PHYSICAL-CHEMICAL AND THERMAL CHARACTERIZATION OF CASSAVA HARVEST RESIDUES FOR APPLICATION IN COMBUSTION AND PYROLYSIS PROCESSES

Alyson da Luz Pereira Rodrigues (alisonluz93@outlook.com)
Ceuma University - Master Science in Environmental, São Luís - MA, Brazil

Arthur Vinicius Silva Sousa (arthsilva6@gmail.com)
Federal University of Maranhão - Department of Mechanical Engineering, São Luís - MA, Brazil

Carlos Eduardo Mendes Braz (carlosedumb@yahoo.com.br)
Federal University of São Carlos – Chemistry Department, São Carlos – SP, Brazil

Wolia Costa Gomes (woliacg@gmail.com)
Ceuma University - Master Science in Environmental, São Luís - MA, Brazil

Glauber Cruz (glaubercruz@gmail.com)
Federal University of Maranhão - Department of Mechanical Engineering, São Luís - MA, Brazil

Abstract: Significant increases in the use of renewable resources are urgently needed to attemptthe needs of a growing population and build a more sustainable society.The literature presents several studies on the determination of the physicochemical characteristics of the crop residues, such as corn cobs and straws, rice husk, olive seed, sugarcane bagasse and others.However, there is still a lack of detailed information about the use of cassava harvest residues for energy applications.This work aims to characterize the cassava residues (husks, stems and leaves) for application in combustion and pyrolysis processes.The physico-chemical characterization was carried out for the cassava residues samples and was determined their ultimate analysis:carbon, nitrogen, hydrogen, sulfur and oxygen and proximate analysis:volatile material, fixed carbon, ash and moisture contents. High Heating Value (HHV) of cassava residues was also determined, ranging from 18.2 MJ kg^{-1} to 23.1 MJ kg^{-1}. The values for moisture (10 %), ash (mean of 6.3% in air), volatiles (68%) and fixed carbon (16%) for the cassava different parts were determined. Thermal analysis (TG/DTG) under air and nitrogen atmosphere were used to simulate the combustion and pyrolysis processes, respectively, and determination of hemicellulose (25%), cellulose (45%) and lignin (25%) contents of the cassava residues. Results presented in this research are useful for the application of this biomass in industrial thermal conversion processes.

keywords: biomass, cassava, residues, combustion, pyrolysis

1. INTRODUCTION

The bioenergy production from biomass or agricultural wastes has gained significant interest due to increased consumption, prices and emissions of pollutants from fossil fuels (EZUI *et al.,* 2015). The literature presents several studies on the determination of the physical and chemical characteristics of crop residues, such as corn and cob, rice and coffee husk, olive seed, sunflower and sugarcane bagasse among others (CRUZ and CRNKOVIC, 2015).

Cassava is a perennial plant of the genus *Manihot esculenta Crantz*. The main producing countries of cassava in the world are Nigeria, Brazil, Thailand and Ghana in order (SUTTIBAK *et al.,* 2012). Cassava is a shrub grown extensively as an annual agricultural crop in tropical and subtropical regions, and its root is an edible starch tuber. Cassava biomass residues are available in the fields after harvesting and can cause environmental problems (EDHIREJ *et al*., 2017). The roots are collected and transported, while some stems are used to replant the crops and most of the green mass is left in the soil, which decomposes and some nutrients return to the soil (LIU *et al.,* 2013; SÁNCHEZ *et al*., 2017).

It was noted that few studies have discussed the use of cassava harvest residues as an energy source. For example, Pattiya (2011) characterized physically and chemically the cassava (stem and stalk) residues for use as biofuel in Thailand. Wei *et al.* (2015) discussed the possibility of extracting the starch from the cassava branches to produce ethanol, evaluating aspects such as the production region. Veiga *et al*. (2016) sought to quantify and characterize the cassava residues by thermogravimetric analysis under oxidizing and inert atmospheres to study the behavior of these

wastes as biofuels. Rodrigues *et al* (2018), in their research recently published reported that cassava harvest residues, is a Brazil biomass with great potential for use in biochemical and thermochemical processes with bioenergy purposes.

In this work used two thermal conversion processes (combustion and pyrolysis) for the thermal characterization of the cassava harvest residues.

Combustion is the process most used for the biomass conversion and contributes to over 97% for the bioenergy production in the world (MADHIYANON, 2010). Considered as a proven low-cost but highly reliable technology, combustion is relatively well understood and commercially available. Large-scale biomass combustion is still considered a complex process with technical challenges associated with biomass fuel characteristics, types of combustors and challenges of co-combustion processes (DERMIBAS, 2007).

Other studied process is pyrolysis, understood as a thermal decomposition process that occurs in the oxygen absence to convert the biomass into solid coal, liquid (bio-oil) and gaseous fuels at moderate temperatures ($\approx$ 600 ºC). Pyrolysis is considered an industrially developed process for the biomass conversion (ISAHAK *et al.* 2012). Pyrolysis of agricultural residues, for example, sugarcane bagasse and cassava plantations was carried out in a laboratory-scale free fall reactor to investigate the effects and conditions of the biomass pyrolysis, such as reactor temperature, condensation temperature, nitrogen flow rate and operation duration (ISAHAK *et al.* 2012).

Due to lack of detailed information about the use of cassava harvest residues (husks, stems and leaves) for energy applications, this research aims to physico-chemical characterization (proximate and ultimate analysis, calorimetry and metal composition) and thermal analysis of this biomass for the application in combustion (synthetic air) and pyrolysis (nitrogen) processes by thermogravimetric analysis (TG/DTG) for the determination of their hemicellulose, cellulose and lignin contents.

2. MATERIALS AND METHODS

In this study, samples of Brazilian biomass – cassava harvest residues (*Manihot esculenta*) from the Northeast region (Maranhão State) were studied. Cassava residues (husk, stems and leaves) originated from Itapecuru Mirim city, located at 3° 23'42"North and 44° 21'36"West. Table 1 shows the different bands used to compose each mean particle size of the biomass used.

Table 1 - Different bands used to compose each mean particle size of the biomass

Screening plant used (mesh in mm)	Average particle size (mm)
0.125 - 0.177	0.151
0.420 - 0.500	0.460

Elemental analysis for the determination of carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) was performed on an Elementary Analyzer Perkin Elmer brand, 2400 CHNS model. Metals and inorganic contents were determined by Inductive Coupled Plasma – Optical Emission Spectrometer (ICP-OES).

The oxygen content (O) was calculated based on the difference between the results for the elemental analysis or ultimate analysis. Proximate analysis was performed according to ASTM E 1617-94 and ASTM E 1755-01 for the determination of volatiles material, fixed carbon, ash and moisture contents (TORQUATO *et al.*, 2017).

A calorimeter pump (IKA C 2000 model) was used - this equipment measures the High Heating Value (HHV) of the liquids and solid fuels samples. The evaluation of the use of this equipment is in accordance with ASTM E711.

The thermal analysis (TG/DTG) was performed in the Shimadzu equipment, TGA-51 model, for the determination of vaporization and volatilization temperatures, hemicellulose, cellulose and lignin contents and ignition temperature. All analyzes for the studied samples were performed under inert (100% nitrogen) and oxidizing (synthetic air - N_2/O_2: 80/20%) atmospheres, heating rate of 10 ^{o}C min^{-1} and gas carrier flow rate of 100 mL min $^{-1}$.

3. RESULTS AND DISCUSSIONS
3.1. Elementary analysis and chemical structures

For stem samples, nitrogen concentration (N) was between 0.58 and 0.81%. Knowledge of N content is necessary to estimate NO formation through the NO-fuel mechanism in the combustion of waste and formation of pollutants (Madhiyanon *et al.*, 2015). The results for the carbon content (C) of the cassava residue samples ranged from 41 to 45%, which differed slightly from the results observed by Pattiya (2011 and 2012), that is, reported a content of C close to 51% and Veiga *et al*. (2016) around 44%.

In the main conversion processes for the biomass combustion (JENKINS *et al.*, 1998), elements such as Si, K, Na, S, Cl, P, Ca, Mg and Fe are involved in the reactions that lead to the ashes formation, fouling and slagging. Table 2 shows the results of the metals composition analysis for the biomass used in this project. Where the limits of detection (LOD) and limits of quantification (LOQ) were determined according to IUPAC (reference). Figure 1 shows the metal composition analysis for the *in natura* cassava residues parts. A high amount of potassium (766 nm) and sodium (589 nm) was observed in Figure 1.

Table 2 - Metal composition analysis of the *in natura* cassava residues (husk, stem and leafe)

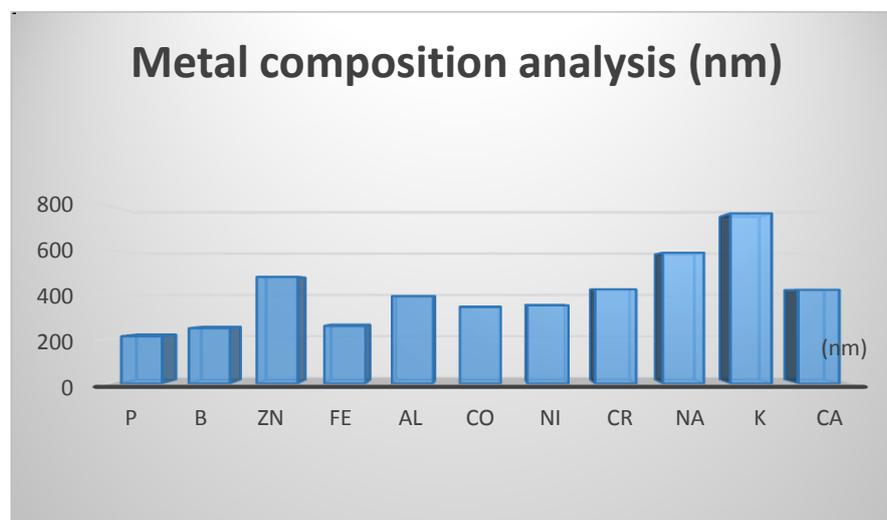| Elements	P	B	Zn	Fe	Al	Co	Ni	Cr	Na	K	Ca
(nm)	213.6	249.8	481.1	259.9	394.4	345.35	352.5	425.4	589.6	766.5	422. 7
leaf (mg kg^{-1})	< LOQ	< LOQ	32.4 ± 1.1	57.6 ± 3.8	113.1 ± 7.7	14.8 ± 1.0	6.8 ± 0.1	22.9 ± 0.3	331.3 ± 47.0	11182 ± 69.2	6116.8 ± 40.4
Stem (mg kg^{-1})	2029.8 ± 93.4	17.9 ± 0.8	122.5 ± 7.6	301.6 ± 4.4	330.3 ± 28.3	16.1 ± 1.5	7.5 ± 0.2	21.9 ± 0.6	240.8 ± 25.8	15052 ± 1103.4	18379 ± 1509.3
husk (mg kg^{-1})	938.8 ± 41.2	< LOQ	24.2 ± 1.1	206.2 ± 8.0	425.7 ± 34.2	14.7 ± 0.9	9.4 ± 0.2	23.8 ± 0.4	164.7± 27.2	12621 ± 492.1	3894.2 ± 213.9

Figure 1: Metal composition analysis for the stalk of the cassava harvest samples

3.2. Proximate Analysis

Considering that the determination of the immediate, elemental and calorific value analysis are fundamental to characterize a material as fuel, proximate analysis of cassava residues was carried out. Ash content were found 4.30% for cassava husk, 4.73% for cassava stalk and 9.85% for cassava leaves. The ash content causes problems of agglomeration, scale and slag in the interference of the feed in the heat transfer in the thermoelectric plant (SAENGER *et al.,* 2001).

It is important to emphasize that elemental analysis provides is the relationship between hydrogen and carbon, oxygen and carbon. These relations allow the calculation of HHV and LHV, since there is a correlation between the HHV proportions and H/C and O/C ratios (Van Krevelen diagram). Therefore, theoretical Higher Heat Value (HHV) was calculated using Dulong equation. HHV values close to the 18.2 MJ kg^{-1} were recently found by Veigas *et al* (2016), *i.e*, 23.1 MJ kg^{-1}.

Proximate analysis was performed and moisture content of 10.60% for husks was identified and 68.85% for the volatiles material are similar to those in other woody biomass (DEMIRBAS, 2007). For the stem the moisture content of 15.56% and 64.99% for the volatile material was analyzed. Finally, for the leaves, moisture contents of 8.82% and 64.78% were found for the volatile material.

The immediate analysis showed the amount of ash for the bark of 4.3%, 4.79% for the stem and 9.85% for the leaves. Higher attention the leaves that presented higher percentage. These ashes are composed of oxides that in the solid state. This considerable percentage shows the importance of choosing refractories with chemical behavior similar to that of ash in combustion processes.

3.3. Thermal analysis (TG/DTG curves)

Thermal analysis was carried out for the samples obtained from three cassava plant parts (husk, stem and leaves) under air synthetic (80% N_2 – 20% O_2) and nitrogen (100% N_2) atmospheres.

Figure 2 shows the TG/DTG curves for the stem samples obtained from cassava residues under air synthetic and nitrogen (N$_2$) atmospheres. Thermal analysis showed for moisture loss a percentage of 11.2% under synthetic air and 10.2% for N$_2$. The first event is related to the thermal decomposition of the organic matter or holocellulose present in the biomasses and this degradation occurs between 130 °C and 380 °C, with a temperature peak 286 °C, characterized as maximum combustion rate. At 450 °C is observed a peak (high intensity and fine), which is related to the lignin thermal degradation. The residues generated in the combustion process are called of ash and were detected of 5% for synthetic air and 23% for N$_2$, which showed a total organic material oxidation (800 °C). It is also noted by curves TG/DTG (Figure 2) a single decomposition step for hemicellulose/cellulose together (holocellulose) under nitrogen atmosphere.
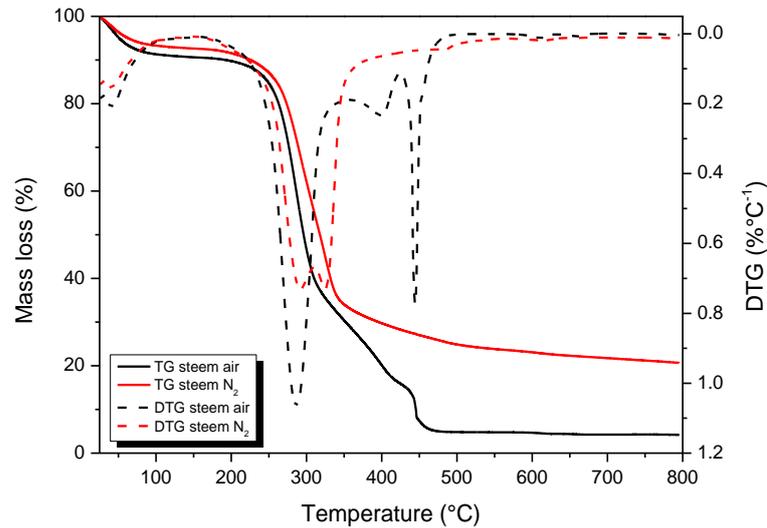

Figure 2: TG/DTG curves for the stems in synthetic air and nitrogen (N$_2$) atmosphere.

Figure 3 shows the TG/DTG curves for the husk samples from cassava residues under synthetic air and nitrogen (N$_2$) atmospheres. For this sample, the moisture loss presented a percentage of 8% under synthetic air (peak temperature close to 44 °C) and 17.1% for N$_2$. The first event (organic matter decomposition) occurred between 120 °C and 467 °C, with a peak temperature of 384 °C. Ash percentages were found of 5% for air and 22% for N$_2$ atmospheres, such values are consists with the other cassava parts analyzed in this research.
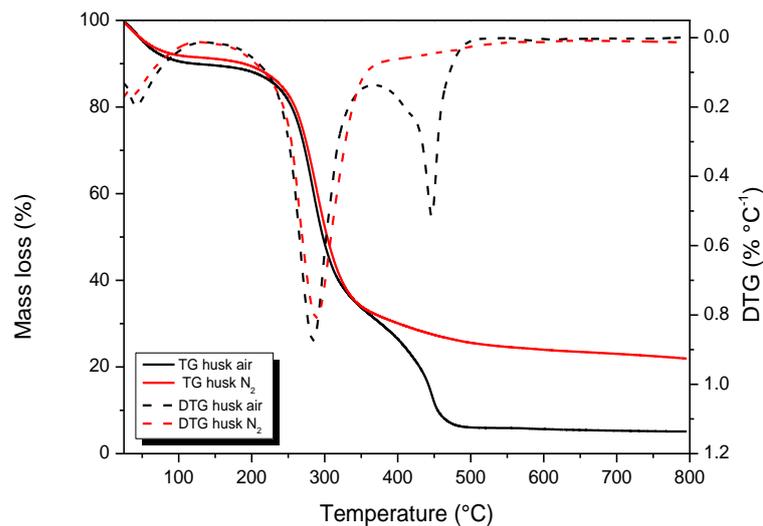

Figure 3: TG and DTG curves for the husk in synthetic air and nitrogen (N$_2$) atmosphere.

Figure 4 shows the TG/DTG curves for the cassava leaf samples under of synthetic air and nitrogen (N$_2$) atmospheres. A different behavior was observed in the TG/DTG curves in relation to the other cassava parts, such as: 2.5% lignin content and low moisture loss (5.3% under air). In this sample, the first event represented the hemicellulose loss of 51.1% for air and 47.25% for N$_2$. The second event showed the cellulose thermal degradation around 31.7% for air and 16.2% for N$_2$. The ash amount (5% for air and 23% for N$_2$) is close to other cassava parts analyzed.

A single extended peak, which is a characteristic of the volatile materials release, was observed a peak temperature around 487 °C, is also observed through of the DTG curves under synthetic air atmosphere. A shoulder was observed around 320 °C for nitrogen atmosphere, which is common for other biomasses, such as sugarcane bagasse and rice husk (Cruz, 2015).
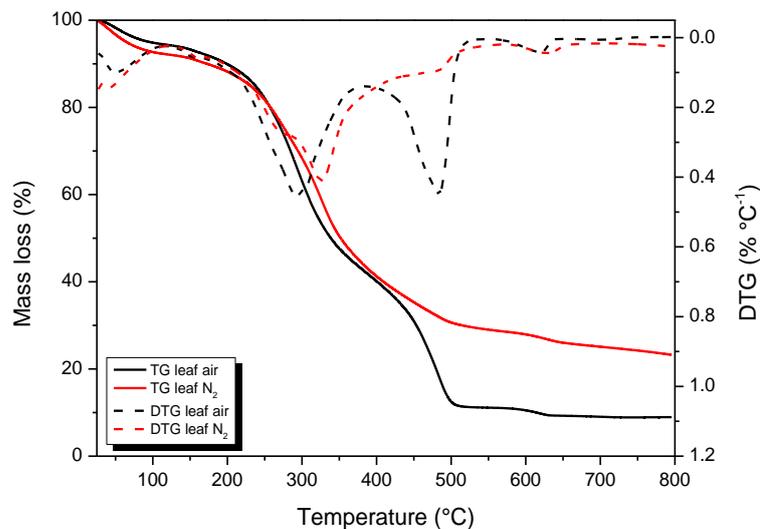

Figure 4: TG and DTG curves for the leaf in synthetic air and nitrogen (N$_2$) atmosphere.

Table 2 shows the temperature ranges of the biomasses thermal degradation stages, whose were obtained in the heating rate of 10 ° C min^{-1} under of synthetic air (80% N$_2$) and 100% N$_2$ atmospheres.

Table 2. Temperature ranges for each stage of thermal degradation under two atmospheres (combustion and pyrolysis)

Cassava Parts	Thermal degradation stages	Temperatures (°C)	
		Air	N$_2$
husk	1	135 - 374	139- 450
	2	378 - 520°	143 - 457
	3	-	-
stem	1	145 - 384	120 - 384
	2	367 - 533	369 - 527
	3	-	-
leaf	1	139.5 -293	140.5 - 399
	2	386.2 - 478	367 - 487.1
	3	-	-

Therefore, it was observed that for the two atmospheres (synthetic air and N$_2$) of the three analyzed parts, these presented the same thermal degradation behavior after ≈ 500 ºC, mainly in pyrolysis atmosphere (100% N$_2$). This is a main indicative that all organic matter was degraded in the thermal processes.

4. CONCLUSION

This study analyzed the physic-chemical properties of cassava residues (husk, stem and leaves). The ash content of the samples ranged from 5% to 25%. The high alkali metal (Na=589.592 nm and K=766.491 nm) content in the samples of cassava residues showed a strong tendency in the occurrence and ashes formation during the combustion and pyrolysis processes.

Thermal analysis (TG / DTG curves) showed the ignition temperatures and thermal degradation stages, mass loss percentage under different atmospheres and thermal degradation of hemicellulose, cellulose and lignin contents for the cassava harvest residues under two atmospheres (combustion and pyrolysis), which showed the behavior and applicability of the studied samples.

In Brazil, cassava harvest residues presented great potential for use as a source of bioenergy, but some care should be taken when used as fuel due to the high ash occurrence.

Finally, it is understood that correct and adequate use of cassava harvest residues in a sustainable and environmentally friendly way, which would be discarded of an unplanned manner, is an important factor for a socio-environmental awareness more concerned with the future of the Planet.

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6. Copyright

7. Acknowledgments

CARACTERIZAÇÃO FÍSICO-QUÍMICA E TÉRMICA DE RESÍDUOS DA COLHEITA DE MANDIOCA PARA APLICAÇÃO EM PROCESSOS DE COMBUSTÃO E PIRÓLISE

Alyson da Luz Pereira Rodrigues (alisonluz93@outlook.com)
Ceuma University - Master Science in Environmental, São Luís - MA, Brazil.

Arthur Vinicius Silva Sousa (arthsilva6@gmail.com)
Federal University of Maranhão - Department of Mechanical Engineering, São Luís - MA, Brazil.

Carlos Eduardo Mendes Braz (carlosedumb@yahoo.com.br)
Federal University of São Carlos – Chemistry Department, São Carlor – SP, Brazil

Wolia Costa Gomes (woliacg@gmail.com)
Ceuma University - Master Science in Environmental, São Luís - MA, Brazil.

Glauber Cruz (glaubercruz@gmail.com)
Federal University of Maranhão - Department of Mechanical Engineering, São Luís - MA, Brazil.

Resumo: Aumentos significativos no uso de recursos renováveis são urgentemente necessários para atender as necessidades de uma população crescente e construir uma sociedade mais sustentável. A literatura apresenta diversos estudos sobre a determinação das características físico-químicas dos resíduos da cultura, como espigas de milho e palhas, casca de arroz, semente de oliveira, bagaço de cana e outros. No entanto, ainda faltam informações detalhadas sobre o uso de resíduos de colheita de mandioca para aplicações energéticas. Este trabalho visa caracterizar os resíduos de mandioca (cascas, caules e folhas) para aplicação em processos de combustão e pirólise. A caracterização físico-química foi realizada para as amostras de resíduos de mandioca e foi determinada sua análise final: carbono, nitrogênio, hidrogênio, enxofre e oxigênio e análise aproximada: material volátil, carbono fixo, cinzas e umidade. O alto valor de aquecimento (HHV) dos resíduos de mandioca também foi determinado, variando a 18,2 MJ kg^{-1}. Foram determinados os valores de umidade (10%), cinza (média de 6,3% em ar), voláteis (68%) e carbono fixo (16%) para as diferentes partes da mandioca. Análises térmicas (TG / DTG) sob atmosfera de ar e nitrogênio foram utilizadas para simular os processos de combustão e pirólise, respectivamente, e determinação dos teores de hemicelulose (25%), celulose (45%) e lignina (25%) dos resíduos de mandioca. Os resultados apresentados nesta pesquisa são úteis para a aplicação desta biomassa em processos de conversão térmica industrial.

Palavras-chave: biomassa, mandioca, combustão, pirólise