infrared, as explained by Nandiyanto, Oktiani, Ragadhita [13]. Also according to Nandiyanto, Oktiani, Ragadhita [13], the mid-infrared spectrum is divided into four regions: single bond (2500-4000 cm^{-1}); (ii) triple bond (2000-2500 cm^{-1}); (iii) double bond (1500-2000 cm^{-1}) and; fingerprint (600-1500 cm^{-1}). Figure 2 shows the main clusters found in this analysis.

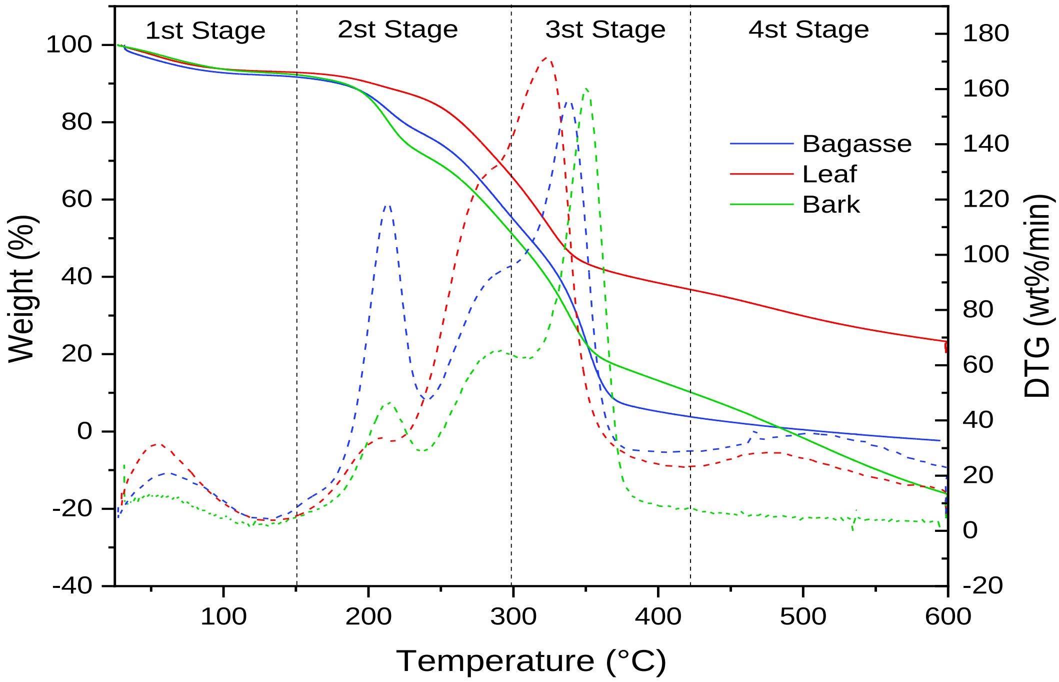
Figure 2 - FTIR analysis for sugarcane residues.



For the three residues, stretching of hydroxyl groups (O-H) and hydrogen bonds in the region 3400-3200 cm^{-1} can be observed, due to the polymeric association. For the bark, in this range, a greater amplitude of the curve is observed due to a greater presence of water in the bark in relation to the leaf and bagasse. A similar analysis was performed by Silva et al. [10] for samples of bagasse natural and chemically activated. Between 2600-3100 cm^{-1}, the unsaturated and saturated stretching of the C-H cluster is verified. Functional groups with aldehydes, ketones, esters, and carboxylic acid (1600-1735 cm^{-1}). Between 1500 and 1600 cm^{-1} is characteristic of the C=C aromatic functional group. Similar analyzes were performed by Ordonez-Loza et al. [3] in sugarcane bagasse bio-oil, in which similar bands were observed. The comparison between the residues studied here and the bio-oil could be carried out because, despite having different treatments, they are the same material. Below 1500 cm^{-1} is the fingerprint region where alcohols, esters, ethers, and aromatic rings can be found. The analyzes are also in agreement with the results obtained for the sugarcane straw [14].

In general, lignocellulosic materials (a combination of cellulose, hemicellulose and lignin) are complex and each part can still be considered a mixture of biopolymers. Seye, Cortez, Gomez [11] explain that the analysis of the thermal decomposition of this type of material is based on the fact that the main families of polymers that make up the biomass present different rates of decomposition temperatures. Seye, Cortez, Gomez [11] consider the beginning of the decomposition of hemicellulose and cellulose below 330 °C depending on the experimental conditions and the heteropolymers present in the biomass, it is worth mentioning that hemicellulose decomposes before cellulose; and lignin above 300°C.The curves with the thermal profiles of the sugarcane residues are presented in Figure 3, indicating the stages of degradation of the biopolymers.

Figure 3 - Thermal degradation curves of sugarcane waste materials.



In the three residues, is the first stage (up to 150 °C) characteristic of the removal of moisture from the materials, with a slight loss of mass. Up to 200 °C, in addition to the removal of water, alcohols, acids and some aromatic oxygenates such as monophenols and furans are lost [3]. According to Santos et al. [6], between 230 and 260 °C the degradation of cellulose and hemicellulose occurs and the beginning of the degradation of lignin, between 260 and 290 °C is considered the end of hemicellulose decomposition (end of the second stage). Observing the DTG curves for the three residues (in the third stage), the difference in the amplitude in the peaks (~230 °C) in the three materials can be noted, this may be related to the amount of lignin present in each biomass [11]. Entering the second stage (300-420 °C), cellulose degradation occurs with different peaks for the three residues; it is noticed that the sugarcane leaf degrades more quickly, having a less accentuated weight loss than the others. In the fourth stage (from 420 °C) is the final degradation of lignin, which has a wide temperature range, starting its degradation at temperatures above 220 °C according to Ponte et al. [9].

4. CONCLUSION

It is concluded that the analyzes of the functional groups are similar for the studied biomasses, however, there are differences regarding the behavior during the thermal degradation; with the leaf degrading faster than the bark and bagasse, possibly due to a lower percentage of lignocellulosic materials present in the leaf. Sugarcane residues have several uses and biotechnological potentials. Thus, studies that promote more knowledge about the behavior in the face of thermal degradation and the variability of existing functional groups are guarantors of reliability on the existing data, in addition to exploring more applicability of these biomasses.

Acknowledgments

This study was financed in part by the Conselho Nacional de Desenvolvimento Científico e Tecnológico, the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) – Finance Code 001.

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