Eucalyptus wood evaluation for pulp production: the choice of key indicators and the kenowledge of the variables role on the processes as a toll for raising the productivity

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Abstract

Ensuring the quality of pulp at a competitive production cost represents a challenge for industries. In this context the quality and availability of the wood appears as a decisive factor. Therefore the genetic improvement programs associated with good silvicultural practice are always present in the pulp industry. However, even with a high level of development, the improvement programs usually do not cover the whole range of variables which involves the cellulose pulp production. The recommendation of a hybrid or clone often follows an orientation focused on silvicultural factors such as resistance to pests, annual growth, soil and climatic conditions. Therefore, a second evaluation of the wood, based on industrial factors such as yield, bleachability and pulp quality becomes an important tool, both for the mill, supplying their expectations regarding the raw material, and for the forest management that can use this information to planting accelerate or withdraw a clone or hybrid from the program. With the purpose of discussing the main technological variables that may join the forestry and industry to improve the productivity, were used the quality wood data matrix concerning of a monitoring program conducted by CENIBRA since 2006. From the industrial point of view the wood density is an important quantitative variable but very unclear to express the wood quality for pulping. The wood chemical parameters has been shown as an great indicator for its quality and relationship with the industrial productivity, especially the extractive content , lignin content and the type of lignin structure (S/G). From the data was demonstrated that the evaluation of variables by the robust statistical techniques like PCA , PLS and Clusters may help to grouping clones or hybrid by similarity, contributing to greater operational stability. However, some aspects should be reviewed, as the approach taken about the amount of lignin, mainly as regards the acid soluble lignin content. The investigation of the filtered soluble lignin by FTIR and PY-GC/MS allowed to show further that the amount of soluble lignin appears to be overestimated by the current technique.

Keywords: Eucalyptus, Pulping, Bleaching, Lignin, Wood quality.

Introduction

The massive growth of the Brazilian production with the advent of new industrial plants and the planning of bigger projects for the next year's show that the cellulose sector remains very interesting for investors. In this context optimize the production and sustaining the quality requirements demanded by the market represents two of the major challenges on daily production of cellulose pulp.

Through the years, the genetic improvement programs, intrinsic in pulp mills, have reached the most promising results for every range of clones and hybrids of Eucalyptus developed. The forests growth rate of the major Brazilian mills currently exceeds 35,0 m^3/ha.year (GOMIDE, et al., 2005) with handling of 6 to 7 years, values that may vary in function of region and the genetic material. Compared to Brazilian Pines forest, Eucalyptus are much superior to wood production; Pinus have been presenting productivity of 20 m^3/ha.year to 30 m^3/ha.year for 20 years handling (BASSA et al., 2007).

Nevertheless, the pulp production involves a complex variables matrix and requires an evaluation which transcends the forest productivity in terms of wood. For this reason the improvement programs get a new direction, to the better technological evaluations, and began to observe the relationship between the variables analyzed. Wood density was initially utilized to classify and infer about it behavior at the mill. However, this variable is still very complex to establish a relationship between industrial and forestry productivity. Nevertheless, the wood segregation by density conducted the industry to develop important concepts about the relationships with final product and wood quality, inserting another variable for decision making (FERREIRA et al., 2006; MOKFIENSKI, et al., 2008).

Currently improvement programs are much more complex and have a quality verification spreadsheet

of wood that include, besides the evaluation of silvicultural requirements and density, the chemical parameters as lignin content and quality (syringyl and guaiacyl ratio), extractives content and pulping yield. This evaluation has been contributing to the development of genetic material optimized in terms of forestry, industrial production and better final product quality. In addiction represent cost reductions per ton of pulp due to the planning of wood harvest more favorable to the pulping and bleaching.

Nevertheless, most comprehensive programs are not yet frequent. Despite having a large range of variables, the traditional wood improvement program is not able to cover the whole spectrum that implies the production of pulp and often overlooked factors like lignin chemistry, bleachability, yield production and quality of the final product. Insert new variables to the genetic selection worksheet becomes somewhat complex due to intrinsic variations of the process, changes of technology for processing besides of the large increase of selection time.

In order to fill this gap, since 2006 CENIBRA implemented a program aiming to better estimate the material already available for pulp production. In this evaluation are determined pulping yield, bleachability and physico-mechanical properties of pulp. The results of this work may be employed by industrial area to fit the process to the characteristics of incoming material and for forest management to recommend the continuation or acceleration of planting a particular clone or hybrid based on their industrial performance. Recently was added to the program the evaluation of chemistry of lignin, the amount of acid soluble and insoluble and the ratio of syringyl and guaiacyl units.

The segregation of the wood or better adjustments of the process according to the wood characteristics still a challenge. Mainly due to the feeding mixture of clones and hybrids in the mill, limiting the use of the information. However, large fluctuations of wood quality may be avoided bringing the mill to a new reality. In this regard will be presented in this paper the results obtained in the evaluation of genetic material recommended for planting and possible inferences regarding product quality, stability, and process cost.

Experimental

In this paper was showed the results from evaluation of 8 clones, totaling 11 samples according to the region source. Each sample was composed by four trees and all experiment was performed in duplicate for each tree. The samples represent clones pre-selected and ready to be used at the mill with an average age of 7 years. After harvesting, the samples were processed into chips in a laboratory chipper and further sorted and selected (sieves 4 mm and 6 mm). Was determined on wood samples the basic density, lignin and extractives content. Samples were sequentially identified by a letter (A through H) followed, if necessary, by a number. The letter identifies the clone while the number the source region.

The pulping were performed in duplicate (400 g of chips per batch) at a temperature of 165 °C, liquor ratio of 4:1 and sulfidity of 30%, in order to kappa number of 17.0. The time to reach the cooking temperature was 90 minutes with 60 minutes retention. After the pulping was determined in the pulp the kappa number, screened yield, rejects content and content of HexA. At the sequence the samples were bleached by the sequence OD(EP)DP to the target brightness of 90 %ISO. The results was grouped and evaluated by a parametric statistical (ANOVA) and multivariate statistics (PCA and Cluster).

Table 1. Standards

Standard	
Lignin content	NBR 7989
Extractives content	NBR 14853:2010
Rejects content	-
Kappa number	NBR ISO 302
Brightness	NBR 14528:2002
Hexenuronic acids	Tappi 282 pm07
Effective alkali	Scan-N 33:94

Another 35 industrial sorted samples were selected to investigate the lignin composition relationship

with the amount of lignin soluble and insoluble. The syringyl (S) and guaiacyl (G) ratio was performed by pyrolysis coupled to the gas chromatography and mass spectrometry (PY-GC/MS). The characterization of the soluble lignin was performed by infrared with Fourier transform (FTIR), GC/MS and PY-GC/MS.

The pyrolysis was realized on Frontier pyrolyzer model Py-2020iS coupled to the Shimadzu chromatograph, GC-MS QP2010 Ultra. The wood sample was introduced to the pyrolyzer on helium atmosphere at 100 kPa and pre-adjusted temperature (550 °C). The gas from pyrolysis was conducted to the chromatograph heated at 100 °C on helium flow of 1 $mL.min^{-1}$. The split ratio was 1/10 and column was TR-5 (60 m x 0,25 mm x 0,25 μm). The temperature program was adjusted to 45 °C for 4 minutes and then heat rate of 4 $°C.min^{-1}$ until 240 °C, keeping at this temperature for 10 minutes. The mass spectrometer was adjusted for electron impact ionization with 70 eV and mass range of 50 to 350 DA. The temperature of detector and interface was 250 °C and 290 °C respectively. The markers of S and G were defined according to Guimarães (2013).

For characterization of soluble lignin, the filtrate from Klason lignin was neutralized with CaO and then the excess of sulfate was precipitated with barium chloride to remove the interferences on infrared analysis. The FTIR spectrum was obtained on spectrometer Thermo Nicolet Avatar 330-FTIR from 600 cm^{-1} to 4000 cm^{-1} and 64 scans. For the FTIR analysis the soluble lignin was previously dried at atmosphere temperature on nitrogen flux for 72 hours. The remaining solids were direct analyzed on FTIR spectrometer and PY-GC/MS. A fraction of solid obtained were also extracted with acetonitrile, the extract was isolated and introduced on chromatograph at the same conditions of pyrolysis. After complete evaporation of acetonitrile solvents, the remaining solids were analyzed by FTIR.

Results and Discussion

The results of eight clones analysis was statistically significant ($p < 0.05$), as may be seen in Table 2. In general was observed that the same clone from different location has distinct characteristics, especially to the basic density (clones A, B and E). The characteristics of the wood influenced the pulping results.

Table 2. Wood characterization, pulping and bleaching results.

	Dens., kg/m^3	Extractives, %	Lignin, %	EA, %	Yield.,%	HexA, m Mol/kg	O_2 Efficiency, %	ClO_2, kg /tad	*BPP, t/ha .year
A1	507.8^{e}	1.23^{b}	29.0^{bc}	14.3^{bc}	51.5^{b}	44.4^{cde}	48.0^{bc}	9.2^{bc}	10.0^{bc}
A2	459.0^{a}	0.91^{a}	29.5^{c}	14.1^{bc}	51.3^{ab}	47.0^{e}	45.7^{b}	7.5^{a}	9.0^{a}
B1	484.5^{bc}	1.19^{b}	28.2^{ab}	13.5^{a}	53.8^{cd}	39.1^{a}	49.7^{c}	10.6^{de}	10.5^{d}
B2	511.0^{e}	2.31^{e}	29.9^{c}	15.4^{de}	51.4^{ab}	55.2^{f}	41.6^{a}	10.7^{de}	10.6^{d}
C	493.0^{cd}	1.93^{d}	32.0^{d}	15.7^{e}	50.1^{a}	53.4^{f}	43.3^{a}	9.2^{bc}	9.6^{b}
D	510.5^{e}	1.62^{c}	29.6^{c}	14.1^{bc}	52.2^{b}	40.8^{ab}	48.2^{c}	8.9^{b}	9.7^{b}
E1	483.0^{bc}	1.21^{b}	29.4^{c}	14.0^{b}	52.6^{bc}	40.3^{ab}	53.5^{d}	9.8^{bcd}	10.2^{cd}
E2	538.3^{f}	1.27^{b}	29.4^{c}	14.5^{c}	51.9^{b}	42.7^{bc}	53.0^{d}	10.2^{cd}	11.2^{e}
F	474.0^{b}	2.05^{de}	29.7^{c}	14.5^{c}	54.3^{e}	44.0^{cd}	53.5^{d}	11.5^{f}	10.0^{bc}
G	505.0^{de}	2.18^{de}	28.9^{abc}	15.2^{d}	52.1^{b}	45.7^{de}	53.1^{d}	10.8^{de}	10.3^{cd}
H	471.6^{ab}	1.25^{b}	28.0^{a}	13.5^{a}	52.2^{b}	38.7^{a}	54.2^{d}	9.3^{bc}	9.6^{b}

Means followed by the same letters in the same column may be considered identical according to the Tukey test at 95% confidence.

*BPP: bleached pulp production.

It was observed an alkali demand variation from 13.5% to 15.7% to reach kappa number 17.0, which directly impacted the yield that ranged from 50.1% to 54.3%. The pulp obtained from the clones even showed significant variation in their bleachability with ClO_2 consumption to reach 90% ISO brightness, ranging from 7.5 kg/adt to 11.5 kg/adt. The global clones productivity (Bleached Pulp Production - BPP) vary from 9.0 t/ha.year to 11.2 t/ha.year. This difference may represent, for example, the need to increase of approximately 19.5% in the cultivated area if used clone A2 against clone E2 to maintain the same production rate.

Table 3 shows the matrix of correlations between the variables measured, assuming a linear model $f(x)=\alpha[xi] + \beta + \varepsilon$, using the least squares method. The values in bold type represent statistically significant correlations ($p < 0.05$). The results show that the alkali consumption was impacted mainly by the content of extractives and lignin of wood, $r > 0.70$, whereas the wood density had only half the correlation obtained with those. The pulping yield was directly influenced by the alkali load and the lignin content also was significantly

correlated. However, this relationship is just a consequence of the interrelationship between variables. The HexA content was also strongly influenced by the alkali charge (r> 0.80). The variation in the pulps bleachability showed no direct correlation with the variables that may explain it satisfactorily.

Table 3. Correlation matrix.

	Extractives, %	Lignin, %	AE, %	Yield.,%	HexA, mMol/kg	ClO_2, kg/adt
Dens., kg/m^3	0.27	0.13	**0.37**	-0.22	0.16	0.25
Extractives, %		**0.42**	**0.76**	-0.05	**0.58**	**0.57**
Lignin, %			**0.71**	**-0.51**	**0.67**	-0.11
EA, %				**-0.52**	**0.85**	0.23
Yield,%					**-0.55**	**0.49**
HexA, mMol/kg						0.01

Parametric statistical methods such as ANOVA are important in the evaluation of data containing a restrict universe of variables. However, multivariate techniques are more suitable for the analysis of variables in a multicomponent system. The cluster analysis is indicated to evaluate the interaction of variables that may not be visualized directly in a two or three dimensional matrix. This technique is useful for filtering less important variables or separation into distinct groups. On dendograms the variables are graded according to their similarity, measured by criteria like the covariance or correlation being generally the n-dimensional spacing expressed by Euclidean distance (Neto et al. 1998).

As may be seen in Fig. 1, there is strong similarity of alkali load (EA) with the chemical characteristics of the wood (lignin and extractives) and pulp (HexA), confirming the results obtained on correlation analysis (Table 3). On this evaluation may also be observed that the variable nearest to this first group is the consumption of ClO_2, which could not be observed in the correlation analysis. Therefore, based on these results it may be affirmed that both yield pulping and bleachability are driven primarily by the chemical characteristics of wood and pulp. This analysis also showed that the basic density, although widely used for the selection and classification of wood quality, has much less interference on the process of pulping and bleaching in comparison to the wood chemical characteristics.

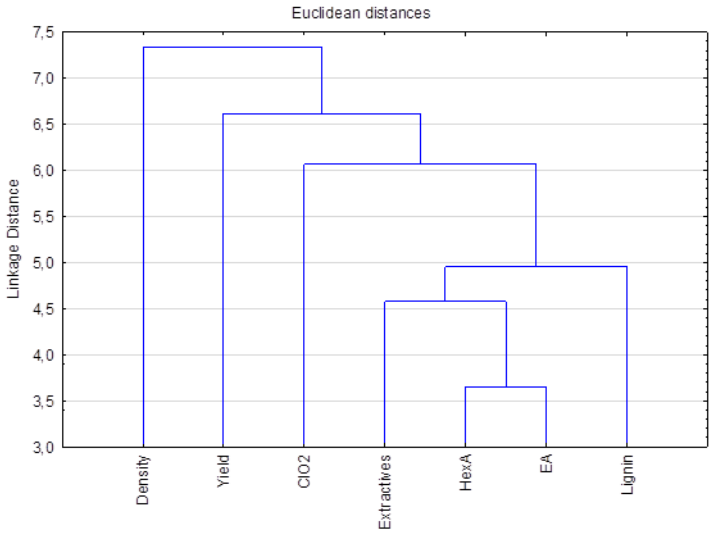

Figure. 1. Cluster analysis.

The principal component analysis (PCA) is another useful technique to obtain groups by similarity or dissimilarity. The evaluation of clones characteristics by PCA may be used for recommendation of blends of clones aiming process stability. The Fig. 2 shows the principal components analysis for the clones evaluated according to basic density, extractives content, lignin content, alkali load to kappa number 17.0, screened

yield, HexA content, efficiency of oxygen delignification and ClO_2 consumption to reach 90% ISO of brightness.

For PCA analysis (Fig. 2) were used the first two components accounting 74.24% of the sample variance. In a general way clones located in positive side of Factor 1 (quadrants I and II) possess the trend of high content of extractives and lignin which impacts directly on the pulping alkaline load and consequently on yield and HexA content. Clones located in the negative side of Factor 1 (quadrants III and IV) are characterized by reduced lignin content, in particular, clones located in quadrant III also have the tendency of low-density, directly impacting on BPP. Despite the low density of quadrant III the reduced lignin content and thus low alkaline load consumption in pulping led to a satisfactory industrial yield, reducing the effects of density.

Some cases may be highlighted illustrating what was said; it may be observed that clones A1 and D were overlaid showing strong similarity between their features. This result is function of the statistical similarity observed in the mean of the basic density, lignin content, alkali load, yield, efficiency of oxygen delignification and ClO_2 consumption (Table 2). Clone B1 showed excellent productivity as function of the growth rate of wood, low alkaline consumption for pulping due to its reduced lignin content. Nevertheless, the clone B2 on Quadrant I have lower pulping yield, however keeping acceptable BPP due to it density.

The bleachability was better represented on the Factor 2, where the positive side is a region of low bleachability while the negative side has good bleachability. The Fig. 2 shows that the clone A2, which is distinguished by reduced consumption of ClO_2 (Table 2) is located on the negative side Factor 2, while clones with higher consumption are located in the positive part of this factor (F, G, B1 and B2).

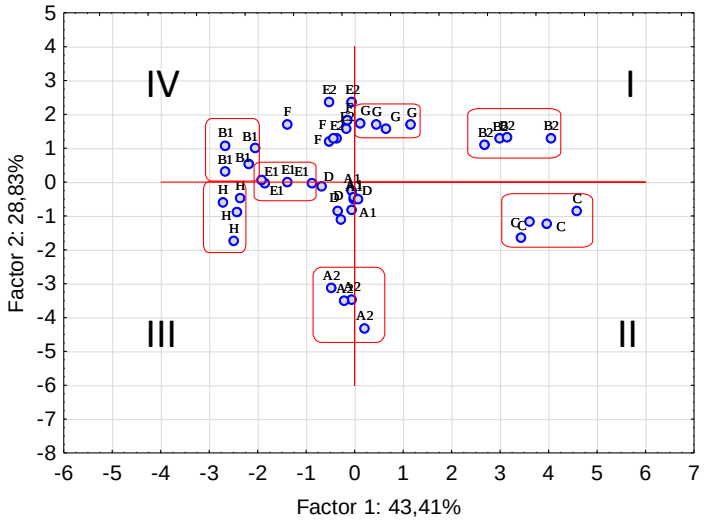

Figure. 2. Principal components of clones results.

All results pointed the important role of lignin on pulping. However, besides the lignin content (the amount of acid soluble and insoluble lignin) the ratio of syringyl (S) and guaiacyl (G) units of Eucalyptus lignin may be used as an important and decisive factor to select a clone, thinking on pulping facility (GOMES et al., 2008). Nowadays, the pyrolysis associated to the GC/MS has been used to get the SG ratio (GUIMARÃES, 2013). The Fig. 3 shows the chromatogram from a pyrolysis of Eucalyptus wood where the relative area of the S and G markers (as a chromatogram peaks) are used to calculate the SG ratio.

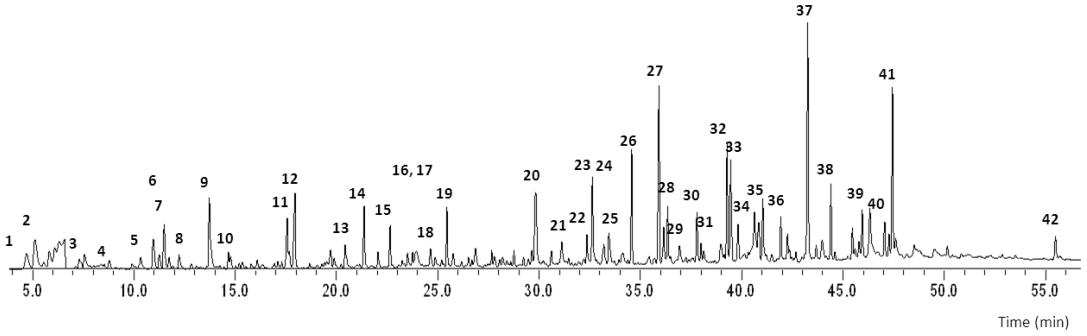

Figure. 3. Chromatogram of Eucalyptus wood pyrolyzed at 550 °C.

The contrast of relative area of the markers of S and G units against soluble and insoluble lignin shows that insoluble lignin is associated only with G markers while the soluble lignin is associated to de S markers as may be seen on Fig. 4. This result led to the obvious association of SG ratio and acid soluble and insoluble lignin. Not all markers may be related to the amount of acid soluble and insoluble lignin however acid soluble lignin does not correlate with any G markers.

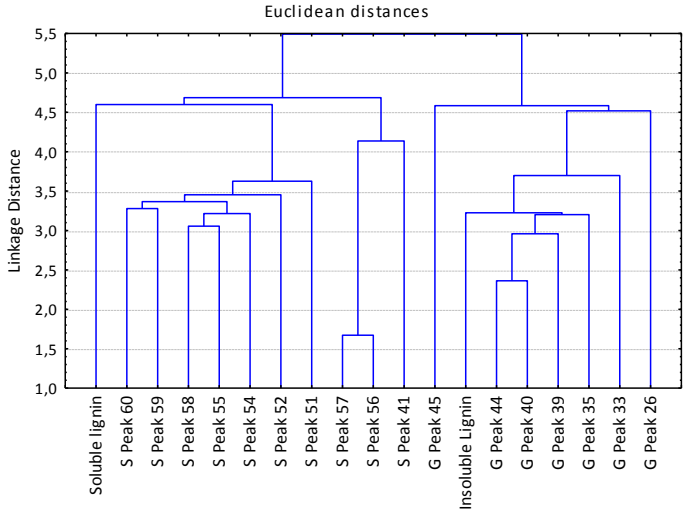

Figure. 4. Cluster analysis for soluble lignin, insoluble lignin, S and G units peaks

Historically the filtrate of Klason lignin is used to define the amount of acid soluble lignin for Eucalyptus, with their evaluation by ultraviolet. For Eucalyptus wood the filtrate of Klason lignin is a complex mixture of compounds like hydrolyzed and products of degradation of carbohydrates, organic acids as uronics acids and acetates. These compounds may interfere on acid soluble lignin analyses due to overlap of ultraviolet peaks absorption.

The analysis by FTIR (FIG. 5) and GC/MS do not show the intense presence of aromatic-lignin units on the soluble extract of Klason lignin. The peaks in 3454 cm^{-1}, 3330 cm^{-1}, 1636 cm^{-1}, 1602 cm^{-1} and 1370 cm^{-1}, indicate the presence of salt of carboxylic acids (FIG. 5-1). The peaks in 1636 cm^{-1}, 1602 cm^{-1} may be attribute to stretch of C=C linkages of aromatic rings, however needs confirmation with another peaks who are absent at the spectra. The presence of carbonyls from acids and other compounds also may interfere on this interpretation.

The extract in acetonitrile (FIG. 5-2) show the presence of hydroxyl groups (3300 cm^{-1} region) and intense peaks related to hydrocarbons (mainly 2923 cm^{-1} and 2856 cm^{-1}). The spectra of acetonitrile extract also presented an intense carbonyl peak in 1721 cm^{-1}. The peak in 680 cm^{-1} may be attributed to the chloride from barium chloride used to eliminate the sulfate. The axial deformation of C(=O)O from acetate may be observed at 1249 cm^{-1}.The peaks near to 1050 cm^{-1} could be attributed to C-O linkage. From the infrared

spectra cannot be stated about the presence of aromatic groups in the extracts.

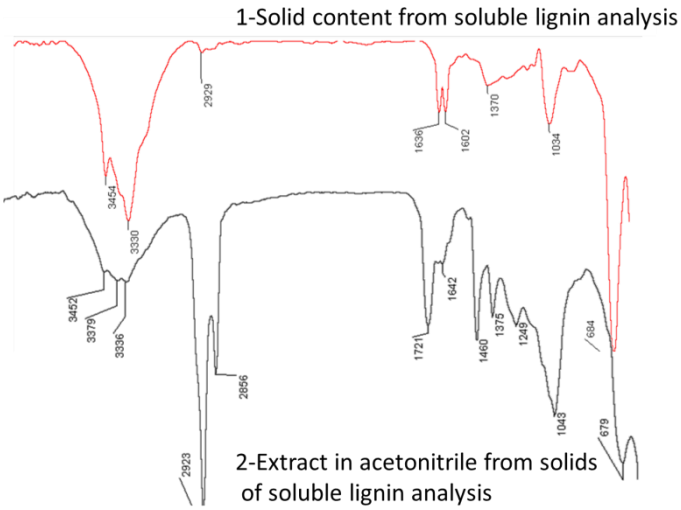

Figure. 5. FTIR of dried extract from Klason lignin (1) and extract in acetonitrile from solids of soluble lignin.

The PY-GC/MS analysis of dried extract from Klason lignin presented 113 peaks which just eight could be assigned to aromatic compounds and from these eight peaks only two may direct related to lignin structure (Table 4). The relative area of the eight aromatic peaks represent 14.5% of sample while the two lignin related aromatics represent 3,39% of sample. These results shows that the soluble extract of Klason lignin is mainly composed by non-aromatic and structures just a small part of aromatic compounds, confirming the super estimation of lignin named as acid soluble.

Table 4. Aromatic compounds from Klason filtrate.

Compound	%
Phenol	3,48
3-Methyl-Phenol	1,75
2-Methyl-Phenol	2,18
Guaiacol (methoxi-Phenol)	**0,66**
3,4 Dimethyl-Phenol	0,37
1,2 Benzenodiol	2,1
3-Methyl-1,2-Benzenodiol	1,23
Siringol (2,6-Dimethoxi-Phenol)	**2,73**

Conclusions

The results of the study showed that the pre-evaluation of characteristics of the clones available for processing, together with appropriate statistical techniques may provide significant benefit to the mill from the viewpoint of stability of process. This information may also be used by the forest area to the control or removal from the program clones with characteristics unsuitable for the reality of the mill.

The results also showed that the density is not the best parameter to segregation of the wood, since the chemical characteristics are more significantly and consequently has a very important role in the resulting properties.

The lignin content represent a important role for pulping and the extract of Klason lignin, historically named as acid soluble lignin present good relation with syringyl units peaks from PY-GC/MS. However, this

extract presented just 3,39% of lignin structures, led to the conclusion that the “Klason soluble lignin” is not suitable to relate the lignin content.

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