Influence of hexenuronic acid content and pH on refining and physical-mechanical properties of pulps produced by ECF and TCF processes

Vanessa L. Silva: Ph.D Candidate, UFV, Brazil, vanessa.silva@ufv.br
Thalita M. Mendonça: Undergraduate student, UFV, Brazil, thalitamr@yahoo.com.br
Bianca Barbosa: Undergraduate student, UFV, Brazil, bianca.barbosa@ufv.br
Jorge L. Colodette: Full Professor, UFV, Brazil, colodett@ufv.br

Abstract

Brightness reversion has become an important issue for high-brightness hardwood pulp producers, particularly for those operating using low chemical doses. Structures that are able to be oxidized, such as hexenuronic acids (HexA), can alter the brightness stability in the pulp. In a previous study involving accelerated aging tests, it was revealed that brightness reversion can be alleviated by an increase of in pulp pH. In this work, the bleaching sequences Q(EP)QP and D(EP)DP were carried out to achieve pulp with a variable content of hexenuronic acid. The bleached pulps were then submitted to a refining process at pH 4.5 and 8.0 and their physical-mechanical properties were evaluated. The bleached pulps with high kappa factors had better brightness stability, and pulp produced by the bleaching sequence Q(EP)QP obtained less stability. The carboxylic group content followed the same trend as HexA content in the pulp. The cooper number (reducing groups) and organically-bound chlorine (OX) content was high in pulps with increased chlorine dioxide doses. Additional tests were carried out to evaluate the effect of HexA on pulp refining. The tests revealed that these oxidizable structures introduce hydrophilicity in the pulp. Regarding the refinability and the physical-mechanical properties of bleached pulps, the pH 8.0 was more favorable than pH 4.5. Significant differences between the physical-mechanical and optical properties were observed in pulp with varied hexenuronic acid content. Pulps with high hexenuronic acid content alter the refinability of the pulps, especially in relation to the tear index, MOE, TEA, specific volume, and energy consumption.

Keywords: hexenuronic acid, pH, bleaching, refining

Introduction

Bleached Eucalyptus kraft pulp is becoming the most important source of market pulp. Brazil is the largest exporter of Eucalyptus pulps, and almost all of the fibres produced in Brazil are bleached. Overall, the main drivers affecting the choice among bleaching technologies are chemical demand, yield, water consumption, effluent load & treatability, pulp OX, brightness stability, refinability and strength, and capital costs.

Brightness reversion has become an important issue for high brightness hardwood pulp producers, particularly for those operating with low chemical doses. While the use of low chemical doses is an indication of high mill efficiency, brightness reversion is not. Recent work has demonstrated that high hexenuronic acids content represent a significant factor of brightness reversion in a pulp [1]. Sevastyanova and Gellerstedt [1] claim that under acidic conditions these colorless structures are hydrolyzed, giving rise to structures such as reductic and 5-formyl-2 furancarboxylic acids that cause thermal yellowing.

Hexenuronic acids (HexA) are formed by the elimination of methanol from the 4-O-methylglucuronic acid group (MeGlcA) in the kraft pulping process [2]. The presence of HexA in hardwood kraft pulps contributes to 25-30% of the pulp kappa number and thus explains the low efficiency of oxygen delignification in hardwood kraft pulps. However, the HexA content can be reduced by inserting acids stages, using ozonation; hot acid treatment; chlorine dioxide; peracetic acid for this purpose [3-5].

Although the hexenuronic acid can be removed from the pulp, it is not a viable option because the pulp yield decreases. In a previous study, it was reported that if pulp has a high hexenuronic content, a better way to establish the brightness reversion is to calibrate the pH of the pulp at about 8.0 [6]. In this work, the bleaching sequences Q(EP)QP and D(EP)DP were carried out to achieve pulp with a variable content of hexenuronic acid. Bleached pulps were then submitted to a refining process at pH 4.5 and 8.0 and their physical-mechanical properties were evaluated.

Experimental

Pulp bleaching

Industrial delignified Eucalyptus pulp was used to produce pulps with varied hexenuronic acid content. For this, the pulp was bleached using ECF technology with the sequences D(EP)DP and TCF technology with the sequence Q(EP)QP. The general bleaching conditions are shown in Table 1.

Table 1. Bleaching conditions

Bleaching conditions	**First stage**			**Second stage**	**Third stage**		**Fourth stage**
	D	**D_{HT}**	**Q**	**(EP)**	**D**	**Q**	**P**
Consistency, %	10.5	10.5	11.0	11.5	11.2	11.0	10.2
Time, min	120	120	60	60/240	125	60	120
Temperature, °C	60/70	95	70	80/95	80/95	70	80/95
Kappa Fator	0.05/0.12/0.18	0.24	-	-	-	-	-
Final pH	3/4	3	6	11	5.5	6	10
H_2O_2, kg/tod	-	-	-	1-25	-	-	0.5-25
ClO_2, kg/tod	2-7	9.4	-	-	0.5-4	-	-
EDTA, kg/tod	-	-	2	-	-	2	-
$MgSO_4$, kg/tod	-	-	-	1	-	-	1
NaOH, kg/tod	0-1	2.5	-	4-16	0-0.6	-	1.8-11
H_2SO_4, kg/tod	0-1.5	0	0.5	-	0-2.2	2.1	-

Physical-mechanical properties

The bleached pulps were refined in a PFI mill laboratory, according to TAPPI standard 248 wd-97, at varying speeds: 0, 1000, 1500, 2000, and 3000 rpm for the pulps refined at pH 4.5 and 0, 1000, 2000, 3000, and 4000 rpm for the pulps refined at pH 8.0. These samples formed handsheets with a weight of about 60 g/m^2. The procedures used to evaluate physical and mechanical properties are described in Table 2.

Table 2. TAPPI methods used to evaluate physical and mechanical properties

Parameters	Tappi Standard Methods
Grammage	TAPPI T410 om-08
Tensile energy absorption - TEA	TAPPI T494 om-96
Thickness	TAPPI T551 om-06
Tear index	TAPPI T414 om-04
Burst Index	TAPPI T403 om-02
Tensile index	TAPPI T494 om-06
Modulus of elasticity - MOE	TAPPI T494 om-96
Forming Handsheets for physical tests	TAPPI T205 sp-95
Freeness of pulp	TAPPI T227 om-04
Apparent density	TAPPI T220 sp-96
Specific volume	TAPPI T220 sp-96
Air resistance	TAPPI T460 om-02
Drainage resistance – Schopper Riegler, ^{o}SR	TAPPI T423 cm-07
Opacity of paper	TAPPI T425 cm-91
Light scattering coefficient	TAPPI T220 om-88

Statistical analysis

For analysis of the mechanical-physical properties of pulp treated with different bleaching conditions at different levels of refinement, the software Curve Expert 1.4 was used to obtain the specimens. The adjusted equations were compared by an F test, using the identity test models and adopting a significance level of up to 5% probability, according to the methodology presented by Regazzi for linear models and Regazzi and Silva for nonlinear models [7, 8].

Results and Discussion

ECF and TCF bleaching

Modern bleaching sequences have been developed to produce pulps with minimum HexA content and reducing groups. Sequences containing chlorine dioxide at high temperatures (DHT) or hot acid (AHT) as the first stage and hydrogen peroxide (P) as the final stage are usually quite effective in minimizing HexA and reducing groups. Examples of such sequences are AHT/D(PO)DP and DHT(EP) DP, which gained acceptance in recent years for bleaching Eucalyptus kraft pulp. They allow the production of pulp with high brightness and high brightness stability. However, even bleached pulps with these sequences still present brightness reversion (1.5-2 % ISO of brightness loss).

In this part of the work, an industrial pulp delignified with oxygen was bleached using ECF and TCF technologies. For these technologies, the sequences D(EP)DP and Q(EP)QP were used, as shown in Table 3. The bleaching aimed to produce pulps with different amounts of hexenuronic acid that were given different dosages of chlorine dioxide, which is a reagent that has the ability to degrade HexA. During the sequence Q(EP)QP, there was no chlorine dioxide added to the process, and the pulp had the highest HexA content. Pulp *6* with FK=0.24 had higher brightness stability, i.e. lower post color number (PCN=0.06), but to achieve a brightness above 90% ISO and a low HexA content, this sequence required a high dosage of chlorine dioxide on D stages. Pulp *1* bleached by the TCF sequence demonstrated the highest brightness reversion (PCN =0.28) and also required a high dosage of hydrogen peroxide (H_2O_2) on (EP) (25 kg/tas) and P (25 kg/tas) stages to achieve brightness above 90 % ISO. However, the high dosage of H_2O_2 resulted in a loss of pulp viscosity. The HexA content correlates positively with brightness reversion, while the chlorine content of organically-bound chlorine (OX) correlated negatively with brightness reversion (Figures 1 and 2). The results shown in Table 3 suggest that reversion is influenced by a combination of several factors that probably occur synergistically.

Brightness reversion, measured after the accelerated dry aging test, decreased with an increasing dose of chlorine dioxide (ClO_2). The pulps were exposed to different doses of hydrogen peroxide and chlorine dioxide. When the dose of chlorine dioxide was reduced to 3.0 kg/tod (Pulp *2*) and 0 kg/tod (Pulp *1*) in the sequence D(EP)DP, it was observed that brightness reversion increased substantially.

It was observed that the kappa number and HexA content of the bleached pulps decreased with increasing doses of chlorine dioxide, it can be noted for Pulp *6*. High values of brightness reversion were obtained from the pulp treated with the sequence Q(EP)QP, suggesting that nucleophilic bleaching with hydrogen peroxide is unable to remove certain substances that cause brightness reversion. On the other hand, Pulps *2* and *3* also had low brightness stability. This can be explained by the use of low doses of chlorine dioxide in these sequences, which resulted in less oxidized material removed during bleaching.

In short, good brightness stability is achieved when the oxidized materials in the pulp are easily removed with a large number of electrophilic reagents (such as chlorine dioxide) and pulp is then treated nucleophilically to remove some substances that cause reversion or when the pulp is submitted to conditions that can keep these materials without degradation [9, 6].

Table 3. Chemical characteristics and brightness reversion values of bleaching of oxygen-delignified kraft pulp* by ECF and TCF technologies

Characteristic of Bleached pulps	**1** **Q(EP)QP** ***TCF***	**2** **D(EP)DP** ***ECF***	**3** **D(EP)DP** ***ECF***	**4** **D(EP)DP** ***ECF***	**5** **D(EP)DP** ***ECF***	**6** **DHT(EP)DP** ***ECF***
Kappa Factor (FK)	0	0.05	0.12	0.12	0.18	0.24
ClO_2, kg/tod	0	3	5.7	8.7	9	13.4
H_2O_2, kg/ tod	50	13	9	5	6	1.5
EDTA, kg/ tod	4	0	0	0	0	0
H_2SO_4, kg/ tod	2.7	2.5	1.8	0.8	0.6	0
NaOH, kg/ tod	27	12.4	12.8	10.6	11.5	8.9
$MgSO_4$, kg/ tod	0.5	0.5	0.5	0.5	0.5	0.5
Viscosity, dm^3/kg	659	856	867	876	900	905
Brightness, % ISO	90.4	89.6	90.4	90	90.9	90.6
Post Color Number (PCN)	0.28	0.23	0.17	0.12	0.08	0.06
Kappa Number	4.8	3.9	3.1	1.9	1.4	0.4
HexA, mmol/kg	41	36.1	29.3	16.9	11.9	2.3
Copper Number, $gCu_2O/100g$	0.11	0.06	0.03	0.09	0.2	0.2
Carboxyl groups, meq/100g	10.5	9.63	8.8	7.54	7.13	5.13
OX, mg Cl^-/kg	0.6	43	81	125	130	165

* Kraft-O_2 original pulp: Kappa number = 10.3; Viscosity = 999 dm^3/kg; HexA =51.6 mmol/kg

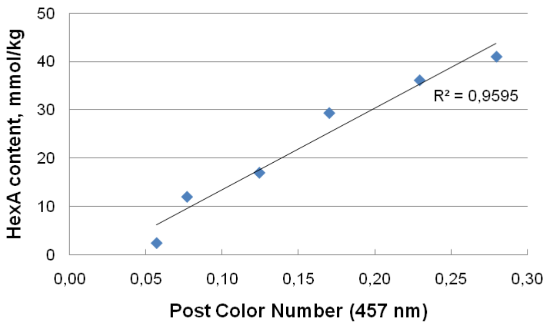

Figure 1. Correlation between post color number (PCN) and HexA content of bleached pulps.

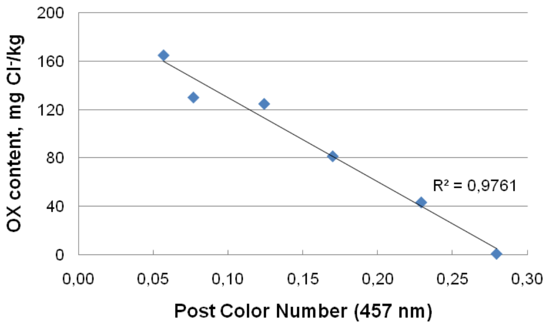

Figure 2. Correlation between PCN and organically-bound chlorine content (OX) of bleached pulps.

Analysis of physical and mechanical properties of bleached pulps

To assess the impact of hexenuronic acid content and pH on refining and the properties of pulps, samples of cellulose pulp, bleached by sequences D(EP)DD and Q(EP)QP were refined in a PFI mill and evaluated regarding their physical, mechanical, and optical properties. However, only the properties of great importance to quality control in paper mills are discussed below, as such as, tear and tensile index; modulus of elasticity, tensile energy absorption; specific volume; opacity and light scattering coefficient . The properties of the pulps are presented as a function of the corresponding energy spent during the refining process. Each graph shows curves describing the models adjusted for energy consumption. They show common curves for one or more samples, showing the same behavior between the pulps studied indicating that the hypothesis of equality between the equations, tested by an F test for the model identity. When there are distinct curves on the graph, the adjusted models differ statistically at a 5% probability, and therefore show different behaviors between the pulps studied.

In all these experiments, the pH affected the refinability and the pulp quality and the value of alkaline pH was more favorable than the acid, especially regarding refinability. This explains why some Eucalyptus pulp mills are converting their sequence type from D(EP)DD to D(EP)DP, which means they are changing the last bleaching stage to an alkaline stage.

Figure 3 shows the relation between tensile index and energy consumption for the pulps studied at pH 4.5 and 8.0. Because of the increase of pH from 4.5 to 8.0, higher values of tensile index were noted for the same power consumption. This can be explained by the fact that at alkaline, pH facilitates the separation of the fibers, thus promoting greater hydration and improving refining. In relation to the hexenuronic acid content, a lower tensile index may be noted for the samples with a lower content of this acid.

The tensile index is related to the durability and utility of paper, such as packaging and other uses subject to direct tension. In the case of printing papers, the tensile strength indicates the probability of rupture when subject to stress applied during the printing process [10].

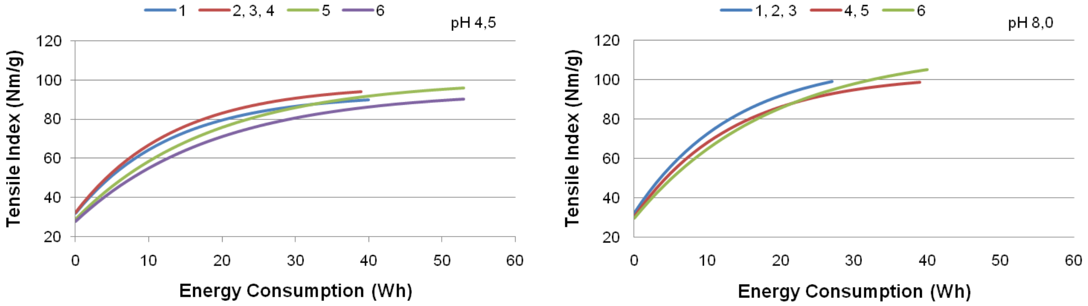

Figure 3. Tensile index as a function of energy consumption for refined, bleached pulps at pH 4.5 and 8.0.

The relation between the tear index and energy consumption at pH 4.5 and 8.0 can be seen in Figure 4. It was observed that the tear index showed a small increase at the beginning of refining, but begins to fall with the later stages of refining. The initial increase in tear index is explained by the increased ability of the pulp to form hydrogen bonds, however, a reduction in this property indicates that it depends more on fiber length than the bonds between them.

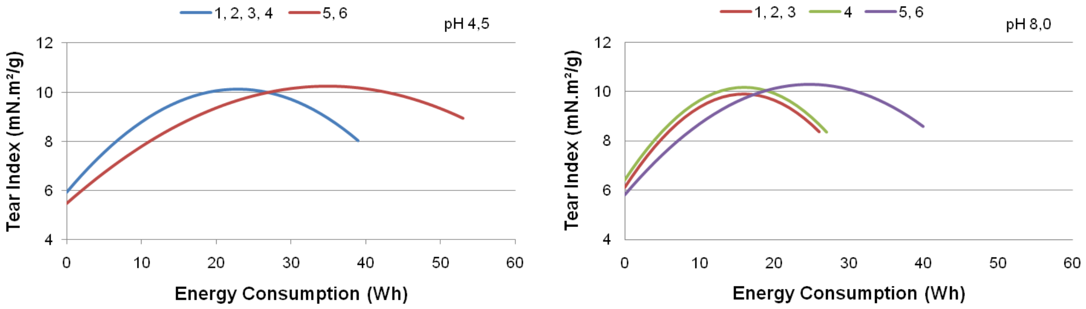

Figure 4. Tear index as a function of energy consumption for pulp refined at pH 4.5 and 8.0.

Based on the F test, the tear index for Pulps *1*, *2*, *3*, and *4* and for Pulps *5* and *6* at pH 4.5 shows no significant difference (P> 0.05), which may be represented by two common curves. At pH 8.0, the Pulps *1*, *2*, and *3* had the same common curve and the Pulps *5* and *6* also had the common curve. When comparing the curves, note that pulps with higher concentrations of hexenuronic acid (Pulps *1-4*) had a maximum tear index with lower energy consumption, and the energy consumption at pH 8.0 was lower than at pH 4.5. However, for Pulps *1-3* at pH 8.0, low power consumption was not enough to obtain a good tear index value. This can be explained by the drastic conditions used for bleaching to brightness values close to 90% ISO, causing a decrease in pulp viscosity.

Figure 5 shows the behavior of the modulus of elasticity (MOE) as a function of energy consumption at pH 4.5 and 8.0. Higher values of modulus of elasticity were obtained from the pulps with high hexenuronic acid content. Moreover, the high content of carboxylic groups also affected the refinability of the pulp.

Page and Seth reported that the main factor that influences the elastic modulus of paper, in addition to the number of interfiber bonds, is the rigidity of the fibers, which on the formed paper increases the modulus of elasticity [11]. More rigid fibers do not elongate as much and are therefore more resistant to deformation when force is applied.

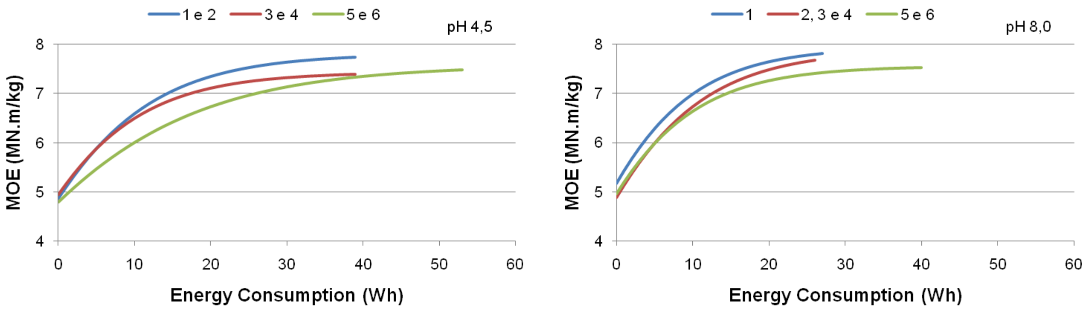

Figure 5. Modulus of elasticity (MOE) as a function of energy consumption for pulp refined at pH 4.5 and 8.0.

Tensile energy absorption (TEA) is shown in Figure 6. At the beginning of refining, the pulps with higher levels of HexA had higher energy of for deformation, however, as refining continued, these pulps tended to stabilize. At pH 8.0, Pulp *3*, despite having a high content of HexA (29.3 mmol/kg), showed the same trend of as the pulp with low acid. This property is very dependent on the characteristics of formation and potential for conformity of the fibers in paper, which indicates that the morphological characteristics of the fibers are very important, especially the fiber length, the cell wall thickness, and lumen diameter [12].

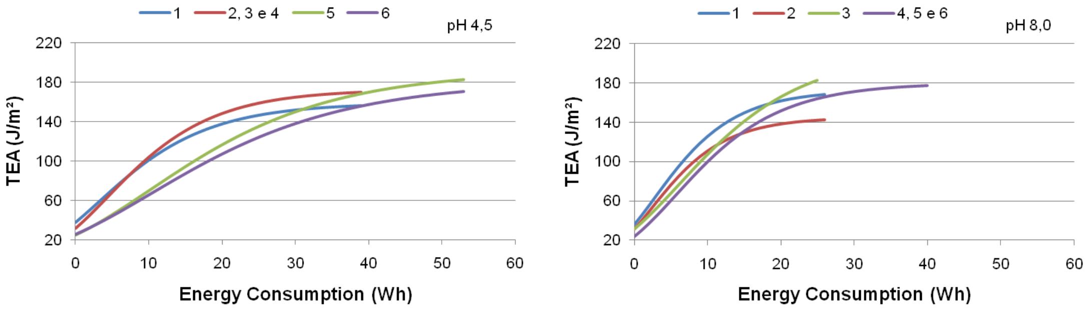

Figure 6. Tensile energy absorption (TEA) as a function of energy consumption for pulp refined at pH 4.5 and 8.0.

Specific volume or *bulk* is a very important property when considering printing papers, since it is closely related to the opacity of the paper. Figure 7 shows the behavior of the specific volume as a function of energy consumption, at pH 4.5 and 8.0.

The pulps with lower levels of hexenuronic acid obtained higher values of bulk during the process of refining the pulp. As the pulp was refined further, there was a fall in specific volume. At pH 4.5, the decrease in bulk was less pronounced than at pH 8.0.

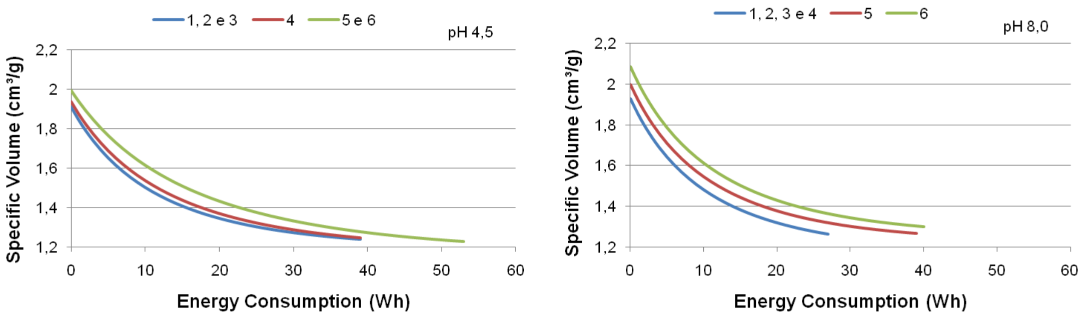

Figure 7. Apparent specific volume as a function of energy consumption for refined pulp at pH 4.5 and 8.0.

The opacity and light scattering coefficient are optical properties of great importance for various applications of paper such as printing, writing, and decorative purposes. Properties involving the scattering of light are closely related and may interact, as is the case for opacity, which is dependent on the coefficients of light scattering and absorption of light, according to the theory of Kubelka and Munk. The results showing the opacity of the pulp as a function of energy consumption during the refining process are shown in Figure 8. Refining had a negative effect on the opacity of the pulp, which may be explained by the increased compaction of the paper structure (reduction of the internal spaces), reducing the number of fiber-air interfaces and providing less light scattering and therefore greater transparency [12]. The pulps refined at pH 8.0 had a greater decrease in opacity than the pulps refined at pH 4.5.

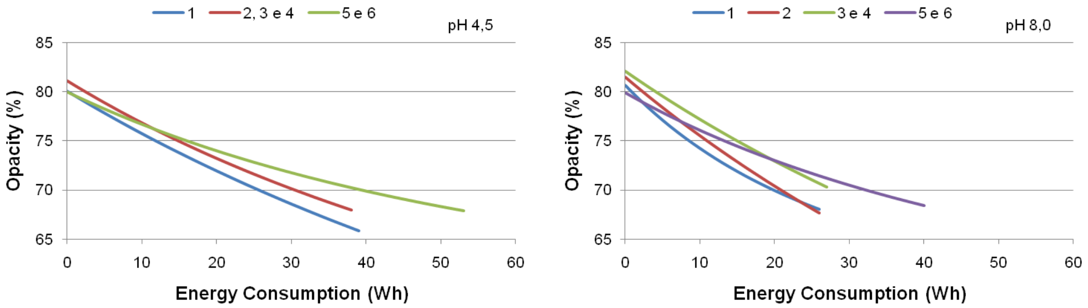

Figure 8. Opacity as a function of energy consumption for refined pulp at pH 4.5 and 8.0.

Figure 9 presents the behavior of the light scattering coefficient as a function of energy spent at pH 4.5 and 8.0. It was observed that the properties of opacity and the light scattering coefficient are reduced with the process of refining. Despite refining increasing the surface area, it also increases the bonding surface between the fibers, which reduces opacity and light scattering [12].

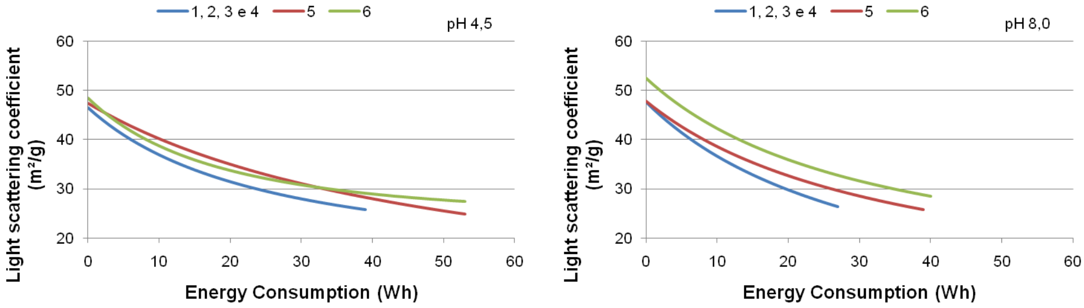

Figure 8. Light scattering coefficient as a function of energy consumption for pulp refined at pH 4.5 and 8.0.

Conclusions

- The bleached pulps with high kappa factor had better brightness stability, and pulp produced by bleaching sequence Q(EP)QP obtained worse stability.
- The TCF pulp, which had lower viscosity due to bleaching, achieved dramatic brightness exceeding 90% ISO.
- The content of carboxylic groups followed the trend of HexA content in the pulp.
- The number of small groups (copper number) and organically-bound chlorine content were higher for the pulps that used high doses of chlorine dioxide.
- The brightness stability given as a function of the PCN correlated positively with the hexenuronic acid content and negatively with OX content.
- Regarding the refinability and the physical-mechanical properties of bleached pulps, the pH value of 8.0 was more favorable than pH 4.5, because of low energy consumption.
- Pulps with high hexenuronic acid content alter the refinability of the pulps, especially in relation to the tear index, MOE, TEA, and specific volume.
- Lower energy consumption was required from the pulps with high hexenuronic acid content.

References

[1]. SEVASTYANOVA, O.; LI, J.; GELLERSTEDT, G. (2006) On the reaction mechanism of the thermal yellowing of bleached chemical pulps. Nordic Pulp and Paper Research Journal. 2006, 21(2)188-192.

[2]. GELLERSTEDT, G.; LI, J. (1996): An HPLC method for the quantitative determination of hexeneuronic acid groups in chemical pulps. Carbohydr. Res. 294 41-51

[3]. EIRAS, K. M. M.; COLODETTE, J. L. SILVA, V. L. (2009) The role of bound chlorine in the brightness reversion of bleached hardwood kraft pulp. Quím. Nova, v.32, n.1, p. 51-55.

[4]. EIRAS, K. M. M.; COLODETTE, J. L. SILVA, V. L.; BARBOSA, L.C.A. (2008) New insights on brightness stability of eucalyptus kraft pulp. Nordic Pulp and Paper Research Journal, v.33, n.1, p. 102-107.

[5]. BARROS, D.P.; SILVA, V. L.; HÄMÄLÄINEN, H.; COLODETTE, J. L. (2010). Peracetic acid for pulp bleaching. BioResources, 5(2), 881-898.

[6]. FORSSTRÖM, A.; WACKERBERG, E. SILVA, V. L. (2009). On the methods for assessing and the causes of brightness reversion of hardwood kraft pulps. In: 4th International Colloquium on Eucalyptus Pulp – ICEP 2009, Concepcion, Chile.

[7]. REGAZZI, A. Teste para identificar a identidade de modelos de regressão e igualdade de alguns parâmetros num modelo polinomial ortogonal. Revista Ceres. Viçosa, v. 40, n. 228, p. 176-195, 1993.

[8]. REGAZZI, A.; SILVA, C. H. O. Teste para verificar a igualdade de parâmetros e a identidade de modelos de regressão não-linear. I. Dados no delineamento inteiramento casualizado. Revista Matemática Estatística, São Paulo, v. 22, n. 3, p. 33-45, 2004.

[9]. EIRAS, K M M, COLODETTE, J L (2005): Investigation of eucalyptus kraft pulp

brightness stability. JPPS 31(1):1.

[10]. D'ALMEIDA, M. L. O. Celulose e papel: tecnologia de fabricação da pasta celulósica. São Paulo: IPT/SENAI, v. 1, 1988.

[11]. PAGE, D.H.; SETH, R.S. A note on the effect of fiber strength on the tensile strength of paper. Tappi Journal, 71(10)182-183, 1988.

[12]. SILVA, R. P.; OLIVEIRA, R. C. Efeitos da ação do refino e da reciclagem nas propriedades de papéis de pinus e eucalipto. Revista Árvore, v. 24, n.3, p. 349-360, 2000.