

Can Acceptable Pulp be Obtained from *Eucalyptus globulus* Wood Chips after Hemicellulose Extraction?

Francisco López,^aM. Trinidad García,^bVicente Mena,^aJ. Mauricio Loaiza,^a Minerva A. M. Zamudio,^cand Juan C. García^{a,*}

This study investigates the operating conditions used in the soda-anthraquinone pulping of *Eucalyptus globulus* wood after autohydrolysis pretreatment on the yield, kappa number, and brightness of the resulting unbleached pulp. Moreover, strength-related properties of the resulting handsheets was examined to identify the best pulping conditions and compare the outcome with that of a conventional soda-anthraquinone pulping process. The paper strength properties of the pulp were similar to or better than papers made from soda-AQ delignified pulps conducted in a single step. Also, a liquid fraction with a substantial content in hemicellulosic extracts was recovered in the simplified process. Autohydrolysis of the raw material facilitates carrying out soda-AQ pulping under milder conditions. In addition, autohydrolysis improves other properties relative to paper from raw cellulose pulp. Yield, kappa number, and brightness for pulp from solid residues of autohydrolysed eucalyptus wood were similar to those for pulp from untreated eucalyptus wood.

Keywords: Autohydrolysis; *Eucalyptus globulus*; Hemicelluloses; Pulp; Paper; Soda-AQ

Contact information: a: PRO²TEC- Chemical Engineering Department, Campus “El Carmen,” University of Huelva, Av. 3 de marzo s/n, 21071 Huelva, Spain; b: Agrifood Campus of International Excellence (CeIA3), Parque Huelva Empresarial, 21007 Huelva, Spain; c: Master studies and Research Section, Technological Institute of Ciudad Madero, J. Rosas y J. Ureta s/n, Col. Los Mangos, 89440 Ciudad Madero, Tamaulipas (Mexico); *Corresponding author: juan.garcia@diq.uhu.es

INTRODUCTION

There is wide consensus in the pulp and paper industry that pre-extracting the hemicelluloses from pulp detracts somewhat from the mechanical properties of handsheets obtained with prior autohydrolysis/hot water extraction, from exploded chips, or with sodium hydroxide extraction (Martín-Sampedro *et al.* 2010; Mendes *et al.* 2011; Vila *et al.* 2012). However, the industry has recently shown increasing interest in the concept of forest product biorefining, by which wood is hydrolysed prior to conventional pulping and papermaking; thereafter, the hydrolysate, consisting of hemicellulose sugars, can be used as feedstock for biofuels and bioplastics as well as for various other purposes (Duarte *et al.* 2010).

Traditional processes for obtaining alkaline cellulose pulp require partial extraction of the hemicellulose fraction. Hemicelluloses are typically encountered in the spent cooking liquor (black liquor) in the form of various degradation products of xylan and other polysaccharides. Alkali processes are relatively selective towards the extraction of lignin; also, these processes lead to the extraction or the degradation of the cellulose fraction, albeit to a lesser extent. A drawback to alkaline pulping is the considerable degradation of the hemicellulose fraction.

Lignin has a relatively high heating value (*ca.* 27.0 MJ•kg⁻¹), whereas hemicelluloses barely have one-half that heating value, and hence, contribute little to profitability to the pulping process (*i.e.*, an energy surplus exists). As a result, separating the hemicelluloses prior to pulping, a central argument of the “biorefinery” concept, might be useful for increasing the profitability of pulp manufacturing in the future (Fava *et al.* 2013). In fact, pulp mills can be regarded as the starting points for development of integrated biomass refineries enabling the production of a wide spectrum of chemicals and biofuels from biomass (Clark 2007; Kamm and Kamm 2007; Sanders *et al.* 2009).

Removing hemicelluloses prior to conventional alkali pulping can clearly reduce the amount of this fraction remaining in the pulp, and hence, affect the strength-related properties of the resulting paper. This is particularly so with respect to pulp refinability, which is very strongly affected by the presence of hemicelluloses as the main agents of surface effects of links between fibers (Neves 1986).

However, some studies have revealed that it is indeed possible to obtain paper with acceptable strength-related properties by using a two-step biorefining process involving the extraction of hemicelluloses prior to pulping. Thus, the process provides a recoverable liquid phase that essentially contains the xylan, xylooligosaccharides, and xylose derivatives (in Garrote *et al.* 2003 under similar operation conditions, the extraction percentages, in liquid phase, with respect to initial raw material were: glucose 0.17%, xylose 1.01%, xylooligomers 8.70%, furfural 0.12%, and acetyl groups 0.21%. This represents extraction of approximately 59% of the hemicelluloses initially present); moreover, an extracted wood material is produced that is amenable to chemical pulping to afford a pulp which is suitable for paper production. Additionally, residual liquid pulping liquid (black liquor) can be used to obtain energy (Garrote *et al.* 2003; García *et al.* 2011a,b; Feria *et al.* 2012).

In this work, we examined the influence of the pulping conditions used in the soda-anthraquinone pulping of the solid residual from *Eucalyptus globulus* wood that has been autohydrolysed (*i.e.*, soda concentration, temperature, and pulping time). The yield, kappa number, and brightness of the resulting pulps were measured, as well as the strength-related properties of the handsheets made from the pulp (*i.e.*, tensile index, burst index, and tear index), to identify the optimum pulping conditions. The results are compared to that of a conventional soda-anthraquinone pulping process (*i.e.*, no wood autohydrolysis).

EXPERIMENTAL

Materials

Characterisation and storage of the raw material

Eucalyptus globulus samples from local plantations in Huelva (Spain) were milled to pass through an 8-mm screen. Preliminary tests confirmed the absence of diffusional restrictions at this particle size. These experiments were made with widths of particles between 1 mm and 20 mm. There were no problems of diffusion of water or chemical reagent to the interior of a particle. After sieving, the wood particles were air-dried and homogenised into a single batch to avoid differences in composition while in storage prior to use.

Samples of the raw material were milled to a particle size < 0.5 mm and analysed for moisture and extractable compounds (TAPPI T264 om-88 1996 and TAPPI T204 cm-071996); also, the 1% NaOH soluble fraction was determined (TAPPI 212 om-981996), as

well as the Klason lignin content (TAPPI T222 om-981996). Glucose, xylose, arabinose, and acetic acid in the acid hydrolysates of the Klason lignin test were determined by high performance liquid chromatography (HPLC) (Parajó *et al.* 1995). The ash content in raw material was determined by calcination (TAPPI 211 om-071996).

Methods

Autohydrolysis process: Pulping procedure and formation of handsheets

Wood chips and water were mixed in the desired proportions and reacted in a 10 L stainless steel reactor from M/K Systems, Inc. (Danvers, MA) equipped with a recirculation pump. The operating conditions were as follows: a temperature of 180 °C, an operation time of 30 min (also, the heat-up time during autohydrolysis was 43 min), and a liquid/solid ratio of 8 kg water/kg raw material. Once loaded, the reactor was closed and simultaneously heated and homogenized to ensure efficient mixing and uniform swelling of the eucalyptus chips. After the autohydrolysis time elapsed, the reactor was cooled to 25 °C. The Liquid phase was separated by filtration and moisture was evaluated in solid phase.

Cellulose pulp from the autohydrolysed wood and from the untreated wood were obtained in the same reactor used for the hydrothermal treatment. Experimental conditions of pulping were: alkali concentration (13 to 21 %), temperature (153 to 173 °C) and cooking time (65 to 115 min). Following cooking, each pulp was separated by filtration from its liquor and disintegrated, without breaking the fibers, during 10 min to 2000 rpm.

Pulping yield and kappa number were determined according to TAPPI Standard T257(1996) and T236(1996), respectively. Handsheets were prepared from pulps with an ENJO-F-39.71 sheet machine (Metrotec, S.A., San Sebastián, Spain) according to TAPPI Standard T205 sp-95(1996). Sheets were analysed for grammage (TAPPI T220 sp-961996), burst index (TAPPI T403 om-971996), tear index (TAPPI T414 om-981996), tensile index (TAPPI T494 om-961996) and brightness (TAPPI T525 om-921996).

Experimental pulping design: Multiple regression model

To relate the dependent variables (*i.e.*, yield, kappa number, ISO brightness, tensile index, burst index, and tear index) to the independent variables of the pulping process (*i.e.*, NaOH concentration, temperature, and processing time) with a minimum number of test runs, a 2ⁿ central composite factor experimental design was used. This allowed a second-order polynomial fit of the independent variables to be established, and allowed statistical significances in the dependent variables to be assessed. The independent variables were normalised (*i.e.*, coded) using the following equation,

$$X_n = \frac{X - \bar{X}}{(X_{\max} - X_{\min})/2} \quad (1)$$

where X is the absolute value of the independent variable concerned, \bar{X} is the mean value, and X_{\max} and X_{\min} are the maximum and minimum values, respectively. Three levels each of alkali concentration (13, 17, and 21 dry wt%, as NaOH concentration), temperature (153, 163, and 173 °C) and cooking time (65, 90, and 115 min) were used for the untreated raw material. The conditions used for the pulping of the wood after autohydrolysis were: alkali concentration 9, 13, and 17 dry wt% (as NaOH concentration); temperature 143, 153, and 163 °C; and cooking time 40, 65, and 90 min. A liquid/solid ratio of 8/1 and an anthraquinone dosage of 0.1 dry wt% were used in all experiments.

The minimum number of tests required was calculated as $N = 2^n + 2 \cdot n + n_C$, with 2^n being the number of points constituting the factor design, $2 \cdot n$ that of axial points, and n_C that of central points. Under our conditions, $N = 16$. The experimental results were fit to the following second-order polynomial:

$$Y = a_o + \sum_{i=1}^n b_i X_{ni} + \sum_{i=1}^n c_i X_{ni}^2 + \sum_{i=1; j=1}^n d_i X_{ni} X_{nj} \quad (i < j) \quad (2)$$

The independent variables used in the equations relating the two types of variables were those having a statistically significant coefficient (*i.e.*, those not exceeding a significance level of 0.05 in Student's *t*-test and having a 95% confidence interval excluding zero). The results were assessed with STATISTICA 8.0 (StatSoft, Inc., Tulsa, OK).

RESULTS AND DISCUSSION

Characteristics of the Raw Material

Table 1 summarises the chemical constituents of *E. globulus* wood as determined in this work and reported by other researchers. The major fraction was cellulose (analysed as glucan according to TAPPI T203 om-93 1996), which accounted for 42.8%, followed by Klason lignin with 21.2% (after quantitative acid hydrolysis), and hemicelluloses (calculated as the combination of xylan, araban, acetyl groups, and various others compounds) with 28.5%.

Table 1. Average Reported Chemical Constituents of *Eucalyptus globulus*¹

	<i>Eucalyptus globulus</i>					
	Present study	Garrote and Parajó 2002	López <i>et al.</i> 2008	Leschinsky <i>et al.</i> 2009	Rencoret <i>et al.</i> 2011	Miranda <i>et al.</i> 2013
1% NaOH sol. (%)	13.1 ± 1.6	12.4	nd	nd	nd	6.5
Ethanol extracts (%)	2.7 ± 0.1	1.2	nd	1.7	0.6	1.3
Ash (%)	0.7 ± 0.1	n.d.	0.5	0.4	0.4	12.1
Glucan (%)	42.8 ± 2.4	46.3	46.8	41.7	46.1	68.4
Klason lignin (%)	21.2 ± 1.7	22.9	19.9	22.9	19.8	26.6
Xylan (%)	17.1 ± 1.4	16.6	23.9	15.3	17.1	23.2
Arabinan (%)	0.7 ± 0.1	0.54	0.37	0.4	0.8	2.7
Acetyl groups (%)	3.5 ± 0.2	3.54	4.32	3.3	nd	nd
Others (%)	7.2 ± 0.4 ²	10.1 ³	nd	nd	nd	nd

¹Raw material percentages (100 kg dry matter)
Data provided as the average ± standard deviation
nd: not disponible
²Calculated as: 100-(ash + glucan + Klason lignin + arabinan + Acetyl groups + soluble lignin contents). Soluble lignin content was 6.84 % in present study.
³Calculated as: 100-(glucan + Klason lignin + arabinan + Acetyl group contents).

This composition is similar to what others have previously reported (Garrote and Parajó 2003; Rencoret *et al.* 2011). Based on our analysis, *E. globulus* can be a suitable raw material for the industrial production of hemicellulosic sugars, pulp, and paper. For example, the liquid fraction from the autohydrolysis process could be used to produce furfural, which requires a minimum pentosan content of 15 to 20% (Yahyazadeh 2011).

Chemical and Physical Characteristics of Cellulose Pulp and Handsheets

Tables 2 and 3 show the normalised values of the independent variables and summarise the properties of the handsheets obtained by using the proposed experimental designs with and without autohydrolysis. Each experimental value was the average of five results for pulp properties or twelve handsheets. Deviations from the respective means were all less than 5%.

Table 2. Normalised Values of Independent Variables, Chemical Properties of the Pulp, and Physical Properties of the Handsheets; Pulping with Autohydrolysis of the Raw Material (A)

Normalised (coded) values of independent variables ¹ : X_T , X_t , X_A			Yield (%)	Kappa No.	Brightness (%)	Burst index (MPa·m ² ·kg ⁻¹)	Tensile index (N·m·g ⁻¹)	Tear index (mN·m ² ·g ⁻¹)
0	0	0	55.1	69.2	16.60	1.01	17.98	1.13
0	0	0	56.6	67.8	18.01	0.99	18.15	1.08
-1	-1	-1	64.4	65.1	13.40	1.05	15.74	0.79
-1	-1	1	55.9	62.8	27.90	0.88	22.78	1.37
-1	0	0	67.2	76.2	16.70	1.06	16.76	1.26
-1	1	-1	64.3	87.9	12.01	0.84	11.31	0.98
-1	1	1	63.3	54.3	28.60	1.07	21.02	1.66
0	-1	0	58.7	77.5	12.70	0.82	18.20	1.06
0	0	-1	50.9	44.7	19.80	1.06	16.86	0.98
0	0	1	45.3	33.2	30.80	0.91	19.44	1.11
0	1	0	52.9	86.4	17.50	0.83	15.42	1.01
1	-1	-1	52.9	64.5	15.08	1.32	23.34	1.55
1	-1	1	45.1	75.9	24.22	0.59	14.23	0.87
1	0	0	51.9	83.9	16.60	1.06	16.64	1.16
1	1	-1	42.5	84.7	12.60	1.04	17.56	1.04
1	1	1	43.4	39.1	31.93	0.89	16.12	0.90

¹: X_T , X_t , and X_A : Pulping temperature, cooking time, and alkali concentration, respectively

The yields of soda-anthraquinone pulping of *E. globulus* wood with autohydrolysis (A) (Table 2) and without autohydrolysis (NA) (Table 3) were comparable if one considers that the autohydrolysed raw material was subjected to two chemical processes to remove lignocellulosic components. In fact, kappa numbers were very similar; thus, they ranged from 32.9 to 76.7 for the NA pulp (*i.e.*, control) and from 33.2 to 87.9 for the A pulp. Similarly, brightness ranged from 12.9 to 31.9% ISO for the A pulp and from 11.8 to 26.8% ISO for the NA pulp.

As can be seen from Tables 2 and 3, the strength-related properties of the handsheets (*i.e.*, tensile index, burst index, and tear index) were also similar. Removing the hemicelluloses by autohydrolysis led to handsheets with improved properties. Although the results were only moderately good, the laboratory handsheets were not of a commercial grade; *i.e.*, the pulp contained no papermaking additives, nor was it refined (beaten).

Table 3. Normalised Values of Independent Variables, Chemical Properties of the Pulp, and Physical Properties of the Handsheets; Pulping without Autohydrolysis of the Raw Material (NA)

Normalised (coded) values of independent variables ¹ : X_T, X_t, X_A			Yield (%)	Kappa No.	Brightness (%)	Burst index (MPa·m ² ·kg ⁻¹)	Tensile index (N·m·g ⁻¹)	Tear index (mN·m ² ·g ⁻¹)
0	0	0	68.7	64.4	18.6	0.72	12.0	1.16
0	0	0	69.0	64.0	18.5	0.72	12.1	1.15
-1	-1	-1	73.3	65.4	19.8	1.05	17.5	0.95
-1	-1	1	69.1	60.4	22.4	0.72	6.5	0.55
-1	0	0	72.9	68.7	18.3	1.04	9.1	0.82
-1	1	-1	70.2	76.7	12.6	1.11	16.8	1.4
-1	1	1	73.7	51.9	20.1	0.76	7.0	0.76
0	-1	0	66.3	67.5	20.9	0.83	13.1	0.95
0	0	-1	70.6	67.4	13.4	0.88	11.4	1.42
0	0	1	66.9	45.2	22.1	0.45	7.0	0.94
0	1	0	65.3	65.8	17.5	0.90	15.3	1.13
1	-1	-1	68.1	71.6	14.9	1.10	8.1	1.21
1	-1	1	57.1	58.7	24.7	0.52	7.0	0.62
1	0	0	62.8	68.6	18.3	0.87	10.1	0.74
1	1	-1	57.4	74.3	11.8	1.12	14.7	1.12
1	1	1	57.6	32.9	26.8	0.52	15.7	0.67

¹: X_T , X_t , and X_A : Pulping temperature, cooking time, and alkali concentration, respectively

Substituting the normalised (coded) values of the independent variables for each of the dependent variables in Tables 2 and 3 into the non-linear regression model (Eq. 2) yielded the expressions listed in Table 4. All regressed polynomial models exhibited an overall good fit, with $r^2 > 0.94$ and Snedecor's $F > 30$ in all instances. Residuals, which constitute a measure of consistency between experimental and predicted values, were also very small; in fact, the differences between the experimental values and those calculated by the expressions in Table 4 equations never exceeded 10% of the former. As can be seen from Table 4, the concentration of active alkali had the largest influence on the resulting kappa number, brightness, burst index, tear index, and tensile index. The autohydrolysed wood chips, however, were more markedly affected by the pulping time than by the active alkali concentration for the resulting tensile index. In any case, the temperature was the most influential variable on the papermaking performance of the brownstock.

To better envisage the influence of the operational variables on brownstock strength and chemical properties, and to compare directly the pulps obtained from the control (NA process) and the solid fraction after autohydrolysis (A process), the response surfaces of Figs. 1 to 3 were constructed. The space between two response surfaces represents the whole range of values for each dependent variable at both extremes (*i.e.*, -1 and +1). Two levels of pulping temperature were examined for brightness because this independent variable had no effect on brightness during the pulping of the previously autohydrolysed pulp. A combined plot of NA *versus* A revealed a significant overlap between spaces and made it possible to identify the specific operating conditions affording a brownstock derived from autohydrolysis wood (A) to be comparable to the brownstock of the raw material (NA).

Overall, soda-anthraquinone pulping of *E. globulus* wood chips after autohydrolysed (A) resulted in better paper physical properties (tensile index, burst index, kappa index, and brightness). Also, the tear index and yield exhibited wide ranges of

overlap for the dependent variables where the pulping conditions required for the autohydrolysed wood chips (A) were much milder than the control (NA). The economy was inherent in two aspects: (1) using a lower pulping temperature, cooking time, or alkali concentration and (2) the obtainment of a highly valorisable liquor containing abundant sugars and oligomers (García *et al.* 2011a).

Table 4. Equations for Each Dependent Variable of the Pulping Processes With and Without Autohydrolysis

Equation		r ²	F-Snedecor
Pulping process (NA)			
(1)	$Y_i = 68.51 - 5.63 X_T - 0.94 X_t - 1.53 X_A - 2.70 X_t^2 - 1.47 X_T X_t - 1.24 X_T X_A + 2.36 X_t X_A$	0.98	68
(2)	$KN = 65.06 - 2.21 X_t - 10.63 X_A + 4.30 X_T^2 - 8.04 X_A^2 - 3.22 X_T X_t - 3.07 X_T X_A - 6.05 X_t X_A$	0.96	35
(3)	$BI = 0.77 - 0.05 X_T - 0.23 X_A + 0.16 X_T^2 + 0.07 X_t^2 - 0.13 X_A^2 - 0.06 X_T X_A$	0.98	70
(4)	$TI = 11.30 + 1.73 X_t - 2.53 X_A - 1.31 X_T^2 + 3.29 X_t^2 - 1.71 X_A^2 + 1.9 X_T X_t + 2.58 X_T X_A$	0.94	43
(5)	$Tel = 1.09 + 0.08 X_t - 0.26 X_A - 0.29 X_T^2 + 0.11 X_A^2 - 0.09 X_T X_t$	0.95	30
(6)	$B = 18.22 + 0.34 X_T - 1.39 X_t + 4.36 X_A + 0.93 X_t^2 + 1.06 X_T X_t + 1.84 X_T X_A + 1.26 X_t X_A$	0.94	44
Pulping process after autohydrolysis (A)			
(7)	$Y_{iAut} = 55.44 - 7.94 X_T - 2.21 X_A - 1.05 X_t - 6.55 X_A^2 + 4.89$	0.98	68
(8)	$KN_{Aut} = 67.7 - 8.17 X_A - 28.39 X_A^2 + 14.64 X_t^2 + 12.76 X_T^2 - 11.02 X_t X_A - 3.86 X_T X_t$	0.96	35
(9)	$BI_{Aut} = 1.10 - 0.10 X_A + 0.10 X_t^2 - 0.28 X_A^2 - 0.08 X_T X_A + 0.14 X_t X_A$	0.98	70
(10)	$TI_{Aut} = 17.60 - 1.29 X_t + 0.88 X_A - 3.41 X_T X_A + 1.29 X_t X_A$	0.94	43
(11)	$Tel_{Aut} = 1.12 + 0.09 X_A - 0.08 X_T - 0.04 X_t - 0.11 X_A^2 - 0.18 X_T X_A - 0.05 X_T X_t$	0.95	30
(12)	$B_{Aut} = 17.47 + 7.06 X_A + 6.85 X_A^2 - 3.35 X_t^2 + 1.54 X_t X_A$	0.94	44
Dependent variables: Y_i : yield (%); KN : kappa no.; BI : brightness (%ISO); TI , BI , Tel : tensile index ($N \cdot m \cdot g^{-1}$), burst index ($MPa \cdot m^2 \cdot kg^{-1}$), and tear index ($mN \cdot m^2 \cdot g^{-1}$), respectively. Independent variables: X_A : alkali concentration, X_t and X_T : time and temperature of operation, respectively The differences between the experimental values and those estimated using the equations never exceeded 10% of the former. Independent variables are expressed in coded units (Eq. (1))			

This idea, which was confirmed in this work, contradicts the results of other authors who examined pine (Saukkonen *et al.* 2012), eucalyptus (Vila *et al.* 2011; Chirat *et al.* 2012), and birch wood (Helmerius *et al.* 2010), among other raw materials. For example, Vila *et al.* (2011) used autohydrolysis to remove hemicelluloses from *E. globulus* wood, and the extracted wood was subjected to kraft pulping and bleaching.

The typical operating conditions of a batch kraft pulp mill are: a liquid/solid ratio of 3.5, 25% sulfidity, 165 °C cooking temperature, and 50 min cooking time. The suitability of the autohydrolysed wood for kraft pulp was assessed under identical operating conditions typical of a kraft pulp mill for the autohydrolysed wood and untreated wood and an active alkali concentration leading to bleachable pulp from the wood and the solid residue after autohydrolysis. Also, the autohydrolysis process was carried out under conditions to extract the maximum amount of oligomers from the hemicelluloses. The

operating conditions used considerably detracted from the physical properties of the handsheets relative to the material subjected to autohydrolysis. Martín-Sampedro *et al.* (2014) obtained similar results with *E. globulus* wood. They extracted hemicelluloses by steam explosion or steam treatment prior to kraft pulping; the two methods were similarly efficient and led to similar reductions in pulp strength.

Figure 1 shows the present tensile index results at two different levels of pulping time (+1 and -1). As can be seen, the tensile index exceeded $22 \text{ N}\cdot\text{m}\cdot\text{g}^{-1}$ even with prior autohydrolysis for a 90 min cooking time, a 9% active alkali concentration, and a pulping temperature of $163 \text{ }^\circ\text{C}$; this value is higher than those obtained at higher alkali concentrations, pulping temperatures, and cooking time in the absence of prior autohydrolysis. Thus, based on models (4) and (10) in Table 4, a tensile index of *ca.* $20.0 \text{ N}\cdot\text{m}\cdot\text{g}^{-1}$ in the A process can be obtained by using an active alkali concentration of 13%, a pulping temperature of $143 \text{ }^\circ\text{C}$, and a cooking time of 90 min. Obtaining a similar value with the NA process would require an active alkali concentration of 17.0%, a pulping temperature of 153°C , and a cooking time of 115 min. Therefore, the A process uses much less severe pulping conditions. The tensile index values obtained by soda-anthraquinone pulping reported here are higher than those reported by Martín-Sampedro *et al.* (2014) for unrefined eucalyptus kraft pulp obtained after hydrothermal steaming or steam explosion (*i.e.*, 8 to $16 \text{ N}\cdot\text{m}\cdot\text{g}^{-1}$ autohydrolysis *versus* $21 \text{ N}\cdot\text{m}\cdot\text{g}^{-1}$ control).

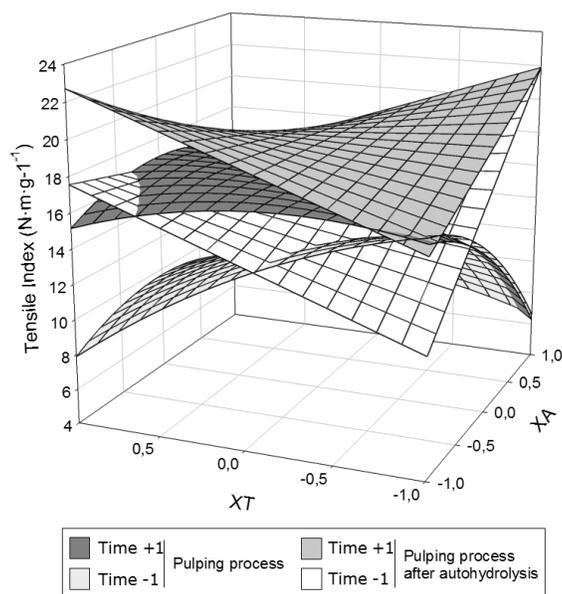


Fig. 1. Variation of the tensile index as a function of the pulping temperature and the active alkali concentration at two cooking time levels

The present results are also higher than those reported by Garrote *et al.* (2003), who obtained handsheets with acceptable physical properties (*e.g.*, tensile index values of 9.1 to $23.7 \text{ N}\cdot\text{m}\cdot\text{g}^{-1}$) by autohydrolysis and organosolv delignification of eucalyptus wood, using an ethanol concentration of 55%, a pulping temperature of $175 \text{ }^\circ\text{C}$, and an operation time of 90 min.

Figure 2 shows the variation of burst index and tear index with the pulping conditions. As can be seen, the burst index was greater with A than with NA (1.32 *vs.* 1.12

MPa•m²•kg⁻¹). The lowest tear index was very similar (approximately 1.5 mN•m²•g⁻¹) in both processes. Also, the overall hyperspaces of the tear indices were highly overlapped, but the A process had the advantage that it used less stringent pulping conditions. These results are higher than those obtained by Garrote *et al.* (2003) with the autohydrolysis-organosolv delignification of eucalyptus wood (*e.g.*, the tear index was 0.57 to 1.11 mN•m²•g⁻¹) and slightly lower than those obtained by Martin-Sampedro *et al.* (2014).

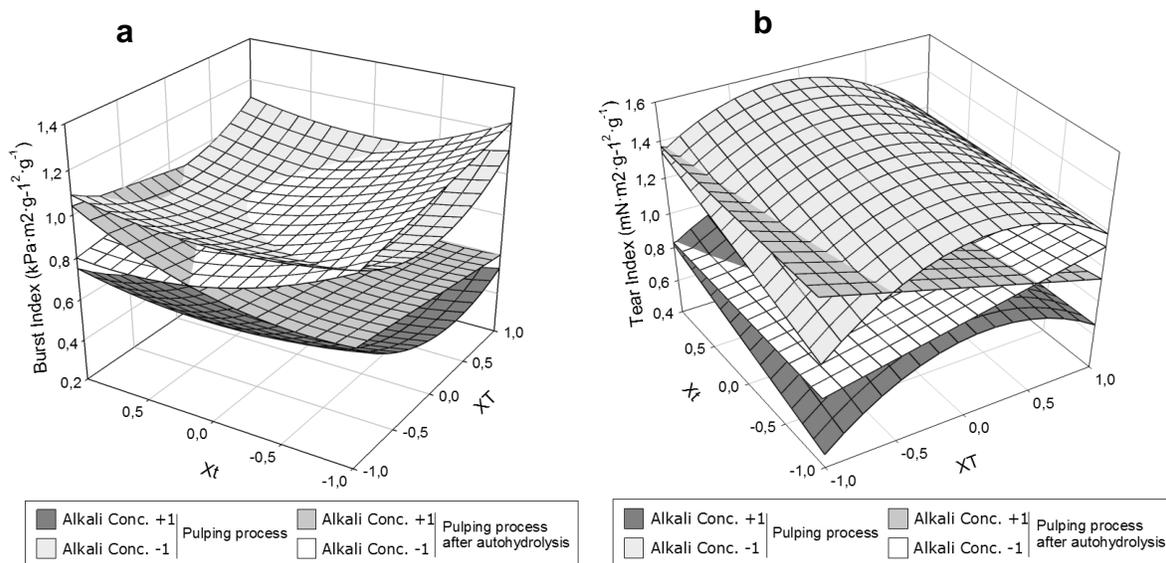


Fig. 2. Variation of the (a) burst index and (b) tear index as a function of the pulping temperature and the cooking time at two active alkali concentration levels

The results presented above confirm that, as previously found in other wood materials, it is indeed possible to obtain a brownstock with acceptable strength-related properties from eucalyptus wood that has been subjected to autohydrolysis. In fact, the removal of hemicelluloses from wood prior to pulping resulted in pulps with strength properties that were as good as or even better than those provided by traditional soda-AQ pulping of unextracted wood.

García *et al.* (2011b) found a hydrolysis temperature of 187.5 °C and an extraction time of 15 min was an effective compromise for maximising the glucan content while minimising the xylan content in paulownia wood chips. The kappa number of soda-AQ pulp ranged from 12.2 to 69.2, and its brightness ranged from 18.2% to 30.6%. Also, the viscosity and the physical properties of the pulp were substantially improved by the autohydrolysis of the starting material.

Feria *et al.* (2012) found the autohydrolysed-treated *Leucaena leucocephala* required less severe soda-AQ pulping conditions than the non-treated *Leucaena leucocephala* (177 °C, 21% active alkali, and 120 min *vs.* 185 °C, 25% active alkali, and 150 min). Also, the resulting pulp had similar or even better properties including yield (27.6 *vs.* 34.0%), brightness (39.3 *vs.* 31.6% ISO), tensile index (7.8 *vs.* 10.5 N•m•g⁻¹), and burst index (0.43 *vs.* 0.29 MPa•m²•kg⁻¹).

With both paulownia and *Leucaena leucocephala*, wood autohydrolysis prior to pulping led to soda-AQ pulps of similar or even better physical properties than without autohydrolysis pretreatment. In any case, the strength-related properties of the handsheets from eucalyptus wood were higher than those from paulownia and leucaena.

Based on other response surface expressions of Table 4 (results not shown), yield was the only property where the untreated raw material exceeded the autohydrolysed material, an obvious result of the latter being subject to a double fractionation process.

Based on the response surfaces for kappa number (Fig. 3), there was a statistically significant overlap at high active alkali concentrations (21 % for NA and 17% with A). As can be seen from Fig. 3, delignification was more efficient following autohydrolysis pretreatment; in fact, the kappa number was greater for the control (non-autohydrolysed). These results are consistent with those of brightness (Fig. 3), which was higher with autohydrolysis (about 32 % ISO). A similar behavior in kraft pulp production processes can be assumed. Cellulosic pulp more easily bleachable using a previous autohydrolysis process would be obtained as well.

Overall, the present results were better than those reported by Garrote *et al.* (2003) for the autohydrolysis-organosolv pulping of eucalypt wood (kappa numbers of 53.5 to 100.7) and somewhat worse than those reported by Martin-Sampedro *et al.* (2014) (brightness 34% to 45% ISO).

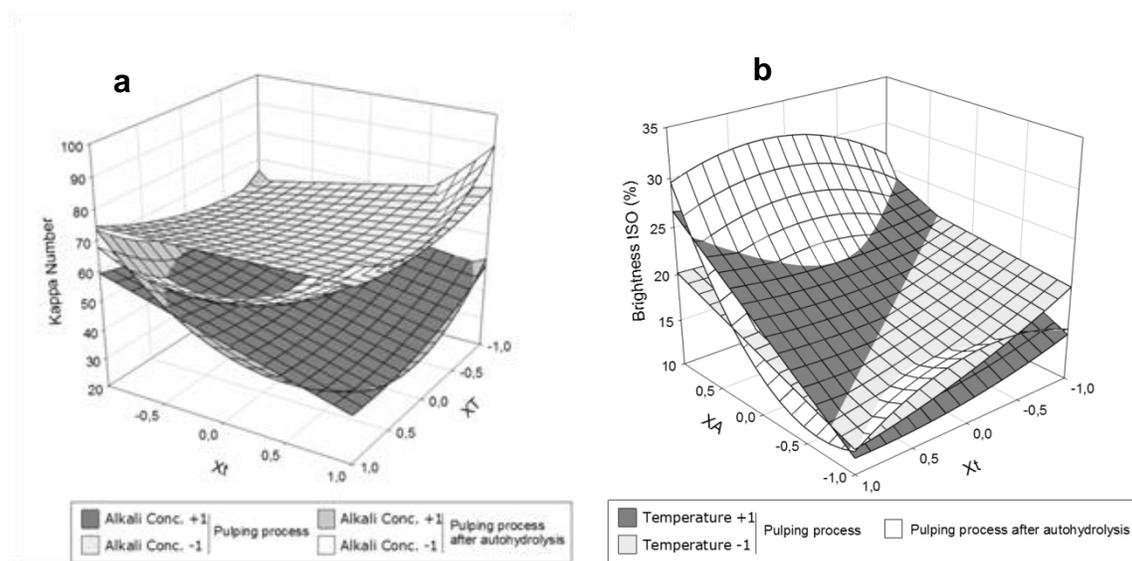


Fig. 3. Variation of the (a) kappa number and (b) brightness as a function of pulping temperature and cooking time at two active alkali concentration levels

CONCLUSIONS

1. Soda-anthraquinone pulping can be an effective choice for processing autohydrolysed eucalyptus wood. In fact, autohydrolysis pretreatment allows soda-AQ pulp to have strength-related properties similar to or even better than those provided by conventional soda-AQ pulping of non-autohydrolysed wood. In addition, the pretreatment process provides a recoverable liquid fraction that is high in hemicellulosic extracts.
2. Autohydrolysis enables soda-AQ pulping to be conducted under milder operating conditions. Thus, a tensile index in the region of $20.0 \text{ N}\cdot\text{m}\cdot\text{g}^{-1}$ can be obtained by using an active alkali concentration of 13%, a pulping temperature of $143 \text{ }^\circ\text{C}$, and a pulping time of 90 min to delignify autohydrolysed *E. globulus* wood; in contrast, obtaining a similar tear index with the non-autohydrolysed wood requires using an active alkali

concentration of 17.0%, a pulping temperature of 153 °C, and a pulping time of 115 min. The results obtained with the autohydrolysis of the starting material are better than those previously reported for unrefined (beaten) brownstocks. Also, the yield, brightness, and kappa number for the pulps made from the autohydrolysed eucalyptus wood are similar to those made from the non-autohydrolysed wood.

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