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INVESTIGATION OF CHARACTERISTICS OF CELLULIGN BY THERMOGRAVIMETRIC ANALYSIS

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ABSTRACT - *Agricultural fuels like energy forest, straw fuels, sugar cane bagasse, oil crops and grain can be used for heat, electricity or transports and may become an important complement to forest fuels in replacing the fossil fuels. The biomass of this study is the celulignin of Eucalyptus grandis forestry residues – composed mainly of cellulose and lignin and a small amount of hemicellulose remainder of the acid hydrolysis process. The decomposition of this biomass was investigated by simultaneous thermogravimetric analysis and differential scanning calorimetry using a SDT-Q600 TA Instruments equipment with the software TA Advantage 5008TGA. Samples between 5 and 9 mg were pyrolyzed to a maximum temperature of 600 ºC at synthetic air (<5 ppm* H_2O*, 50 mL* min^{-1}*), and to a maximum temperature of 1400 ºC at* N_2 *(<5 ppm* H_2O*, 50 mL* min^{-1}*) using a heating rate of 10 ºC* min^{-1}*. The mass calibrations were carried through temperature (zinc standard), base line and heat flow (sapphire standard) in the analysis conditions. Results obtained of thermal decomposition of this biomass show that the transition temperatures in oxidant atmosphere were between 28 and 160 °C for moisture elimination, 160 and 374°C for hemicellulose remainder and cellulose and 374 and 494°C for lignin decomposition. In inert atmosphere of nitrogen, three exothermic intervals were also observed, between 28 and 105°C for moisture elimination, 105 and 325°C for hemicellulose remainder and cellulose and 325 and 540°C for lignin decomposition.*

Keywords: biomass, renewable energy, pyrolysis, combustion, thermal analysis.

1- INTRODUCTION

The technological human development generated the dependence of energy in our lives as a question of survival. Energy independence of a nation guarantees development, economic power and national safety. Fossil fuels as main energy sources have been questioned due their scarcity and contribution to the increase of CO_2 concentration and other greenhouse gases (GHG) in the Earth's atmosphere, provoking global climate change. With the objective of decreasing this effect it is clear that a combination of approaches will be required, including increased energy efficiency, energy conservation and, mainly, alternative energy sources.

The conversion of biomass waste to bioenergy has been fundamental to the development of new technologies of renewable energy sources to substitute the fossil fuel. According to McKendry (2002), biomass can be converted into three main products: two related to energy – power/heat generation and transportation fuels – and one as a chemical feedstock. The biomass is constituted mainly of cellulose, hemicellulose and lignin and its thermal decomposition takes place through a set of complex chemical reactions with heat and mass transfer. Previous studies showed that biomass pyrolysis can be divided into four individual stages: moisture evolution, hemicellulose decomposition, cellulose decomposition and lignin decomposition. Knowledge of the pyrolysis characteristics of the three main components is essentially important for a better understanding to biomass thermal chemical conversion Yang *et al*. (2007).

Thermogravimetric analysis have been widely used to study solid-state decomposition reactions and it is the general approach applied to determine the mass loss of pyrolyzed samples at various reaction temperatures (Chen *et al.* 2013; Stanger *et al.* 2013; Carrier *et al.* 2011; Huang *et al.* 2011; Vamvuka & Zografos, 2004; Lapuerta *et al.,* 2004; Mansaray & Ghaly, 1999; Ghetti *et al.,* 1996). In the case of organic materials (lignocellulosics, plastics, municipal solid residues, among others), thermogravimetric techniques have been used for identification of different polymer fractions of material and its ratio, to determine the kinetic decomposition constant or in previous study of residues incineration. It is also a useful instrument to study coal gasification in order to know the reactivity of the coal under active atmospheres (CO_2, oxygenate mixtures or vapor). It is therefore accepted that thermal analysis can contribute to knowledge of thermal decomposition of biomass.

The purpose of present study was to investigate thermal decomposition of celulignin through techniques of thermal analysis in an oxidant and in an inert atmosphere, followed by comparison of the TGA and DTG curves of the samples.

2. MATERIALS AND METHODS

2.1. Raw Material

The raw material used was celulign obtained from acid hydrolysis of *Eucalyptus grandis* forestry residues of plantation of Cia. Suzano de Papel e Celulose – São Luiz do Paraitinga – SP – Brazil. Air dried samples were milled on the 20 mesh.

2.2. Thermal analysis

Thermal analyses were carried out using a SDT-Q600 TA instrument equipped with software TA Advantage 5008. The TGA curves were obtained directly from the apparatus while the DTG curves were obtained by software. The sample mass used was 5 and 9 mg. To obtain the burning profiles, the content of the combustible part (volatile matter and fixed carbon) were considered. For volatile release profiles, the volatile matter alone was considered. Consequently, the DTG curves are normalized and peak heights are directly comparable. Samples were placed in an alox cylindrical crucible and heated from room temperature to 500 °C with air and to 1400 °C with N_2 at 10°C min $^{-1}$ using a 50 mL min^{-1} flow of air and N_2. Figure 1 show a schema of a generic device for differential thermal analysis (DTA) and differencial scanning calorimetry (DSC).

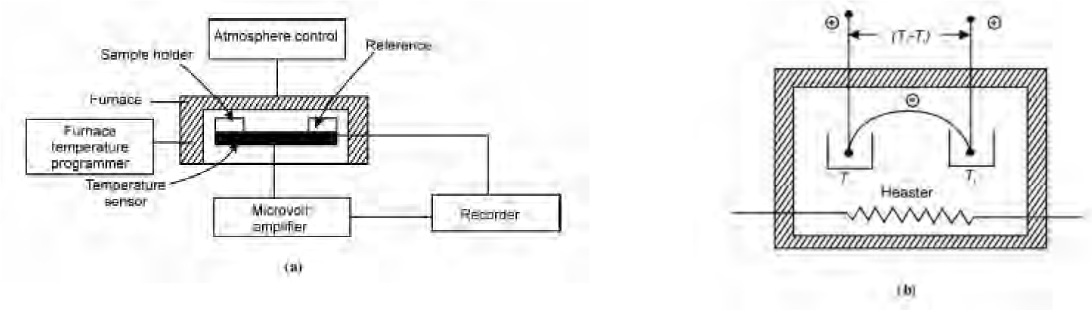

Figura 1. Schematic of a generic device for differential thermal analysis (DTA) and differential scanning calorimetry (DSC) ; a) complete layout, b) furnace part sharing continuous heating of sample and standard (adapted by Bernal *et al.,* 2002).

3. RESULTS AND DISCUSSION

For each sample, graphics were drawn with crossed curves as shown in the figures 2, 3, 4 and 5 (TGA, DTA and DTA). The mass loss was determined from DTG peaks according to temperature intervals. The DTA peak (maximum) temperature is also shown, although this curve must be analyzed with caution, because until 250ºC it did not distinguish itself from the base line of the equipment. These curves represent the decomposition of the cellulose, lignin and a small residual fraction of hemicellulose resultant of acid hydrolysis from forestry eucalyptus residue in inert and oxidant atmosphere. There are a great number of peaks in the DTG curves as shown in figures 2, 3, 4 and 5 making it difficult to attribute to each mass loss the decomposition reaction of each biomass component.

The cellulose is a linear macromolecule with units of β- (1→4) - D-glucopiranose. According to Kilzer & Broido (1965), mentioned by Mangut *et al.* (2006), the pyrolysis of these polysaccharides initiates with intramolecular dehidratation to form anidrocellulose, then levoglucosana is formed and finally a great number of reactions that splits C-C, C-O and reactions of radicals to form volatile gases and composites.

In TGA curves using air atmosphere (figures 2 and 3), it can be observed that the sample mass loss occurred in three stages between 105 and 494ºC, while DTA curve indicates two exothermic processes. The presence of peaks in the temperature versus time curve showed that the heat release was enough to raise the temperature of the sample above of the programmed. The format of curve TGA between 373 and 494ºC suggests the occurrence of combustion of the sample, with almost total consumption of the same one. Comparison with DTG curves obtained by Orfão *et al.* (1999) suggest that the mass loss between 105 and 373ºC either caused by the decomposition of the cellulose and a small fraction of hemicellulose, whereas the mass loss between 373 and 494ºC can be attributed to lignin. Font *et al.* (1995) studied the decomposition of the almond shell, with a heating rate of 10 ºC min $^{-1}$ and these authors had determined through DTG curves, two peaks, a peak centered around 310°C and the other clearest around 368 °C. The first peak can be mainly produced by the decomposition of hemicellulosic fraction of almond shell while than the second peak could correspond the decomposition of cellulosic fraction. At the same time, the charring of lignin fraction occurs on a scale of ampler temperature overlapping with these two processes. Ergüdenler & Ghaly (1994) studied the thermal decomposition of four straws of cereal (wheat, barley, oats and rye) in oxidant atmosphere and noticed three peaks of mass loss, the first peak was in 100°C, attributed the evaporation of water, the second peak appeared in 250-350°C and the third in 350-500°C, both must be to combustion process. The mass losses in the combustion stages were different of one biomass for another, what it predominated was that in the second reaction of combustion the mass loss was bigger for the species with bigger lignin content, suggesting that the extension of the second reaction of combustion was correlated with the lignin content.

In nitrogen inert atmosphere (figures 4 and 5), TGA the curve between 105 and 540ºC shows two regions of mass loss; after this temperature interval the mass loss is continuous and with constant rate until the end of heating, with residue of (23±1) % at 1000ºC e (18±2) % at 1370ºC. DTA curve contains small endothermic with maximum in 274ºC, coincident with the maximum of DTG peak in this region, whereas the DTA curve remain suggests the occurrence of endothermic processes in the region of 1000ºC and above of 1200ºC. Ghetti *et al.* (1996) studied the thermal decomposition of some lignocellulosics materials and TGA curves in helium atmosphere shows that are most homogeneous than air atmosphere. The volatilization process started in 200 °C and the maximum mass loss occurred in 330-350°C. In 380-400°C interval the inclination of curve change abruptly and a slow mass loss continues until high temperatures (800°C).

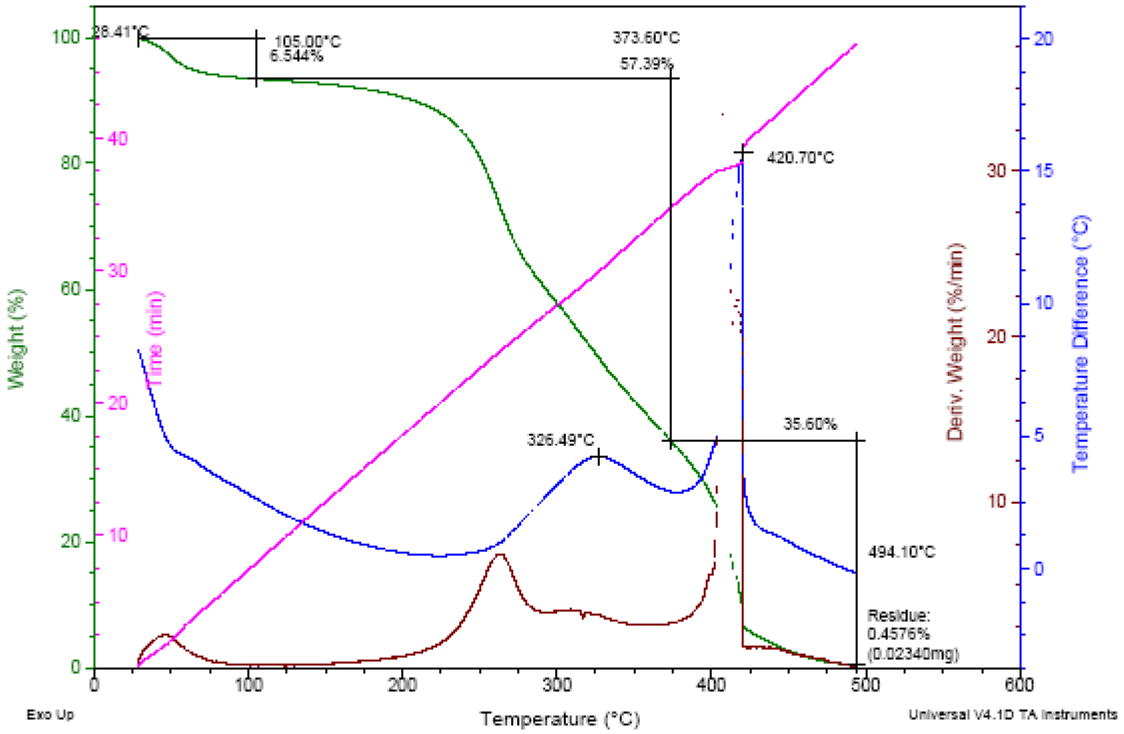

Figure 2. DSC-TGA simultaneous curves of cellulignin from forestry eucalyptus residues, with 10°C min^{-1} air, 50 mL min^{-1}; m $_{i}$ = 5 mg.

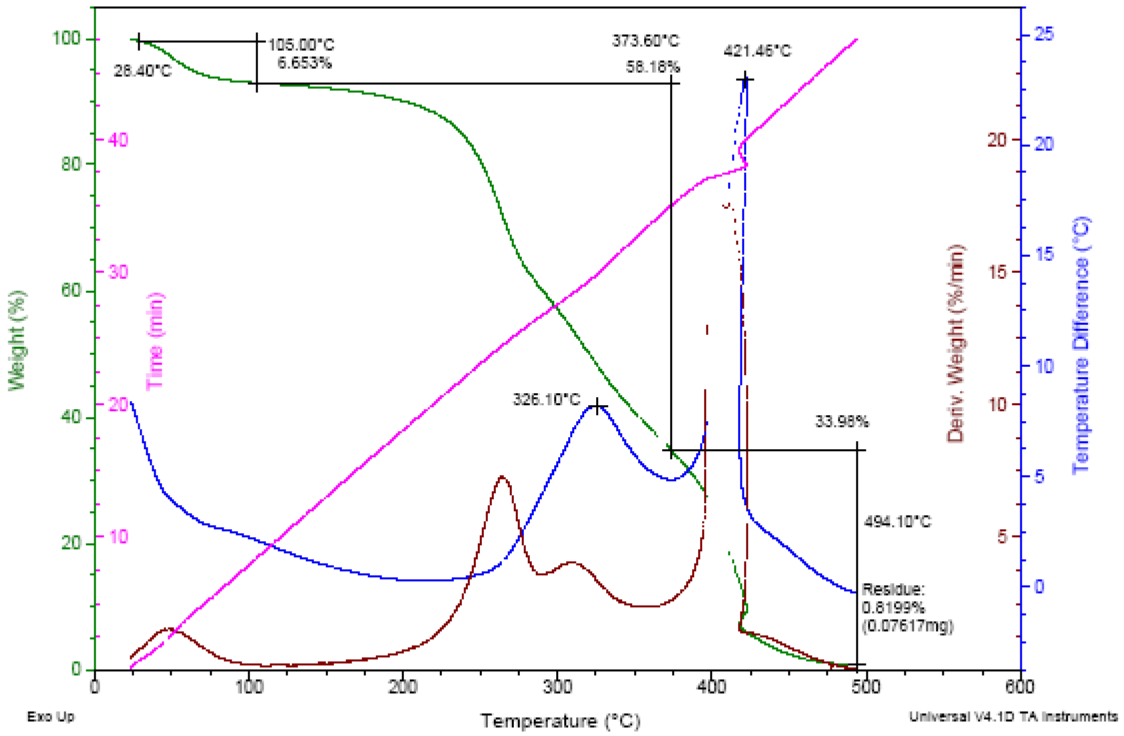

Figure 3. DSC-TGA simultaneous curves of cellulignin from forestry eucalyptus residue, with 10°C min^{-1} air 50 mL min^{-1}; m $_{i}$ = 9 mg.

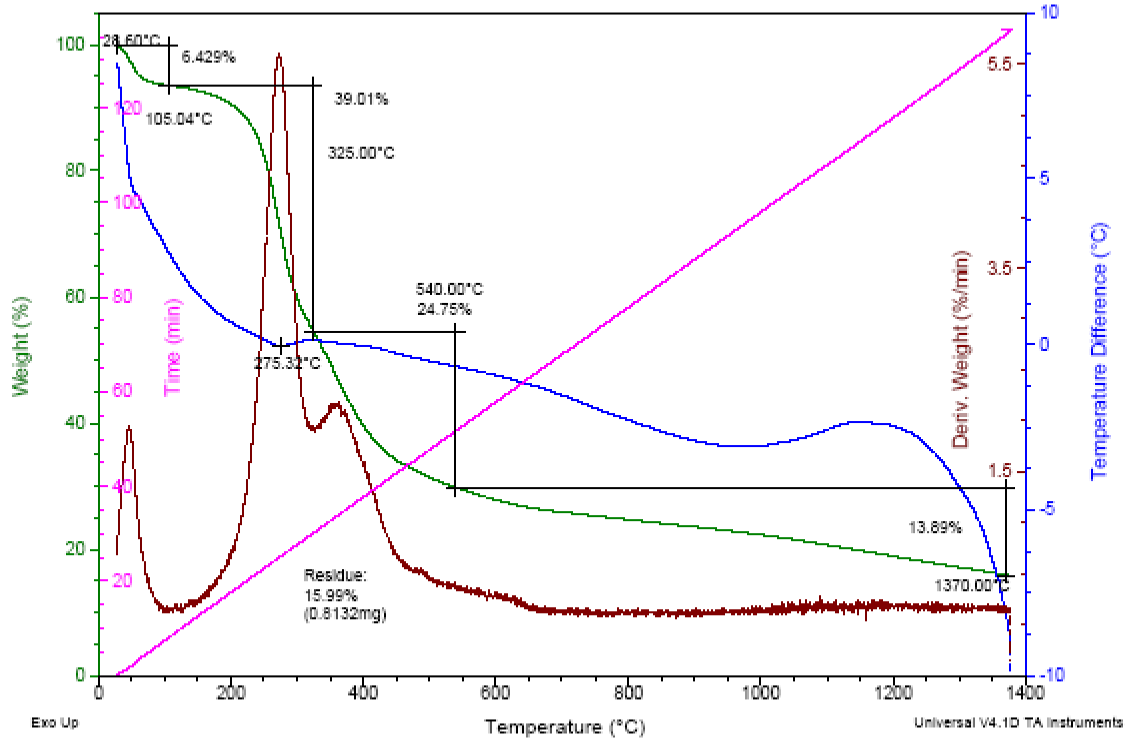

Figure 4. DSC-TGA simultaneous curves of cellulignin from forestry eucalyptus residue, with 10°C min^{-1} N_2, 50 mL min^{-1}; m $_i$ = 5 mg.

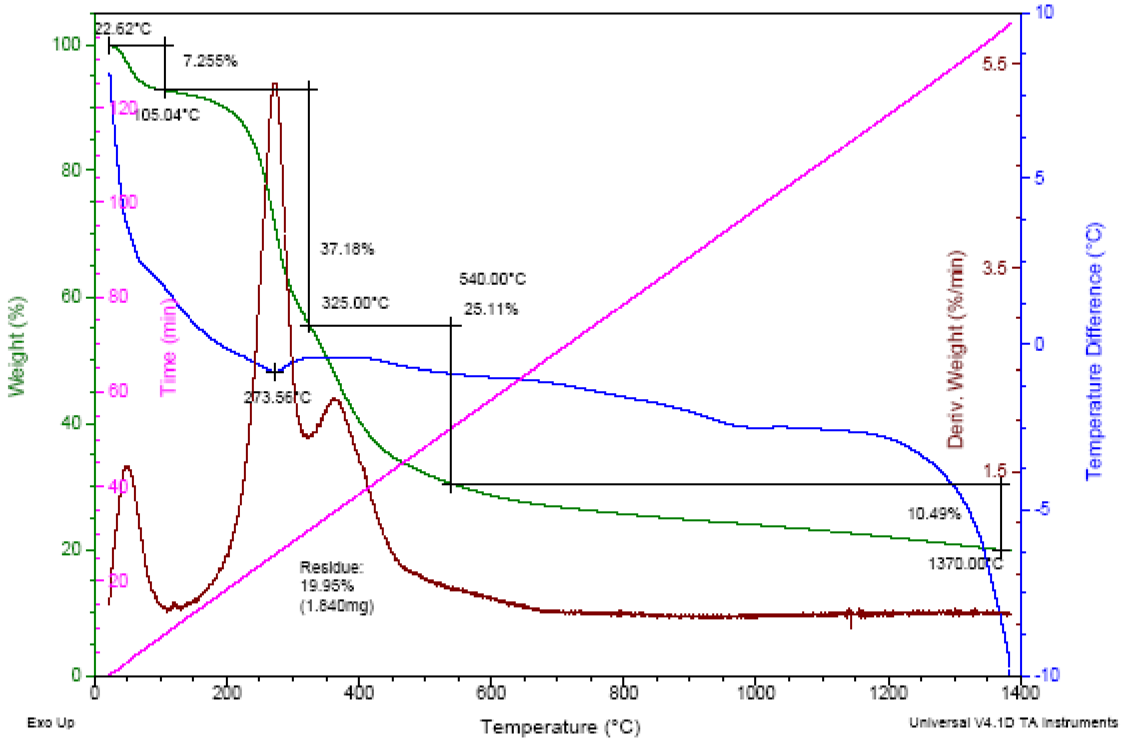

Figure 5. DSC-TGA simultaneous curves of cellulignin from forestry eucalyptus residue, with 10°C min^{-1} N_2, 50 mL min^{-1}; m $_i$ = 9 mg.

Table 1 shows the values of cellulignin mass loss percentage with the respective averages and deviation in the temperatures intervals for each sample. Although different masses have been used, the repetitiveness was adequate. The initial mass was modified to 5 mg in air to diminish the effect of the release of reaction heat and in N_2 to try to increase the intensity of DTA peaks. The same behavior was observed in both studied atmospheres (air and nitrogen) the first stage of mass loss can be attributed to the elimination of present humidity in the sample. The average between these two atmospheres can be used as a representative value for the humidity; the sample presented 6.7 ± 0.3% of humidity content.

Table 1. Results of DTA-TGA analysis from cellulignin.

Air	Mass loss (%)*				DTA (ºC)	
T (ºC)	28-160	160-374	374-494	RESÍDUE 494	Tp 1 exo	Tp 2 exo
Cellulignin, $m_i = 5mg$	6.54	57.39	35.6	0.46	326.49	420.7
Cellulignin, $m_i = 9mg$	6.65	58.18	33.98	0.82	326.1	421.46
Average	6.60	57.79	34.79	0.64	326.30	421.08
Standard deviation	0.06	0.40	0.81	0.18	0.19	0.38

N_2	Mass loss (%)						DTA (ºC)
T (ºC)	28-105	105-325	325-540	540-1370	RESIDUE 1000	RESIDUE 1370	Tp 1 endo
Cellulignin, $m_i = 5mg$	6.43	39.01	24.75	13.89	22.31	15.99	275.32
Cellulignin, $m_i = 9mg$	7.26	37.18	25.11	10.49	23.91	19.95	273.56
Average	6.85	38.10	24.93	12.19	23.11	17.97	274.44
Standard deviation	0.42	0.91	0.18	1.70	0.80	1.98	0.88

TGA curves presented a similar behavior to both atmospheres with 9 mg sample and its DTG and DTA curves suggested different processes for each atmosphere because the form and position of the peaks are different. DTA curves show that the process of decomposition is very exothermic in air and endothermic processes are observed in nitrogen atmosphere.

Lapuerta *et al.* (2004) analyzed *Pinus pinaster* forest residues thermal decomposition and identified three distinct volatility regions. In the first region the moisture was removed until 127°C. In second, between 177-377 °C, the lighter volatile compounds are produced and it is attributed to hemicellulose and cellulose decomposition. Finally, in inert atmosphere the more weighed volatile compounds are produced while than in oxidant atmosphere the char is oxidize around 527 °C and the remainder become ashes. This third volatility is generally identified as lignin decomposition, this process occur slowly and under a wide temperature scale.

Rajeswara Rao *et al.* (1998) studied the pyrolysis of different species of biomass (hazelnut, wood, rice and olive shell) and these authors concluded that the temperature transition for the cellulose, lignin and xylan occurs approximately at 350°C, 390°C e 270°C, respectively.

Yang *et al.* (2006) compared third commercial products of Sigma-Aldrich Chemie GmbH of cellulose, lignin and xylan representing hemicellulose with different biomasses (shell, fibers and branches of fruits) and related that the pyrolysis process of this biomasses can be divided in four regions: < 220 °C, relative the moisture; 220-315 °C, predominantly hemicellulose decomposition; 315-400 °C, cellulose decomposition; > 400 °C, lignin decomposition.

The results of present paper show that the cellulignin consist mainly of cellulose and lignin and a small amount of hemicellulose remains of acid hydrolysis process. The study of thermal decomposition of this biomass attributes the transition temperatures in oxidant atmosphere: 28-160°C, relative the moisture elimination; 160-374°C, hemicellulose and cellulose decomposition, 374-494 °C, lignin decomposition. In nitrogen inert atmosphere, three exothermic intervals were also observed: 28-105 °C, relative the moisture elimination; 105-325 °C, hemicellulose e cellulose decomposition; 325-540 °C, lignin decomposition. Further studies are needed to achieve a better knowledge of biomass thermal decomposition. The purpose of a future work can be the use of other types of biomass, because different proportions of its fractions must influence significantly the thermal decomposition process. Energy and environment policies affect the future of agricultural fuels. The weight that policy makers attach to the greenhouse effect is of vital importance. Sustainable energy supply by means of balanced political steering instruments increases the demand for biofuels and makes it possible for agricultural fuels to expand.

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