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THERMAL DEGRADATION OF THE AGROINDUSTRIAL RESIDUES BY THERMOGRAVIMETRY AND CALORIMETRY

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ABSTRACT: Vegetal residues, in general, have variable characteristics and caloric values, difficulty in combustion control and relatively fast burning. Thus, indicating certain materials for energy production, there is a need for thermal analysis studies. The aim of this work was evaluating by thermal analysis the behavior of agro industrial residues for energy production. Coffee bean parchment and coffee plant stem residues; bean stem and pod; soybean stem and pod; rice husk; corn leaf, stem, straw and cob; sugar cane straw and bagasse; wood processing (planer shavings and sawdust); elephant grass stem and leaf; and coconut husk were submitted to thermo gravimetric analysis and differential scanning calorimetric. The results indicated that the presented residues has potential for energy production; the highest energy peaks occurring around 350 °C; the temperature range of greatest mass loss was 250-350 °C and coconut husk was more resistant to thermal decomposition.

Keywords: energy, biomass, lignocellulosic residues.

DEGRADAÇÃO TÉRMICA DE RESÍDUOS AGROINDUSTRIAIS POR MEIO DE TERMOGRAVIMETRIA E CALORIMETRIA

RESUMO: Os resíduos vegetais, em geral, possuem características e valores calóricos variáveis, dificuldade no controle da combustão e queima relativamente rápida. Assim, para indicar certos materiais para produção de energia, é necessário estudar sua análise térmica. Este trabalho foi realizado com o objetivo de avaliar o comportamento de resíduos agroindustriais mediante análise térmica visando à produção de energia. Os resíduos pergaminho do grão e caule do cafeeiro; caule e vagem do feijão; caule e vagem da soja; casca de arroz; folha, caule, palha e sabugo de milho; palha e bagaço da cana-de-açúcar; resíduos do processamento da madeira (serragem e maravalha); caule e folha do capim-elefante e casca do coco-da-baía foram submetidos à análise termogravimétrica e de calorimetria exploratória diferencial. Com os resultados pode-se concluir que os resíduos apresentaram potencial para produção energética; os maiores picos de energia ocorrem por volta de 350 °C; a faixa de temperatura de maior perda de massa foi 250 - 350 °C e a casca de coco foi o material de maior resistência à decomposição térmica.

Palavras-chaves: energia, biomassa, resíduos lignocelulósicos.

1 INTRODUCTION

The discussion of alternative forms of energy has great importance for the current energy setting, as the population demand is increasing. Therefore, the rational use of misused or wasted natural resources is essential, adding value to them.

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The Brazilian energy matrix presented in 2016 an internal supply of energy equal to 58.5% of non-renewable resources (petroleum and oil products, natural gas, coal and coke, uranium and other) and 41.5% from renewable sources, the latter corresponding to 7.8% of firewood, 17.2% of sugarcane products, 11.1% hydraulic, 1% wind and 4.3% from other fonts (BRASIL, 2017). Although Brazil is predominantly an agricultural country, the use of biomass for energy production is still not significant.

An alternative to increasing the share of biomass in the Brazilian energy matrix is the use of lignocellulosic residues from the agroindustry, which are abundant in the country.

The vegetal residues, in general, have variable characteristics and caloric values, difficulty in combustion control and relatively fast burning. Thus, in indicating certain materials for energy production, there’s a need for characterization and evaluation of its behavior when subjected to thermal analysis.

According to Orfão and Figueiredo (2001), thermal analysis is a set of techniques in which a physical property of a substance and /or its products is measured as a function of time or temperature while the sample is subjected to a controlled temperature program.

The thermal gravimetric analysis (TG) provides information on the composition and thermal stability. Thermal analysis is a technique essentially quantitative, used to measure weight changes experienced by the specimen, resulting from a physical or chemical transformation as a function of temperature or time. In order to facilitate the interpretation of the results obtained in the thermogravimetric analysis, the derivative thermogravimetry (DTG) is performed, which is the mathematical representation of the first derivative of the thermogravimetric curve by time or temperature; it allows a more precisely definition for the beginning and end of thermal events and check the presence of concurrent events (MOHTÉ; AZEVEDO, 2002).

Differential scanning calorimetry (DSC) is a technique that measures the difference in energy supplied to the substance and to a reference material, technically inert. In the process, the substance and the reference material are subjected to a controlled temperature program so that the sample and the reference are maintained at isothermal conditions (IONASHIRO; GIOLITO, 2004; MOTHÉ; AZEVEDO, 2002).

Thus, the objective of this study is to analyze the behavior of agro-industrial residues through thermal analysis aimed at producing bioenergy.

2 MATERIAL AND METHODS

In order to conduct this study, coffee parchment waste of grain and stem; bean stem and pod; soybean stem and pod; rice husk; corn leaf, stem, straw and cobs; sugar cane straw and sawdust bagasse; wood processing residues (planer shavings and); elephant grass stem and leaf and coconut husk underwent to analysis at the Laboratory of Forest Biomass Energy of the Federal University of Lavras.

The material was grinded by a Wiley blade apparatus, using the fraction that passed through a 200-mesh screen but was retained in a 270-mesh screen. The residues were stored under controlled temperature (20±3)°C and relative humidity (65±2)% for moisture homogenization.

The differential scanning calorimetry (DSC) was performed using a DSC 60AH Shimadzu apparatus. Approximately, 2 mg of material were weighed in an aluminum crucible and were inserted in the device. The DSC measured the material energy variation (in mW or mW.mg^{-1}), which was compared to a reference sample of α-alumina. The analysis was performed from room temperature to 550 °C using nitrogen gas atmosphere with constant flow of 50 mL.min^{-1} and a heating rate of 10 °C.min^{-1}.

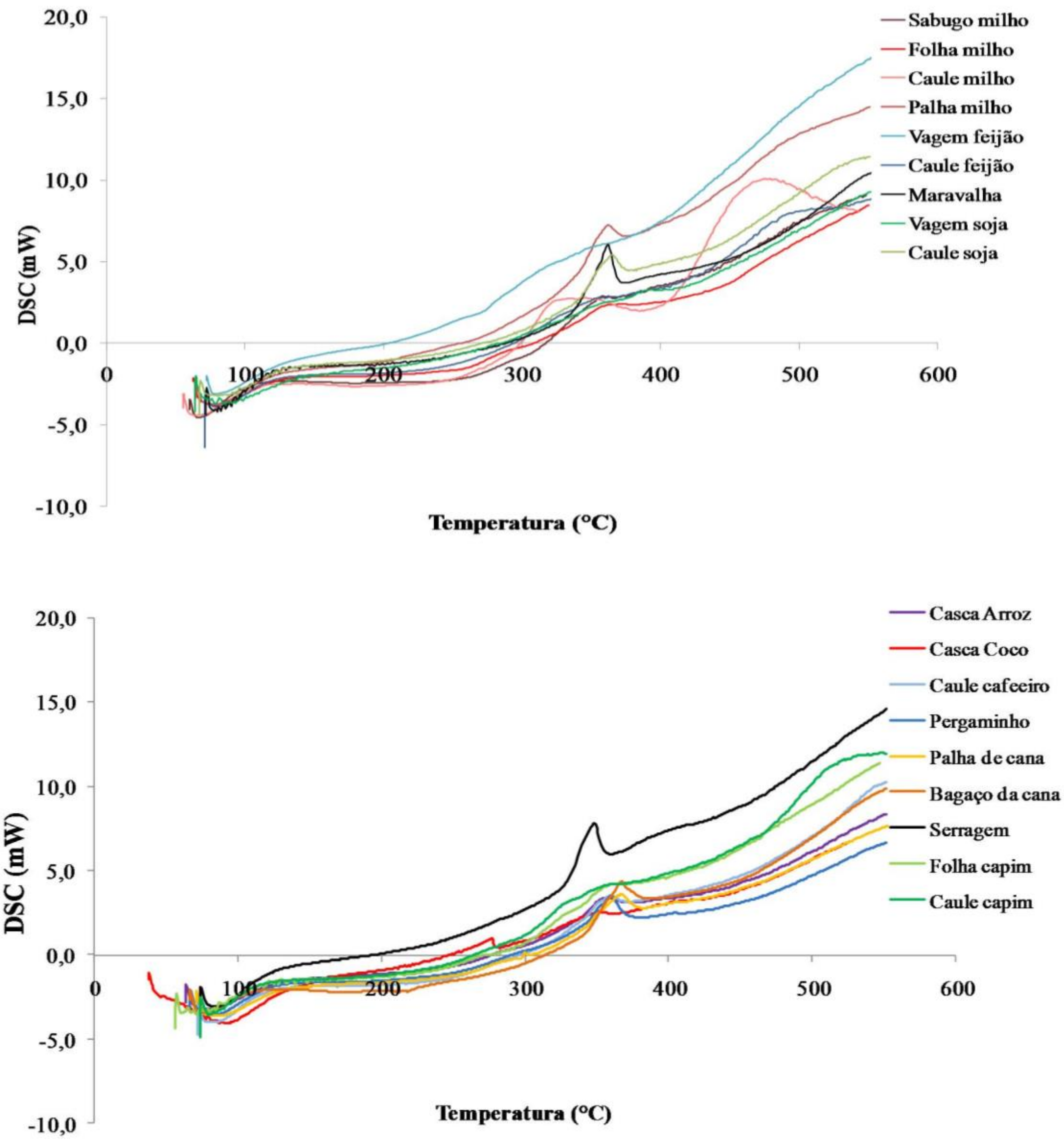
Subsequently, the residues were subjected to thermogravimetric analysis (TG) on an DTG 60 AH Shimadzu apparatus connected to a computer. About 4 mg of the sample were placed in an alumina crucible, and then the same is inserted into the apparatus. The crucible was linked to this sensor and a scale which measured the weight loss of the material as a function of time and temperature. An empty aluminum recipient was used as reference. The process took place in nitrogen gas atmosphere with constant flow of 50 mL.min^{-1} and the temperature was measured with a thermocouple device.

After the analysis, it was possible to obtain curves called thermograms, which showed the weight loss (in mg or %), from room temperature to 550 ° C with heating rates of 5, 10 and 15 °C.min^{-1}. From the thermogravimetric curves the first derivative for identifying points where occurred the weight loss peaks was calculated.

3 RESULTS AND DISCUSSION

Figure 1 shows the DSC curves for residues. In order to a better study on the energy variation, the curves were divided into two groups.

Figure 1. DSC curves for studied residues



The DSC curves represent the heat variations that occur during heating. Early in the process, for all wastes, it was possible to identify a valley that features an endothermic phase of heat absorption. This region, from the beginning to 120 °C approximately, is related to the drying of the material, when the process provides heat for the water to be removed from the sample. In the rate that goes from 120 to 200°C a stabilization occurred and, from 200 to 250°C, there was a slight variation in energy in the process, however still in the endothermic phase.

Pinheiro, Sampaio and Rezende (2008), while studying species of *Eucalyptus* sp. subjected to DSC, analysis, revealed that between 20 and 110°C, the wood has absorbed heat and lost water as steam. Between 110 and 175°C, final traces of water were released and dehydration reactions involving the holocellulose hydroxyl groups occurred. Between 175 and 270°C, the reaction rate increased, giving the onset of the release of volatiles and gases and wood decomposition, with carbon monoxide, carbon dioxide, acetic acid and methanol releasing. According to the authors, this phase is called pre-carbonization or torrefaction and all reactions in reaching it are endothermic.

The release of heat, exothermic phase, begins at temperatures around 280°C, showing that the chemical components begin to decompose at this temperature. In this phase, the exothermic peaks are obtained.

The behavior of waste in the analysis was different and this fact is evident in the energy release phase. Although having lignocellulosic constitution, this happens because they have different component concentrations (Table 1). The sources cited in Table 1 used the same material of the present study.

Table 1. Chemical composition of residues.

Material		Extr. (%)	Lign. (%)	Ash(%)	Hol. (%)	Reference
Coconut	Husk	9.8	51.41	8.21	30.57	Baliza (2011)
Elephant grass	Stem	14.14	22.97	3.00	59.89	
	Leaf	16.04	23.40	8.05	52.51	
Rice	Grain husk	4.06	26.90*	16.43	52.61	Paula et al. (2011)
Coffee	Plant stem	10.49	22.88	1.12	65.51	
	Bean parchment	7.63	23.04	1.46	67.87	
Sugar cane	Bagasse	31.76	20.88	0.80	46.56	
	Straw	9.18	20.85	4.32	65.65	
Bean	Stem	7.55	21.61	4.61	66.23	
	Pod	18.19	11.99	6.65	63.17	
Wood	Sawdust	9.37	21.88	0.18	68.57	
	Planer shavings	5.60	20.62	0.13	73.65	
Corn	Stem	11.31	20.49	3.43	64.77	
	Leaf	10.51	19.26	3.53	66.70	
	Straw	5.85	9.29	1.58	83.28	
	Cob	5.85	15.75	1.16	77.24	
Soybean	Stem	6.87	21.64	2.28	69.21	
	Pod	21.77	17.16	7.25	53.82	

* Adjusted value, deducting 8.32% of silicon.
Extr., Lign., Ash, Hol. = Extractives, lignin, ash and holocellulose contents.

According to Byrne and Nagle (1997), in the biomass pyrolysis is possible to identify three stages of degradation. The first, at temperatures between 200 and 260°C, results from the loss of the most reactive fraction, composed mainly of hemicellulose. In the second case, the degradation of the cellulose at 240 to 350°C and in the last step the degradation of lignin from 280 to 500°C.

The regions of exothermic DSC curves (Figure 1) showed different peaks, some less and others more defined with variable intensity. However, for most samples, it was only possible to identify a peak, which occurred at around 350°C. Although this temperature is high compared to the previously mentioned, some authors, such as Pereira et al. (2013) and Leroy, Leoni and Cancellieri (2010), identified this peak and attributed to the thermal decomposition of hemicellulose. These authors also found a second peak in the DSC curves at around 370°C, characterizing the decomposition of the cellulose.

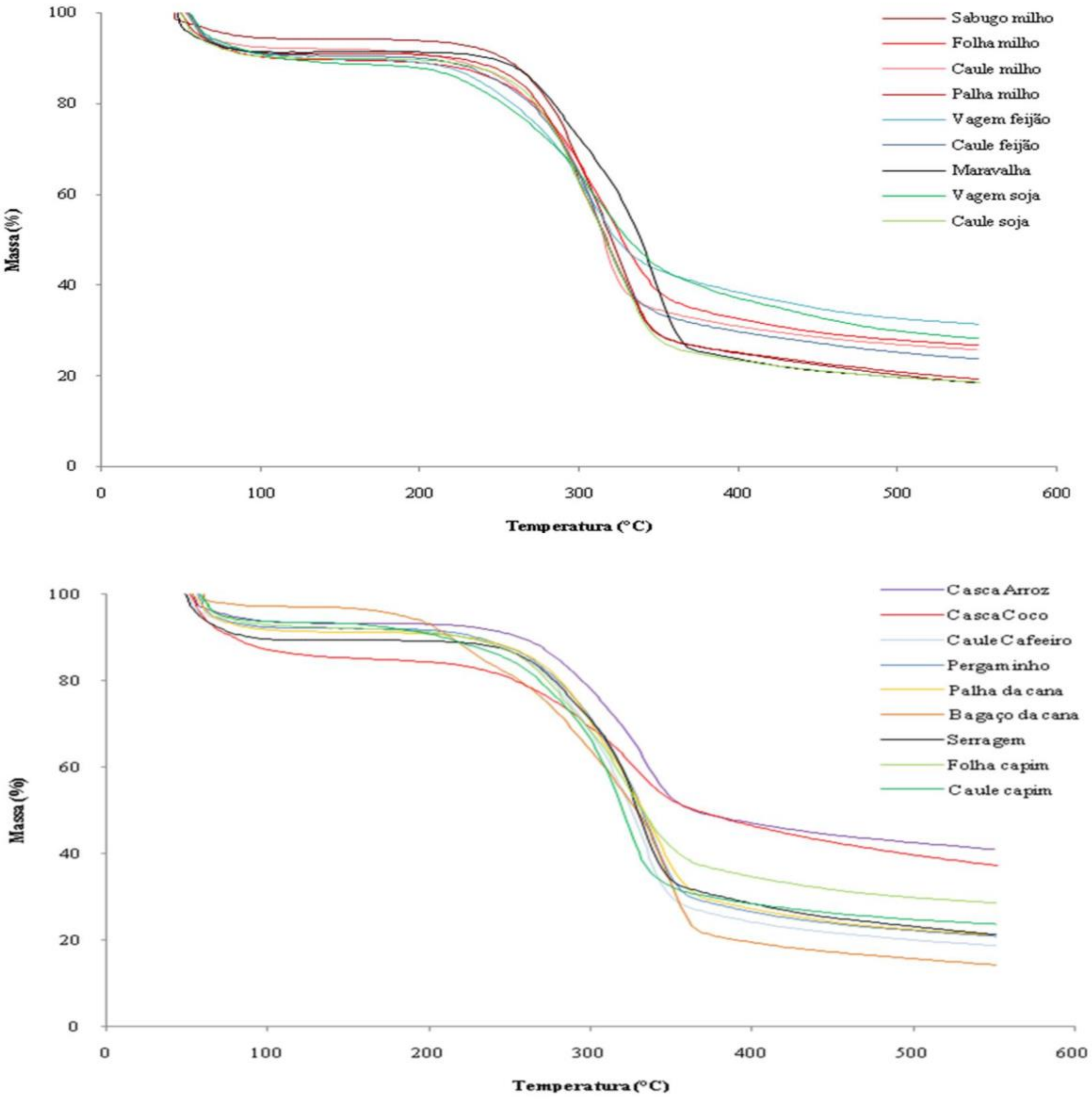
In the present study, which treats on different biomasses, it is believed that this peak was due to the degradation of hemicellulose and cellulose together, since the materials (sawdust, shavings and corn straw) that showed greater deterioration in these phases contain high holocelulose content (cellulose + hemicellulose), as can be seen in Table 1.

The stem of corn showed a DSC curve with two distinct peaks at temperatures 313 and 464°C, probably due to decomposition of lignin and holocellulose, respectively. For the majority of residues, as mentioned, only one peak was identified; for some others it was not possible to point some peak. This fact is probably due to the occurrence of simultaneous events, which prevented the identification of three stages of thermal degradation of the biomass.

According to Branca and Di Blasi (2003) and Órfão and Figueiredo (2001), the steps of thermal decomposition of biomass overlap, since the degradation of the lignin begins in the second step, the hemicelluloses are converted to the end of this step and cellulose degradation ends in the third step.

Figure 2 shows the TG curves for the evaluated residues. From the curves, the weight loss by temperature range was determined (Table 2). An initial mass loss phase can be seen in the TG curve, an, which occurred from room temperature to approximately 120° C, due to drying of the sample. Then, as in the DSC curves, a stabilization of up to 220 °C with low mass loss was observed, as shown in Table 2.

Figure 2. Profile of residues thermal degradation.



The second weight loss band is steeper. It begins at around 220°C for most residues and continues to increase up to approximately 380°C, according to Santos (2013). For elephant grass stem and sugar cane bagasse, mass loss in this stage began at a lower temperature, around 155°C. According to Fernández et al. (2012), this phase indicates the reactivity of the sample. Noticing the weight loss ranges from 250 to 350 °C, presented in Table 2, it appears that corn cobs showed a sharper peak, a more vertical profile indicating a greater mass loss in a shorter time, which means a shorter combustion time. The coconut husk, in its turn, had a linear profile that requires a longer combustion, which is interesting for a fuel.

The peculiar behavior presented by the coconut husk is probably due to its high content of lignin and low holocelulose, as can be seen in Table 1. The thermal decomposition of lignin takes place in a wide temperature range and is the most thermally stable lignocellulosic component (MÜLLER-HAGEDORN et al., 2002), which explains the high residual mass of coconut husk.

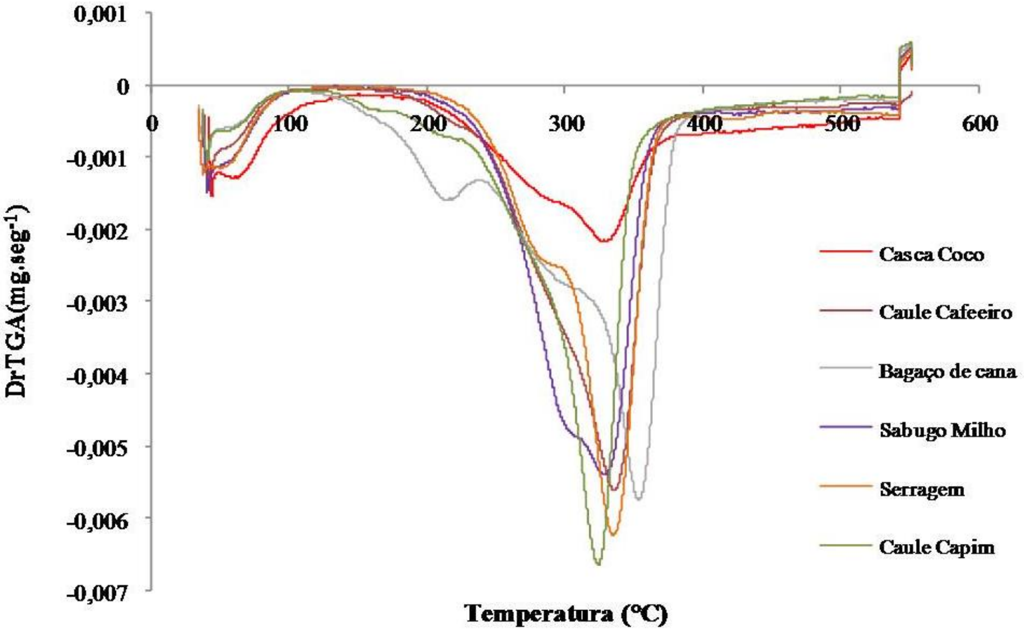
The behavior exhibited by wood residues are at accord with Santos et al. (2012), who studied the wood of Eucalyptus. From 370°C, the weight loss slowly decreases for most waste until the final temperature. The greater residual mass was found to rice hull, however, it has a high ash content (Table 2).

Table 2. Weight loss (%) of residues per temperature range.

Material		30-100	100-250	250-350	350-550	100-550	30-550
Rice	Grain husk	6,39	2,95	37,71	11,94	52,60	***58,99***
Coconut	Husk	12,89	6,61	***28,05***	15,03	***49,69***	62,58
Coffee	Plant stem	7,77	5,35	56,93	11,21	73,48	81,25
	Bean parchment	7,64	4,91	52,91	13,43	71,24	78,88
Sugar cane	Straw	8,37	4,08	50,42	15,84	70,33	78,70
	Bagasse	2,93	**15,68**	48,64	18,39	**82,71**	**85,64**
Corn	Cob	5,48	3,93	**61,36**	10,65	75,94	81,42
	Leaf	9,59	5,40	46,26	11,82	63,49	73,08
	Stem	7,53	6,54	51,20	8,78	66,52	74,05
	Straw	8,76	3,79	57,99	10,00	71,78	80,54
Bean	Pod	8,92	9,04	38,63	11,89	59,56	68,48
	Stem	8,89	6,10	51,07	10,10	67,27	76,16
Wood	Sawdust	10,49	***2,73***	52,97	12,52	68,21	78,70
	Planer shavings	8,53	1,97	50,49	**20,28**	72,74	81,27
Soybean	Pod	9,10	10,23	36,43	15,80	62,46	71,56
	Stem	9,55	4,14	58,14	9,45	71,73	81,28
Elephant grass	Leaf	7,20	6,02	45,20	12,80	64,02	71,22
	Stem	6,41	8,94	52,24	***8,59***	69,76	76,17

Figure 3 shows the DTG, the first derivative of the thermogravimetric curves of the coffee stem, coconut shell, sugarcane bagasse, the corn cobs, sawdust and stem of elephant grass.

Figure 3. DTG curve of residues



The DTG curves showed that the coconut shell, corn cob and sawdust exhibited behavior characteristic with three weight loss steps. The first occurred around 100 ° C due to water loss and the two others with greater thermal degradation.

The second stage of thermal decomposition was the temperature range between 200 and 300°C. This mass loss phase was expected, as it has already been identified by Polleto et al. (2012), in reference to the region of DTG curves, called "shoulder". According to these authors, this temperature range occurs mainly the degradation of hemicellulose and the onset of decomposition of the cellulose.

The third phase, where the rate of decomposition of biomass was maximum (major peaks), caused a greater weight loss in the temperature range 300 to 400°C due to the degradation of cellulose and especially of the lignin.

The two thermal degradation bands occurred because the hemicellulose has an amorphous structure, branched and easily decomposed by heat. In contrast, the cellulose molecule is a long polymer of glucose units and their crystalline regions increases the thermal stability (JOHN; THOMAS, 2008).

The analysis of bagasse showed four decomposition regions, differing from the other due to a decomposition phase at a temperature of 200°C, which is probably due to the extractives decomposition. In Table 1, these residues contains with a higher content of extractives compared to the others.

Thermogravimetry derived from stem of elephant grass presented only two regions of decomposition. The first, due to the outflow of water and the second possibly related to the decomposition of hemicellulose and cellulose.

4 CONCLUSIONS

Based on the results obtained, it can be concluded that the waste showed potential for energy production; the highest energy peaks occur around 350°C; the largest mass loss temperature range was 250-350°C; DTG curves showed three stages of degradation for the coconut husk, corn cob and the sawdust and four steps to the sugarcane bagasse; and the coconut husk showed the highest resistance to thermal decomposition.

5 ACKNOWLEDGEMENTS

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