EFFECTS OF SULFIDITY REDUCTION AND ANTHRAQUINONE ADDITION ON POLLUTANT EMISSION AND QUALITY OF *EUCALYPTUS* KRAFT PULP

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ABSTRACT

The objective of this study was to evaluate the impact of sulfidity reduction and anthraquinone (AQ) addition on TRS emission, chemical characteristics and bleachability of *Eucalyptus* kraft pulp. Identical effective alkali charge (16.3%), cooking time (100 minutes) and cooking temperature (160°C) were used for all experiments. Different sulfidities levels and several AQ charges were used to obtain different kappa numbers. The results were used to establish a mathematical model ($Ln(k) = b_0 + b_1 Ln(S) + b_2 Ln(AQ)$) using multi-regression analysis. This equation was used to calculate diferrent combinations of sulfidities and AQ chrges to obtain the same kappa number (17 ± 0.5). The pulps produced were bleached by the sequence (OO)DEoD(PO). The results obtained showed that reduction of sulfidity from 33% to 15% and AQ addition decreased methylmercaptan formation up to 63%. AQ addition resulted in higher yield, lower pulp viscosity, better xylan retention and presented no effect on hexeneuronic acid content. Sulfidity reduction and AQ addition decreased pulp bleachability.

Key Words: Methylmercaptan, Sulfidity, Anthraquinone, Xylans, Hexenuronic acid, Bleachability.

INTRODUCTION

Emissions of total reduced sulfur compounds (TRS) in a kraft pulp mill have been an environmental concern. They are corrosive and responsible for the bad odor of the kraft process. TRS compounds are generated during pulping and are liberated mainly from digester together with steam. Smaller amounts are dissolved in the cooking liquor. Steam liberated from digester are usually condensed, stripped and separated into two phases: the non-condensable gases (NCG) and the condensate. The NCG phase is rich in TRS, while the condensate is basically composed of volatile organic compounds (VOC), which is contaminated with TRS.

During kraft pulping, due to its strong nucleophylic characteristic, the HS^- ions react with lignin methoxyl groups and methylmercaptan compound (CH_3SH) is formed. The CH_3S^- ions can subsequently react with another methoxyl group to form the dimethylsulfide compound $(CH_3)_2S$ or by oxidation reaction can originate dimethyldisulfide, $(CH_3)_2S_2$. The hydroxyl ions (HO^-) can also react with lignin methoxyl groups but being a weaker nucleophile than HS^- this reaction occurs in a small extension (1, 2, 3). Methylmercaptan has been identified as the main TRS component (4, 5) present in NCG.

TRS formation during pulping depends on sulfidity level, pulping time and pulping temperature (6, 7, 9, 10, 11). Some decrease in sulfur reduced compounds emissions have been obtained by reducing pulping sulfidity (4, 11, 12). Use of low sulfidity and addition of AQ can be an alternative to reduce pollutant emission without decreasing delignification efficiency. However, very few publications are available describing use of additives to reduce pollutant emissions. AQ has been used by the pulp industry to increase yield, decrease solids concentration in black liquor and to reduce kappa number (13). Those applications usually aim to decrease bottlenecks in some sectors such as recovery furnace, caustification, digesters, and bleaching plant (14).

The volatile organic compounds (VOC) present in condensates have also been an environmental concern. VOCs constitute an important source of biodegradable organic material. They increase the biochemical oxygen demand (BOD) of the condensates from the pulping process and are responsible for about 20% of the total BOD load in these effluents (15). Methanol is the main organic volatile compound produced during alkaline pulping (4, 16, 17). It can be formed by reaction of hydroxyl ions in two different ways: alkaline hydrolysis of 4-O-methylglucuronic acid groups in xylans and demethylation reaction of the methoxyl groups present in lignin (15, 18). However, lignin demethylation by HO^- is less intensive than by HS^- ions (17).

Modification of pulping conditions can be an alternative to reduce pollutant emission but it has been demonstrated that it may significantly affect pulp quality including viscosity, chemical characteristics, bleachability, and physical-mechanical properties (19, 20, 21). Pulping conditions may have a detrimental effect on reactivity of residual kraft lignin during oxygen delignification (22). Several authors have demonstrated that use of anthraquinone and/or polysulfides affect not only yield and delignification efficiency but also pulp bleachability (20, 21, 23, 24).

The objectives of this study were to evaluate the impact of sulfidity reduction and AQ addition on methylmercaptan generation, chemical characteristics and bleachability of eucalyptus kraft pulps.

EXPERIMENTAL

Pulping

Pulping experiments were carried out in a laboratory M&K digester using 500g of eucalyptus wood chips and liquor to wood ratio of 4/1. The digester was heated up for 90 minutes to reach cooking temperature (160^{o}C) and this temperature was maintained for 100 minutes. The same effective alkali charge (16.3%, as NaOH) was applied for all cooking. Different levels of sulfidities (20, 25, 30 and 35%) and several AQ charges (0.0, 0.03, 0.06 and 0.10%) were used for each sulfidity level. The kappa number results, sulfidity levels and AQ charges were used to establish a mathematical model, using multi-regression analysis. The equation was used to calculate diferrent AQ charges to obtain the same kappa number (17 ± 0.5) at severals sulfidity levels (33, 28, 20 and 15%). These pulps were labeled as S33, S28, S20 and S15, respectively. At the end of each cooking and just before discharging, the non-condensable gases and the condensed phase were collected, as shown in Figure 1. After washing, pulp kappa number and viscosity were determined using Tappi standards.

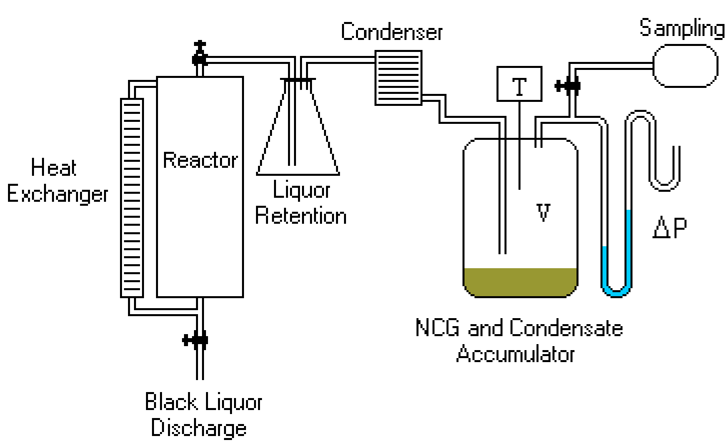

Figure 1 – Sampling system of non-condensable gases and condensates.

Methylmercaptan Analysis

Some methods for analysis of volatile organic sulfur compounds are described in literature (4, 25). In this study the non-condensable gases were collected in polyethylene bag and were analyzed by gas chromatography using the technique of direct injection. Concentrations of CH_3SH were determined using a gas chromatograph SHIMADZU GC-17A equipped with flame ionization detector and a capillary column DB-5 (30m x 0,25mm). Analysis conditions were: injector at 40°C, capillary column at 40°C, detector at 170°C, split ratio of 1:50, injection volume of 400µL, nitrogen as gas carrier and run time of 5 minutes. Analytical grade standard of CH_3SH was used to build the calibration curve.

Carbohydrate Analyses

Pulp samples of approximately 0,3g were treated with 3mL of 72% H_2SO_4 for one hour at 30°C. The acid was diluted to 3% and hydrolysis was completed in an autoclave at approximately 120°C and 103 Kpa for one hour. The mixture was filtered and the hydrolyzate was collected in a 250ml flask. Known amount of internal standard (eritritol) was added to 50mL of hydrolyzate. The mixture was neutralized with barium hydroxide to pH 5.3 and centrifuged. It was necessary to concentrate a sample to 1:10 for sugar determination. Sugars concentration was determined by HPLC using a SHIMADZU SCL-10A chromatograph, equipped with a refraction index detector, RID-10A, columns HPX 87P (7,8mm x 300mm) and SCR 101P (7,9mm x 300mm) coupled and heated to 80°C. Deionized water was used as an eluent at 0,4mL/min for 70 minutes. Analytical grade standards of glucose and xylose were used for calibration curves and sugars quantification.

Hexenuronic Acid (HexA) Groups Analysis

Several methods for HexA analysis have been reported (26, 27, 28). The methodology used for this study was based on a recent method (JIANG et al., 1999). Pulp samples of approximately 0.3g were treated with 3 mL of 72% H_2SO_4 for one hour and after that time the acid was diluted to 3%. Hydrolysis was completed in an autoclave at approximately 103 KPa and 120°C. After filtration the hydrolyzate was analyzed by HPLC technique using a SHIMADZU SCL-10A chromatograph, equipped with an UV-visible detector and a SCR 102H (8mm x 300mm) column heated to 40°C. The eluent was 5 mmol/L $HClO_4$ at 1,0 mL/min for 40 minutes. Commercial standard of 2-furoic acid was used for calibration curve and quantification of hexenuronic acid groups.

Bleaching

Effects of sulfidity reduction and anthraquinone addition on pulp bleachability were evaluated using an ECF bleaching sequence, O/ODEoD(PO). The brightness target for all pulps was 90±0.5% ISO. The bleaching conditions used are shown in Table 1.

Table 1- Bleaching Conditions

Conditions	Bleaching Stage				
	O/O	D_0	Eo	D_1	(PO)
Consistence, %	10	10	10	10	10
Temperature, °C	95/95	55	80	75	95
Time, min	30/60	20	20+70	210	60
Pressure, kPa	600	-	200	-	300
Final pH	11.5-12.0	2.5-3.0	±11.0	3.5-4.0	±10.8

RESULTS AND DISCUSSION

Pulping

Figure 1 shows the results of kappa number obtained in different cooking conditions. These results demonstrated that delignification degree was increased up to 0,6% of AQ charge. Above this dosage the number kappa was only slightly affected, being AQ more effective at lower sulfidity levels. Data shown in Figure 1 were used for a multiple regression analysis, obtaining a mathematical model (Equation 1). The kappa number (K) was a function of sulfidity (S) and AQ charge. From this equation different kappa numbers curves were established (Figure 2).

Equation 1: $Ln(k) = 3{,}2430 - 0{,}2060 Ln(S) - 0{,}0722 Ln(AQ)$

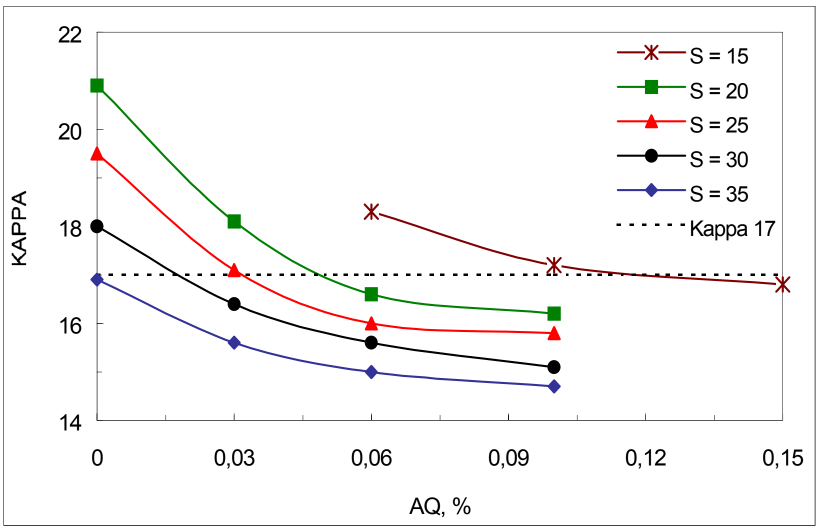

Figure 2 – Effect of AQ in delignification rate at several sulfidities.

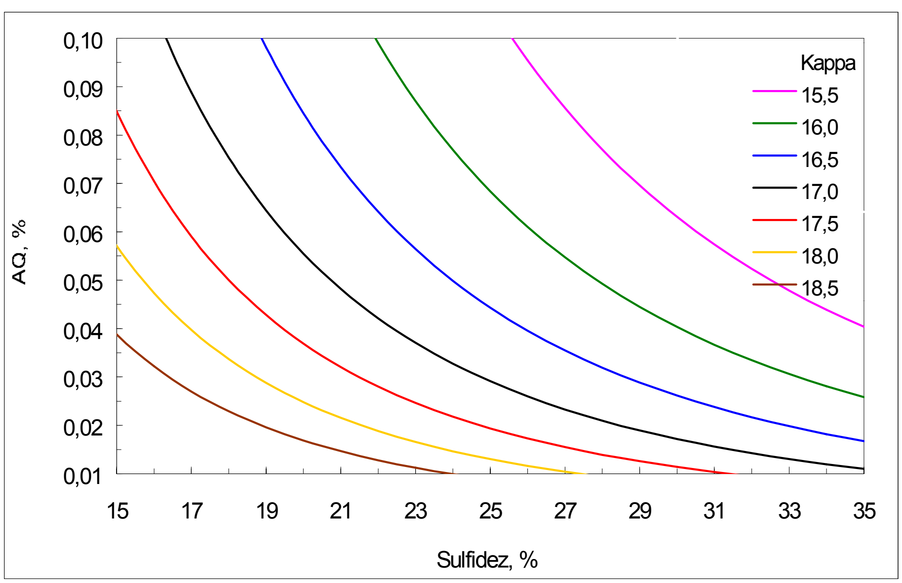

Figure 3 – Kappa numbers as function of different sulfidity levels and AQ charges.

From Equation 1 it was calculated the AQ dosages necessary to obtain pulps with same kappa number (17 ± 0.5) at several sulfidity levels (33, 28, 20 and 15%). Results presented in Table 2 demonstrate that AQ addition compensated the sulfidity reduction. The same delignification degree was maintained and a yield increase up to 1% was obtained. AQ presented an important action in carbohydrates preservation. However, yield increase was accompanied by a decrease in pulp viscosity. Such viscosity reduction could be explained by stabilization and higher retention of short chains carbohydrates (xylan) as shown in Table 4.

Table 2 - Effect of sulfidity reduction and AQ addition in kraft pulping

Sulf., %	AQ, %	Kappa	Yield, %	Viscosity, $mPa.s^{-1}$
33	0.00	16.8	51.3	45.1
28	0.02	16.7	51.5	43.0
20	0.06	17.4	51.8	39.7
15	0.12	17.3	52.3	38.7

Table 3 shows that sulfidity reduction and AQ addition did not affect residual effective alkali (AE). This suggests that the same amount of OH^- ions was required for lignin and carbohydrate degradation reactions. However, there was a decrease in the amount of solids in black liquor. This could be explained by the higher yields (lower organic solids in black liquor) and lower sulfide charges (lower inorganic solids in black liquor) when part of the sulfidity was replaced by AQ addition.

Table 3 – Effects of sulfidity reduction and AQ addition on black liquor characteristics

Black Liquor	Cooking			
	S 33	S 28	S 20	S 15
NaOH, g/L	3,0	3,6	5,5	6,0
Na_2S, g/L (as NaOH)	8,1	6,6	2,9	1,6
Effective alkali, g/L	7.1	6.9	7.0	6.8
Total solids, %	16.1	15.5	14.5	13.0
Organic solids, %	9.6	9.3	8.9	8.0
Inorganic solids, %	6.5	6.2	5.6	5.0

Carbohydrates and Hexenuronic Acid Contents

Table 4 shows the effect of sulfidity reduction and AQ addition on kraft pulping yield and carbohydrates content. These results demonstrated that yield increase was accompanied by higher carbohydrates stabilization, especially xylans. This suggests that xylans were quite sensitive to stabilization by the AQ oxidizing capacity, resulting in yield increase. Hexenuronic acids content was not affected by sulfidity reduction and AQ addition. This phenomenon was expected because formation of hexenuronic acids is dependent on temperature, cooking time, and OH^- ions concentration (29, 30), which were maintained constant in all pulping experiments.

Table 4-Effect of sulfidity reduction and AQ addition on pulp chemical characteristics

Pulp	Yield, %	Glucans, %	Xylans, %	HexA, mmol/kg
S 33	51.3	73.5	12.8	58.5
S 28	51.5	72.6	13.0	58.6
S 20	51.8	73.8	13.1	57.9
S 15	52.3	75.4	13.6	58.5

NCG and Condensate Analysis

Figure 4 shows the effect of sulfidity on methylmercaptan formation when it was partially replaced by AQ. Sulfidity reduction from 33% to 15% and AQ addition decreased CH_3SH formation up to 63% for the same kappa number (17 ± 0.5). Condensate analysis presented in Figure 5 shows that COD and BOD_5 concentrations decreased with sulfidity reduction and AQ addition. At the end of a kraft cooking, although most of the TRS produced is found in the NCG phase, some part is retained in black liquor and contributes to COD and BOD.

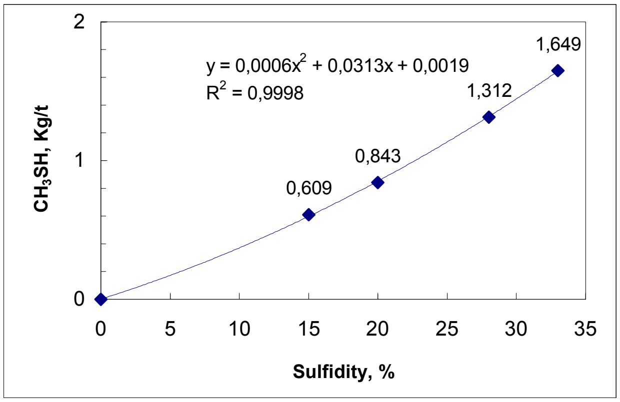

Figure 4 - Effect of sulfidity reduction and AQ addition on methylmercaptan formation.

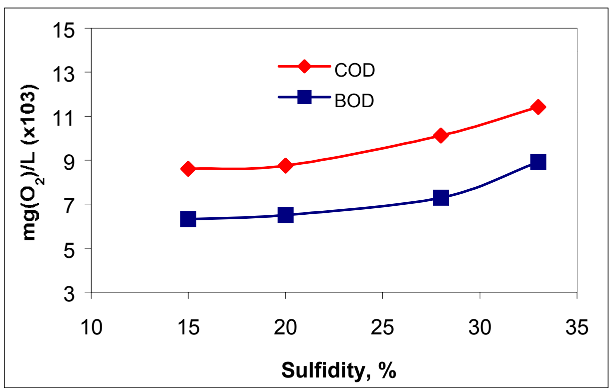

Figure 5 - Effect of sulfidity reduction and AQ addition on BOD and COD in condensates.

Oxygen Delignification

Table 5 summarizes the effects of pulping conditions on oxygen delignification. Kappa number reduction close to 41% was obtained for all pulps. However, Figure 6 shows that selectivity of oxygen delignification was improved by sulfidity reduction and AQ addition. This phenomenon could be explained by the higher initial viscosities, before oxygen delignification, presented by pulps produced with higher sulfidities.

Table 5- Results of oxygen delignification

Pulp	Kappa Reduction, %	Pulp Brightness, %ISO		Viscosity, $mPa.s^{-1}$	
		Brown	O_2	Brown	O_2
S 33	41.1	38.6	57.3	45.1	29.1
S 28	41.3	38.8	58.0	43.0	27.4
S 20	41.4	37.9	56.3	39.7	27.1
S 15	41.3	37.6	56.3	38.7	27.2

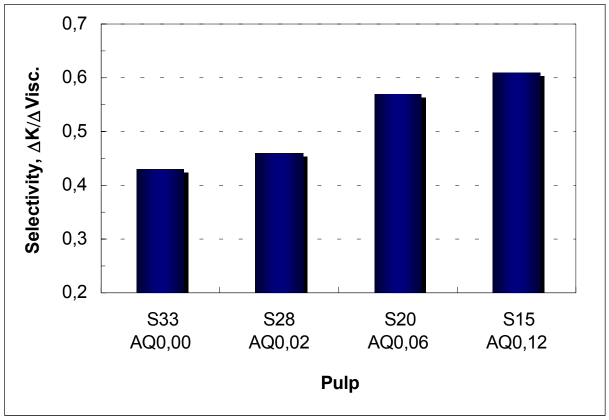

Figure 6 - Effect of sulfidity reduction and AQ addition on selectivity of oxygen delignification.

Bleaching

Table 6 shows that pulps produced with higher sulfidity levels presented higher brightness along the bleaching sequence. Hence, sulfidity reduction and AQ addition resulted in higher chemicals requirement to reach final brightness of 90% ISO (Table 7 and Figure 7). The chemical consumption was noted in the final (PO) bleaching stage as shown in Figure 7. These results are in agreement with others studies (19,20,21).

Table 6 - Profile of pulp brightness during bleaching.

Pulp	Pulp brightness, % ISO				
	Marrom	Polpa O_2	D_0	Eo	D_1
S 33	38,6	57,3	76,5	79,5	86,4
S 28	38,8	58,0	76,0	78,7	87,2
S 20	37,9	56,3	75,8	77,2	85,2
S 15	37,6	56,3	75,7	77,3	84,4

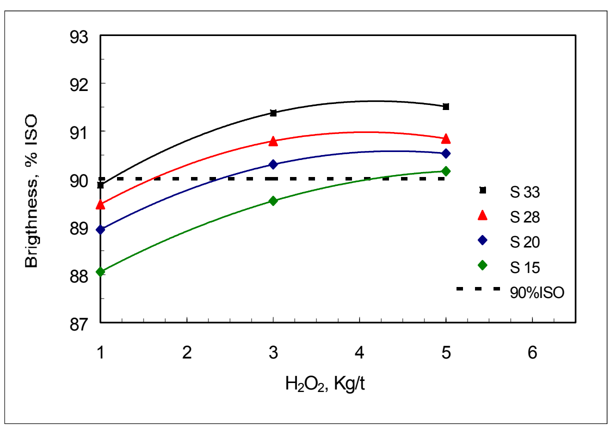

Figure 7 – H_2O_2 charged in PO stage to reach the final brightness of 90% ISO.

Table 7 – Viscosity and bleaching conditions used to obtain a pulp brightness of 90±0.5% ISO

	Pulps			
	S 33	S 28	S 20	S 15
O_2, Kg/ton	25	25	25	25
ClO_2*, Kg/ton	26.8	26.6	27.4	27.4
H_2O_2, Kg/ton	1.1	1.6	2.2	4.0
Viscosity, $mPa.s^{-1}$	19.8	19.5	18.0	17.8

* Kappa factor: 0.20

Physical-mechanical properties

Pulps produced with 33% and 15% of sulfidity were refined. Physical-mechanical properties were evaluated as function of tensile index and refining energy consumption. The results (Figure 8) demonstrate that sulfidity reduction and AQ addition increased pulp refinability, requiring less energy to reach the same tensile index. This effect can be attributed to hemicelluloses retention (xylans), favouring fibers hydration and interfibers bonding.

Decrease in pulp viscosity due to sulfidity reduction and AQ addition could indicate pulp strength losses. However, no difference in pulp strength was observed (Figure 9 e 10). According to Figure 10, sulfidity reduction and AQ addition contributed to pulp bulk. This it is an important pulp property for tissue paper because it correlates to paper softness.

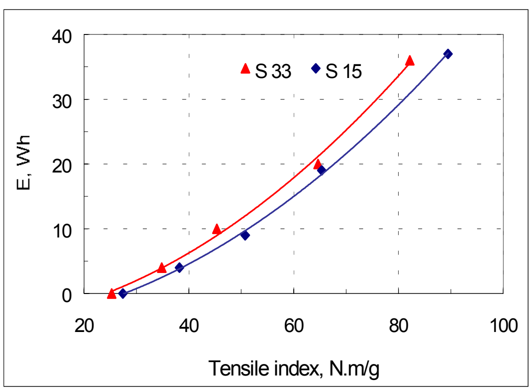

Figure 8 – Energy requirement and tensile index relationship.

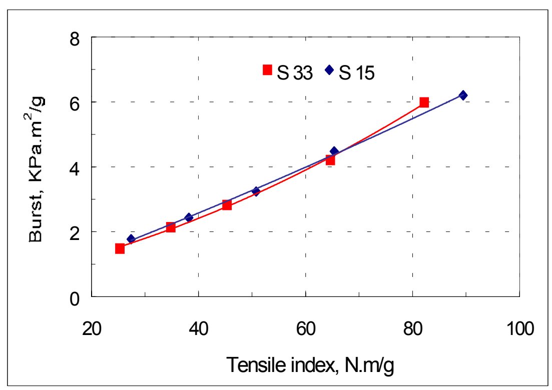

Figure 9 – Burst and tensile index relationship.

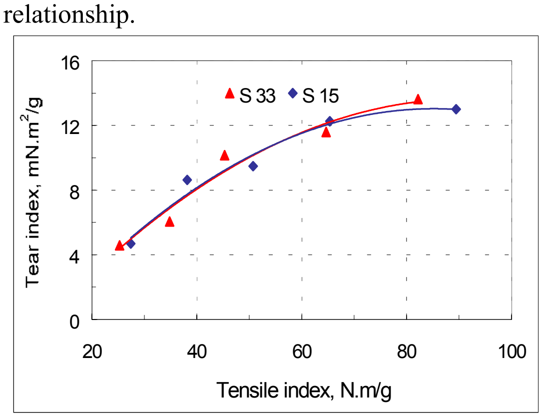

Figure 10 – Tear index and tensile index relationship.

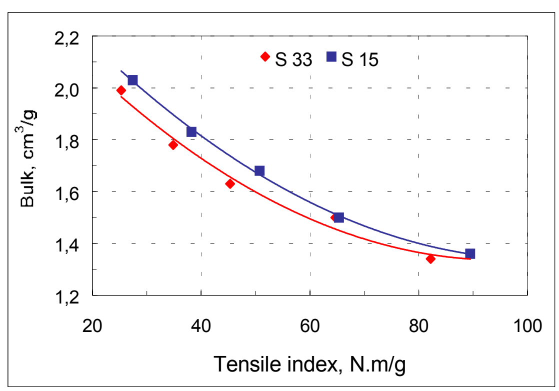

Figure 11 – Bulk and tensile index relationship.

CONCLUSIONS

Decrease in sulfidity could be compensated by AQ addition to maintain the same degree of delignification. Sulfidity reduction and AQ addition decreased methylmercaptan formation and, thefore, air pollution load. BOD_5 and COD in condensate were also reduced. AQ addition increased pulping yield due to higher xylan retention but the hexenuronic acid content was not affected. Sulfidity reduction and AQ addition decreased pulp bleachability. Pulp refinability was improved but physicist-mechanical properties were not affected.

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