The effect of alkali charge on *Eucalyptus spp*. kraft pulping

Ana Gabriela Monnerat Carvalho Bassa*, Francismara A. Sanches Duarte*, Francides Gomes da Silva Jr**, Vera M. Sacon***
*Master in Forestry Sciences at University of São Paulo - Brazil
**Professor - University of São Paulo - Brazil
*** R&D Technical Manager - Votorantim Celulose and Papel - Brazil

Abstract

The objective of this study was to evaluate the behavior of the pulping process in industrial *Eucalyptus spp* chips under different alkali charges. The alkali charge applied varied between 10 and 20%, at 1% intervals. The parameters analyzed were: total yield, screened yield, kappa number, pH, viscosity, lignin content in the pulp and hexenuronic acid content. For all these parameters variations in the results were noticed as the alkali charge was changed. For total yield the values varied between 65.4 and 50.6%. For screened yield the values varied between 9.2 and 54.5%. The high total yield and the very low screened yield can be explained by the high content of rejects in some of the pulping conditions, indicating that during the pulping process there was a lack of alkali. The reject content was high for the lowest alkali charges, but by the 13% alkali charge it reached values of around zero. For the kappa number, the values varied from 82.4 to 13.4. For viscosity the results varied from 807 up to 1225 cm^3/g, and for lignin content in the pulp from 12.7 up to 3.02%. The hexenuronic acid formed varied between 23.0 and 65.7.

1. Introduction

Many researchers have been studying kraft pulping of *Eucalyptus* with a view to increasing knowledge and technology in this area.

Certain factors, such as alkali level, temperature and cooking time, are of fundamental importance in the pulping process. The objective of this study was evaluate the influence of alkali level on the kraft production process using eucalypts as a raw-material.

The main objective of kraft pulping is the individualization of fibers through the dissolving of the lignin present mainly in the middle lamella.

According to Bassa (2002) the active alkali is one of the main parameters in the pulping process, as it is directly related to the intensity of the delignification reactions and the breaking down of carbohydrates.

According to Silva et al (1997) one of the cooking parameters that significantly affects pulp quality is the total active alkali level applied, mainly in the case of conventional cooking. The effective need for alkali applied fully at the beginning of this stage makes the process less selective, being reflected in the reduced quality of the pulp.

The kraft pulping process presents relatively low selectivity in the lignin-removing reactions, resulting in significant breaking down of the carbohydrates during the delignification of the wood. To improve selectivity during industrial processing of the wood, technical and scientific knowledge of the reactions that take place during pulping and the effects of these reactions on the constituent parts of the wood is essential. Complete knowledge of the dissolving and consequent removal of both lignin and carbohydrates during kraft pulping can be of great importance for the production of pulp with maximized quality and yield. (Gomide & Fantuzzi Neto, 2000).

Gomide (1979) says that the kraft process has a number of advantages, such as: high pulp quality, efficiency in recovery of chemical reagents and energy and the possibility of sing practically all kinds of wood. The same author presents the disadvantages of the process as low yield, pulp production of approximately 50% the wood weight, and the fact that only about 30% of the alkali used in the process is used in the breaking down and dissolving of the lignin, the rest being consumed in the dissolving pf the polysaccharides and the neutralization of the organic acids formed.

Silva Jr. (2001) says that as the main characteristic of the kraft process is the high quality of the pulp obtained. This quality is assessed basically by the level of residual lignin (the kappa number), the extent to which the carbohydrates are broken down (viscosity), and the physical-mechanical properties. However, these characteristics can be altered by some variables in the productive process, such as: alkali charge, cooking time and temperature, amongst other things.

According to Bassa (2002), reactions to the removal of hemicelluloses aid the diffusion of chemical reagents in the liquor for the interior of the cell walls and the access of this liquor to the middle lamella, a region that has a higher concentration of lignin. The polysaccharides located mainly in the cells' secondary wall react with the chemical components in the liquor. These reactions cause structural alterations that reduce the fibers' intrinsic resistance and conformity, besides sharply reducing the yield of the process, the viscosity and the physical properties of the fiber.

In the alkaline pulping process, the alkali is consumed by the following phenomena:

i. Reactions with the lignin.
ii. Dissolving of the carbohydrates.
iii. Reactions with various organic acids, both those present originally in the wood and those produced by hydrolyzing reactions during the pulping.
iv. Reactions with resins in the wood.
v. Absorption by the fibers.

Most of the alkali used in pulping is consumed in the neutralization of the acids that are formed in the breaking down of the hemicellulose and cellulose. Such breaking down begins at a temperature of 60ºC, being almost completed when the temperature reaches approximately 150ºC (Gomide, 1979).

Amongst the points that hinder good development of cooking, we can mention the penetration of reagents into the structure of the wood that occurs basically according to two mechanisms.

i. Penetration of cooking liquor.
ii. Diffusion of the ions (Na^+, S_2^-, Hs, OH^-) from the cooking liquor in the water inside the chips.

2. Objective

The objective of this study was to evaluate the behavior of the pulping process in *Eucalyptus spp* chips under different alkali charges. The alkali charge applied varied between 10 and 20%, at 1% intervals. The parameters analyzed were: total yield, screened yield, kappa number, pH, viscosity, and the level of lignin and hexenuronic acids in the pulp.

3. Materials and Methods

3.1. Material

Industrial *Eucalyptus spp* chips supplied by the Luiz Antônio Unit of Votorantin Celulose e Papel were used for this study.

The chips were classified using a vibrating classifier containing four sieves with 16mm, 7 mm (thickness), 10 mm and 5 mm gaps. The chips retained in the sieve with 16 mm gaps and those that passed through the sieve with 5 mm gaps were discarded – oversized and undersized, respectively.

After classification, the chips were homogenized, the moisture level was determined, and 70-gram samples were prepared for kraft cooking.

3.2. Method

3.2.1. Basic density

Basic density was determined through the maximum moisture level method (Foelkel, Brasil & Barrichelo, 1972) using 5 samples of approximately 20g of chip each.

3.2.2. Pulping

The cooking was done in a rotative digester with 8 capsules. An absolutely dry mass of 70 grams of chips per cooking was used. The cooking conditions are shown in table 1.

Table 1. Cooking conditions

Parameters	Conditions
Alkali charge (%)	10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20
Sulfide level (%)	25
Maximum temperature (°C)	160
Heating time (min)	90
Cooking time (min)	90
Liquor - wood ration	4:1

3.2.3. Cooking analyses

After cooking, the analyses described in table 2 were carried out.

Table 2. Analyses carried out on the pulp and liquor and their respective methods.

Parameters		Norms
Pulp	Total Yield	Difference between o.d.weight of cellulose and o.d. weight of wood.
	Screened Yield	Difference between o.d weight of screened cellulose and o.d. weight of wood.
	Reject Level	Difference between o.d. weight of rejects (material taken from sieve with 0.2mm slot screened in the laboratory) and o.d. weight of wood
	kappa Number	Tappi – T236 cm-85
	Viscosity	Tappi – T230 cm-94
Liquor	pH	pH meter reading

4. Results and Discussion

4.1. Basic Density

The chips' basic density results are in table 3. The results are the averages of 5 repetitions.

Table 3. Eucalyptus spp. chip basic density results, standard deviation and variation coefficient.

Sample	Wood density (g/cm^3)	Average	Standard deviation	Coefficiant of variation (%)
	0,494			
	0,472			
Eucalyptus spp.	0,481	0,483	0,0087	1,8
	0,488			
	0,479			

In table 3 it can be seen that the chips basic density was 0.483g/cm^3. Foelkel (1992) recommends that eucalyptus raw material used for pulp production should have a basic density of 0.450 to 0.550 g/cm^3.

Bassa (2002) assessed the basic density of two samples of eucalyptus wood, one being a sample of *E. grandis* and the other being a hybrid of *E. grandis* and *E. urophylla*; this author found values of 0. 424 and 0. 543 g/cm^3, respectively.

Alencar et al (2002) assessed the basic density of a clone hybrid of *E. grandis* and *E. urophylla* between 1 and 7 years' old and found values between 0.431 and 0.521 g/cm^3.

Hence, the basic density determined for the raw material studied is in line with the authors cited.

4.2. Cooking

Table 4 shows the average results (2 repetitions) from the pulping process carried out.

Table 4. Pulping.

Active Alkali	Total yield	Screended yield	Reject level	kappa number	pH	Viscosity	Pulp lignin	Hexenuronic acid content
%	%	%	%			g/cm³	%	µmol/g
10	65,36 a	9,2 a	56,2 A	82,5 a	10,3 a	808 a	12,7 a	23,0 a
11	62,23 a	20,4 b	41,8 B	53,9 b	10,6 ab	891 a	9,5 ab	27,3 a
12	57,10 b	53,3 c	3,80 C	22,6 c	11,2 abc	1226 a	5,4 c	39,8 c
13	53,50 bc	52,9 c	0,70 C	20,0 cd	12,2 abcd	1169 a	5,7 bc	56,0 d
14	53,40 bc	53,4 c	0,02 C	17,6 de	12,5 bcd	1106 a	5,2 c	61,1 de
15	54,60 bc	54,5 c	0,05 C	17,1 def	12,9 cd	1137 a	6,1 bc	58,2 de
16	52,90 bc	52,8 c	0,045 c	16,6 ef	12,6 cd	1129 a	4,4 c	60,6 de
17	51,30 c	51,2 c	0,04 C	16,3 efg	12,3 abcd	1062 a	3,2 c	65,7 de
18	51,10 c	51,1 c	0,00 C	15,1 efg	13,4 d	967 a	3,1 c	61,5 de
19	50,80 c	50,7 c	0,075 c	14,6 fg	13,7 d	889 a	2,9 c	46,4 cd
20	50,60 c	50,6 c	0,00 C	13,4 g	13,8 d	998 a	3,0 c	34,2 ac

* The values with the different letters differ significantly ($p>0.05$)

From the results of the experimental cooking it is noted that for the different levels of active alkali applied, the values for the total and screened yields, reject levels, kappa number, pH, viscosity, levels of lignin and hexenuronic acids in the pulp varied.

Statistical analysis of the data presented in table 3 shows that there is a difference between the parameters assessed, with the exception for viscosity.

For the total yield, very high values are seen for the levels of active alkali 10, 11 and 12. This is due to the low alkali level applied in these treatments; that is to say, there was a lack of active alkali to get a good delignification of the wood, which caused a high reject level, as shown in figure 3. For the levels of active alkali between 13 and 20, values total yield between 50.6 and 54.6% were found, as shown in figure 1.

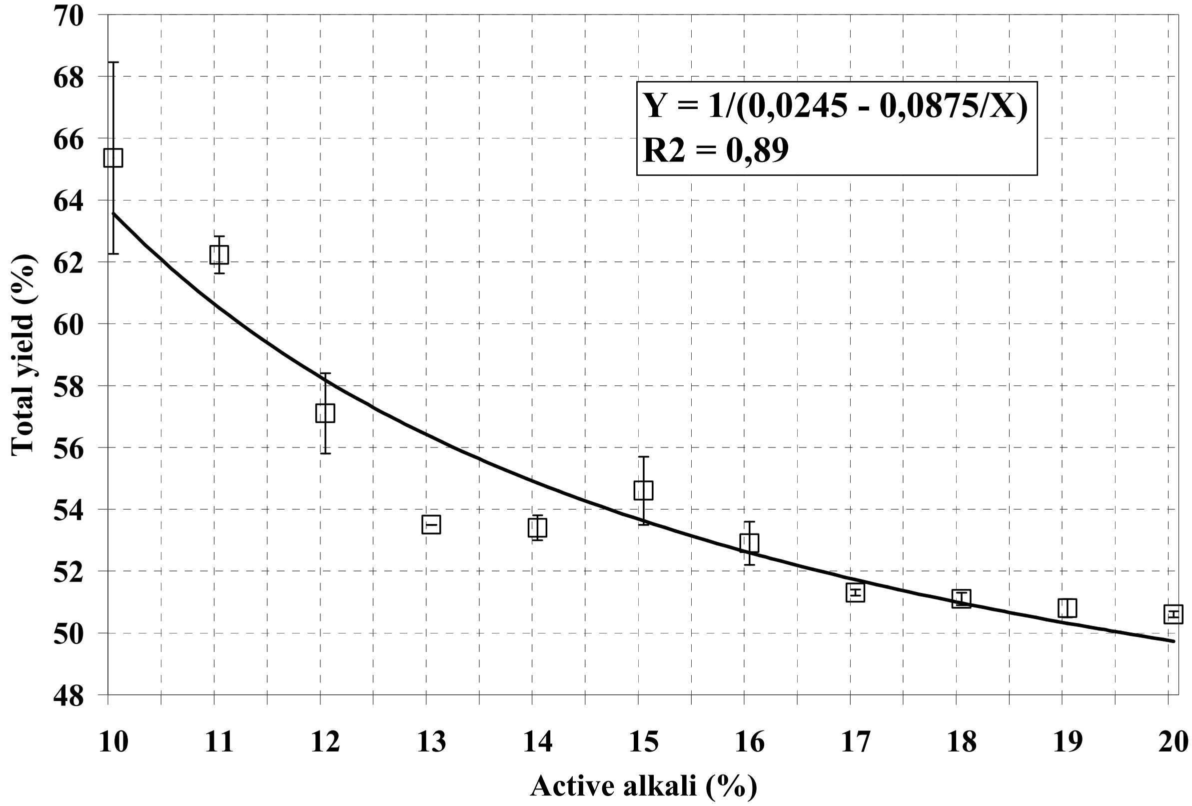

Figure 1. Total yield/ active alkali.

For levels of active alkali between 12% and 20% values of screened yield between 50.6 and 54.5% are seen, as shown in Table 4 and figure 2. In figure 2 it is also seen that maximum yield is reached at around 15% active alkali applied and for higher levels of active alkali, a tendency to fall is seen.

According to Gomide (1979), carbohydrates, both cellulose and hemicellulose, can be very unstable in alkaline solutions. During alkaline cooking cleavages occurr in the glycosidic bonds, causing the separation of groups or lateral chains and the cleavage of carbohydrates' main chains. These cleavages result in the formation of soluble compounds with low molecular weight and consequently a reduction in yield. This reaction is more pronounced in hemicellulose than in cellulose, resulting in the formation of some organic acids, such as saccharine acid, which consumes about 60% to 65% of the effective alkali used in the alkaline cooking. This breaking down is related to the rearrangement of the monomer molecules, resulting in the breaking of glucosidic bonds in the sugar units with carbonyl groups. When the carbonyl group is part of an aldeidic structure in the extremity of the carbohydrate chain, successive eliminations occur from the terminal sugar unit. The same author also says that the chemical breakdown of the carbohydrates during alkaline pulping involves different kinds of reactions, which are influenced by the concentration of –OH, but which are independent of the presence of sulfur ions ($S^{=}$ and –SH) used in the kraft process.

Almeida et al (2000) studied the dissolving of the chemical constituents of eucalyptus wood throughout the conventional kraft pulping process and stated that the alkali charge applied has a considerable affect on the rate of delignification and on the breaking down of the hemicellulose, mainly in the initial stages of cooking.

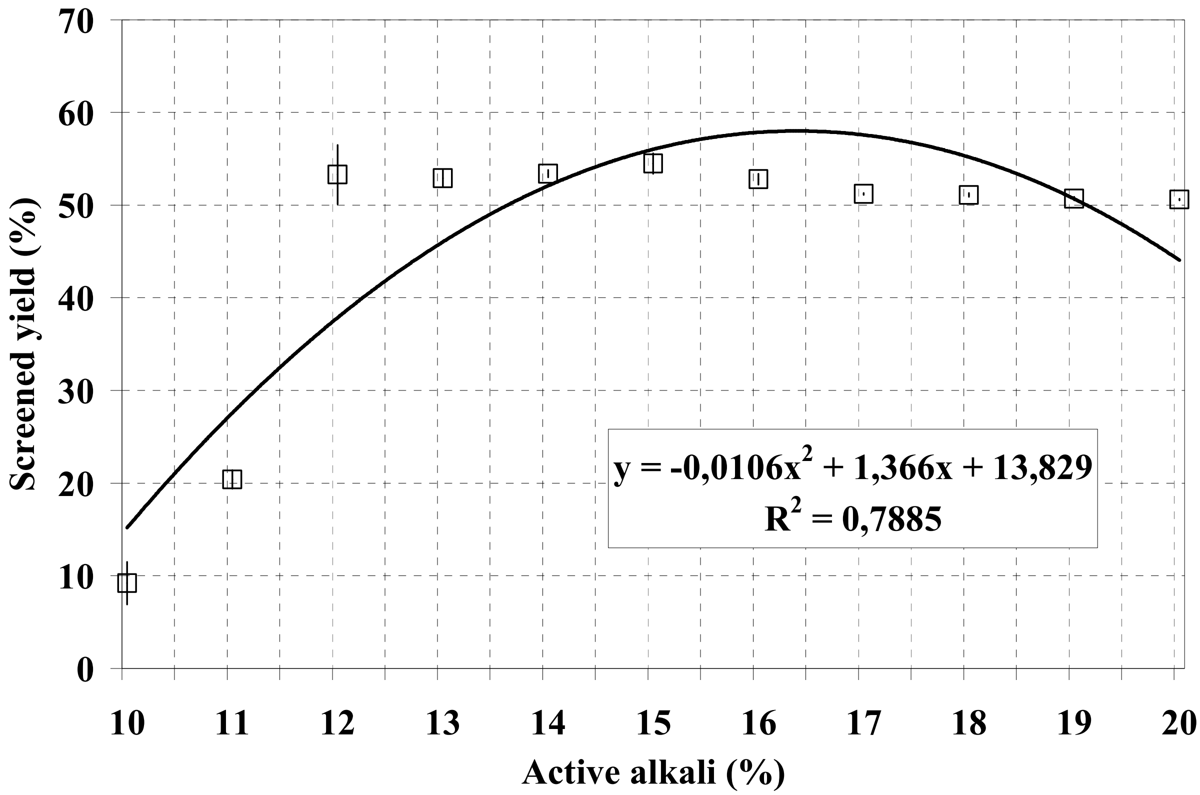

Figure 2. Screened yield/ active alkali.

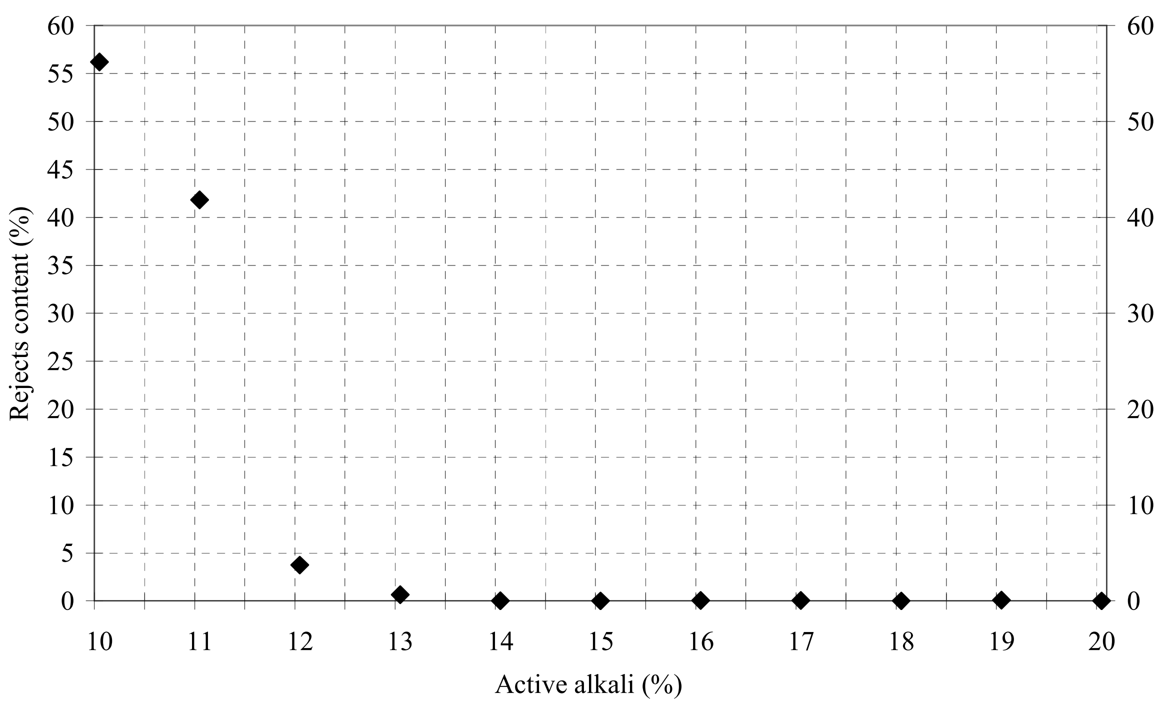

Figure 3. Reject levels/ active alkali.

In figure 3 the elevated reject levels cited above are observed for 10%, 11% and 12% levels of active alkali, with the remaining levels of alkali rejects being close to zero.

The reject levels in the pulping process are related to the characteristics of the wood and the parameters of the pulping process, mainly time and temperature of impregnation, factor H and alkali charge. When assessing the effect of the dosage of different levels of alkali, Almeida (2003) found high values of rejects for active alkali level 13%, and attributed this to the lack of active alkali in this treatment, showing the importance of the alkali charge in the pulping process.

For the kappa number parameter, a downward trend is noted as the active alkali level increases, as shown in figure 4.

For eucalyptus species, the kappa number commonly target at pulp mills varies from 15 to 20. So, it can be said that the levels of active alkali from 13 to 18 reach the level of delignification (kappa number) in the range applied commercially.

Bassa (2002) did a study based on defined kappa numbers (14, 16 and 18 ± 0.5), in which the strategy adopted to get these levels was alkali charge variation. This study proves the influence of the alkali level on the kappa number.

Alencar et al (2002) say that the increase in the alkali charge in the pulping process leads to the reduction if the kappa number, representing a higher removal of lignin.

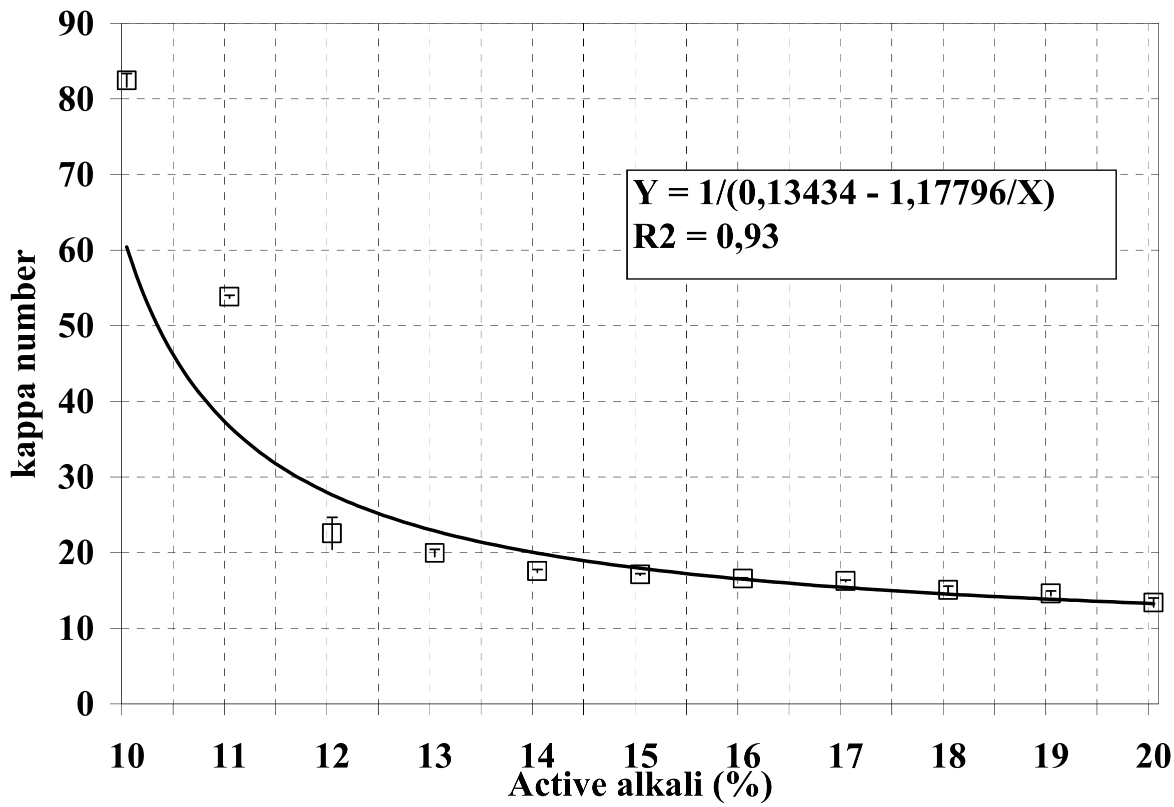

Figure 4. kappa number/ active alkali.

Almeida (2003), studying the behavior of the screened yield compared with the kappa number, reported that for kappa values less than or equal to 18 there is practically a linear effect by the kappa number on the screened yield in the pulping process, showing the importance of non-isolated assessment of parameters such as yield, alkali charge applied and, consequently, level of delignification. For kappa values of around 30 there is also a reduction of the screened yield due to higher generation of rejects, which is associated with the low alkali charge applied in the cooking.

Pulp viscosity is a widely used parameter in the control of pulp quality in the different phases of the production process. The viscosity parameter is associated with the average degree of polymerization and the correspondent molecular weight of the cellulose and hemicellulose polymers, this measurement being used to indirectly estimate the degree of polymerization and the extent to which carbohydrates are broken down during the phase when cellulose pulp is obtained. Thus, generally, greater viscosity indicates greater preservation of carbohydrates and, consequently, better physical resistance properties, mainly those that depend on the bond between fibers (Almeida, 2003).

Figure 5 shows the values obtained for the viscosity parameter of the pulp and its behavior depending on the alkali charge applied. The results achieved varied from 808 to 1226 g/cm^3.

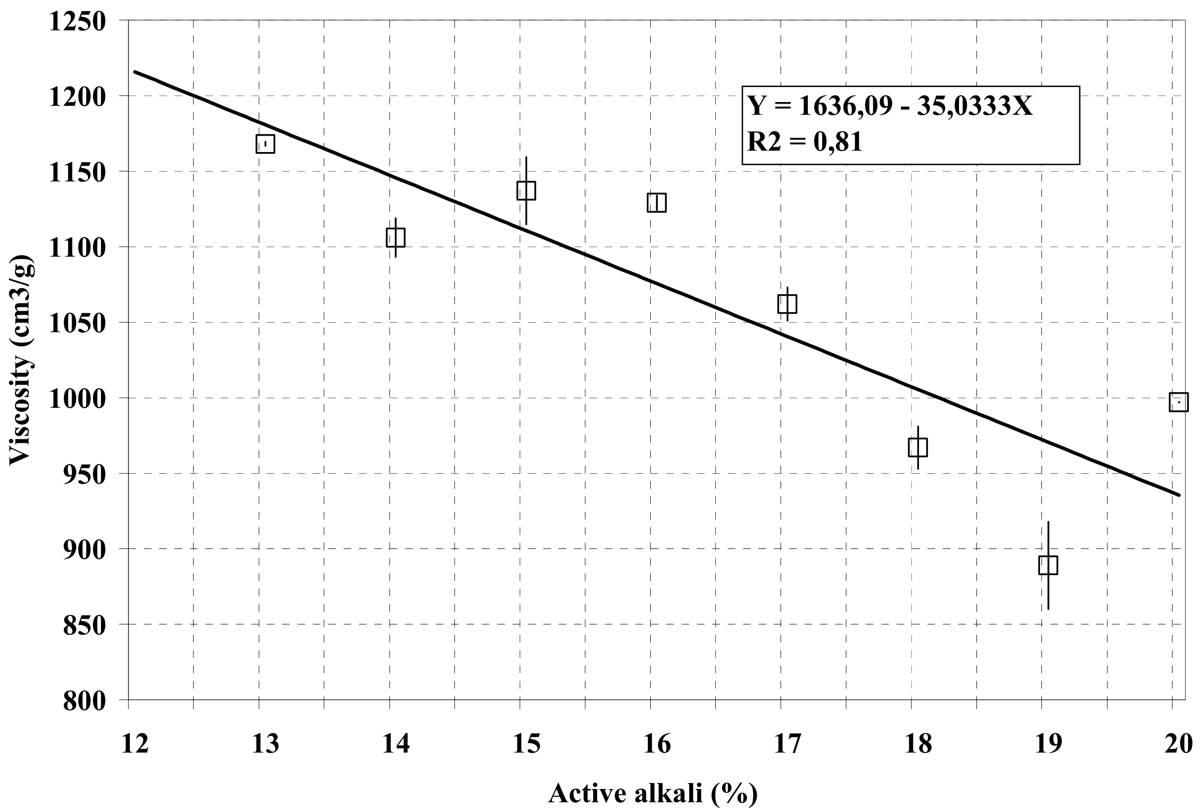

Figure 5. Pulp viscosity / active alkali

Costa et al (2001) say that the hexenuronic acids are formed during the alkaline pulping through the modification of 4-O methylglucuronic acids, present in the xylanase. The pulping conditions that have most influence over the hexenuronic acid content in the pulp are: active alkali, sulfide level, and temperature.

In this study the results on hexenuronic acids varied from 23.0 to 65.7 (µmol/g) pulp.

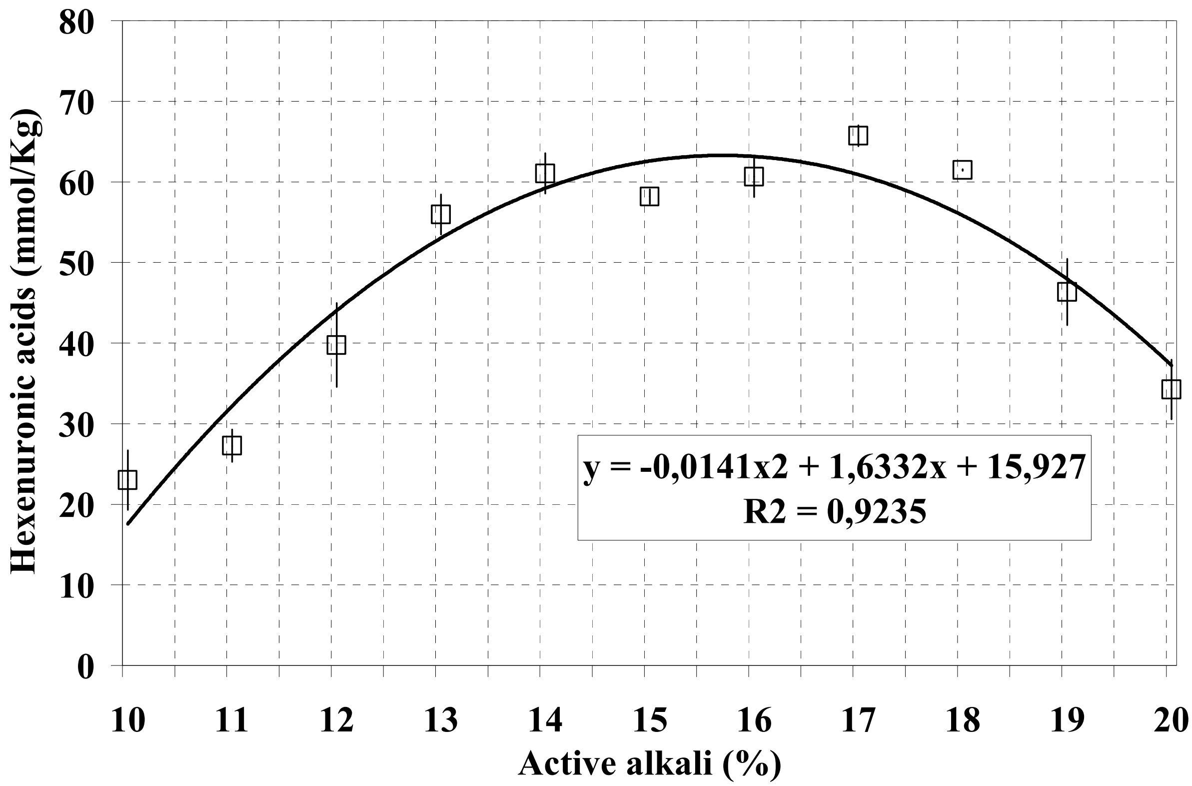

Figure 6. Level of hexenuronic acids/ active alkali.

Gidnert et al (1998) saw that the kappa number is influenced by the level of hexenuronic acids in the pulp, chemical compounds formed during the pulping phase after the conversion of 4-O methylglucuronic acids in the wood. Hexenuronic acids consume the potassium permanganate, a reagent used in determining the pulp kappa number, contributing in this way to an increase in the kappa number. Studies have suggested some conversion factors to calculate the corrected kappa number, it being common to use the factor proposed by Li et al (1997), in which a kappa number unit corresponds to 11.9 mmol of hexenuronic acid/kg of pulp.

The contribution of hexenuronic acids to the kappa number is greater in short-fiber pulp (up to 6 kappa number units) than in long-fiber pulp (up to 3 kappa number units) (Costa et al. 2001).

6. Conclusions

For total yield, values from 65.4 to 50.6% were obtained, with the highest total yield values showing a high reject level, indicating that there had been a lack of alkali during the cooking.

For screened yield, the values obtained varied from 9.2 to 54.5%. The lowest screened yield values are those in which cooking was compromised due to the lack of active alkali (high rejects content).

The levels of rejects were high for the lowest charges of active alkali and were close to zero at around 13% alkali charge.

The kappa number curve began with high values and these were reduced as the alkali dose was increased. The values were from 82.4 to 13.4.

In relation to viscosity, values from 807 to 1,225 cm^3/g were observed.

For the total yield and screened yield parameters, kappa number and viscosity, a downward trend was noted as the active alkali increased.

The levels of hexenuronic acids formed with 10% active alkali were lower, with the values increasing as the alkali dose increased, until about 16%. After this, the level of hexenuronic acids showed a tendency to reduce. For the sample used in the study, it was shown that the ideal alkali charge would be of around 15%, as in this condition a good delignification rate was observed, measured through the kappa number, of 17.1 and the highest screened yield and pulp viscosity were obtained.

7. Bibliographical References

1. GIERER, J. Chemical aspects of kraft pulping. **Wood Science and technology,** v. 14. p. 241-266, 1980.

2. BASSA, A. Processos de Polpação kraft Convencional e Modificado de Madeiras de *E. grandis* e Híbrido (*E. grandis* x *E. urophylla*). Piracicaba, 2002. 103p. Dissertação (Mestrado) – Escola Superior de Agricultura "Luiz de Queiroz", Universidade de São Paulo.

3. SILVA, D.J.; OLIVEIRA, R.C.; COLODETTE, J.L., GOMIDE, J.L. Impacto da qualidade da madeira na deslignificação, no branqueamento e na qualidade da polpa kraft de clones de eucalipto. **O Papel** n.2, 1997.

4. GOMIDE, J.L.& FANTUZZI NETO, H.. Aspectos Fundamentais da Polpação Kraft de Madeira de Eucalyptus. **O Papel**, v.61 n. 3 p 62-68. 2000.

5. SILVA Jr. F.G.; McDONOUGH, T.J. Polpação Lo-Solids® de Eucalipto: Efeito do Ritmo de Produção. In: 34° CONGRESSO ANUAL DE CELULOSE E PAPEL, ABTCP 16p. 2001.

6. GOMIDE. J. L.. Reação dos carboidratos de dissolução dos constituintes da madeira, durante polpação alcalina. **O Papel,** v. 40 n.11 p.119-128. 1979.

7. FOELKEL, C. E. B; BRASIL M.A.M.; BERRICHELO, L.E.G. Métodos para determinação da densidade básica para folhosas e coníferas. O Papel, v.33, n.8, p.57-61, Agosto, 1972.

8. FOELKEL, C. E. B. & MORA, E. MENOCHELLI, S. Densidade básica: Sua verdadeira utilizada como índice de qualidade da madeira de eucalipto para a produção d celulose. **O papel**, v.53, n5, 5p. 1992.

9. ALENCAR, G.S.B., BARRICHELO, L.E.G.; SILVA Jr., F.G. Qualidade da madeira de híbrido de *E. grandis* x *E. urophylla* e seleção precoce. In: 35º Congresso e Exposição Anual de Celulose e Papel. **Anais**, 2002.

10. ALMEIDA, J.M.; GOMIDE,J.L.;SILVA,D.J. Dissolução dos constituintes da madeira de eucalipto ao longo dos processos kraft contínuo convencional e aditivado. **Revista Árvore**, v.24, n.2, p. 215-222, 2000.

11. ALMEIDA, F. S. Influência da Carga Alcalina no Processo de Polpação Lo-Solids para Madeiras de Eucalipto. Piracicaba, 2003. 115p. Dissertação (Mestrado) - Escola Superior de Agricultura "Luiz de Queiroz", Universidade de São Paulo

12. COSTA, M.M.; MOUNTEER, A.H.;COLODETTE, J.L. Ácidos Hexenurônicos Parte I: Origem, Quantificação, Reatividade e Comportamento durante a Polpação kraft. **O Papel** v.62 n.5 p. 75-85. 2001.

13. GIDNERT, E.B.; TOMAI, P.E.; DAHLMAN, O. Influence on pulp quality of conditions during the removal of hexenuronic acids. **Nordic Pulp and Paper Research Journal**, v.13, n14, p.310-316, Apr. 1998.

14. SANTOS, S.R. Influência da qualidade da madeira de híbridos de *Eucalyptus grandis* x *Eucalyptus urophylla* e do processo kraft de polpação na qualidade da polpa branqueada. Piracicaba, 2005 160p. Dissertação (Mestrado) – Escola Superior de Agricultura "Luiz de Queiroz" Universidade de São Paulo.