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Particle Size Influence on the Chemical Composition from Waste *Eucalyptus* in the Processing for Industrial Production of Cellulose Pulp

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Among the biological materials, wood is a chemist and biochemist collection formed and organization still is of secrets and unknowns, despite the great technological advances in recent decades. Today the chemistry of wood takes new directions and new challenges with the technological improvement of the analysis and the emergence of wood modified by genetic modification, mutation and genetic improvement, therefore, new skills are required with new sources of information. Thus the present assessed chemical characterization a residue derived from Eucalyptus processing for the industrial production of cellulose pulp. Ten grams of sample were subjected to a milling process. The following particle sizes were studied (10, 14, 20, 30, 40 and 50 mesh). It was determined the moisture content, ash content and lignin were determined by the sum of Klason lignin insoluble and soluble lignin. The filtrate produced by the method insoluble Klason lignin was analyzed by spectroscopy. The holocelulose content, pulp and polyoses were determined through analysis by líquidade high performance liquid chromatography. The results showed that particle size influences the chemical properties of lignocellulosic material, and the smaller the particle size the greater was the amount of extractives and ash, which resulted in lower amounts of cellulose and hemicellulose. Lignin showed no significant changes.

1. Introduction

The wood from eucalyptus is the main source of fibers in the countries of South America for the production of pulp and paper. Brazil occupies a prominent place in world production of eucalyptus fiber pulp (Magaton et al., 2008).
The pulp and paper companies generate a lot of waste and its use is based primarily on power generation by burning and animal feed. However, new applications are emerging and provided a better use of these materials. The pulp and paper companies have the potential for the implementation of bio-refinery, where it aims to take full advantage of biomass.
Eucalyptus logs processing in pulp mills generate large amounts of sawdust that are burned to produce water vapor / electricity.
The pulp and paper industry generates around 10% of biomass per ton per day, which is not used for the production of cellulose pulp, being conducted burning steps to water vapor production and electricity.
The chemical composition of wood can be divided into low and high molar mass fractions (Fengel; Wegener, 1989; and Gellerstedt Henriksson, 2009). The low molar mass fraction consists of organic substances, generally referred to as extractives, and inorganic substances which are metal ion salts (Sjostrom; Wetermark, 1999; Gellerstedt and Henriksson, 2009). The extractives include various chemical compounds that can be extracted with organic solvents, although some are also soluble in water (Fengel; Wegener, 1989; and Gellerstedt Henriksson, 2009). These compounds are responsible for characteristics such as odor, color and flavor of lignocellulosic and are present in small quantities (from 2 to 8%) (Sjostrom; Wetermark, 1999). The

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inorganic compounds are present in even smaller quantities in lignocellulosic (1 to 2%) (Fengel; Wegener, 1989; and Gellerstedt Henriksson, 2009).
The macromolecules represent almost all plant tissues and comprise only three classes of compounds: cellulose, polyoses (hemicellulose) and lignin (Fengel; Wegener, 1989).
The cellulose is the most abundant component in wood (about 50%), being a linear polymer formed exclusively of anhydro-glucose molecules (Fengel; Wegener, 1989; Sjostrom; Wetermark, 1999; and Gellerstedt Henriksson, 2009).
The hemicelluloses (polyoses) are composed of the sugars glucose, mannose and galactose (hexoses) and of xylose and arabinose (the pentoses) they may also provide varying amounts of uronic acids and deoxy-hexose in some types of wood. These sugars present in the form of branched polymers of lower molar mass than cellulose. The polyoses content in different types of wood is very variable and may be assumed an average value of about 20% (Fengel; Wegener, 1989; Sjostrom; Wetermark, 1999; and Gellerstedt Henriksson, 2009).
The lignins are complex and abundant structures present in plants, linked to cell vegetable wall, responsible for the rigidity of the cell wall, reducing the permeability of the cell wall to water, protection of the wood against micro-organisms and plant resistance to compression to allow its growth (De Almeida et al., 1988; Willför et al., 2002).
The lignin is the second component in larger quantities in lignocellulosic and its presence provides all the complexity existing in pulping processes, because it has a quite complex structure. A part of the lignin molecules is chemically linked with polyoses, i.e. there is a lignin-carbohydrate complex in the chemical structure of the plant cell wall. (Ralph et al., 2004).
The great structural complexity of lignin makes it one of the hardest natural macromolecules to characterize chemically. The majority of the lignin cannot be removed from the lignocellulosic matrix without structural changes during the extraction step. Furthermore, no method of characterization *in situ* is informative enough to be used conclusively without the aid of other methods. So the best way to study the structure of this macromolecule appears to be through the use of several complementary methods that provide corroborative results.
Importantly, the wood components are closely linked, so they constitute the cell complex of plant biomass. In the cell wall of the plant, such compounds are organized forming different layers.
Thus this study aims to chemically characterize, at different levels of granularity, the waste from the processing of eucalyptus for industrial production of cellulose pulp.
The knowledge about characterization in different grain size of this waste is very important for the production of bio products, such as oligosaccharides, with higher added value, which would prevent its loss for burning it to produce electricity.

2. Materials and Methods

The feedback used in this study was the residue of Eucalyptus *grandis and urophylla* (in 1:1 ratio).
The preparation of samples for chemical analysis was performed according to TAPPI standard T 264 cm-97.
In a first step, the timber was subjected to a grinding process (slicer), yielding 10 grams of sample with particle size, and the mesh pattern 42 is by means of sieving. This process was conducted with the objective of promoting greater surface of the wood contact with the reagents used in the analysis. The following particle size were studied: 10, 14, 20, 30, 40 and 50 mesh.
All analyzes were performed in triplicate.
With the results, it was performed the analysis of variance and then the Tukey test, to see if there is a significant difference between the samples.

2.1 Determination of extractive content

Four grams of each sample were extracted on organo-soluble solvent in an extractor type Soxhlet with no less than four refluxes per hour, consisting of two steps: a) extracting 1: 1 (v / v) cyclohexane parts/ethanol for 8 hours, in order to remove the extractive organo-soluble; b) boiling water for 3 hours. After extraction, the sample was dried in an oven with a maximum temperature of 100 ° C, until constant mass.
The extractive content was calculated according to equation 1 in terms of dry weight:

$$\%\ Extrativos = \frac{m_i - m_f}{m_i} \cdot 100 \quad (1)$$

Where:
a = initial mass (g);
mf = mass end (g)

2.2 Determination of ash content

The ash content were determined according to TAPPI standard T 211 om-02, in order to obtain the percentage of inorganic material from the sample. From 1.0 g of sample placed in crucibles that were brought into oven at temperature of 525 ± 25 ° C for 4 hours. The calcined samples were placed in a desiccator to cool. The determination of the masses was held in analytical balance.
The ash content was determined according to equation 2:

$$\% Cz = \frac{m_r}{m_i} \cdot 100 \quad (2)$$

Where:
% Cz = Ash content (%);
mr = mass of ash (g)
m = mass of dry sample before burning (g).

2.3 Determination of lignin and carbohydrates

The lignin contents were determined by the sum of Klason lignin insoluble and soluble lignin. The determination of lignin by Klason method involves two steps. The first is a hydrolysis reaction ether linkages and glycosidic under reflux in a concentrated sulfuric acid solution. The second step is carried out under reflux after dilution of the acidic solution. In this step, the hydrolysis is completed, the sulfates groups incorporated substrado are removed and condensation can occur between the lignin fragments.
The complete treatment results in a solid which is immiscible with lignin and a sugar containing solution oligomers or polysaccharides, degradation products of the reaction and a small fraction miscible lignin.

2.4 Lignina Klason insoluble

The determination of the modified method by Klason lignin was performed based on TAPPI standard T 222 om-98. It was weighed 800 mg of the milled lignocellulosic material with granulometry shown above (samples 1 to 6), pre-extracted, i.e., free of extractives transferred weighed together with 12 ml of H_2SO_4 72% (d = 1.631 g. ml-1) for a borosilicate tube autoclavable 500 ml, under magnetic stirring for a period of two hours. Thereafter was added 450 ml of distilled water in borosilicate glass tube, which was closed and taken to an autoclave until the temperature of 120 ° C and pressure of 2 bar for a period of one hour. Then, the tubes were cooled on ice to about 25 ° C. The residue was filtered on a glass filter porosity of 10 - 15 M and taken to drying in an oven at 100 ° C ± 3 ° C until constant weight. The generated filtrate was used for the determination of soluble lignin and polysaccharides (cellulose and polyose), then transferred to a volumetric flask of 500 ml, and the volume of the filtrate was completed to 500 ml, thereby diluting the acid solution for 3%.
After this, the plate with the funnel-immiscible lignin was again calcined, obtaining in this way the amount of ash for correcting the value of the insoluble lignin. The calcination was carried out at a temperature of 525 ° C for a period of 4 hours, with a heating ramp 100 ºC.h-1.
The filtrate produced by the method of insoluble Klason lignin was analyzed in a UV-VIS spectrophotometer, Hach DR-5000. The absorbances were measured at 215 and 280 nm, with reference to a sulfuric acid solution in the same proportions. The dilution factor is the dilution of the solution in which the spectrum was recorded and is used dilution factor 5, or 1 ml of the filtrate was diluted 4 times in the sulfuric acid solution in the same proportions.
The total lignin content (LT) was obtained from the sum of the Klason lignin insoluble and soluble Klason lignin.
The filtrate produced by the Klason lignin method insoluble was used for the determination regarding the hydrolyzed sugars of the compounds (glucose, xylose, arabinose and acetic acid) by analysis by liquid chromatography on a brand chromatograph Shimadzu model LC-10 . For determination of the sugars it was coupled to a refractive index detector R10-6A model, using an Aminex HPX-87H column (300 x 7.8 mm Bio-Rad); H_2SO_4 mobile phase was 0.005 mol L-1 at a flow rate of 0.6 ml.min-1 at 45 ° C. The masses of glucose proportional to the areas obtained in HPLC chromatograms of standards were converted to cellulose. Likewise, the masses of xylose, arabinose were converted to hemicellulose (Abreu, et al., 2006).
The obtained masses were divided by the dry weight of the original material and multiplied by hydrolysis factors. The conversion factors used for glucose to xylose and acetic acid were 0.90, 0.88 and 0.7 respectively.

The determination of the insoluble Klason lignin was calculated by equation 3.

$$L_I = \frac{(m_L - m_C)}{m_S} \cdot 100 \quad (3)$$

Where:
L_i= Klason lignin is insoluble in the sample (%);
mL = lignin immiscible dry mass (g);
mC = mass of ash (g);
mS = weight of dry sample (g).

2.5 Lignin Klason soluble

The filtrate produced by the method insoluble Klason lignin was analyzed in the ultraviolet spectroscopy (UV-VIS) since, due to the aromatic nature of lignin, it absorbs strongly ultraviolet light. It used a UV-VIS spectrophotometer, Hach DR-5000. The absorbances were measured at 215 and 280 nm, with reference to a sulfuric acid solution in the same proportions. The dilution factor is the dilution of the solution in which the spectrum was recorded and is used dilution factor 5, or 1 ml of the filtrate was diluted 4 times in sulfuric acid solution to the same extent (commonly referred to as blank).
The determination of soluble Klason lignin was calculated by equation 4.

$$L_S = \frac{(4{,}53 \cdot A_{215} - A_{280}) \cdot V_f \cdot F_d}{3 \cdot m_S} \cdot 100 \quad (4)$$

Where:
L_s= Klason lignin is soluble in the sample (%);
A215 = absorbance value at 215 nm;
A280 = absorbance value at 280 nm;
Vf = Final volume (L);
Fd = dilution factor acid in 1: 4 (v: v);
ms = mass of dry sample (g). The total lignin content (LT) was obtained from the sum of the Klason lignin insoluble and soluble Klason lignin, equation 5:

$$L_T = L_I + L_S \quad (5)$$

3. Results and Discussion

From the experiments performed to determine the particle size it can be observed in Table 1 the distribution of particles on sieves of different meshes. It is observed that the sample 1 passed through the 10 mesh sieve and it was retained on the 14 mesh, and so on. Furthermore, it was made the average diameter of the sieves in which the sample was not retained and the ones it was retained.

Table 1: Average diameter of sieves (retained and not retained samples)

Samples	Sieves (not retained samples)	Sieves (retained samples)	Average diameter of sieves (mm)
1	10(2,000mm)	14(1,410mm)	1.705
2	14(1,410mm)	18(1,000mm)	1.205
3	20(0,841mm)	30(0,585mm)	0.718
4	30(0,585mm)	40(0,420mm)	0.507
5	40(0,420mm)	60(0,250mm)	0.335
6	50(0,297mm)	70(0,210mm)	0.253

Table 2 and figure 1 show the chemical composition of the residue under study at different levels of particle size, as shown in Table1. The residue at different levels of particle size presented content of extract, total lignin, cellulose, hemicellulose and ash which ranged from 3.0% to 3.8%, 30.9% and 31.2%, 37.5% and 34.1%, 18.7% and 17.5% and 0.4% to 3.6%, respectively. The summation of all components ranged from

90.5% to 90.2%. Some components such as hydroxymethylfurfural, furfural and glucuronic acid were not analyzed which explains the level of the value of the presented sum (Masarin et al., 2011).
Table 2 show that the sample 1 retained on the 14 mesh sieve showed the lowest amount of extractives and ash (3.0% and 0.4%, respectively), which resulted in a higher amount of cellulose and hemicellulose (37.5% and 18.7%, respectively). However, the sample 3, 4, 5 and 6 retained on the sieve size showed the highest amount of ash. These results showed that the chemical composition of the residue from the studied Eucalyptus is affected by particle size. The particles from the sieves with smaller diameters, showed results that are not desirable (higher amounts of ash and extractives) for the production of bio products, unlike the samples 1 and 2, which had greater diameters.
With this result, we may say that there is evidence that the ashes would be more concentrated in the cell walls of parenchyma cells.
Esses resultados
Statistical analysis, which was performed using the Tukey test, showed that all components analyzed of the sample of Eucalyptus *grandis and urophylla* waste, except lignin, showed significant differences between the different particle sizes studied.

Table 2: Chemical composition of the waste at different levels of particle size. Levels presented in grams / 100 grams of biomass (data on a dry basis).

Samples	Extractives (%)	Total Lignin (%)	Cellulose (%)	Hemicellulose (%)	Ashes (%)	Total (%)
1	3.0 ± 0.1^{a}	30.9 ± 0.1^{a}	37.5 ± 0.4^{a}	18.7 ± 0.8^{a}	0.4 ± 0.01^{a}	90.5
2	2.8 ± 0.1^{b}	31.4 ± 1.2^{a}	38.2 ± 0.5^{ab}	18.0 ± 0.4^{ab}	0.2 ± 0.01^{a}	90.6
3	3.0 ± 0.1^{a}	30.9 ± 1.0^{a}	35.3 ± 0.5^{c}	17.3 ± 0.3^{bc}	3.5 ± 0.30^{b}	90.0
4	3.2 ± 0.1^{c}	31.2 ± 0.4^{a}	34.8 ± 0.4^{bd}	17.7 ± 0.2^{abcd}	3.6 ± 0.05^{bc}	90.6
5	3.2 ± 0.1^{c}	31.4 ± 0.4^{a}	34.8 ± 0.2^{c}	17.6 ± 0.3^{abcde}	3.6 ± 0.09^{bcd}	90.6
6	3.8 ± 0.1^{d}	31.2 ± 0.2^{a}	34.1 ± 0.3^{abd}	17.5 ± 0.2^{abcde}	3.6 ± 0.04^{bcd}	90.2

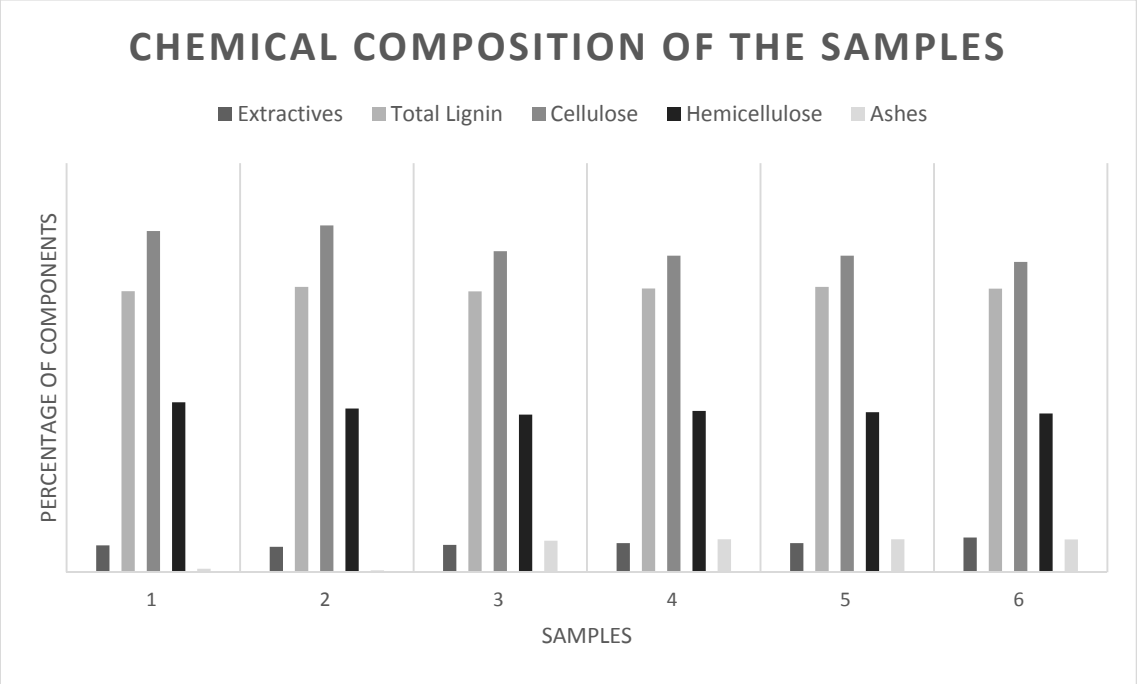

Figure 1: Graphic of the relation of residue chemical composition with different particle size levels. Levels presented in grams / 100 grams of biomass (data on a dry basis).

4. Conclusions

It is concluded that the size of residue particles under study has a direct influence on the chemical composition of the lignocellulosic material. The smaller the particle size of the residue levels, the higher the proportions of ash and extractives. However, the larger the particle size of the material, the greater the proportions of cellulose and hemicellulose. There were no significant variations for the total lignin content.

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