

STUDY OF COMPOSITIONAL AND MORPHOLOGICAL ANALYSIS OF LOCAL BIOMASS WITH AIM TO EXPLORATION OF THEIR ENERGY POTENTIAL

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ABSTRACT

Biomasses of sugarcane straw (Sample PC), banana straw (Sample PB) and brewer's exclusion (Sample MT) were subjected to a structural and compositional analysis in order to study the relationship between their composition and the quality of the bio-oil produced from fast pyrolysis. The samples were chemically defined to obtain lignin, cellulose and hemicellulose contents. In addition, they were also detailed by X-ray diffraction, thermogravimetric analysis, scanning electron microscopy and Fourier transform infrared spectroscopy. The results showed that the PC and PB Samples had a high cellulose and hemicellulose content, tending to form a better-quality bio-oil, however the ash samples could cause coke. Crystallographic planes referring to cellulose I were observed. The surfaces of the samples did not present pores, denoting a low surface area. The FTIR showed bands in regions that indicate the presence of aromatic compounds and other groups that refer to lignin and hemicellulose. Four stages of observation were identified, with good mass loss being observed in the region between 400-500°C for all samples. Therefore, Samples PC and PB will be the most promising biomasses for delivering bio-oil with a low oxygenate content, expanding the application of this biofuel

Keywords: Bio-oil. Pyrolysis. Biomass. Composition.

1. INTRODUCTION

To meet the increase in energy demand triggered by population growth and urbanization processes, oil became the pillar of civilization. There is no shortage of everyday examples of consumer goods derived from this dark liquid, ranging from chemical inputs to energy generation for industries. The major disadvantage in using this resource of fossil origin lies in its contribution to the intensification of environmental problems associated with global warming, due to emissions of greenhouse gases (NO_x, SO_x, CH₄ and CO₂). Given the severity of the damage caused to the environment, it is necessary to diversify the global energy matrix through the adoption of alternative sources such as lignocellulosic biomass. Around 105 million tons of biomass are generated annually (1), including agricultural, industrial and municipal waste, which has a high potential for replacing fossil sources due to its low cost and abundance. Among the existing processes used to valorize biomass, pyrolysis has stood out because it is a consolidated and easy-to-execute procedure, which involves burning plant material in an oxygen-poor environment, converting it into biogas, charcoal and bio-oil (1). Among them, bio-oil is the most promising to be used as a fuel, due to the similarities with the petroleum derivatives currently used, allowing its use alone or mixed with fossil fuels, in order to reduce the environmental impact (2). Bio-oil consists of a complex mixture of several organic compounds such as phenols, alcohols, aldehydes, esters and oligomers derived from lignin, resulting in a dark oil. One of the main problems limiting the application of bio-oil is the high content of oxygenates found in its constitution. It is known that biomasses rich in lignin contribute significantly to a high yield of phenols, while biomasses rich in hemicellulose and cellulose tend to produce bio-oil with a low oxygenate content (3). In this context, the present work aims to study the composition and the morphology of the biomasses sugarcane straw (Sample PC), brewery residue (Sample MT) and banana straw (Sample PB) aiming at their future application for the production of bio-oil by fast pyrolysis, thus contributing to the national energy production.

2. MATERIAL & METHODS

2.1. Preparation of *in natura* biomass

The PC, MT and PB samples were subjected to washing processes in running water to remove surface impurities, then dried at 60°C for 24h, crushed and sieved (32-60 mesh).

2.2. Chemical Characterization

Chemical characterization of samples was performed according to the National Renewable Energy Laboratory (NREL) standard method (4).

2.3. X-ray diffraction (XRD)

-ray diffraction analyzes were carried out on an X-ray diffractometer, Shimadzu, model XRD-6100, with radiation ($K\alpha$) of copper ($\lambda = 1.5418 \text{ \AA}$), in the range of 10 to 80° , with speed of $10^\circ \cdot \text{min}^{-1}$.

2.4. Thermogravimetric Analysis (TGA)

Thermogravimetric analyzes were conducted on Shimadzu DTG-60 equipment, with a heating ramp of $20^\circ \text{C}/\text{min}$ up to 700°C , in an inert atmosphere (N_2), with a flow rate of $20 \text{ mL}/\text{min}$.

2.5. Scanning electron microscopy (SEM)

The morphological analysis of biomass samples was carried out using a Tescan model Vega 3 LMU scanning electron microscope.

2.6. Fourier Transform Infrared Spectroscopy (FTIR)

A spectrophotometer was used, Perkin Elmer 100 FT-IR, model Spectrum 100S, operating in the region of 4000 to 450 cm^{-1} , with a resolution of 4 cm^{-1} and 32 accumulations per spectrum.

3. RESULTS & DISCUSSION

3.1. Chemical Characterization

The MT sample has the highest lignin content (Table 1), which can favor the production of bio-oil rich in oxygenates, such as phenols, aldehydes, ketones, carboxylic acids and alcohols. The presence of these compounds is not desirable for obtaining a good quality biofuel, since the presence of carboxylic acids makes the bio-oil corrosive (5). Furthermore, oxygenates such as phenols are highly reactive, resulting in storage problems due to chemical instability (6). Biomasses rich in lignin also favor the formation of charcoal, as its decomposition is hampered by the high thermal stability it has (6). On the other hand, Samples PC and PB exhibited higher cellulose and hemicellulose contents compared to brewing residue, showing the greatest tendency to produce bio-oil with a low oxygenate content (6). Sample PC presented the highest ash content, indicating the possibility of formation of species with high molecular weight similar to coke (7). Ash consists of traces of alkaline metals, alkaline earth metals and other metals, such as molybdenum and zinc, and can catalyze or sometimes even inhibit the decomposition of the majority fractions of biomass (8). On the other hand, the PB Sample exhibited the highest extractive content. During the thermal degradation of biomass, this fraction is capable of promoting the formation of light molecules such as water, CO and CO_2 at low temperatures, in addition to catalyzing secondary reactions that lead to the release of carboxylic acids (9). The presence of water in bio-oil causes a reduction in its HHV, distancing its properties from those found in fuels such as raw diesel.

Table 1. Chemical composition of the main constituents of *in natura* biomasses.

Biomass	Cellulose(%)	Hemicellulose(%)	Lignin(%)	Extractives (%)	Ashes (%)
PC	28,98	17,59	18,47	$16,124 \pm 0,006$	$5,30 \pm 0,04$
MT	15,60	14,66	27,19	$24,5 \pm 0,3$	$1,061 \pm 0,002$
PB	22,70	19,10	17,20	$28,431 \pm 0,005$	$1,345 \pm 0,005$

3.2. X-ray diffraction (XRD)

Intense diffraction peaks were observed at $2\theta = 22^\circ$, in the diffractograms of all Samples, corresponding to the crystallographic planes of cellulose I (002), which is cellulose in its native form (10). The pyrolysis of lignocellulosic biomasses that have cellulose I as one of their constituents can lead to the production of bio-oil rich in anhydrous sugars and derivatives, furfural, furans and light oxygenated compounds (hydroxy acetaldehyde and 1-hydroxy-2-propanone) (11). In this process, cellulose also interacts with lignin to form new compounds such as benzene, phenol and p-xylene (12). However, only in Samples PC and PB were peaks identified at $2\theta = 15^\circ$, which also corresponds to one of the crystallographic planes of cellulose I (110) (12)

3.3. Scanning electron microscopy (SEM)

The surface of the three samples (Figure 1) appears to be free of pores, resulting in a low surface area, characteristic of fresh biomass (13). The PC Sample presented a voluminous fibrous structure, resulting from its higher cellulose content (13). An internal pore structure resembling honeycombs ($109 \mu\text{m}$) was also observed. For the MT Sample, no pores or cracks were observed, a fact that can be attributed to the presence of wax and the high lignin content in its composition (14). Some white dots can be identified on the surfaces of all analyzed samples, which indicate the presence of non-volatile elements such as magnesium (Mg), aluminum (Al), and other volatile elements such as chlorine (Cl) and potassium (K). On the surface of the PC Sample, biomass with the highest ash content, this can be clearly observed.

Figure 1. Scanning electron microscopy for MT, PB and PC samples

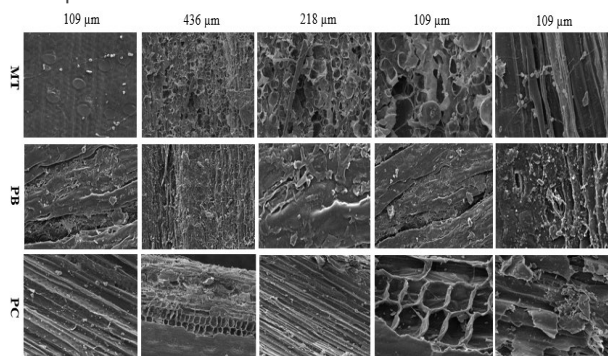
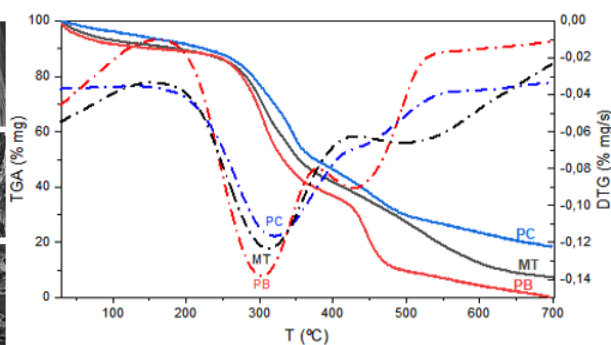


Figure 2. TGA/DTG curves (dashed) for *in natura* biomasses.



3.4. Fourier Transform Infrared Spectroscopy (FTIR)

Absorption bands characteristic of C-H bonds in carbon belonging to the aromatic ring (900–690 cm^{-1}), present in lignin, were identified, as well as bands characteristic of the methyl group (1450-1373 cm^{-1}), typical of lignin, cellulose and hemicellulose (Figure 2). Furthermore, bands were observed at 1635 and 1728 cm^{-1} , possibly of carbonyl (C=O) present in cellulose and lignin, and an O-H band at 3441 cm^{-1} , which may be due to the phenol group or the alcohol, associated with lignin (15).

3.5. Thermogravimetric analysis

The TGA curves (Figure 2) obtained for biomasses exhibit four main stages: (i) evaporation of moisture and decomposition of extractives, from room temperature to approximately 210 °C; (ii) degradation of cellulose and hemicellulose between 210 and 402 °C; (iii) decomposition of cellulose and part of the lignin, between 402 and 506 °C; (iv) decomposition of the remainder of the lignin, from 506 to 629 °C. From the TG/DTG curves, it is also possible to determine the pyrolysis temperature. Considering that fast pyrolysis, ideal for the production of bio-oil, is carried out at temperatures that are neither too high nor too mild, it can be inferred that the range of 400 to 500 °C is the most suitable for the pyrolysis of the biomasses under study, for ensuring good mass loss (around 70% for the MT and PC samples and 90% for the PB sample) and maximizing the yield of the desired liquid phase.

4. CONCLUSION

The techniques adopted made it possible to verify the possible applicability of biomass in fast pyrolysis, for the production of bio-oil. Among the biomasses studied, sugar cane straw and banana straw are the most promising for the production of bio-oil through pyrolysis, as they tend to produce bio-oil with a low oxygenate content, helping to mitigation of problems associated with corrosion caused by the presence of high concentrations of oxygenated compounds, thus enabling its application as biofuel.

5. REFERENCES

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