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BIOENERGY VALORIZATION OF THE BLENDS (FOOD WASTE AND URBAN PRUNINGS) AS A POSSIBLE CANDIDATE FOR SOLID BIOFUELS PRODUCTION

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Abstract. *The exacerbated consumption of natural resources directly impacts food waste - in Brazil this fact is a serious socioenvironmental issue. Another problem faced by large cities is urban afforestation. Although it is a common practice and beneficial, their pruning service results in a significant amount of organic solid waste. The present study evaluated food waste (FW) and urban prunings (UP), regarding their potential for bioenergy production. Physicochemical and morphological properties were employed for the pure samples (100%UP and 100%FW), and their blends in the ratios (75%UP:25%FW; 50%UP:50%FW; and 25%UP:75%FW). XRD analysis showed that the pure samples and blends constitute an amorphous and reactive biomass for the thermoconversion process. SEM images detected structures with high levels of disorder for all samples. From FTIR, a predominance of functional groups and/or linkages formed by carbon, hydrogen, and oxygen were detected, elements these of extreme importance for the biofuels generation. The proximate analysis identified the contents of moisture (W < 6.0%), volatile materials (VM > 79.0%), fixed carbon (FC > 7.0%), and ash (ASH ≈ 8.0%), reflecting optimal operating conditions in thermochemical systems (combustion, pyrolysis, and/or gasification). By calorimetry, it was found average values for Higher Heating Value (16.96±0.69 MJ kg^{-1}) and Lower Heating Value (15.53±0.06 MJ kg^{-1}). Samples with higher percentages of UP (100%UP and 75%UP) presented higher HHV (≈ 17.69±0.25 MJ kg^{-1}). The wastes studied and their blends showed significant energy properties. These are justified by presence of large quantities of volatile materials and fixed carbon, and low quantities of inorganic elements that are potentially harmful to the environment and can deteriorate the equipment used during thermoconversion processes.*

Keywords: *biomass, green energy, natural resources, thermoconversion, thermal systems.*

1. INTRODUCTION

The exacerbated population growth has led to some anthropic actions on the planet. According to the United Nations (UN, 2022), the population will have surpassed 8 billion and is expected to reach 9 billion by 2037. Due to global densification, the need for water and food increases for the survival of humanity. Due to this, some serious effects of the exploitation of nature may occur, such as the reduction of non-renewable resources, loss of biodiversity, and climate change (dos Santos *et al*., 2020).

In this sense, more than 2 billion tons of food are thrown away every year in the world, corresponding to about one third of the food produced (Cao *et al*., 2021). In this context, Brazil is the seventh most populous country on the planet

(≈ 214 million inhabitants), being one of the ten countries that waste the most food (Borges *et al*., 2019). This waste disposed of incorrectly generates leachate, a substance responsible for the contamination of surface water, groundwater, and soil (Duarte *et al*., 2022). Although incineration and the use of landfills are common practices, such methods are increasingly criticized in terms of sustainable development (Qin *et al*., 2021).

The generation of municipal solid waste in Brazil increased from 67 to 79 million tons between the years 2010 and 2019 (Duarte *et al*., 2022). From this waste, about 45% is composed of organic fraction, corresponding to approximately 36 million tons of urban pruning (UP) and food waste (FW) (Duarte *et al*., 2022). Thus, in addition to food waste, urban prunings also represent a huge problem for cities, such as inadequate disposal.

In this scenario, the present work aims to analyze the physicochemical (ultimate and proximate analysis, X-ray diffraction - XRD, Fourier transform infrared - FTIR, and calorimetry analysis) and morphological (scanning electron microscopy - SEM images) properties were employed for the pure samples (100%UP and 100%FW), and blends in the different proportions (75%UP:25%FW; 50%UP:50%FW, and 25%UP:75%FW).

2. MATERIALS AND METHODS

The following subsections report the main experimental steps for the physicochemical and morphological characterization of the biomasses from urban prunings, food waste and their mixtures, according the methodology presented by Cruz (2015).

2.1 Samples selection and preparation

The food waste (100%FW) was collected in a market located in São Luís (MA) city (latitude: -2.542218; longitude: -44.213387), and the urban prunings (100%UP) were collected in a public square located in São Luís (MA) (latitude: -2.539795; longitude: -44.214367). In the preparation stage, the samples were washed in running water to remove impurities. Afterwards, these went through a drying process in a sterilization oven (Tecnal TE-393/80L) for a period of 120 h at 70 °C for the food waste sample and 48 h at 60 °C for the urban prunings. After this process, the biomasses were ground in a knife mill (Tecnal R-TE-648) to reduce them into a particle size range. The particles were sieved to an average particle size of ≈ 275 µm (ASTM meshes 50 and 60), and blends were formed between the two biomasses (75%FW:25%UP; 50%FW:50%UP, and 25%FW:75%UP). Thus, both pure samples and blends were used in the study.

2.2 Ultimate Analysis

The chemical compositions of the biomasses were obtained using Elementary Analyzer (Perkin Elmer, 2400 CHNS-O). Thus, the carbon (C), Oxygen (O), Hydrogen (H), Nitrogen (N), and Sulfur (S) contents of the samples were exposed. The oxygen percentage is calculated by the difference of 100%.

2.3 Proximate Analysis

Proximate analysis was applied to determine the moisture (W), volatile materials (VM), ash (ASH), and fixed carbon (FC) contents of the samples. For this study, an adaptation of the methodology described by Torquato *et al*. (2017) was performed, which is as described below.

First, 3.0 g of sample of the biomasses were used, previously cleaned, dried, ground and deposited in a porcelain crucible (≈ 36.7 g) with a capacity of 50 mL. The INTI MLVC 1300/7 vacuum muffle furnace (220 V, 4,000 W, 18 A, with a maximum temperature of 1800 °C) with electronic controller FLYEVER FE50RPN (90-240 VAC, 9 W, 50/60 Hz) was employed to perform this step. The experiments were done in triplicate and the average values of the proximate compositions will be exposed.

The first composition obtained was the percentage of moisture. For this, the initial mass (m_0) of 3.0 g was raised from room temperature (≈ 30 °C) to 110 °C and held at this temperature for a 30-minute isotherm at a heating rate of 10 °C min $^{-1}$. After this, the sample was cooled naturally to the initial temperature (≈ 30 °C), the resulting mass is weighed (m_1). Eq. (1) shows the calculation for the percentage moisture (W) (ASTM D3173-00, 2000):

$$\%W = \frac{m_0 - m_1}{m_0} \cdot 100\% \tag{1}$$

To find the volatile materials, the sample on a dry basis (m_1) was subjected to a temperature of 600 °C for a 30-minute isotherm at a heating rate of 10 °C min^{-1}, and then cooled naturally to room temperature. The resulting mass is weighed proximately after decomposition of the volatile materials (m_2). Thus, the content of volatile materials (VM) is described by Eq. (2) (ASTM D3175-02, 2002):

$$\%VM = \left[\left(\frac{m_0 - m_2}{m_0}\right) \cdot 100\%\right] - \%W \tag{2}$$

For the ash content (ASH), the resulting sample after release of volatile materials (m_2) and fixed carbon is subjected to a temperature of 900 °C for a 7-minute isotherm at a rate of 10 °C min^{-1}. Then the sample is cooled naturally to room temperature, and its mass is measured (m_3). Eq. (3) refers to the percent ash of the samples (ASTM D3174-02, 2002):

$$\%ASH = \frac{m_3}{m_0} \cdot 100\% \quad (3)$$

The fixed carbon (FC) is found by the difference in 100% of the other components quantified by the process as showed in Eq. (4) (ASTM D3172-07A, 2007):

$$\%FC = 100\% - \%W - \%VM - \%ASH \quad (4)$$

2.4 Calorimetry Analysis

The Higher Heating Value (HHV) is the quantification of the heat produced by biomass in relation to its mass (Silva *et al*., 2019). The calorimetric analysis, therefore, was performed experimentally using a calorimetric pump (IKA C200) and in duplicate. In this sense, the measurement of such property represents the amount of heat that the sample transfers to the water present in the pump, in a combustion process (Flowers *et al*., 2021). The combustion of biomass is an exothermic reaction, *i.e*., the heat transferred to the water causes a change in temperature. Thus, knowing the heat capacity of the pump (C_{bomb}) and the temperature change of the water (ΔT_{H_2O}), the HHV also can be calculated through Eq. (5) (Flowers *et al*., 2021):

$$HHV = C_{bomb} \cdot \Delta T \quad (5)$$

For calculating the Lower Heating Value (LHV), the empirical equation using proximate analysis and described by Erol; Haykiri-Acma; Küçükbayrak (2010) was applied, which is expressed by Eq. (6):

$$LHV = 5{,}9 + 0{,}836FC - 0{,}0116CF^2 + 0{,}00209VM^2 + 0{,}0325ASH^2 \; (MJ\,kg^{-1}) \quad (6)$$

2.5 Fourier transform infrared spectroscopy (FTIR)

The FTIR analysis was applied in the range of 4000 to 400 cm^{-1} in a Shimadzu Fourier Transform spectrophotometer (IR-Prestige-21), in transmittance mode. The analyses were performed on KBr pellets for a particles size of ≈ 275 µm:

2.6 X-Ray diffraction (XRD)

The function of X-ray diffraction is to evaluate the crystallography of the sample structures. For this, an X-ray diffractometer (Bruker D8 advance) was used applying CuKα radiation (λ = 1.541 Å, 40 kV - 40 mA). The diffraction angle (2θ) varied from 5 to 70°, with an increment of 0.05° s^{-1}.

From the above, the crystallinity index (%CI) was calculated using Segal's method, which is represented by Eq. (7). Where, I_{002} indicates the intensity of the crystalline region and I_{am} refers to the intensity of the amorphous region (Yu *et al*., 2009). The analyses were performed both on FW and UP pure biomasses and their blends:

$$\%CI = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \quad (7)$$

2.7 Scanning Electron Microscopy (SEM) images

Morphological and structural analyses were made by means of Scanning Electron Microscopy (Leo Electron Microscope 440). The biomasses were arranged on an aluminum support with a double-sided adhesive tape produced from carbonaceous material and subjected to a gold bath. Magnified images at 200 times were obtained.

3. RESULTS AND DISCUSSION

The values for ultimate, proximate, and calorimetry analyses are shown in Table 1.

Table 1. Ultimate, proximate, and calorimetry analyses for the urban prunings, food waste, and their blends in different proportions.

Properties	**100%UP**	**75%UP:25%FW**	**50%FW:50%UP**	**25%UP:75%FW**	**100%FW**
			Ultimate Analysis		
Carbon (%C)	46.94±1.93	45.17±1.45	43.41±0.97	41.64±0.48	39.87±0.00
Hydrogen (%H)	5.80±0.14	5.91±0.11	6.03±0.07	6.14±0.04	6.25±0.00
Oxygen (%O)	45.78±0.00	47.39±0.00	49.00±0.00	50.60±0.00	52.21±0.00
Nitrogen (%N)	1.48±0.05	1.53±0.04	1.58±0.03	1.620.01	1.67±0.00
Sulfur (%S)	n.d.	n.d.	n.d.	n.d.	n.d.
			Proximate Analysis		
Moisture (%W)	5.21±0.13	4.59±0.25	4.06±0.08	3.88±0.23	3.57±0.07
Volatile Materials (%VM)	80.10±0.94	79.47±0.42	79.81±0.51	79.05±0.63	79.76±0.53
Fixed Carbon (%FC)	8.57±1.03	9.18±0.54	7.96±0.46	8.97±0.53	8.16±0.46
Ash (%ASH)	6.12±0.15	6.76±0.08	8.17±0.07	8.09±0.05	8.51±0.05
			Calorimetry Analysis		
HHV (MJ kg^{-1})	17.91±0.06	17.48±0.00	16.72±0.05	16.58±0.06	16.10±0.07
LHV (MJ kg^{-1})	15.03±0.31	15.03±0.31	15.50±0.20	15.85±0.21	15.80±0.16

n.d. - not detected or below equipment detection limit.

3.1 Ultimate Analysis

The values of elementary compositions for food waste were close to those found by Singh and Yadav (2021), in which the compositions were: 45.71%, 6.72%, 41.04%, and 2.91% for carbon, hydrogen, oxygen, and nitrogen, respectively. Thus, presenting absolute differences (in relation to the data of this study) of the order of 5.84%, 0.47%, 11.17%, and 1.24% for C, H, O, N, and S, respectively. For the urban pruning samples, Mazzonetto, Obata, and Almeida (2016) obtained values equal to 49.20%, 6.00%, 43.00%, and 0.04% for carbon, hydrogen, oxygen, and nitrogen, respectively. The absolute differences for this studied biomass resulted in 2.26%, 0.20%, 2.78%, and 1.44% for C, H, O, N, and S, respectively.

The values for the nitrogen and sulfur elements presented for both biomasses were below 2.00%. This is a positive point for application of these samples as solid biofuels, since the presence of N and O is directly related to the production of SO_x and NO_x emissions, which are considered air pollutant. Low concentrations of these two elements represents a decrease in air pollutants released during the combustion process of these biomasses (Cruz *et al*., 2021). In addition, the absence of these elements decreases the degradation of combustion equipments, since these can deteriorate the metallic parts of oven and/or boilers and impair heat and mass transfer in these systems (Cruz, 2015).

3.2 Proximate Analysis

From the results of the proximate analysis, it becomes noticeable that the percentage of moisture (W) was higher in urban prunings when compared to food waste, *i.e.*, 5.21% and 3.57%, respectively. For the mixtures, this characteristic was maintained, therefore, for larger proportions of tree prunings (75%UP), the moisture was higher than the other blends (25%UP and 50%UP). This is of extreme importance, since moisture content has a negative influence during the application of biomasses as solid fuel (Santana Junior *et al*., 2020). It is interesting to highlight that combustion and pyrolysis processes are exothermic reactions and water evaporation is a strongly endothermic process, and a greater amount of moisture implies limiting the self-sufficiency of these reaction processes (Bhaskar *et al*., 2011). Furthermore, amounts higher than 65.00% moisture seriously affect the use of biomass as fuel, since the energy released during combustion process will be insufficient in relation to that used for evaporation, and the increase in water temperature, leading to the loss of combustion self-sufficiency (Pasquini, 2014).

Volatile materials (VM) are composed of combustible gases (*e.g.*, C_xH_y, carbon monoxide or H_2) and a non-combustible part (CO_2, SO_2, and NO_x). Biomass that presents higher volatile materials content also presents higher thermal reactivities in the combustion and/or pyrolysis processes, and consequently, the ignition point and heating value of these biomass will also be more representative (Rasam *et al*., 2020). In this sense, when analyzing Table 1, the urban pruning samples indicate higher percentages of volatile materials when compared to the biomass formed by food waste, *i.e*., 80.10% and 79.76%, respectively.

The fixed carbon (FC), along with the ash contents (ASH), represents the amount that remains after the process of removing moisture and volatile materials from the biomass. The FC is directly proportional to the calorific value, *i.e*., the lower its quantity, the lower the heating value (Brun *et al*., 2018). Therefore, the quality of combustion is related to this quantity. Through the proximate analysis, the highest amount of FC is found in the 75%UP:25%FW sample and the lowest amount in the 50%UP:50%FW biomass, *i.e*., 9.18% and 7.96%, respectively.

The ash content represents the solid residue resulting from the complete thermal degradation of the organic material of the biomass, its primary constituents are silica, aluminum, iron, and calcium (small amounts of magnesium, titanium, sodium, and potassium also may be found) (Basu, 2013). Such components, despite being found in small quantities in biomasses, can cause serious problems, such as fouling and/or corrosion in boilers and/or gasifiers (Romero, 2022). In addition, they are not decomposed in the thermoconversion process, which causes the reduction of the UHV (Useful Heating Value) (Santana Júnior *et al*., 2020). The lowest ash contents were reached for the pure samples of urban prunings, *i.e*., 6.12%.

3.3 Calorimetry Analysis

The heating value is closely related to the amount of calories released by the material in a situation of complete combustion (Singh and Yadav, 2021). Thus, when a complete combustion of a unit of fuel occurs, it releases thermal energy that is usually measured in energy per unit mass [MJ kg^{-1}]. The heating value can be divided into Lower, Higher, and Useful Heating Value (Nogueira; Lora, 2003).

The Higher Heating Value (HHV) indicates the amount of energy that a unit of biofuel has in relation to the amount of mass, representing the capacity of biomass to produce biofuel (Sahoo *et al*., 2022) The average of the HHV values was equal to 16.96±0.69 MJ kg^{-1}. The HHV for the pure sample of food waste was close to that described in another study on food waste, in which the value of this property was 15.97±0.07 MJ kg^{-1} (Melo *et al*., 2023). Evidencing, in this sense, a percentage difference of only 0.81%. For urban prunings, the HHV compared with data from the literature was less than 14.14% (da Silva *et al*., 2021).

From the empirical equation Eq. (6) adapted of Erol *et al.* (2010), it was possible to identify the LHV. The Lower Heating Value (LHV) disregards the energy used to evaporate the intrinsic moisture of the biomass. Being better to portray the quality of the fuel (Quirino, 2002). The average LHV for the biomasses was equal to 15.53±0.35 MJ kg^{-1}. From the above, there was a decrease in the heating value from the wet to the dry sample of 8.39%. Thus, the dehydration process decreases the calorific capacity of the biomasses in a minor way.

There is also a greater decrease in heating value for the pure sample of urban prunings (16.08%) and less for food waste (1.86%). This confirms the data obtained in the proximate analysis, in which, 100%UP presents higher moisture in relation to 100%FW. This trend is found in the blends, indicating more intense decreases in heating value for biomasses with larger amounts of urban prunings, in order, 25%UP:75%FW < 50%UP:50%FW < 75%UP:25%FW.

3.4 Fourier transform infrared spectroscopy (FTIR)

The Fourier transform infrared spectroscopy was essential to identify main functional groups in the studied biomasses. Figure 1 represents the spectrum obtained for each of the pure samples and its blends.

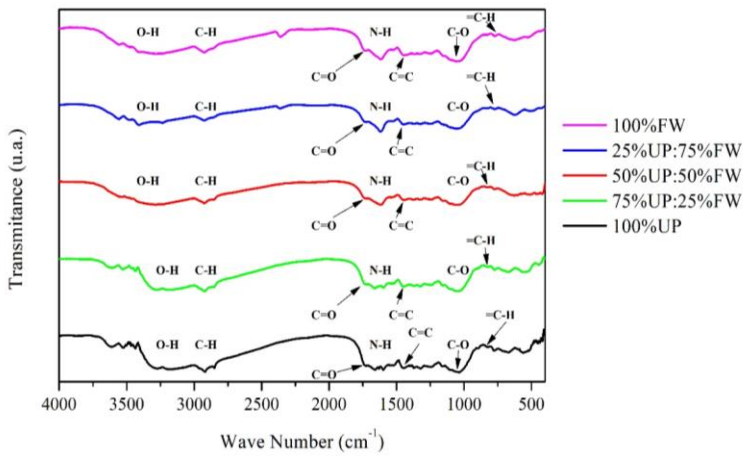

Figure 1. Infrared spectrometers by Fourier Transform for the urban prunings, food waste, and its blends.

The stretching vibration of the hydroxyl group (O-H) and water can be identified in the range 3200-3600 cm^{-1} for all evaluated biomasses (Frost *et al*., 2001). Despite undergoing a drying step, the samples still exhibited residual or intrinsic moisture (HUANG *et al*., 2020). In addition to water, this group indicates the presence of alcohols, phenols, and carboxylic acids (Bouaik *et al*., 2021). Alkanes are identified in the range 2850 - 3000 cm^{-1}, exposed by the stretching vibration of the C-H bond (Chintala *et al*., 2017). The vibration of the C=O groups indicates the appearance of carboxylic acids, esters, ketones, and aldehydes in the biomasses in the range 1750-1719 cm^{-1} (Ellerbrock and Gerke, 2021). Amides were detected by N-H vibration at 1550-1640 cm^{-1} (González *et al*., 2020). The aromatic groups are verified by C=C group stretching vibrations between 1400-1600 cm^{-1}. The C-O bond in the range 1050-1150 cm^{-1} implies the occurrence of alcohol groups. Alkenes are recognized by the =C-H bond between 675-1000 cm^{-1} (Naik *et al*., 2017). The wavenumber for each of the biomasses is shown in Table 2.

Table 2. Main functional groups present in the urban prunings, food waste, and its blends.

	Wavenumber (cm^{-1})				
Functional Groups	**100%UP**	**75%UP:25% FW**	**50%UP:50% FW**	**25%UP:75% FW**	**100%FW**
O-H	3414	3407	3440	3440	3383
C-H	2918	2925	2925	2920	2925
C=O	1740	1737	1735	1733	1735
N-H	1599	1596	1618	1618	1615
C=C	1447	1449	1449	1449	1447
C-O	1052	1052	1053	1052	1058
=C-H	829	826	826	771	769

3.5 X-Ray diffraction (XRD)

From the X-ray diffraction results (Figure 2) for the pure samples (UP and FW) and their blends, the crystallinity indices were calculated Eq. (7). The peaks of the crystalline region ranged from 21.74 to 22.26°, while the amorphous regions were detected in the range of 18.27 to 18.65° for 2θ, as shown in Table 3.

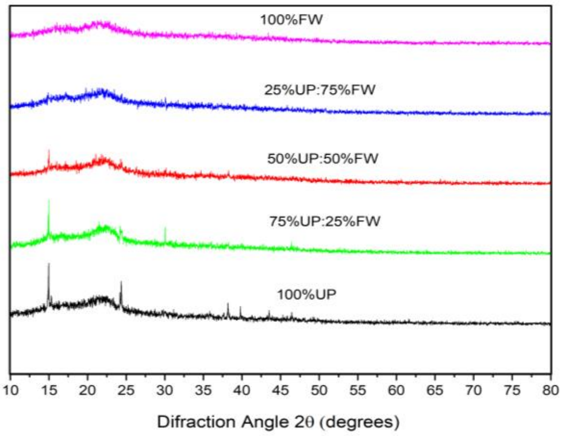

Figure 2. X-Ray diffractograms for the samples of urban prunings, food waste, and its blends

Table 3. Crystallinity index (%CI) for the samples of urban prunings, food waste, and its blends.

Properties	**100%UP**	**75%UP:25%FW**	**50%FW:50%UP**	**25%UP:75%FW**	**100%FW**
I_{002} (°)	21.78	22.26	21.88	21.89	21.74
I_{am} (°)	18.47	18.65	18.58	18.27	18.61
IC (%)	26.28	37.49	31.18	45.98	41.02

The crystallinity index for the pure sample of urban prunings resulted in a value equal to 26.28%, which was close to that value found by Silva *et al*. (2021) for the same sample, describing a percentage difference of only 1.28%. This sample presented many amorphous structures, which may mean a low amount of cellulose (crystalline structure) in these structures (Wang *et al*., 2017). For the pure food waste sample, the %CI showed a higher value, *i.e*., 41.02%, but also presented large amounts of amorphous structures compared to crystalline ones. The blends also showed low crystallinity values, varying from 31.18% to 45.98%.

Another explanation for the low crystallinity index of the materials is their pretreatment through a milling process (responsible for breaking the crystalline structures) (Hu *et al*., 2020). In general, all samples were identified with low %CI. Such characteristic favors the thermal processes, since considerably amorphous substances present higher reactivity when compared to the crystalline substances (Xu *et al*., 2013).

3.6 Scanning Electron Microscopy (SEM) images

Using Scanning Electron Microscopy (SEM) images, it was possible to obtain the morphological and surface characterization of the pure samples (100%UP and 100%FW) and blends (75%UP:25%FW; 50%UP:50%FW, and 25%UP:75%FW). For this, images with 200x magnification were used, facilitating the visualization of the structural characteristics of the biomasses (Figure 3).

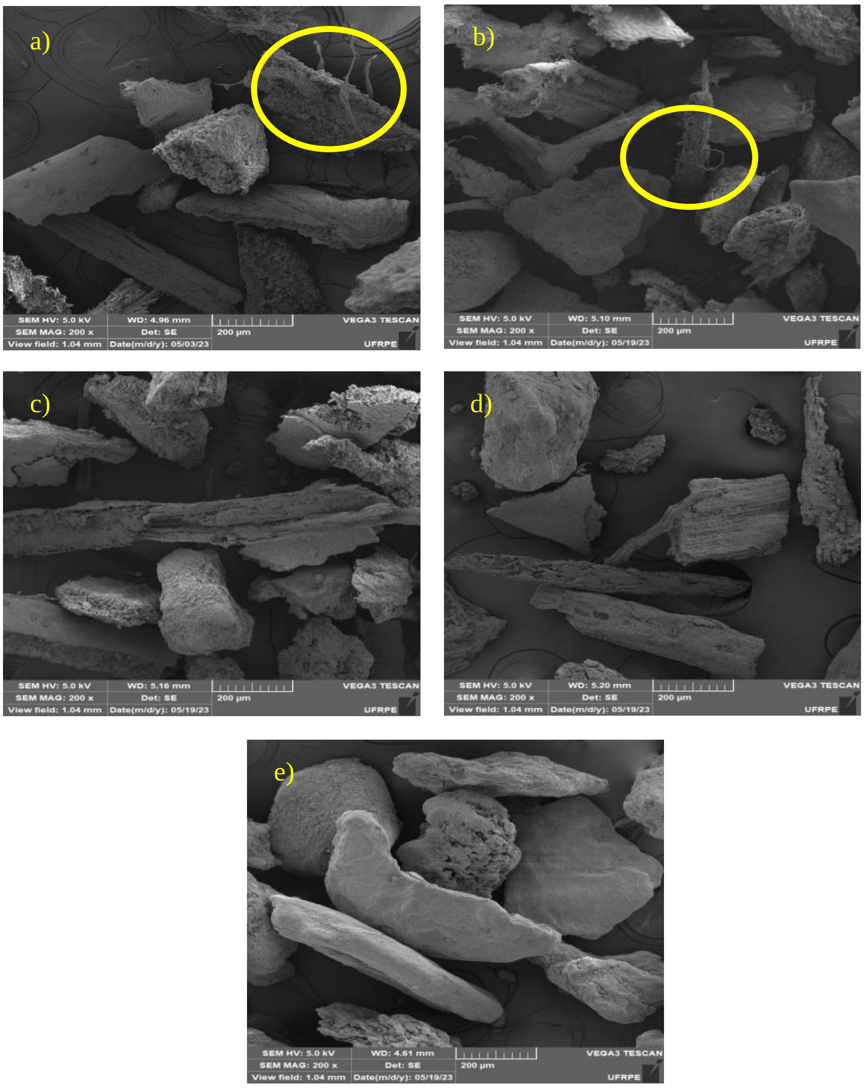

Figure 3. SEM micrographs for the: (a) 100%UP, (b) 75%UP:25%FW, (c) 50%UP:50%FW, (d) 25%UP:75%FW, and (e) 100%FW. All the images used presented the same 200x magnification.

The 100%UP sample showed a high level of structural disorder and fragmentation, besides showing some fibers of the material (yellow circle in Figure 3a). Such aspects were also detected by Silva *et al*. (2021) for sample of urban prunings. In this sense, the structural irregularity can be explained by the grinding process, which occurred in the sample preparation stage (Cruz *et al*., 2018). In addition, it is pointed out that the presence of leaves in the samples was perhaps responsible for the high degree of disorder in this biomass, since the sample only with stems studied by Silva *et al*. (2021) demonstrated a greater regularity.

The biomass from 100%FW (Figure 3e) indicates a compact and irregular surface, with some globular particles having grooves. Similar particularities also were observed in the results proposed by Yadav *et al*. (2016). The grooves displayed on the surface area have the function of facilitating the digestion process of lignocellulosic substances during anaerobic digestion (Yadav *et al*., 2016).

As in the pure samples, disordered surfaces and fragmented particles were also identified in the blends (Figures 3b, 3c, and 3d), being consequences of the grain size reduction process (as placed earlier in this section). Regions with many fibers were also identified in the 75%UP:25%FW sample (yellow circle in Figure 3b). These results are in agreement with the calculated crystallinity index.

4. CONCLUSION

From this study it was possible to determine important properties of biomass from urban prunings, food waste, and its blends. The physicochemical, morphological, and structural properties were crucial to evaluate the application of these materials as alternative energy source in thermoconversion processes for clean energy production. The calorimetry analysis presented satisfactory results, corroborated by other data in the literature. The quantities found for the ultimate analysis showed optimal environmental conditions during thermal processes (low concentrations of nitrogen and sulfur for all samples). As for the proximate analysis, it was confirmed that the heating value, presented high concentrations of volatile materials (essential in combustion and/or pyrolysis), and low concentrations of ash and moisture (negative influence on the heating value). Moreover, it is also pointed out hydrocarbons and other compounds identified by FTIR, which can participate as volatile materials and justify the high concentration of them. Another important observation can be made regarding the low crystallinity of biomass, which implies samples more reactive and better application in thermoconversion processes.

Lastly, the analysis of samples of food waste, urban prunings and their blends showed results favorable in terms of energy properties. The low formation of polluting and corrosive substances in thermal processes, high amounts of fixed carbon and volatile materials, and mostly amorphous structure makes energy generation from these biomasses a feasible process from an economic-environmental point of view.

5. ACKNOWLEDGEMENTS

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