Investigation of the urban pruning wastes as biofuels and possible utilization in thermal systems

Investigação dos resíduos da poda urbana como biocombustíveis e possível utilização em sistemas térmicos

DOI:10.34117/bjdv7n3-265

Recebimento dos originais: 08/02/2021
Aceitação para publicação: 11/03/2021

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ABSTRACT

The urban afforestation is an important part of cities that provide well-being and health for their citizens; however, the urban afforestation needs constant pruning, which generates a considerable amount of waste that are not able to be disposal in land. In the other hand is an emerging need of clean energy production due the damage caused by the fossil fuels. An alternative to solve these issues is to use the urban pruning waste as feedstock for thermochemical conversion with the goal to produce clean energy. However, is necessary investigate the physical-chemical properties of urban pruning waste as possible biofuel, for this propose this study realize several experiments such as: Thermal Analysis (DG/DTG and DTA), Proximate and Ultimate Analysis, Inductively Coupled Plasm – Optical Emission Spectrometry (ICP-OES), Scanning Electronic Microscopy (SEM), Electron Diffraction Spectrometry (EDS) and Fourier Transform Infrared (FTIR). The analysis of the urban pruning waste achieves as result a considerable energy property and low amount of pollutants-forming elements for that biomass, which mean, that the urban pruning is an profitable source for energy generation and also contents a proper chemical composition.

Keywords: biomass, bioenergy, characterization, feedstock, urban pruning, potential.

RESUMO
O florestamento urbano é uma parte importante das cidades que proporcionam bem-estar e saúde para seus cidadãos; no entanto, o florestamento urbano precisa ser podado constantemente, o que gera uma quantidade considerável de resíduos que não podem ser depositados na terra. Por outro lado, há uma necessidade emergente de produção de energia limpa devido aos danos causados pelos combustíveis fósseis. Uma alternativa para resolver estas questões é utilizar os resíduos da poda urbana como matéria-prima para a conversão termoquímica, com o objetivo de produzir energia limpa. Entretanto, é necessário investigar as propriedades físico-químicas dos resíduos de poda urbana como biocombustível possível, para que este estudo realize várias experiências como, por exemplo: Análise Térmica (DG/DTG e DTA), Análise Proxima e Última Análise, Espectrometria de Emissões Ópticas (ICP-OES), Microscopia Eletrônica de Varredura (SEM), Espectrometria de Difração de Elétrons (EDS) e Infravermelho de Transformada de Fourier (FTIR). A análise dos resíduos da poda urbana atinge como resultado uma considerável propriedade energética e baixa quantidade de elementos formadores de poluentes para essa biomassa, o que significa que a poda urbana é uma fonte lucrativa para a geração de energia e também contém uma composição química adequada.

Palavras-chave: biomassa, bioenergia, caracterização, matéria-prima, poda urbana, potencial.

1INTRODUCTION

Renewable energy sources and technologies were widely been studied, discussed and developed is last years since the fossil fuels (oil, coal, natural gas, and others) does not agree with sustainable principles and environmental respect established for well-being of humanity and Earth's health, causing damage such as global warming, greenhouse gas emissions (GHG) and air pollution (Velázquez-Martí et al., 2018; Modesto et al., 2016; Alzate et al., 2017; Nozela et al., 2017).

Biomass is considered as one of the alternative sources for the clean energy generation, which presented greatest potential for growth at last years. This lignocellulosic source remains prominent in the worldwide scenario, because, unlike other energy sources, it can be used to generate different forms of energy, including heat, electricity, and biofuels, possible to transport and storage (Barbanera et al., 2016; Nozela et al., 2017). A promising sustainable method to transform lignocellulosic biomass into biofuel is the thermochemical conversion, which can be adjusted into few reactions such as pyrolysis and combustion (Silva Filho et al., 2019).

The aim of this work is investigating the municipal solid waste obtained from pruning waste of afforestation in an urban area (São Luís - Maranhão State - Northeast - Brazil). Thus, before disposing the urban pruning waste as a feedstock for the biofuel

production, it is necessary to investigate the physicochemical properties and thermal behavior of this biomass as a tool to obtain accurate information on the possibility of excursion and the socioeconomic availability (García et al., 2012).

For a complete investigation of urban pruning waste as a possible biofuel is made by multi-analytical techniques (Velazquez-Martí et al., 2018). Among several techniques the most frequently are Thermal Analysis (DG/DTG and DTA curves) and Calorimetry Analysis (HHV and LHV) to show the thermal decomposition kinetics of pyrolysis and the amount of energy generated during combustion reaction, respectively (Velazquez-Martí et al., 2018). To know characteristics that have influence on energy properties and pollutants formation, it is necessary other analytical techniques such as Ultimate and Proximate Analysis, X-Ray Diffraction, Scanning Electronic Microscopy, Fourier Transform Infrared, and Energy Dispersive Spectrometry, in order to obtain an advanced characterization of the studied samples (Cruz, 2015).

The importance of this study consists in carried out a complete characterization of the main physicochemical properties and thermal behavior of urban pruning waste and their application as possible feedstock for the clean energy production by means of thermochemical conversion processes (combustion and/or pyrolysis).

2 MATERIALS AND METHODS

Sample preparation

The urban pruning samples used in experiments were collected in São Luís (02° 35' 36.45" South and 44° 12' 44.92" West; Maranhão, Brazil) (IBGE, 2007). The tree species of the urban pruning wastes used in this research were not identified, for making them more generalized. In preparation stage, the samples of leaves (L), branches (B), and blends - leaves more branches (LB): 50% w/w) were washed with running water for impurities removal, dried in oven at 50 °C for 48 h, sieved and separated at ≈ 300 μm (average granulometry).

Ultimate and proximate analysis

The ultimate analysis was performed to discover the biomasses chemical composition, and it was possible to obtain the content of carbon, oxygen, hydrogen, nitrogen, and sulfur of the samples, using the Elementary Analyzer of Perkin Elmer brand - 2400 CHNS-O model, the experiment was performed at pure oxygen (99.99%) atmosphere. The oxygen was calculated by difference in 100%. The proximate analysis

of samples was performed in a Simultaneous TG-DTA Thermal Analyzer, SDT-2960 (*TA Instruments; New Castle*, DE, EUA), using the methodology proposed by Torquato et al. (2017).

Calorimetry analysis

The High Heating Value (HHV) was determined according with DIN 51900 (DIN, 2003), ASTM D240 (ASTM, 2019), ASTM E711 (ASTM, 2019), ISO 1928 (ISO, 1987), and NBR 8633 (ABNT, 1984) standards, using a calorimetric pump *IKA* brand and *C-200* model. The calorific analysis was performed at pressure of 30 atm and room temperature (≈ 20 ºC) to 25 °C.

With the hydrogen content (ultimate analysis), HHV measured experimentally, and moisture (proximate analysis) it was possible to obtain the LHV by Equation 1 (Cortez et al., 2008).

$$LHV = [(HHV - \lambda * (r - 0{,}09*H)) * (100 - W)/100] \quad (1)$$

Where λ is water evaporation heat, which is 2.31 MJ kg^{-1} at 25 °C; *W* is moisture content (%), *H* is hydrogen content, and r = W/(100 - W), which is denominated of moisture ratio.

Thermogravimetric Analysis and Differential Thermal Analysis

The Thermogravimetric Analysis and Derivative Thermogravimetry (TGA/DTG) curves were obtained in a TGA-51 Thermogravimetric Analyzer module (Shimadzu), and for the Differential Thermal Analysis (DTA) the measurements were performed in a DTA-50 (Shimadzu) equipment, in triplicate from room temperature (≈ 25 °C) to 800 °C, under synthetic air and nitrogen atmospheres, using a dynamic flow of 100 mL min^{-1} and the heating rate of 10 ºC min^{-1}.

Scanning Electronic Microscopy

The morphological structures and textural of urban pruning waste were observed by LEO440 Scanning Electronic Microscopy (SEM), Leo Electron Microscopy. The experiment was performed at vacuum and the samples were submitted to a golden bath (metallization). The images were obtained in magnifications of 200, 600, 800, and 3000x.

X-Ray Diffraction

The X-Ray Diffraction (XRD) was used to identify the main amorphous and crystalline regions, and to calculate the Crystallinity Index (CrI). The measurements were performed in a Rigaku Multiflex equipment, model Miniflex, with CuKα radiation (λ = 1,541 Å, 40 kV-40 mA), based on the powder methodology. The range (2θ) was from 5º to 70° with a step size of 0.05 min^{-1}. The CrI were calculated by Segal's (peak height) method, using the Equation 2 (Xu, Shi and Wang, 2013).

$$CrI_{(\%)} = \frac{I_{002} - I_{am}}{I_{002}} \cdot 100 \quad (2)$$

where I_{002} is the maximum intensity of the 002 lattice diffraction value at 22.5° (2θ), when a CuKα radiation is used, and I_{am} is the intensity of amorphous scatter value at 18° (2θ).

Fourier Transform Infrared

The Fourier Transform Infrared (FTIR) was used to identify main structural components. The measurements were performed in a spectrophotometer (Shimadzu brand, IR-Prestige-21 model) from 4000 to 400 cm^{-1}, and the samples were prepared with KBr (potassium bromide).

Inductively Coupled Plasma – Optical Emission Spectrometry

To detect the main traces elements (metals and inorganic compounds) present in the samples, the Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) technique was used, in Arcos equipment (Spectro), (ICP-OES 710ES model and Varian brand). This procedure allows to accurately quantifying the chemicals trace elements present in samples, in amount up to 10 mg L^{-1} (Caruso et al., 2017).

Energy Dispersive Spectrometry

In addition, to obtain the qualitative distribution of elements in surface of the *in natura* urban pruning waste samples, the Energy Dispersive Spectrometry (EDS) technique was applied, using the LEO440 scanning electronic microscope (Leo Electron Microscopy). The samples were subjected to compaction in a hydraulic press, to form a tablet that was then fixed in an aluminum bracket. The purpose of this experiment is to get the composition without hiding any element and no metallization was performed.

3 RESULTS AND DISCUSSION

3.1 ULTIMATE, AND CALORIMETRY ANALYSIS

The results of the Ultimate and Calorimetric Analysis are presented in Table 1.

Table 1 – Chemical composition, Calorimetry and DTG analysis of the urban pruning waste.

Ultimate Analysis			
Properties	**Leaves (L)**	**Branches (B)**	**Leaves and Branches (LB)**
Carbon (%)	47.28±1.47	43.99±1.75	46.94±1.93
Hydrogen (%)	5.83±0.21	5.20±0.38	5.80±0.14
Oxygen* (%)	44.94±0.00	49.80±0.00	45.78±0.00
Nitrogen (%)	1.89±0.07	0.98±0.04	1.48±0.05
Sulfur (%)	0.06±0.06	0.03±0.05	n.d.
Calorimetric Analysis			
HHV (MJ kg^{-1})	20.86±0.02	18.65±0.01	19.69±0.02
LHV (MJ kg^{-1})	19.96	17.73	18.74
Proximate Analysis			
Moisture	8.68±0.15	9.07±1.15	9.27±0.14
Volatile matter	66.43±0.54	61.24±0.12	64.61±0.98
Fixed carbon	21.71±0.51	22.95±1.40	22.85±0.40
Ash	3.17±0.19	6.72±0.40	3.24±0.70

*calculated by difference at 100%; n.d.- not detected or below equipment detection limit;

The HHV results showed that **L** presented a value 11.8% higher than the **B**, confirming that the leaves presented major influence on the urban pruning waste. The urban pruning residue that presented HHV close to LB was the almond tree pruning, whose values were only 1.4% smaller (González et al, 2009).

The leaves of this study presented a better behavior than the most leaves listed by García et al. (2012), only one type of leaves has a HHV 0.7% higher than the urban pruning leaves of this study, the *boj* samples with HHV of 20.72 MJ kg^{-1}.The *boj* branches, instead, showed a HHV of 18.79 MJ kg^{-1} (García et al., 2012).

The branches presented a HHV of 1.6% higher than the almond tree branches (González et al, 2009). The B sample demonstrated some similarity with other types of branches, and also with wood and/or sawdust, for example, values found by Cruz and Crnkovic (2019) for the pine sawdust sample was of 18.3 MJ kg^{-1} and by Huron et al. (2017) for a wood waste mixture was of 18.7 MJ kg^{-1}.

The low amount of moisture and hydrogen in the samples promote a slight decrease in HHV, which shows that hydrogen conversion in water is not significant in combustion of pruning waste samples (García et al., 2012; Braz, 2014).

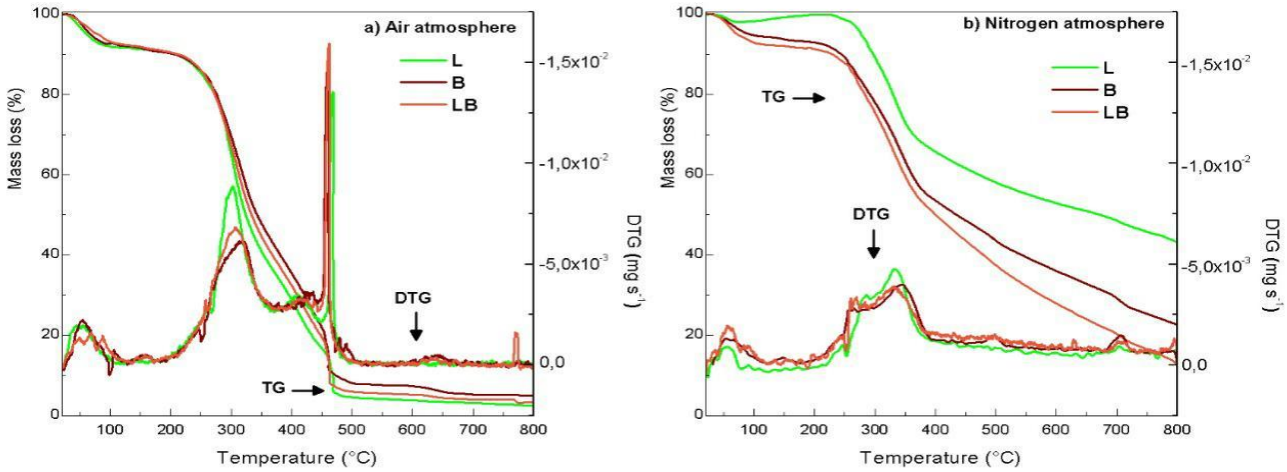
The nitrogen and sulfur content of the samples of urban pruning waste were insignificant presenting values below 2%. The presence of sulfur and nitrogen is directly related to the production of SO_X and NO_X, pollutant gases, and the low amount of these two elements means represents a decrease in the release of these pollutants during the combustion of biomasses (Cruz et al., 2020).

The urban pruning waste due its composition and great HHV, when compared to other tree pruning wastes also presented a low tendency for the pollutants formation, with considerable potential to be used as an energy matrix (or feedstock in thermochemical systems).

3.2 THERMOGRAVIMETRIC ANALYSIS (TG/DTG) AND DIFFERENTIAL THERMAL ANALYSIS (DTA)

Thermogravimetry Analysis (TGA), Derivative Thermogravimetry (DTG), and Differential Thermal Analysis (DTA) was used to evaluate the thermal behavior of urban pruning wastes. Results for the three samples analyzed under synthetic air are shown in Figure 2a. Through the TG/DTG curves it was also possible to obtain the levels of moisture, volatile materials and fixed carbon (proximate analysis) of the samples as presented in Table 1.

Figure 2 – Thermogravimetry and Derivative Thermogravimetric (TG/DTG curves) of the urban pruning wastes: (a) synthetic air and (b) inert atmospheres.



The similarity between the TG/DTG curves for the three samples under synthetic air atmosphere reflects the data obtained to thermal degradation stages. In the first stage between 20 and 150 ºC occurred the mass loss of 8.68, 9.07, and 9.27% for the L, B, and LB samples, respectively, corresponding to moisture evaporation.

According to the Mitu et al. (2018), the volatile materials content contributes to the combustion, pyrolysis, and gasification processes. It is interesting to note that the samples presented an average value of volatiles material content around 64.09%, this value is approximately 9.0% lower than that found by Mitu et al. (2018) for fine-particle sanding wood waste.

The high ash content affects directly the combustion process and is often deposited on the thermochemical reactors bottom, causing clogging and energy efficiency loss (Mitu et al., 2019). Low ash contents of B and L around 6.72% and 3.17%, respectively are higher to the achieved contents found for cotton stalks and sugarcane bagasse of approximately 4.68 and 2.34%, respectively (El-Sayed and Mostafa, 2014). These ash contents are small compared to other solid wastes, such as sewage sludge (43.0%) (Nozela et al., 2018).

After release of moisture and volatile materials, occurs the fixed carbon degradation, combustible material, which presented contents of 22.95% for B and 21.71% for L, higher than the levels found for urban pruning waste from the Araraquara city (São Paulo State - Brazil) of 21.55% reached by Nozela et al. (2018).

The urban pruning waste showed high volatile materials and low ash amounts, making of this biomass a great potential for using as energy matrix in combustion process.

The DTG curves (Figure 2a) show and confirm the three steps of mass loss by increasing the temperature. The first event refers to the moisture release as already discussed for the TG curve analysis. The two remaining steps refer to the thermal degradation of hemicellulose and cellulose together, which is called of holocellulose, and evidenced by the presence of a “shoulder” around 310 ºC (Cruz and Crnkovic, 2016). While that in second event it was evidenced to thermal decomposition of the lignin (Mitu et al., 2019).

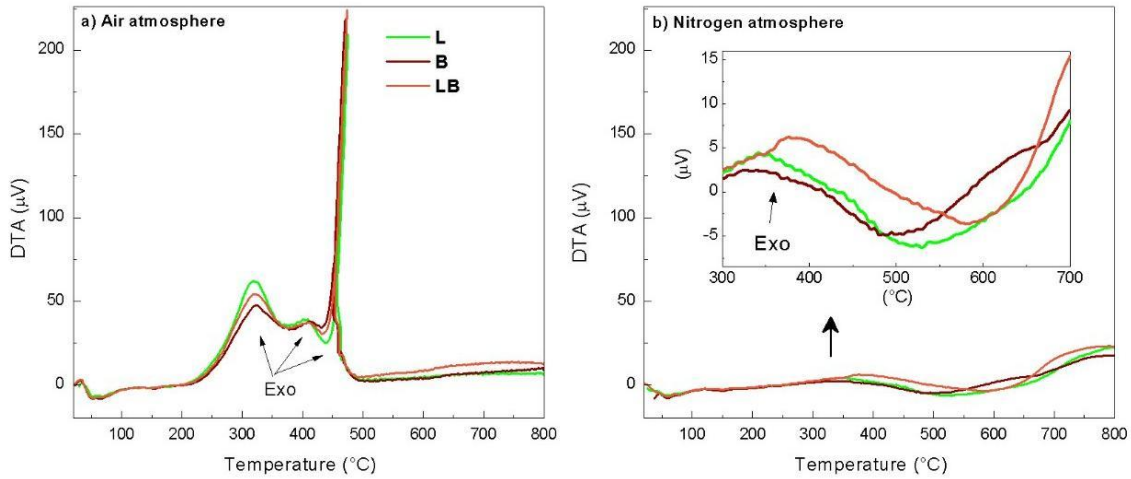
The temperatures that correspond to the maximum thermal decomposition rate of hemicellulose for the B, L, and LB were ≈ 317.31, 303.87, and 307.21 °C, respectively. However, the maximum mass loss rates for the same constituent were ≈ 0.369, 0.530, and 0.409 mg min^{-1}, respectively. These results revealed the existence of a distinct hemicellulose percentage for the tested samples (El-Sayed and Mostafa, 2014).

However, cellulose mass loss percentage can be considered similar between the three materials studied, because the maximum mass loss rate values are near, *i.e.*, 0,208 mg min^{-1} (≈ 415 ºC). Lignin mass loss rate showed an average value 0.893 mg min^{-1} (≈ 460 ºC), which was higher to the average values reached for hemicellulose and cellulose, *i.e.*, 51.2 and 76.5%.

TG, DTG, and DTA curves under nitrogen are showed in Figure 2b. By means of TG curve it was possible to identify a subtle inflection between 300 and 400 °C, which correspond to the maximum degradation step. The mass loss curve, starting from 400 °C increase linearly up to 800 °C, and can be explained by residual lignin decomposition, which is not described by main peaks (Rodilla, Contreras and Bahillo, 2018). The remaining content after thermal processes was of approximately 10 to 50%, for both oxidizing and inert atmospheres, respectively.

The parity observed for the DTG curves in both atmospheres (nitrogen and synthetic air) was evidenced by presence of a "shoulder" between 200 and 300 °C, and maximum degradation peak between 300 and 400 °C.

Figure 3 – Differential Thermal Analysis (DTA curves) under: c) synthetic air and d) nitrogen atmospheres for the urban pruning residues.



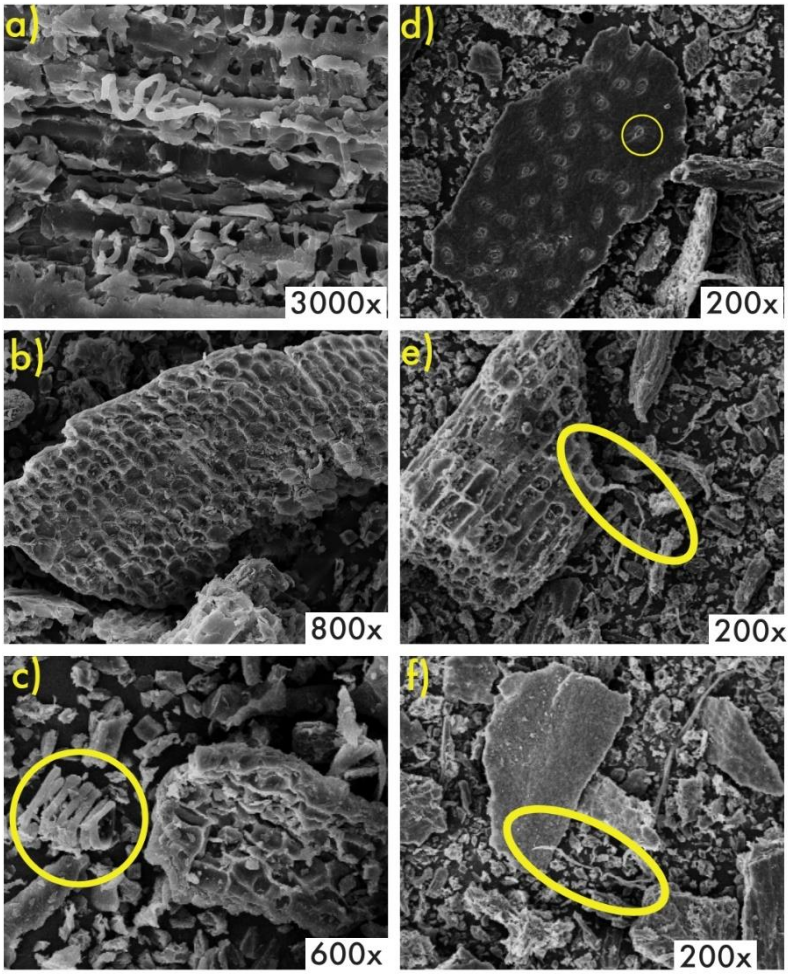
DTA curves shown in Figure 3 (a and b) under air atmosphere revealed that thermochemical conversion process for the three samples were similar. Initially, an endothermic reaction occurred (heat gain), referring to the moisture loss for the samples. It was observed from TG and DTG curves, primarily for the moisture release, which is directly related to conversion reaction of hydrogen and oxygen into water (Braz, 2014). Afterwards, there are two other complex exothermic reactions (heat release), first at 321.34, 319.32, and 320.87 °C for B, L, and LB, respectively. The second exothermic

reaction demonstrated higher intensity and was observed in DTA curve, with peak temperatures around 474 °C (Chen and Kuo, 2011). This increase showed the high reactivity of lignin content present in urban pruning wastes, when compared to the other constituent elements of the same residues.

3.3 SCANNING ELECTRONIC MICROSCOPY

The SEM images of *in natura* urban pruning waste are showed in Figure 4 (a-f). The samples presented a disintegrate structure, such aspect can be probably by the milling process. The B sample presented a structure more regular than the LB, where the particles had high disorder. The magnification of 3000 times allowed to observe that the L sample (Figure 4a) presented a curve and intertwined structure, similar to a spiral or ring.

Figure 4 – SEM images of the leaves (a: 3000x and d: 200x); branches (b: 800x and e: 200x), and leaves and branches (c: 600x and f: 200x).



According to Wang et al. (2017), the hemicellulose in cellular wall has a branched structure similar a “chain” that connects and intertwines with cellulose and lignin. From a resemblance analysis, it was believed that curve structure of the L sample may be probably the hemicellulose present in biomass, which has an important function in the final products of combustion and/or pyrolysis process (Liu et al., 2011).

The B specimen (Figure 4b) presented a porous texture that looks like extent inside of the solid similar to that found in the *in natura* pine sawdust, which was possible to observe at 800 times magnification (Cruz et al., 2018). A biomass particle is made of solid cells, but sometimes presents some visible cavities or slits, that seem to extend inside the particle, forming axial and radial channels (Gil et al., 2015). Other interesting aspect verified at 200 times magnification, was that such magnification allowed identifying the loose fibers that probably happened due the grinding process.

The blend (LB) also presented particles that seem with a similar curve to a spiral or ring at 600 times magnification (Figure 4c). Such aspect was also found by Cruz et al. (2018) for the sugarcane bagasse samples, revealing elongated parallel fibers and massive beams and that swirl shape is possibly caused by milling process.

It was not found any similarly with other vegetable biomasses, and also was not found in literature specific SEM images for any urban pruning wastes. This means that still missing more information about these wastes, and its morphologies and in this sense, our study tries supplementing this scarcity and brings by the firstly this information.

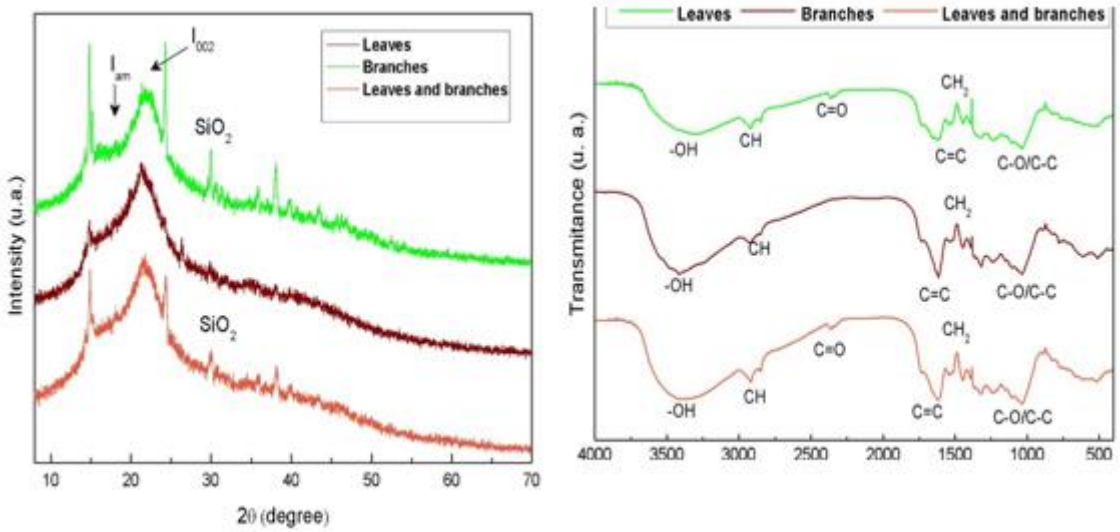
3.4 X-RAY DIFFRACTION

The crystallography investigation of urban pruning wastes was performed an X-ray diffraction (XRD), from which it was possible to calculate the crystallinity index (CrI). The XRD results for the urban pruning specimens are showed in Figure 5a. The crystalline (I_{002}) and amorphous (I_{am}) regions of the samples were detected at 2θ of 22.5º and 18.0º, respectively. The others peak at 30° corresponds to the presence of silica (SiO_2), and was observed for the B and LB specimens (Chen et al., 2016).

The CrI obtained by Segal's method for L, B and LB samples were of 11.0, 14.0, and 25.0%. These results achieved revealed the presence of more amorphous structures for the urban pruning wastes (Xu, Shi and Wang, 2013). These results showed that the urban pruning wastes of this study possibly presented lower cellulose concentration (crystalline structure) than palm pruning wastes, resulting in a CrI for *Petiole* and *Rachis* almost 2 and 2.5 the values of the LB sample, respectively (Ahmadi et al. 2012).

However, determining real crystallinity of cellulose require a complex effort, because this depends of the entire material, including the content of hemicelluloses, lignin and also the nature of bonds between them (Akhtar, Goyal and A.Goyal, 2016).

Figure 5 - (a) – Crystallographic diffractograms of the urban pruning wastes. From top to bottom are presented the curves for the samples of leaves (L), branches (B), and leaves + branches (LB) - (b) - Fourier Transform Infrared spectra for the urban pruning wastes.



The crystallinity index is essential in defining the thermal degradation behavior, in thermochemical processes amorphous structure have higher reactivity when compared to the crystalline structure (Xu, Shi and Wang, 2013).

The high volatility is profitable for direct combustion because the reactivity maintains the burning flame, but is detrimental in charcoal production because decrease the gravimetric yield due the degradation at lower temperatures (Martinez et al., 2019).

3.5 FOURIER TRANSFORM INFRARED

The results for the Fourier Transform Infrared analysis of the urban pruning wastes are shown in Figure 5b. The infrared spectra revealed similar absorptions for L, B, and LB samples, but with different intensities.

The three samples exhibited broad band between 3600 and 3000 cm^{-1} and the smaller peaks between 3000 and 2700 cm^{-1} were attributed to the presence of -OH functional groups and alkyl C-H stretches, respectively. Hydroxyl functional groups stemming from acid and methanol (OH^-) stretching vibration or adsorbed water, while the C-H stretching is due the alkyl, aromatic aliphatic, both related to presence of cellulose, hemicellulose, and lignin (Duranay and Akkuş, 2019).

The band identified at 2362 cm^{-1} for L and LB samples is due the presence of C=O stretching for CO_2, and the C=O stretching is also related to hemicellulose and deformation vibrations of H–O–H in absorbed water, for the B sample was not observed any visible peak in this region (Akhtar, Goyal and A.Goyal, 2016; Müsellim et al., 2018).

The functional group C=C were identified for three species in wavenumber range of 1680-1600 cm^{-1} (Kanwal et al., 2019). The C=O and C=C peaks are due to stretch vibrations, ketones, aldehydes, esters, carboxyl groups in cellulose and hemicellulose, and aromatic structures in lignin (Duranay and Akkuş, 2019). The band presented at 1487 cm^{-1} identified in the three samples spectra corresponds to the presence of mixtures of CH_2 deformations and C-O-H bending vibrations, while the band at 1035 cm^{-1} is due the assignable to coupling modes of C-O and C-C stretching vibrations, also presented for all species (Liu et al., 2016). The C-O and C-C presence is a characteristic signal of cellulose (Aguardo et al., 2020).

The wood-based biomass presented main functional group expected, except by the absence of the C=O in B sample that was not experimentally identified as the others two evaluated samples waste (Duranay and Akkuş, 2019).

3.6 INDUCTIVELY COUPLED PLASMA – OPTICAL EMISSION SPECTROMETRY

Table 3 shows the main inorganic elements and metals present in the studied biomasses measured and/or quantified by ICP-OES analysis.

Table 3 – Metal and inorganic elements detected by ICP-OES analysis and Compositional analysis detected by EDS for the urban pruning wastes.

Metal and inorganic elements detected by ICP-OES analysis (mg kg^{-1})			
Compounds	**Leaves (L)**	**Branches (B)**	**Leaves and Branches (LB)**
Silicon (Si)	1083	314	331
Phosphorus (P)	1422	1393	1270
Magnesium (Mg)	2352	1946	2223
Calcium (Ca)	4235	14974	11026
Sodium (Na)	888	1034	944
Potassium (K)	8611	6256	7957
Energy Dispersive Spectroscopy analysis (%wt/wt)			
Carbon (C)	63.94±1.18	55.35±0.74	58.79±1.87
Oxygen (O)	34.39±0.41	41.92±0.48	39.28±1.38
Sodium (Na)	0.11±0.02	0.12±0.04	0.09±0.01

Magnesium (Mg)	0.14±0.03	0.21±0.06	0.15±0.05
Aluminum (Al)	n.d.	0.10±0.01	0.14±0.05
Silicon (Si)	0.14±0.01	0.26±0.23	0.12±0.02
Phosphorus (P)	0.06±0.01	0.12±0.01	0.08±0.02
Sulfur (S)	0.12±0.03	0.10±0.01	0.09±0.03
Chlorine(Cl)	0.18±0,04	0.07±0.01	0.10±0.02
Potassium (K)	0.67±0.19	0.56±0.13	0.33±0.07
Calcium (Ca)	0.24±0.02	1.06±0.29	0.78±0.51
Iron (Fe)	n.d.	0.13±0.10	0.12±0.07

The compounds of remaining ashes of the biomass can cause heat transfer problems to the bioenergy generation system. It is important a deep knowledge of the biomass thoroughly before designing an efficient power generation system (Nunes, Matias and Catalão, 2016).

The pine bark, which is used as soil fertilizer present a rich composition with the presence of all the components found for the urban pruning wastes, where the contents of Mg, P, K, and Na, were 950.1, 143.1, 1338, and 73.63 mg kg^{-1}, respectively, demonstrating low values compared with the samples of this study (Nunes, Matias and Catalão, 2016). From these results was possible to assume that urban pruning waste ash perhaps can be used as an organic fertilizer or manure.

The two samples (L and B) demonstrated higher calcium contents, when compared to the coffee pulp (2716 mg kg^{-1}) and castor husk (1675 mg kg^{-1}. The LB had a K content of 7957 mg kg^{-1} and 68% higher than the values found by Parascanu et al. (2017) for *opuntia*.

The Si content of biomass are below the average values found for the wood wastes used in recycling centers (Huron et al., 2017). The possible reason for the different composition observed in urban pruning wastes in relation to the agricultural residues may be related to the soil composition in which these different biomasses were cultivated, as well as the specific flow of absorbed nutrients (Nunes, Matias and Catalão, 2016).

The amount of metals and inorganic compounds present in the biomass directly reflects in the chemical composition of the ashes, which can also cause damage such as corrosion, deposition and fouling in thermal reactors, besides heat transfer problems, and the costly maintenance of the thermochemical systems, etc (Nunes, Matias and Catalão, 2016).

3.7 ENERGY DISPERSIVE SPECTROSCOPY

The results for the Energy Dispersive Spectroscopy (EDS) are presented in Table 3. The values obtained indicated a high carbon and oxygen content for the three samples as shown in the ultimate analysis.

The sulfur content was more pronounced, when compared to the elemental analysis, however, the percentage amount remained similar to the values found by other authors, for example, 0.13% sulfur content as noted by Bove et al. (2016) for apple tree pruning.

The samples are constituted mostly by carbon and oxygen (around 97.0%), the same composition was also for the L and LB (≈98.0%) showing low amount of other compounds, which were analyzed in earlier discussion of ICP-OES results.

4 CONCLUSION

This research evaluated the calorimetric properties and thermal behavior of urban pruning waste and correlated with its compositional, morphological, structural, and physicochemical characteristics. The performed characterization it possible the complete analysis of urban pruning waste as a potential biofuel and the comparison with others biomass already employed in real thermal systems, providing an accurate information of this biomass in energetic scenario and afford more data about its use in thermochemical processes for the clean energy production and also correct waste disposal.

Finally, by means of these results was possible to affirm that urban pruning waste present a great energy potential due their profitable calorific value, which suggests a considerable energy release in combustion processes. Others interesting results were a good percentage of calcium and potassium, and low amount of sulfur and nitrogen, which mean that urban pruning waste present a proper composition for the bioenergy production and also the ashes generated can be easily dematerialized.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge Foundation for Research Support, Scientific and Technological Development of Maranhão - FAPEMA (00957/19 and 002261/20), and National Council for Scientific and Technological Development - CNPq (426162/2018-8) for the financial support. Environmental Sciences Laboratory (LACAM) of the Ceuma University, Mercedes-Benz Brazil for the ICP-OES analysis,

and Federal University of Maranhão, São Paulo State University, and University of São Paulo for technical and professional support.

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