PRODUCTION FACTORS AFFECTING THE PERFORMANCE OF EUCALYPT KRAFT PULP FOR TISSUE PAPERS

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ABSTRACT

Nowadays, forced by the substantial growing of tissue market, pulp companies are confronted to improve/optimize the production process in an economically viable and technologically feasible way. Aiming to evaluate the impact of production factors (cooking and bleaching conditions) on the basic consumer properties of bleached eucalypt kraft pulp for the tissue paper applications, such as, softness and absorption capacity, a series of industrial pulps were analyzed by multivariate statistics. The statistical dependence of softness and absorption capacity of pulp resistance properties, morphology and chemical composition were evaluated. These relationships were verified using laboratory-cooked and bleached pulps produced following the industrial references. The main variation parameters were the alkali charge in cooking and the profile of reagents in peroxide (P_O) and chlorine dioxide (D) stages in O-O-D_H-P_O-D-P bleaching sequence. Increasing the active alkali charge in the cooking (while maintaining bleaching parameters) affected positively the pulp softness, with a substantial reduction of xylan content in pulps, decreasing of intrinsic viscosity and the strength properties of pulps. Laboratory-cooked and conventionally bleached pulps showed a clear trend of softness and absorptivity to increase with the decreasing of handsheet stiffness. The pulps showing better softness also revealed better absorptivity. Unexpectedly, softness and absorption capacity of pulps were dropped when in the ECF bleaching sequence the charges of reagents in P_O and D stages were raised by 100% and 50%, respectively. Hence, changes in the pulp composition and structure induced by increment of reagents charge in the cooking and in the bleaching did not showed the same tendencies.

Keywords: tissue paper, softness, absorption capacity, xylan, eucalypt kraft pulp

INTRODUCTION

While demands for bleached paper-grade kraft pulps are declining worldwide, the tissue paper market grows 3-5% annually, exceeding 37 million tons in 2017 [1]. The tissue market is a competitive area, which requires pulps with distinguished specifications, especially as concerns its absorption capacity and organoleptic properties (e.g. softness) [2]. Accordingly, pulp companies are confronted to improve/optimize the production process in an economically viable and technologically feasible way.

Softness is generally recognized as being comprised of two components – bulk and surface softness. It is related to the smoothness, texture and surface uniformity of the tissue and, therefore, is very sensitive to protruding fibers or irregularities at the surface. Absorption capacity refers to the ability of absorb and retain water quickly, which is mainly dependent on the ability to form hydrogen bonds by the surface hydroxyl groups of cellulose [3, 4]. Both softness and absorption capacity are sensible to the fiber´s morphology.Coarseness, curl and kink are three key morphological characteristics that affects directly final tissue paper properties. Fibers with thicker cell wall in association with high density woods represent an advantage for water drainage during the papermaking process and lead to more porous sheets, with higher bulk, coarseness (weight of fiber wall material in specified fiber length), less fiber population per pulp weight and, as a consequence, lower surface area available for interfiber bondings [5]. For pulps made by 100% of short fibers, higher coarseness increases specific volume resulting less compacted papers. During pulping and bleaching processes, fiber deformations like curl and kink occur, as well as modifications in the fiber structure, affecting pulp mechanical strength properties [6]. It is normally accepted that fibers with higher curl cause a reduction in the tensile index, while the kink affects mainly the wet strength of the pulp. On the other hand, fiber deformations lead to significant improvements in paper porosity, bulk, absorption capacity and softness, characteristics which can be enhansed and artificially induced with proper device for pulp differentiation, when desired and advantageous, like for tissue papers [7].

Typically, tissue producers also desire pulps with low fines, low hemicelluloses content and moderate intrinsic viscosity values. Low hemicelluloses give papers with less degree of hydration and fibers with low capacity to maintain the bonds during sheet compacting. Increase them in the system represents an increase of adhesion in the coating, that will cause variations in creping. This feature contrasts almost all the time with the wishes of manufacturers of cellulose, where the retention of hemicelluloses means increase of pulp yield. Moderate intrinsic viscosities are desirable because provide non-stick properties on the Yankee rolls and more absorbent papers [8].

This study reveals the preliminary analysis of a series of industrial bleached eucalypt kraft pulps showed that both mechanical and specific consumer properties (e.g. absorption capacity and softness) are depended on the production conditions (alkali charge in cooking and reagents profile in the bleaching). Further laboratory trials were done dealing with the evaluation of production factors (cooking and bleaching conditions) affecting the basic consumer properties of bleached eucalypt kraft pulp for the tissue paper applications.

EXPERIMENTAL

Materials

Six industrial pulps produced by kraft pulping and ECF bleaching sequence (O-O-D_H-P_O-D-P) under variable conditions were supplied by CELBI SA (Portugal). These pulps were first selected using a multivariate analysis, based on industrial production conditions, to ensure that the final properties would be significantly different for establish correlations with softness and absorption capacity. *Eucalyptus globulus* wood chips were also supplied by this company to perform a series of laboratory cooked and bleached pulps.

Pulp and paper properties analysis

Laboratory hand sheets with basis weight of 65 ± 2 g.m^{-2} were prepared according to ISO 5269-1 procedure and prior to testing these were conditioned for 24 h at a temperature of 23 °C and 50% of relative humidity. The physical strength properties such as tensile, burst and tear index were determined according to ISO 1924-2:2008, ISO 2758:2001 and ISO 1974:2012, respectively. Intrinsic viscosity and Gurley air resistance were evaluated following standard methods ISO 5351:2010 and ISO 5636-5:2013. To analyse softness (HF) were prepared several laboratory hand sheets, mimicking tissue paper of low grammage (20 g/m^2) and measured on EMTEC® Tissue Softness Analyser equipment (TSA). Absorption capacity was measured on water absorption tester S18010 according to ISO 12625-8.

Carbohydrate analyses

The pulps were analysed on the neutral sugars as alditol acetates by GC after the Saeman hydrolysis. The sugars were separated using an analytical column DB-225 J&W (30m x 0,25 mm i.d., with 0,15 µm of film thickness) and FID detector (Thermo Fisher Scientific Focus GC series), using a nitrogen drag gas, with inject temperature of 225°C, column temperature of 220°C and detector temperature of 250°C.

Fibre morphology

Morphological properties of pulps, such as coarseness, curl, kink and length were optically measured using Morfi ® Fiber&Shieves Analyzer (TECHPAP Inc.). In the analysis procedure, the fibres were suspended in a water solution, therefore the results obtained related to the fibre properties in a rewetted state.

Laboratory cooking and bleaching sequences

Eucalyptus globulus wood chips were cooked in a dual vessel M/K digester at 160°C for 2h (time-to temperature 60 min), using different alkali charges with similar sulfidity and hydromodulus 4. Unbleached pulps were submitted to oxygen delignification followed by four bleaching stages D_H-P_O-D-P (standard and modified P_O and D) using a 1.5L glass reactor (Parr 5100 series, USA). Conditions used in each bleaching stages were the same as in the industry. In the modified bleaching sequence the peroxide and NaOH charges in P stage was doubled and ClO_2 charge in D stage was increased of 50%.

Table 1. Conditions used in the laboratory bleaching of kraft pulps.

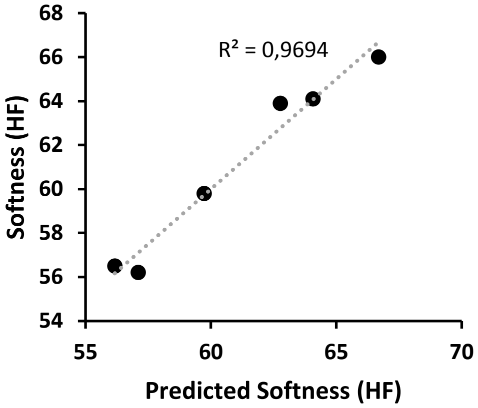
Stage	Variables	Conventional sequence	Modified sequences
O_2	T (°C)	100	100
	t_{ret} (min)	60	60
D_H	T (°C)	95	95
	t_{ret} (min)	110	110
P_O	T (°C)	100	100*
	t_{ret} (min)	60	60*
D	T (°C)	75	75*
	t_{ret} (min)	70	70*
P	T (°C)	90	90
	t_{ret} (min)	65	65

*stages P_O and D with increased reagente charges were designated P_O# and D#, respectively.

RESULTS AND DISCUSSION

Structure-properties relationships of industrial pulps

Among a large group of produced bleached eucalypt kraft pulps, six were pre-selected being significantly different for the softness and absorption capacity. The mechanical properties, fiber chemical composition and morphology were subjected to statistical analysis with respect to the softness and absorption capacity of those pulps. A partial least square analysis was performed to explain the maximum covariance of Y matrix (softness and absorption values) by a matrix X (mechanical properties and fibers morphology values). PLS combines two models of PCA (principal component analysis), one to X and one to Y matrixes, aligned them after to the factors formed by decomposition of matrixes explains the maximum covariance between X and Y. Decomposition of X is then used to predict new values of Y. In this case trustable results were found using this statistical model, Figures 1 and 2. The importance associated to each mechanical and morphological property to predict new values of softness and absorption capacity are presented in Figure 3. In general, VIP values under 0.8 are considered low [9].



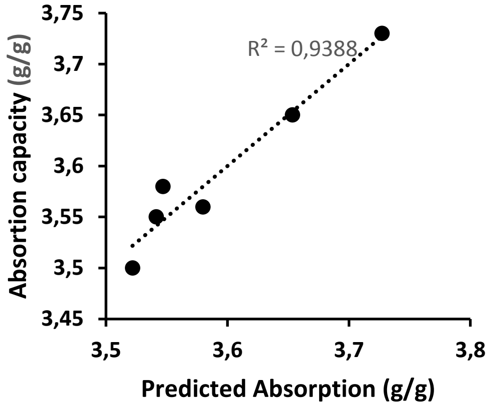


Figure 1. Correlation between softness values and those predicted by PLS model.

Figure 2. Correlation between absorption values and those predicted by PLS model.

The prediction of softness was mainly negatively influenced by xylan content, that affects directly mechanical properties such as burst resistance and tensile strength, and positively influenced by fibers morphology with emphasis on coarseness values. Absorption capacity showed a high negative correlation with Gurley resistance, surface roughness and intrinsic viscosity. At the same time, absorption capacity was positively affected by kink index of fibers. Taken into consideration the results obtained, a series of laboratory cooking and bleaching trials were carried out under extreme conditions to confirm the relationships inferred by statistics of industrial pulps.

Impact of laboratory cooking and bleaching conditions of tissue pulp properties

For a range of cooking severity applied (S1-S4), the extremes in the pulp yield reached of 5.3% and of 6 kappa units (Table 2). Softness values, absorption capacity, xylose content, intrinsic viscosity, final kappa and ISO brightness for each sequence of lab produced pulps are refer to the pulps bleached by O-D_H-P_O-D-P under the conventional (standard) conditions and the reagents charges. The respective mechanical properties of pulps are summarized in Table 3.

Table 2. Cooking yield, softness, absorption capacity, xylose content, final kappa, intrinsic viscosity and brightness of laboratory produced pulps.

Sample	Cooking yield (%)	Softness (HF)	Absorption capacity ($g.g^{-1}$)	Xylose (% w/w)	Kappa	Intrinsic viscosity ($dm^3.kg^{-1}$)	ISO brightness (%)
S1 Standard	55,8	59.0	9.3	23.8	1.46	849	87.6
S1 P_O ≠	-	54.5	7.5	-	1.02	600	88.4
S1 D ≠	-	52.7	7.3	-	0.38	622	88.6
S2 Standard	52,1	61.4	8.6	21.6	1.03	697	88.8
S2 P_O ≠	-	56.3	7.7	-	0.58	575	90.0
S2 D ≠	-	55.5	7.6	-	0.28	634	89.5
S3 Standard	51,5	63.2	9.1	20.8	0.98	659	89.1
S3 P_O ≠	-	60.4	8.3	-	0.55	558	90.1
S3 D ≠	-	58.1	7.8	-	0.23	592	90.0
S4 Standard	50,5	64.7	8.7	19.7	0.38	587	89.4
S4 P_O ≠	-	61.1	7.8	19.1	0.43	484	90.4
S4 D ≠	-	60.1	7.4	-	0.14	564	90.1

Fixing the conditions of bleaching sequence (standard), an increase cooking severity led to gain of +5.7 in HF, which was accompanied by a decrease of 2.4% in xylose content, -262 intrinsic viscosity units, -5 tensile strength units, -1.02 tear index and -0.41 of burst resistance units. Hence, these observations corroborated with the conclusions drawn above by statistical analysis of industrially produced pulps. Absorption capacity was very similar for all the pulps, showing only a significant decrease (≈ -1.7 $g.g^{-1}$) for higher cooking severity. This can be related with an increased degradation of the most hydrophilic counterpart of pulps – glucuronoxylan.

Table 3. Mechanical properties of laboratory produced kraft pulps.*

Sample	Gurley resistance ($\mu m.Pa^{-1}s^{-1}$)	Tensile strength ($N.m.g^{-1}$)	Elongation (%)	Stifness ($kN.m.g^{-1}$)	Tear Index ($mN.m^2.g^{-1}$)	Burst resistance ($kPa.m^2.g^{-1}$)
S1 Standard	2.0	49.2	2.1	6.7	7.13	2.93
S1 P_O ≠	2.0	48.2	2.2	6.8	6.43	2.91
S1 D ≠	1.4	48.9	2.1	6.9	6.45	2.89
S2 Standard	1.5	46.0	2.1	6.9	6.65	2.88
S2 P_O ≠	1.2	43.5	2.0	6.2	6.58	2.63
S2 D ≠	1.3	44.4	2.1	6.7	6.54	2.49
S3 Standard	1.7	45.0	2.0	6.8	6.74	2.80
S3 P_O ≠	1.4	42.2	2.0	6.1	6.29	2.61
S3 D ≠	1.5	43.8	2.1	6.4	6.16	2.54
S4 Standard	1.6	44.2	2.0	6.7	6.11	2.52
S4 P_O ≠	1.2	42.1	2.0	6.4	6.51	2.49
S4 D ≠	1.2	43.7	2.0	6.3	5.53	2.45

*Stages P_O ≠ (double H_2O_2 and NaOH loads) and D ≠ (50% higher ClO_2 load) substituted the stages P_O and D, respectively, in conventional O-O-D_H-P_O-D-P bleaching.

The increasing in bleaching charges (twice peroxide load in P_O stage or 50% ClO_2 increment in D stage) affected negatively either softness or absorption capacity of final bleached pulps (Table 2). In general, mechanical properties were also negatively affected by modified bleaching stages, especially with P_O≠ stage being the one with highest negative impact on the tensile strength, tear and burst resistance and stiffness. This can be explained, at least partially, by decrease of pulp viscosity, e.g. by the fiber weakening. In this series of laboratory simulated pulps (excluding the data for higher severity cooking and some repeating points), a strong correlation between stiffness and absorption capacity and between stiffness and softness was also found (Figs. 4, 5). As stiffness is associated with intensity of interfiber bonds, the loss in absorption capacity looks logical. For the same reason the softness was decreasing.

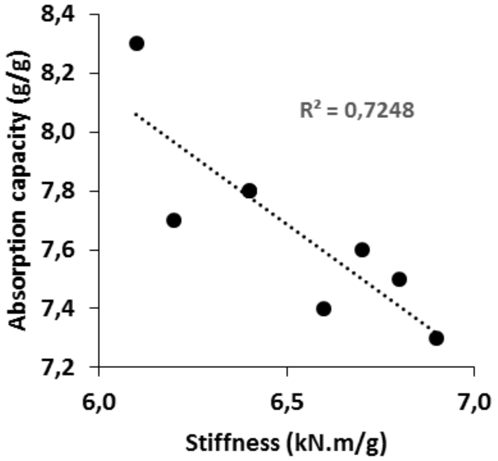


Figure 3. Correlation between absorption and stiffness.

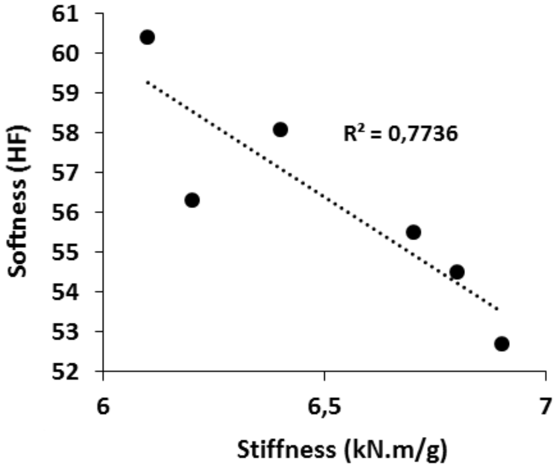


Figure 4. Correlation between softness and stiffness.

For the same pulps, as could be expected from trends in Figures 3 and 4, the positive correlation was found between the softness and the absorption capacities of pulps (Fig.5). Hence the same pulps that showed better absorption capacity showed better softness.

The intension to increase of H_2O_2 and NaOH loads in P_O stage was related to the better purification of the fiber surface and to remove additionally the hemicelluloses thus favoring the pulp softness. The increased load of ClO_2 in D bleaching stage should decrease the residual lignin content on pulp surface thus improving the absorption capacity of pulp. As already mentioned, softness increases with the severity of cooking process and removal of hemicelluloses. However, an increased H_2O_2 and NaOH loads in P_O and ClO_2 in D stages led to opposite results (Table 3). When compared with conventional bleaching, for the same cooking, softness dropped 3-5 HF units in modified P_O≠ and 5-6 HF in modified D≠ stages. Although the content of xylan with modified P_O sequence decreased, any improvement was detected either in softness or absorption capacity of final pulp. The depolymerization of polysaccharides and the decrease in intrinsic viscosity by approximately 100 units did not revealed positive effect as could be expected from previously drawn statistic relationships in bleached kraft pulps. This indicates that the correlations found between softness/absorbency and processual conditions and properties/morphologies of the conventionally produced pulps are not necessary remain when changing the reagents loads in the bleaching. For example, the xylan removal (or polysaccharides degradation) in pulping and bleaching operations leads to different effect on such pulp characteristics as softness and absorption capacity.

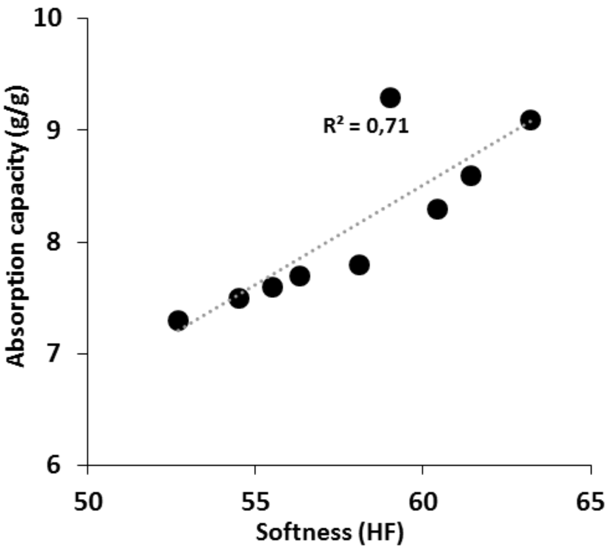


Figure 5. Correlation between softness and absorption capacity of pulps.

CONCLUSIONS

Results of this work demonstrated that processing parameters in the production of eucalypt bleached kraft pulps have significant effect on such final pulp properties as softness and water absorption. The statistic dependency of these characteristics from pulp strength properties, morphology and chemical composition allowed the conclusion that the softness of ECF pulps is negatively influenced by xylan content in pulp and pulp strength properties (tensile strength, burst and tear resistance) and positively affected by fibers morphology. Absorption capacity showed a high negative correlation with Gurley resistance, surface roughness and intrinsic viscosity of industrial pulps. Most of these relationships were sound with those of laboratory pulps produced with different cooking conditions, though not always being straight forwarded to the trends of industrial pulps. The severity of laboratory cooking revealed an increase of softness, being accompanying by lower xylan content, intrinsic viscosity and strength properties of pulps. Laboratory-cooked and conventionally bleached pulps showed a clear trend of softness and absorptivity to increase with the decreasing of handsheet stiffness. In general, the pulps showing better softness also revealed better absorptivity. In contrast to expected softness and absorption capacity of pulps were dropped when in the ECF bleaching sequence the charges of reagents in P_O and D stages were raised by 100% and 50%, respectively. Hence, changes in the pulp composition and structure induced by increment of reagents charge in the cooking and in the bleaching did not showed the same tendencies.

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REFERENCES

[1] P. Bach, “Market pulp: Tissue has become the biggest global buyer | The Tissue Story,” 2018. [Online]. Available: http://www.tissuestory.com/2018/04/26/market-pulp-tissue-has-become-the-biggest-global-buyer/. [Accessed: 14-Jul-2018].

[2] P. Bicho, “Strength and softness – how NBSK pulp fibres deliver,” *Tissue Worl Magazine*, (3): 49-50

(2016).

[3] W. Gallay, "Textural Properties of Paper: Measurements and Fundamental Relationships," in *Fundamental Properties of Paper Related to its Uses, Vol.2*, 1973.

[4] H. Hollmark, "Mechanical Properties of Tissue," in *Handbook of Physical and Mechanical Testing of Paper and Paperboard, Vol. 1*, R. E. Mark, Ed. 1983, pp. 497–521.

[5] R. J. Trepanier, "Pulp fiber quality and the relationship with paper tissue properties," in *Tappi Tissue*, TAPPI Press, Atlanta, pp. 1-30 (2017).

[6] N. H. Shin, B. Stromberg, and G. Falls, "Xylan's Impact on Eucalyptus Pulp Yield and Strength – Myth or Reality ?," *Proceedings of III Int. Colloq. Eucalytus Pulp,* Belo Horizonte, *4-7 March, Brazil 08 pp., 2007.*

[7] C. Foelkel, "Advances in Eucalyptus Fiber Properties & Paper Products," *Proceedings of III Int. Colloq. Eucalytus Pulp*, Belo Horizonte, 4-7 March, Brazil 06 pp., 2007.

[8] H. O. R. Ramires, "ALTERNATIVAS TECNOLÓGICAS PARA MELHORIA DE PROPRIEDADES MECÂNICAS DE PAPÉIS TISSUE E SUA APLICAÇÃO PARA DIFERENTES POLPAS KRAFTS DE EUCALIPTO," Tese de Mestrado, Universidade Federal de Viçosa, Viçosa, Brazil 2013.

[9] L. Eriksson, E. Johansson, N. Kettaneh-Wold, J.Trygg, C. Wikström, S. Wold, Multi and megavariate data analysis : Part I : Basic principles and applications, Umeå :Umetrics, (2006).