Evaluating the Application of an Analytical Method for the Determination of Hexenuronic Acids in Eucalyptus Pulps

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Abstract

The objective of this study is to research the existing methodologies for determining hexenuronic acid (HexA) and evaluate the implementation of one of those, in the laboratory of Valdivia Mill, for process control in eucalyptus fiber line.

The following criteria were applied for the analysis:

- Easiness of implementation (with rapid response time).
- Low investment for Valdivia Mill (materials, equipment and reagents), minimal environmental impact and safety for people.

The methods currently available for HexA measurement are based on hydrolysis (enzymatic mercury acetate, mercury chloride, dilute acids) of the pulp followed by analysis of the hydrolizates with chromatographic separation (HPLC), UV spectroscopic analysis and NMR spectroscopy.
All the methods aforementioned require time consuming and hard work in the laboratory. In the criteria established above, it was mentioned that the VTT, AEC, KTH and UVRR methods require instrumentation and equipment that are not available in the Valdivia Mill. Their implementation would mean investments in order to perform testing in the laboratory.
So, it was concluded that the most appropriate method for implementation at Valdivia would be the one based on simple acid hydrolysis of the pulp with formic acid (Vuorinen et al, 1999), thus producing furoic acid that can be quantified by UV spectroscopy, i.e., an indirect method of quantifying HexA.
This method proved effectiveness in the laboratory testing and produced HexA measurements with low standard deviation compared with other methods reported in literature.
These pulps were produced by varying process variables such as kappa, sulfidity and temperature. It was observed that it is possible to establish quadratic correlations between 53 and 69 % and their trend is similar to those found in literature for the *E. globulus*.

Introduction

Hexenuronic acids have been identified recently in xylans as a result of the pulping process, by partial conversion of 4-O-methylglucuronic acids groups attached in the xylans chain. 4-O-methylglucuronic acids are randomly distributed along the xylan chains located in the secondary wall (S1 and S3) and in the parenchyma cells (80 % xylans in eucalyptus). During the pulp bleaching, HexA groups may undergo electrophilic and nucleophilic attacks (Jiang, 2000), leading to a higher consumption of bleaching agents such as chlorine dioxide, chlorine, ozone and peracids (Ragauskas, 2000) however they do not react with oxygen and peroxide in alkaline stages . Moreover, it is believed that hexenuronic acids interact with metallic ions in the pulp retaining them and therefore increasing brightness reversion of the bleached pulp. In addition, hexenuronic acids can contribute to the formation and deposition of oxalic acid which can precipitate as calcium oxalate in the bleaching equipment (Daniel I.D., 2003).

Taking into account that implementing a suitable technology for removal and quantification of HexA is a topic of great interest for pulping and bleaching mills dealing with Eucalyptus wood, it is necessary to have a rapid laboratory method for the quantification of HexA. This method should allow, together with the kappa analysis, to do a suitable operational control of the Kraft process in the fiber line, because it was found that in unbleached pulps, the kappa number is the comprising mainly of residual lignin and hexenuronic acid (HexA) because both are sensitive to oxidation with permanganate (Ruusumo, 2008). Extractives and carbonyl group also contribute to kappa number in a small extention. Based on the previous work, it has been found

that HexA contributes with approximately the 20 - 60 % of the kappa number in the commercial pulp and that its removal changes substantially among the pulps (Chai, 2001).
Other studies have found that HexA consumes between 8.4 - 8.6 equivalents of $KMnO_4$/mol HexA, 10 mmol of HexA/kg of pulp per 0.70 to 1.05 kappa units. The most widwly accepted value is about 0.85 (Chai, 2001).

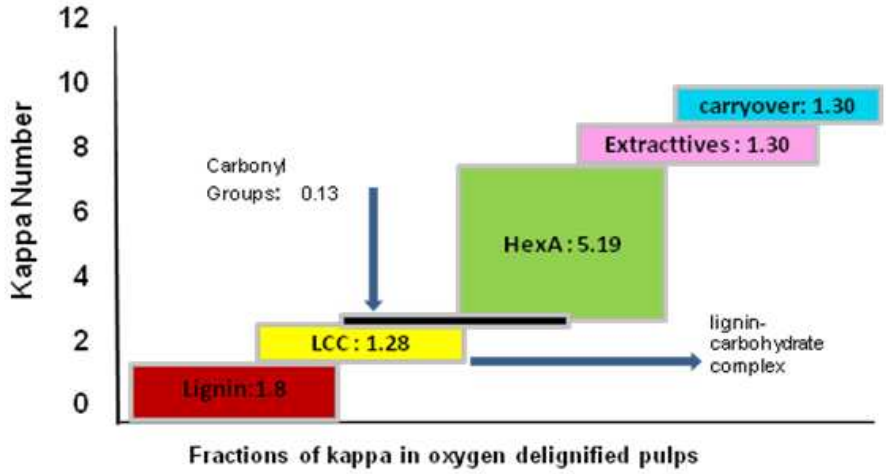

Figure 1.- Contribution of the kappa number in the oxygen delignification of eucalyptus in kraft pulps

The aim of this work is to perform a research of the existing methodologies to determine HexA and to evaluate the application of some of them as process control in pulps of E. *nitens-globulus*, in the laboratory of Valdivia Mill.
Many analytical methods have been proposed to determine the HexA (Buchert, 2003). The different existing methodologies for the determination of HexA are detailed below. These will be theoretically and some of them experimentally analyzed, so as to evaluate which is the most feasible to implement in Valdivia Mill, in order to deliver the best tools to the operation personnel during the pulp production of eucalyptus 100% *globulus* and eucalyptus mixture 70 % *nitens* and 30 % *globulus.*

VTT Method: Teleman et al. (1999) uses xylanase in total enzymatic hydrolysis combined with NMR spectroscopy or anion exchange chromatography up to developing xylo–oligosaccharide, where the replaced HexA are released. This method requires extensive time (more than two days) because of the low enzymatic efficiency (more than two days), and presents values between 11 - 18 % lower than the KTH method.

HUT Method (UFV Method): Vuorinen et al. (1999) presents this method that consists of a selective acid hydrolysis with buffer of sodium formate followed by UV spectrometric detection at 245 nm and / or 285 nm of hydrolysis products like the 2-furoic acid and 5 carboxy-2-furaldeydo (derived from furan). Even though it is a rapid method, it presents interfering elements for the strong absorption in the UV range of the acid soluble fraction and residual lignin. It presents values between 14 - 25% lower than the KTH (Monrroy, 2009), (Petit, 2002).

KTH Method: Gellersted and Li (1999) develops this method using a HPLC by combining hydrolysis with mercury acetate buffer, oxidation with peroxide and thyobarbituric acid forming a colored structure. This can be measured by spectrometry UV after separation by HPLC, measuring in two wave-lengths 260 nm and 290 nm to eliminate the interference of the dissolved lignin. This has a higher efficiency than the hydrolysis with mercury chloride; however, the high absorption of the blank in the buffer solution makes it impossible to apply the method

directly on the products of the hydrolysis. It presents higher values than the previous methods VTT, HUT (Chai, 2001).

Chai Method (2001) (TAPPI Method): uses mercury chloride as hydrolysis agent because it has a relatively low absorption in the UV range. This way, HexA's concentration in the products of the hydrolysis solution can be easily measured. The standard to calibrate is a sample with a known content of hexenuronic acid.
As a summary, Chai method (2001), is more rapid than the KTH method, has fewer steps, fewer equipments and reagents, especially the separation by HPLC.

Method by Spectroscopy in Cadoxen Solutions: Method for the simultaneous determination of lignin and HexA by UV spectroscopy in Cadoxen solution in an absorbency of 231 - 280 nm. This solution is prepared with (EDA) ethylenediamine and cadmium oxide. It is applicable to non-bleached or semi-bleached pulps.

Quantification Method for HexA and Lignin by UV Resonance Raman Spectroscopy (UVRR) (Saariaho, 2003): It is a highly sensitive method, free of fluorescence for the determination of lignin and HexA. This UVRR is calibrated using the least-squares regression method (PLS) to obtain the simultaneous concentration of lignin and HexA. It is possible to determine the concentration of unbleached and bleached pulps, directly from the laboratory sheets without previous treatment.
The calibration requires many lignin and HexA values for different types of pulping and delignification and the readings are performed at two wave-lengths 244 nm and 257 nm. HexA's concentration is determined by the VTT method.

AECT Method: Jiang, et al. (2000) proposed this other method based on selective hydrolysis of the pulp with sulphuric acid to degrade HexA to 2-furancarboxylic acid (FA) and 5-formyl-2-furancarboxylic acid (FFA), followed by the quantification of the products by anionic exchange chromatography (AEC).

Experimental

Eucalyptus pulp samples are taken from the fiber line of Celulosa Arauco y Constitution S.A., Valdivia Mill, Chile, from different production campaigns of eucalyptus 70 % *nitens* - 30 % *globulus* and eucalyptus 100 % *globulus*.
The sampling points are pulp from digesters, pulp from press 3 (post digesters) and pulp from press 4 (post-oxygen). Approximately 500 g of every point were sampled, in a frequency of two samples per shift, these are washed, centrifuged, pelletized and stored.
The statistical software MINITAB 15 is used to calculate the size of the sample, considering a significance level of 5 %, a difference between values of 7 and an error of 0.5, getting a number out of 15 representative samples as a result.
A literature review was performed to evaluate the different alternatives of analytical methods for the quantification of HexA. Then, two methods are selected to be evaluated in Valdivia Mill laboratories as possible methods to quantify HexA's content in eucalyptus pulps with mixture of eucalyptus 70 % *nitens* - 30 % *globulus* and eucalyptus 100 % *globules* and it is complemented with some samples sent to external laboratories.

It was decided to evaluate in Valdivia Mill laboratory:

- **UFV METHOD, VALDIVIA MILL**: According to the procedure of Federal University of Viçosa, Forest Engineering Department, Laboratory of Pulp and Paper. The UFV METHOD is a HUT METHOD modified.

- **TAPPI (OR CHAI) METHOD, VALDIVIA MILL**: According to Tappi (2007) "Hexeneuronic Acid Content of Chemical Pulp". The TAPPI METHOD is a CHAI METHOD modified.

Table 1 – Methods for determining HexA in Valdivia Mill laboratory

	UFV METHOD, VALDIVIA MILL	TAPPI (Chai) METHOD, VALDIVIA MILL
Means of hydrolysis	Formic acid 0.01M	$HgCl_2$ 0.6%/CH_3COONa 0.7%
Volume of reagents	80mL	10mL
Hydrolysis equipment	Autoclave	Thermo-regulated bath
Range of temperatures	100-121ºC	60-70ºC
Hydrolysis time	60min	30min
Analysis time	20min	10min
Reading	245nm	260nm y 290nm

It was decided to evaluate in external laboratory:

- Renewable Resources Laboratory of University of Concepción, Chile (LRR)**.** According to the TAPPI or CHAI METHOD modified; **TAPPI (OR CHAI) METHOD, LRR**.
- Federal University of Viçosa, Forest Engineering Department, Laboratory of Pulp and Paper (U. VIÇOSA). According to HUT METHOD modified; **UFV METHOD, UFV**.

Nine samples are sent to the Laboratory of the Federal University of Viçosa, Brazil (six samples from digesters and three samples from press 4), which are used as reference values for the analysis that is performed in Valdivia Mill (identical samples) with the methodology based on the HUT method modified (UFV METHOD, UFV) (Vuorinen et al, 1999).
Furthermore, 45 samples are sent to the Renewable Resources Laboratory of University of Concepción, Chile (LRR). These are used as reference in the application of TAPPI (OR CHAI) METHOD, VALDIVIA MILL, because this University uses, as a reference, the method proposed by Chai (2001), which is also similar to the method proposed in TAPPI (2007).

Results and Discussion

Table 2 – Comparison between methods for determining HexA in kraft

	UFV METHOD, VALDIVIA MILL	TAPPI (Chai) METHOD, VALDIVIA MILL	TAPPI (Chai) METHOD, LRR	AEC	KTH	UFV METHOD, UFV
Hydrolysis time (minutes)	60	30	45	180	210	60
Estimated time per each analysis (minutes)	20	<5	<5	25	25	<5
Reproducibility	Good	Good	Good	Good	Good	Good
Efficency of HexA hydrolysis	Non determined	Non determined	?95%	?95%	Non determined	Non determined
Quantification of the hydrolysis products	Indirect	Indirect with interfering elements	Indirect	Direct	Direct	Indirect

According to the selection criteria for the most suitable method (costs, time), we can mention that the VTT, AEC, KTH and UVRR methods need instrumentation equipments that Valdivia Mill doesn't have. Therefore, it means an investment to be able to perform the tests at a laboratory level. Furthermore, these methods need as minimum 3 hours of treatment, which is unfeasible for the operational control.
Regarding the methods that allow to quantify the lignin and HexA, the spectroscopy method in Cadoxen solutions, and the UV Resonance Raman Spectroscopy (UVRR) method (Saariaho, 2003) present disadvantages, the first one with the solubility of the solution at high kappa

number and the second one needs, for the calibration, the analysis of many samples that cover all the variables that affect the kraft process (type of wood, pulping, bleaching sequences.)
Since the methods HUT, Chai and TAPPI require a short time in the hydrolysis, and equipments that are available in Valdivia Mill (autoclave and thermostatic bath), they were selected to be evaluated in Valdivia Mill.
By quantifying the content of HexA with both selected analytical methods, we analyzed the results of the trend with the kappa number, comparing them with those of reference (obtained in external laboratories) to define preliminarily in this study, which is most suitable to be operationally applied in Valdivia Mill.

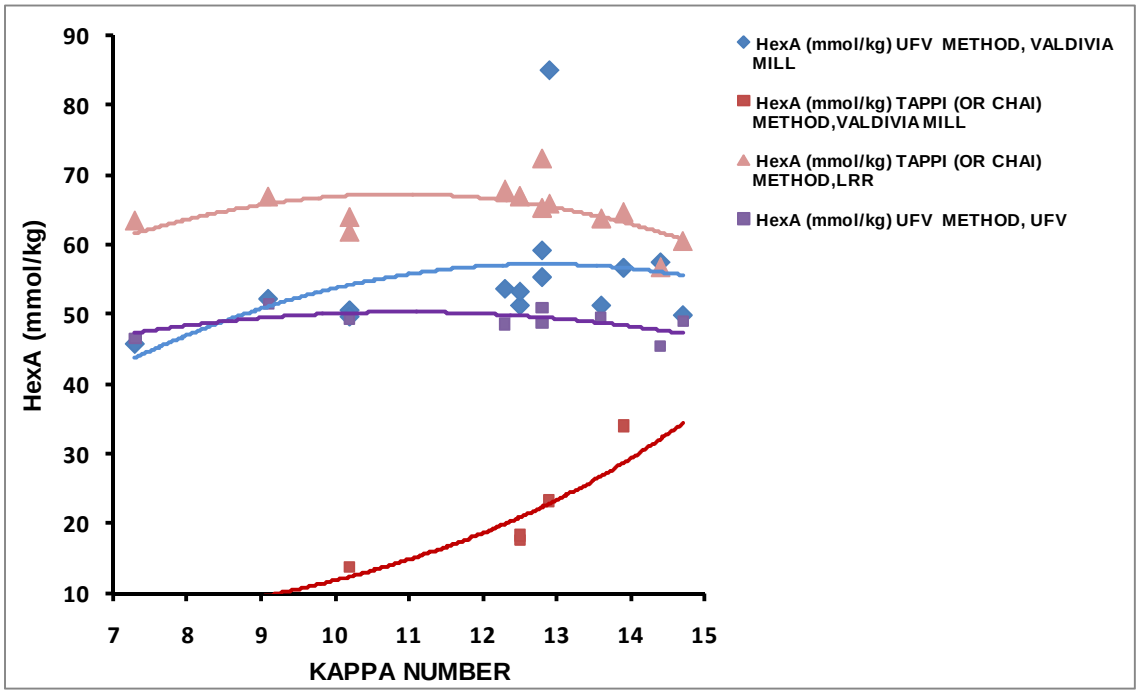

Figure 2- Variation of HexA content to the kappa number in eucalyptus pulp determined by different analytical methods

In Figure 2 it is possible to observe how HexA's values obtained by the UFV METHOD, VALDIVIA MILL are among the values of HexA obtained for the same samples in external laboratories (LRR and U. VIÇOSA).
On the other hand, it is possible to observe that the TAPPI (OR CHAI) METHOD, VALDIVIA MILL presents lower values than the obtained ones for the same samples in the external laboratories. This is explained because of the difference in the reference method they used (Chai, 2001).
The difference in the methodology between UFV METHOD, VALDIVIA MILL y UFV METHOD, UFV was that the 5 hours of disintegration were not used and it was only stirred for a few minutes.
There weren't good results in the application of the TAPPI (OR CHAI) METHOD, VALDIVIA MILL. The difference with other methods can be explained due to the presence of interfering elements in the wave-lengths of 260 and 290 nm (this behavior can be associated with the phenomenon of leaching of the lignin.)

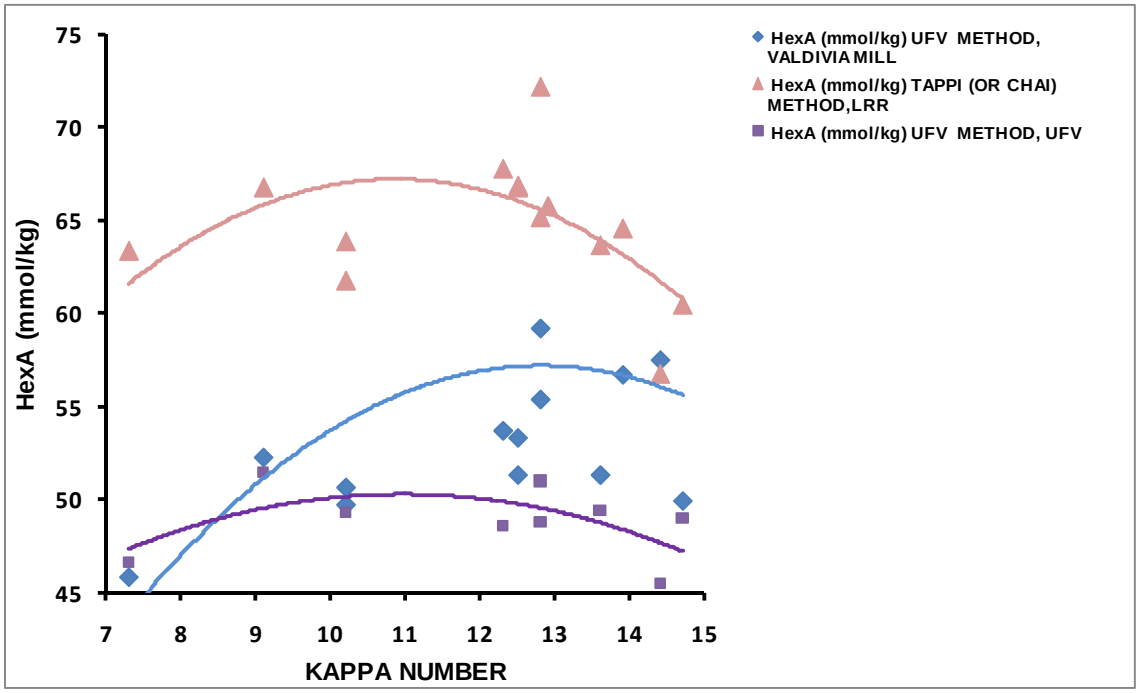

Figure 3- Variation of HexA's content in relation to kappa number in eucalyptus pulp, in samples from digesters and delignified pulp

In the figure 3 it is possible to observe how the values obtained with the UFV METHOD, VALDIVIA MILL follow a behavior similar to the one obtained with the same method in the laboratory of U. VIÇOSA, and it presents a low standard deviation in relation to the results of the literature (Monrroy, 2009). The TAPPI (OR CHAI) METHOD, VALDIVIA MILL shows a very high variability in its measurements

When comparing the selected methods, we can appreciate in the preliminary tests, that in relation to the environmental impact and health risks, the TAPPI (OR CHAI) METHOD, VALDIVIA MILL is not suitable. This is because the work must be performed with mercury and its residuals must be handled very carefully.

According to the results obtained in the laboratory of Valdivia Mill, the UFV METHOD, VALDIVIA MILL. is the feasible one to be implemented for the analysis of HexA's content for the operational control. The main issue, is to find the suitable strategy (optimization), to be able to use this value and correct the kappa number.

In economic terms, the cost per analysis in the laboratory of Valdivia Mill with UFV METHOD, VALDIVIA MILL has a value of 24 USD, much lower than the cost of sending the samples for being analyzed in external laboratories, which fluctuate between 50 - 100 USD.

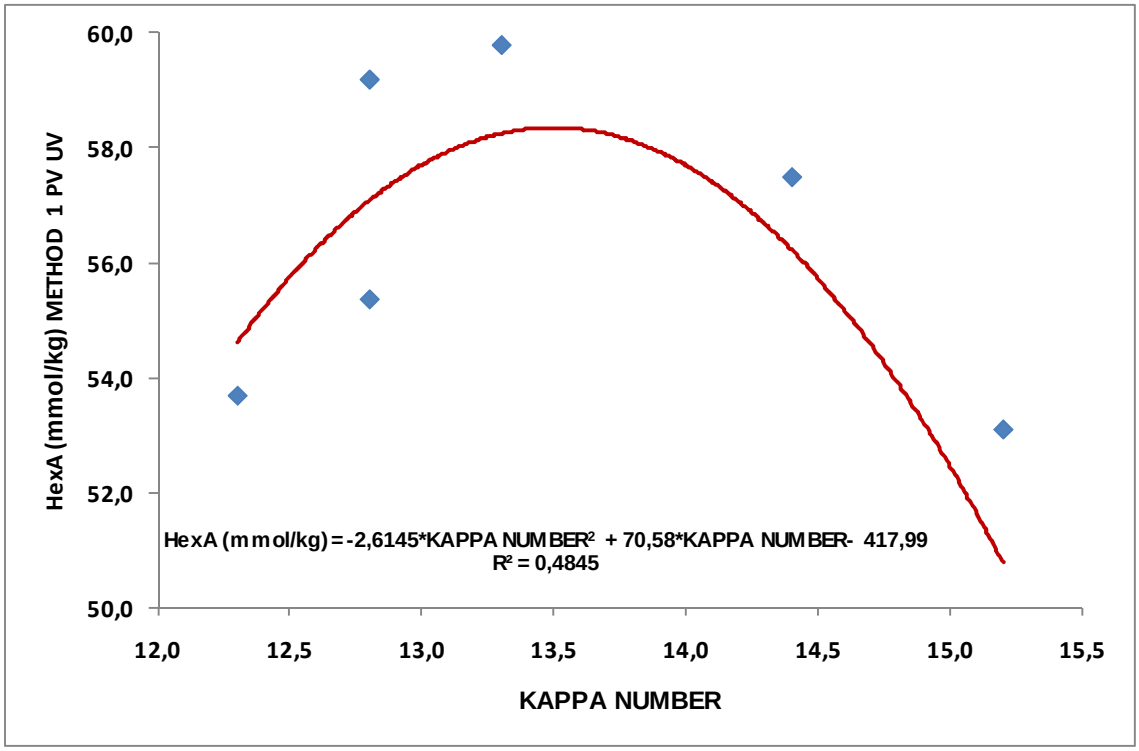

Figure 4- Variation of HexA's content in relation to the kappa index in eucalyptus pulp

Figure 4 shows that HexA's content increases with the kappa number up to a maximum and then decreases. This can be explained because of a higher ratio of degradation / dissolution beyond the formation in more extended cookings. A quadratic correlation of 48.5 % is obtained. This agrees with what was indicated by Chai (2001) and by Daniel (2003).

It can be seen the trend for HexA's content with various operational variables.

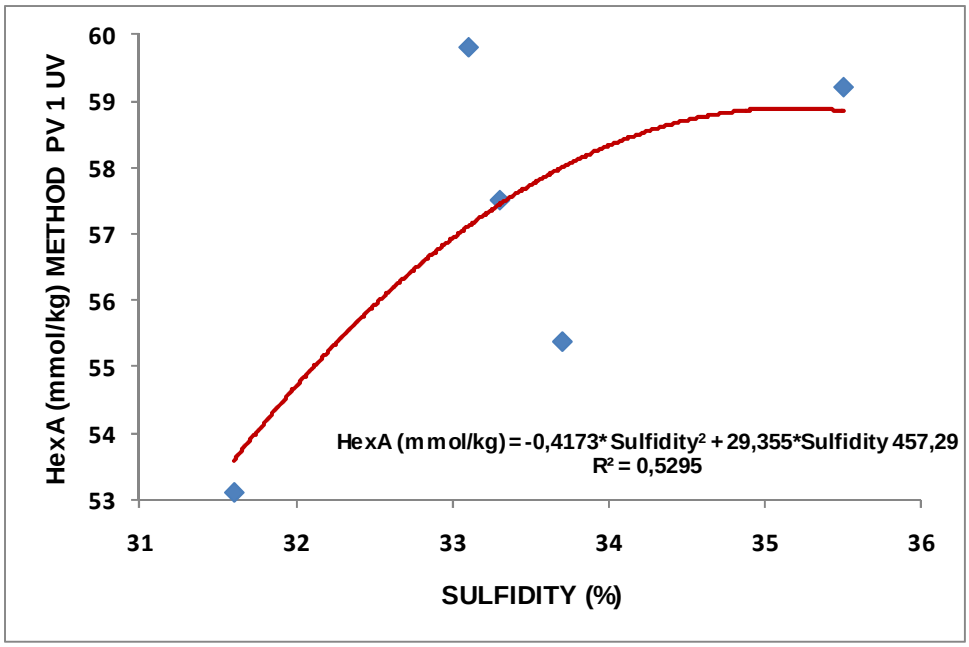

Figure 5 – Variation of HexA's content in relation to sulfidity in eucalyptus pulp

Figure 5 shows that HexA's content increases with the sulfidity in the range of the analyzed samples (31-36 %). A quadratic correlation of 53 % is obtained.

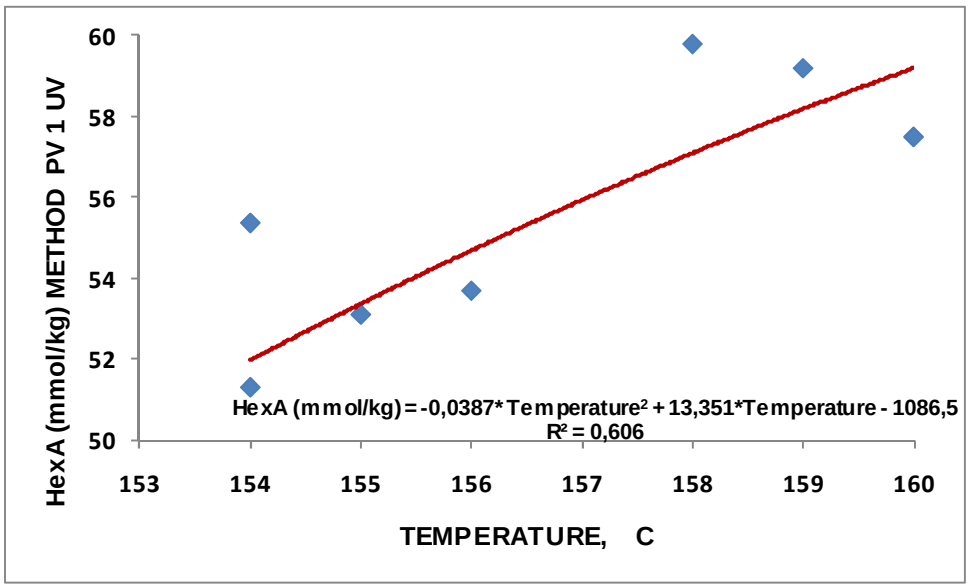

Figure 6 – Variation of HexA's content in relation to the temperature in eucalyptus pulp

Figure 6 shows that HexA's content increases with the temperature, obtaining a quadratic correlation of 60.6 %. This can be explained because of a higher temperature that increases the delignification ratio, therefore increases HexA's formation beyond the degradation.

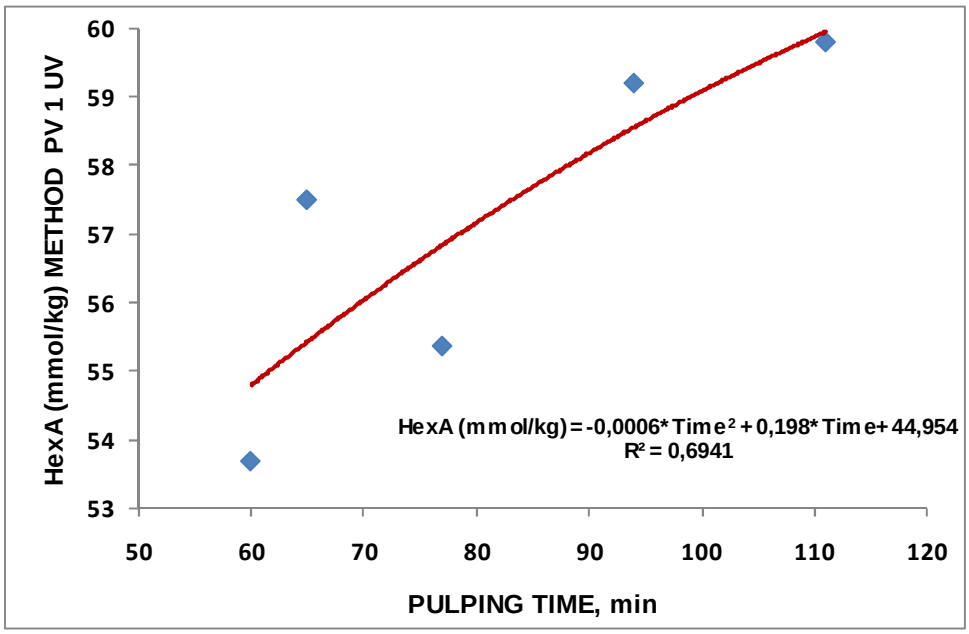

Figure 7 – Variation of HexA's content in relation to cooking time in eucalyptus pulps

Figure 7 shows that HexA's content increases with the cooking time obtaining a quadratic correlation of 69.4 %. This is because a higher cooking time that increases the delignification, therefore increases HexA's formation beyond the degradation.
A brief analysis of HexA's behavior is performed in samples of eucalyptus 100% *globulus* and samples of eucalyptus mixture 70 % *nitens* and 30 % *globulus.*

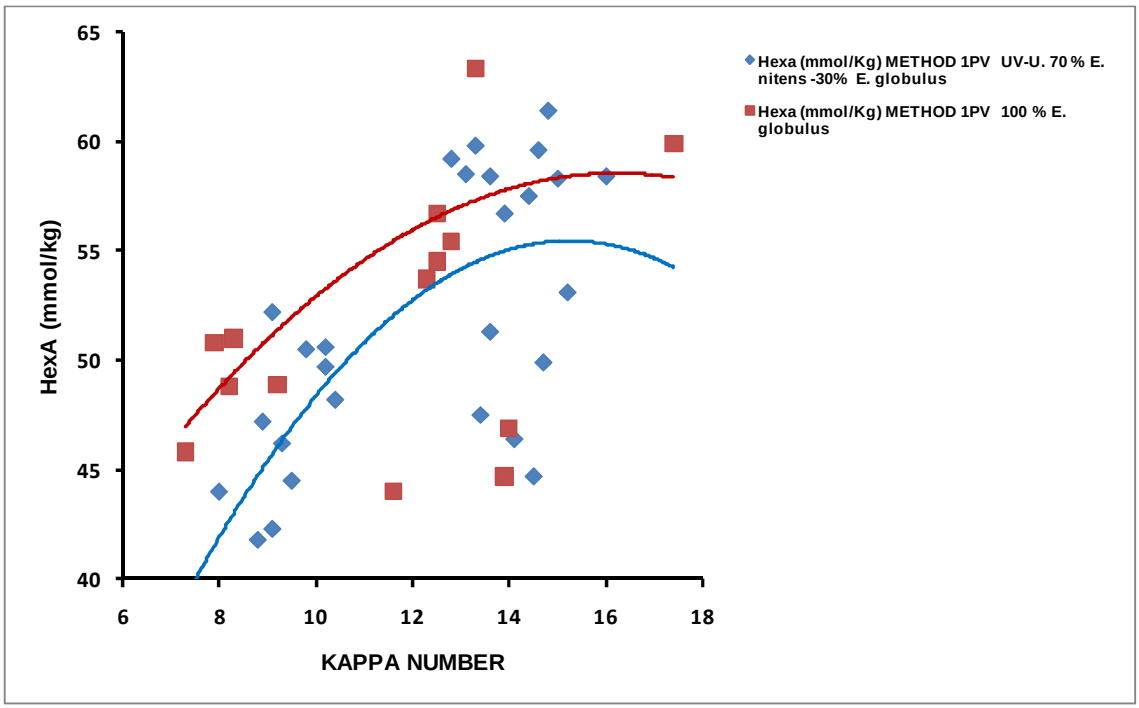

Figure 8 – Variation of HexA's content in eucalyptus pulp 100 % *E. globulus* and mixture samples 70 % *E. nitens* and 30 % *E. globulus*

In Figure 8 it is possible to observe how the pulps 100 % E. *globulus* present a higher content of HexA than the mixture samples of 70 % *E. nitens* and 30 % *E. globulus* mixture,for the same kappa number. This results suggest that *E. nitens* has higher lignin content which contributes to the enhancement of the kappa number.

CONCLUSIONS

- VTT, AEC, KTH and UVRR methods cannot be implemented in the laboratory of Valdivia Mill according to the established criteria for selection (short response time, low cost, safe).
- The selected methods for performing a more complete work (validation) are the ones that have the HUT method and TAPPI method (Chai, 2001) as a reference, both methods used in preliminary tests in this study.
- The methods applied in the external laboratories allow us to conclude that TAPPI (OR CHAI) Method, VALDIVIA MILL not easy to apply in Valdivia Mill and that the magnitude of the results between 17.7 and 34 mmol/ /kg of HexA are very different from other results.
- During the preliminary laboratory testing, we found that the HexA values obtained when applying the UFV METHOD, VALDIVIA MILL, in the laboratory of Valdivia Mill (reference the method used at the University of Viçosa), follow the trend of HexA values obtained in the external laboratories (UFV, LRR). And graphically, the results are between the HexA values obtained in both reference laboratories.
- HexA's content increases with the kappa number up to a maximum and then decreases.
- HexA's content increases with sulfidity, temperature and cooking time, where each of its variations has a quadratic effect on HexA's content.
- 100% *E. globulus* pulps have a higher content of HexA than the samples of a mixture of 70% *E.nitens* and 30% *E.globulus*.

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Acknowledgements

Financial support provided by Celulosa Arauco y Constitución, Vadivia Mill is greatly appreciated.