# Autohydrolysis, Pulping, and Bleaching of *Eucalyptus urograndis* in a Biorefinery Framework

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Autohydrolysis and kraft pulping were sequentially applied to *Eucalyptus* urograndis wood to obtain added-value products from hydrolysis liquor. A biorefinery approach was used to bleach the resulting solid phase containing the cellulose pulp with an optimized O-D-(EP)-D bleaching sequence, where O denotes delignification with the sequence D bleaching with chlorine dioxide and EP alkaline extraction with soda and hydrogen peroxide. The pulp was then beaten to obtain paper sheets. The two-stage process yielded pulp with a small Kappa number relative to conventional delignification (4.9 to 13.7 vs 17.1). Using autohydrolysis temperatures of 160 °C to 170 °C during 0 min to 15 min made the process selective towards the extraction of hemicelluloses (xylan up to 43.9%). Additionally, the Kappa number and brightness obtained after bleaching with an O-D-EP-D sequence were suitable for preparing dissolving grade pulp. The brightness of the pulp obtained was identical with that of the reference pulp (91.0%) and the Kappa number was smaller (0.2 to 0.6). Beating the pulp for 4500 PFI revolutions produced paper sheets with slightly better tensile strength and tear index than those for sheets from the reference pulp (viz., 90.3 N·m·g<sup>-1</sup> and 9.9 mN·m<sup>2</sup>·g<sup>-1</sup>, respectively, versus 89.8 N·m·g<sup>-1</sup> and 9.7  $mN \cdot m^2 \cdot q^{-1}$ , respectively).

Keywords: Autohydrolysis; Biorefinery; Dissolving pulp; Hemicelluloses; Kraft pulping

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## INTRODUCTION

The related paper properties depend not only on the characteristics of the raw material and the pulping method used, but also on how the pulp is refined. Thus, an adequate hemicellulose content is essential for obtaining strong paper. This is difficult to accomplish because of the complex biorefining processes in which the lignocellulosic materials are subjected to the sequential separation of the hemicellulose, cellulose, and lignin fractions for use as feedstock for biofuel and bioplastic productions (Duarte *et al.* 2010).

Technologists serving the pulp and paper industry have long assumed that overextraction of hemicelluloses detracts from some properties of paper sheets obtained from the solid phase remaining after an autohydrolysis treatment (Saukkonen *et al.* 2012). In fact, some strength-related properties of paper are impaired by treatments such as alkaline extraction, vapour explosion, hot water extraction, or autohydrolysis (Martín-Sampedro *et al.* 2010; Mendes *et al.* 2011; Vila *et al.* 2012). Hydrolysis pretreatments are used to open the wood structure of mechanical pulp to facilitate beating and thus save energy. However, with dissolving pulp, acid hydrolysis substantially affects the cellulose fraction (Kencaly *et al.* 2007; Jahan 2009). In any case, the resulting loss of handsheet strength can be reduced by avoiding excessive extraction of hemicelluloses, especially xylan (Chirat *et al.* 2012). Thus, the viscosity of hydrolysed pulp can be preserved by using milder operating conditions than that used in conventional pulping processes (Vila *et al.* 2012). Obviously, those processes initially extract hemicelluloses *via* autohydrolysis and diminish the pulp yields by over-extraction of hemicelluloses and by boosting the peeling reactions in the cellulose fraction (Chirat *et al.* 2012).

Although autohydrolysis is especially interesting for biorefinery schemes, the hemicelluloses can be efficiently extracted with alternative hydrolytic, acidic, or alkaline treatments, which provide liquor containing soluble oligomers or low-molecular weight polymers. These liquid phases can be used to obtain a variety of oligomers with high applicability in the chemical, oil, pharmaceutical, and food industries (Garcia et al. 2013; Adom 2012; Cheng et al. 2008). In a conventional process (i.e., one involving no prior hydrolysis), such polymers are degraded to a great extent and were incorporated into the black liquor, which can thus be used for energy production (Bhaskaran and Von Koeppen) 1970). As new technologies affording renewable and sustainable production emerge (Ragauskas et al. 2006; Kamm et al. 2009), biorefinery is increasingly expected to raise the benefits of processing lignocellulosic biomass fractions and hence to expand business opportunities for the silvicultural sector (Hess et al. 2007; Chambost et al. 2008). In fact, cellulose pulp mills can be the starting point for the integral production of energy and a wide range of chemicals from lignocellulosic biomass (Clark 2007; Kamm and Kamm 2007; Sanders et al. 2009). Additionally, extracting hemicelluloses should facilitate the delignification, thereby expediting reactions or reducing the reagents needed to obtain a given target Kappa number (Vila et al. 2011). However, in some cases, extracting hemicelluloses reduces intrinsic viscosity in the resulting pulp through depolymerisation of cellulose.

Accepting the idea that the extraction of hemicelluloses provides additional value (in the use of lignocellulosic material), kraft pulping process can be used for purposes other than conventional paper production. Dissolving pulp is one example of such an alternative purpose. In fact, the dissolving pulp market requires pulp with a high cellulose purity of typically 95% to 98%  $\alpha$ -cellulose, only 1% to 10% hemicellulose, and less than 0.05% lignin (Christov *et al.* 1998). With kraft pulps, these cellulose purity levels can be obtained with a bleaching process carried out to reach a high brightness degree. Because the yields rarely exceed 30% to 35%, the dissolving pulp is more expensive to produce than the conventional cellulose pulp. For this reason, the dissolving pulp is often used to obtain various value-added cellulose derivatives such as cellulose acetate, viscose, cellulose nitrate, carboxymethyl cellulose, or methylcellulose.

The dissolving pulp can be obtained not only from wood but also from other raw materials, such as cotton linters, which are kraft-pulped following sulphite-hydrolysis (Barba *et al.* 2002).

Returning to the argument of the first paragraphs about that over-extraction of hemicelluloses detracting from some properties of paper sheets, hemicelluloses are hydrophilic and account for most of the water-retention capacity of fibres in beaten cellulose pulp. In fact, the hemicelluloses make fibres more flexible and increase fibre contact areas, thereby improving its intertwining property. The resulting increased fibre cohesion reduces the beating energy required for specific levels of mechanical strength to be obtained (Barzyc *et al.* 1997; Laine and Hynynen 1997; Warberg and Annergren 1997).

However, an increased water-retention capacity of fibres diminishes drainability in the resulting paper and can compromise the operation of papermaking machines, which usually work at their top drainage rate. Whether pulp can be properly refined under these conditions depends on a balance between the mechanical strength and fibre intrinsic performance (Ferreira *et al.* 1998). Because hemicelluloses facilitate refining, they should only be removed to produce pulp for tissue paper (Santos 2005).

Köhnke and Gatenholm (2007) altered cellulose fibres to control their adsorption capacity for hemicellulose and examined their impact on the properties of pulp from leafy wood. They found that the hemicellulose adsorption by fibres increases cellulose stability by preventing microfibril aggregation upon drying and hence minimizing hornification of fibres. According to Oliveira and Sabioni (2002), the hornification causes fibres to harden after drying, which detracts from their suitability for papermaking. This phenomenon arises during the cooking, bleaching, and drying of pulp, which are usually separately completed.

In this work, the authors used *Eucalyptus urograndis* wood as the raw material for pulping. This is one of the most widely grown plant species in Brazil's forests, and also one of the most widely used species for wood for kraft pulping. The material was subjected to sequential autohydrolysis and kraft pulping as a means to valorize the hydrolysis liquor. Additionally, the remaining solid phase (cellulose pulp) was processed under biorefinery principles by using an optimized OD–EP–D bleaching sequence using pressurized oxygen, hydrogen peroxide, and alkali extraction, and then beaten to obtain handsheets.

## EXPERIMENTAL

#### **Raw Material and Autohydrolysis Processing**

The raw material used was *E. urograndis* chips obtained from a pulp and paper mill in central-eastern Brazil (Suzano, Salvador de Bahia, Brazil). The material was subjected to the treatments described below at the cellulose and paper laboratory of the Forestry Engineering Department of the Federal University of Viçosa, Brazil. The wood chips were classified according to the SCANCN 40:94 (1993) standard, dried to approximately 15% moisture, and then stored until further processing. For chemical analysis (the same analysis than hydrolysed material -see below in this section-), the chips were ground and sieved through an 8-mm mesh according TAPPI T-264-cm-07 (2007). No particle diffusion constraints were detected under these conditions. The ground wood samples were allowed to dry at ambient temperature, homogenized in different batches, and stored in air-tight vessels.

The *E. urograndis* chips (chip size: long 25 mm to 30 mm, width 15 mm to 20 mm and thickness 2 mm to 3 mm) used in the autohydrolysis tests were processed in a 10-L jacketed reactor from MK-Systems, Inc. (Danvers, MA, USA) furnished with a liquor recycling system. The operating temperature used was 160 °C to 180 °C, and the treatment time was up to 30 min. The time needed for the reactor to reach the processing temperature was 43 min, and the water to wood mass ratio was 10:1. The recycling system allowed the reactor to be externally cooled down to 25 °C before it was opened.

The hydrolysed material was mechanically beaten and sieved through 40/60-mesh on a Wiley mill (Arthur H. Thomas Co., Philadelphia, PA, USA). The hydrolysed material was allowed to dry under ambient conditions (23 °C and 50  $\pm$  2% relative humidity) prior to storage in air-tight containers. These samples were chemically characterized according to the following standards: TAPPI T264 cm-07 (2007) for moisture content and TAPPI

T204-om-07 (2007) with Soxhlet extraction (95% ethanol for 5 h) for extractables. After removing ethanol extracts, the solid samples were analysed for lignin and sugars after acid hydrolysis according to TAPPI T249-em-09 (2009). Klason lignin content was determined according to TAPPI T222 om-11 (2011).

The sugar monomers in the hydrolysis liquor were determined according to Wallis *et al.* (1996) using a 940 Professional IC Vario ion chromatograph from Metrohm AG (Herisau, Switzerland) that was equipped with a pulsed amperometric detector and a CarboPac PAI column (Thermo Fisher Scientific, Waltham, MA, USA). A sample volume of 25  $\mu$ L was injected at a flow rate of 1 mL/min in each run. The instrument was calibrated with glucose, xylose, galactose, mannose, and arabinose standards, and fructose was used as an internal standard.

## Pulping and bleaching

After the autohydrolysis process, a kraft delignification was completed using the following conditions: alkali concentration, 25% (on dry wood weight); sulphidity, 31% (on dry wood weight); temperature, 167 °C; and operating time of 45 min. As noted earlier, the reactor warm-up time was 43 min. However, the amount of water needed to impregnate the material was much smaller than that used for autohydrolysis, and the liquid/solid mass ratio of 4:1 was used. As in the autohydrolysis tests, recycling the liquor ensured efficient mixing and uniform delignification of the previously hydrolysed wood chips.

Cellulose pulps (from the solid phase after autohydrolysis) were collected in the same reactor used for the hydrothermal pretreatment. In addition, a pulp without autohydrolysis was performed under the same operating conditions as a reference experiment.

The black liquor from the pulping process was filtered off, and the pulp was beaten in a PFI mill at 2000 rpm for 10 min. The pulp samples thus obtained were analysed for yield, Kappa number, and intrinsic viscosity according to TAPPI T257 cm- 85 (1999), TAPPI T236 cm-85 (1996), and TAPPI T230 om-99 (1999), respectively. Paper properties were assessed according to TAPPI T205 sp-02 (2014) using handsheets previously obtained with an ENJO-F-39.71 sheet former (IDM Test, San Sebastián, Spain).

Experiments (Reference 4, 6, 8, and 9)							
Conditions	0	D	EP	D			
Consistency (%)	11.5	10	10	10			
Time (min)	60	120/30×	90	120			
Temperature (°C)	100	95/80×	85	80			
Pressure (kPa)	600	-	-	-			
H <sub>2</sub> SO <sub>4</sub> (kg.t <sup>-1</sup> )	-	*	-	*			
NaOH (kg.t <sup>-1</sup> )	20.0	-	10.0	*			
O <sub>2</sub> (kg.t <sup>-1</sup> )	20.0	-	-	-			
Kappa number	-	0.26	-	-			
CIO <sub>2</sub> (kg.t <sup>-1</sup> )	-	*	-	Ref, 4 and 6			
H <sub>2</sub> O <sub>2</sub> (kg.t <sup>-1</sup> )	-	-	5.0	-			
Final pH	-	2.8		5.0			
*H <sub>2</sub> SO <sub>4</sub> or NaOH for adjustment of pH ×. For exp. 8 and 9							

## **Table 1.** General Conditions Used for Bleaching of Pre-hydrolysis Kraft Pulps

In a kraft process, bleaching can produce large amounts of effluents containing toxic substances. Replacing the typical bleaching sequences based on chlorinated reagents with elemental chlorine-free (ECF) sequences can help to reduce effluent toxicity (García *et al.* 2010). In this work, autohydrolysed kraft pulp was subjected to an O-D-(EP)-D bleaching sequence where O denotes delignification with sequence, D bleaching with chlorine dioxide, and EP alkaline extraction with soda and hydrogen peroxide. The operating conditions for each step in the sequence are shown in Table 1.

## Methods

#### PFI beating, sheet formation, and physical testing

Pulp samples were beaten in a PFI mill (IDM Test, San Sebastián, Spain) in accordance with TAPPI T248 sp-08 (2008). As per TAPPI T200 sp-01 (2002), the beating intensity was expressed in Schopper–Riegler degrees (°SR) or as energy consumption (W·h). The samples (an amount of 30 g oven-dry pulp in each run) were beaten at a variable rate (0 to 4500 PFI revolutions) to obtain three levels of pulp refinement spanning the range of 15 °SR to 50 °SR (0 W·h to 70 W·h).

#### Formation of sheets for physico-mechanical and optical tests

The paper sheets used in the tests were obtained on a sheet former according to TAPPI T205 sp-02 (2014). The sheets, 60 g/m<sup>2</sup> in aerial weight according to TAPPI T205 sp-02 (2014), were conditioned at  $23 \pm 1$  °C and a relative humidity of 50%  $\pm 2\%$  for testing.

The light scatter coefficient was determined on a Datacolor Elrepho 450X instrument (Datacolor Inc., Lawrenceville, NJ, USA) at two different points in each sheet. The readings obtained at each beating level were averaged for subsequent processing. Tensile strength tests were conducted on Instron equipment (Instron, Barcelona, Spain), using a grip distance of 100 mm, a test speed of 25 mm/min, a loading cell of 1000 N, and a computer-controlled data acquisition and processing system. The tear strength, burst strength, and air pass were determined on Elmendorf and Müllen equipment (IDM Test, San Sebastián, Spain).

#### Experimental design for the pulping process - multiple regression modelling

The pulping process was modelled and optimized using a polynomial model approach considering linear and quadratic terms of the process variables, and mutual interactions. Thus, the equations established were fitted by multiple regression. A central composition design was used to reduce the number of tests needed while ensuring the absence of significant covariances between the independent variables. These two tools allow the influence of several process variables on pulp and paper properties to be simultaneously assessed (Dong and Fricke 1996). The dependent variables, such as yield, glucan, xylan, mannose, ethanol extractives, intrinsic viscosity, and Kappa number were thus related to the independent variables of the kraft pulping process after autohydrolysis, *viz.*, autohydrolysis temperature and time.

A  $2^n$  central composite factor design was used to minimize the number of tests needed while avoiding correlation in the covariance matrix. Modelling required previously normalizing the ranges spanned by the independent variables according to Eq. 1 and statistically identifying the significant influences in the coefficients. Thus, no term with a coefficient exceeding p = 0.05 in significance as per Student's t-test, or with a 95% confidence interval, was included in the models,

$$X_n = \frac{X - \overline{X}}{(X_{\text{max}} - X_{\text{min}})/2} \tag{1}$$

where X is the absolute value of the independent variable concerned,  $\overline{X}$  is the mean value, and  $X_{\text{max}}$  and  $X_{\text{min}}$  are the maximum and minimum values, respectively.

Three levels each of the autohydrolysis process (temperature 160 °C, 170 °C, and 180 °C) and operation time (0 min, 15 min, and 30 min) were used. Operational conditions in kraft pulping were fixed: alkali concentration, 25%; sulphidity, 31%; temperature, 167 °C; and operating time, 45 min. A liquid/solid ratio of 4/1 were used in all experiments.

The minimum number of tests needed, N, was calculated to be  $2^n + 2n + c$ , where n is the number of independent variables and c that of replicates of the central point in the experimental design (Eq. 2). Therefore, N was  $2^2 + 2 \times 2 + 2 = 10$ . The experimental results were fitted to the following second-order polynomial,

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

where X are the independent variables and Y are the dependent variables. The coefficients,  $a_0$ ,  $b_i$ ,  $c_i$ , and  $d_{ij}$  are constant unknown characteristics, estimated from the experimental data.

The results were assessed with STATISTICA 10.0 software (StatSoft, Inc., Tulsa, OK, USA). In addition, global model adjustment statistics, such as  $R^2$  and Snedecor-F have been used. Levels of  $R^2$  higher than 0.85 or Snedecor-F higher than 5 were found as suitable.

#### **RESULTS AND DISCUSSION**

#### **Characteristics of the Raw Material**

The chemical characterization of *Eucalyptus urograndis* was determined. The ethanol extractives content obtained was 3.7%. The chemical compositional analysis revealed that the major content was cellulose, which accounted for 47.0% of the mass, followed by Klason lignin (24.4% after quantitative acid hydrolysis), and hemicelluloses (In the present case, to estimate the efficiency of autohydrolysis, hemicellulose was calculated as the combination of xylose 11.0%, arabinose 0.25%, galactose 0.85%, mannose 1.1%, and acetyl content 3.1%) with 16.3%. According to the Wise *et al.* (1964) method, the holocellulose content was 71.9%. Therefore, the hemicelluloses content could also be calculated as hollocellulose – glucan (or  $\alpha$ -cellulose) = 25.0%

This composition was similar to other eucalyptus varieties used in biorefinery (Table 2): *Eucalyptus globulus* (Garrote and Parajó 2002; López *et al.* 2008; Loaiza *et al.* 2016), *E. grandis*, and *Eucalyptus urograndis* (Da Silva Morais *et al.* 2016).

#### Autohydrolyzed Solids and Kraft Pulping

The main purpose of an autohydrolysis treatment preceding kraft pulping is to obtain a liquor containing abundantly extracted xylo-oligosaccharides and monomeric sugars, such as xylose and acetic acid. Some authors have suggested that the resulting solid phase can be used to obtain added-value products (Testova *et al.* 2011). For example, if it

contains more than 15% to 20% pentosans, then it can be useful to produce furfural (Yahyazadeh 2011).

Component	Е.	E. grandis	E. globulus	E. globulus	E. globulus	
	urograndis	(Da Silva	(Loaiza <i>et al.</i>	(López et	(Garrote	
	(Da Silva	Morais et	2016)	<i>al.</i> 2008)	and Parajó	
	Morais et	<i>al</i> . 2016)			2002)	
	<i>al.</i> 2016)					
Total Extractives (%)	1.8	2.9	2.7	nd	1.2	
Insoluble Lignin (%)	23.2	21.9	21.2	19.9	22.9	
Holocellulose (%)	86.2	80.8	64.4	75.4	77.1	
Cellulose (%)	42.8	40.8	42.8	46.8	46.3	
Hemicelluloses (%)	43.4	40.0	21.3	28.6	30.8	

**Table 2.** Results of Chemical Characterization of *Eucalyptus globulus, E. grandis*, and *E. urograndis* from the Literature

Table 3 shows the results of the pulping process, and the normalized values of the dependent variables in accordance with the proposed experimental design (autohydrolysis with kraft delignification). It also shows the results of a reference experiment (kraft pulping without autohydrolysis). Each result is the average of 5 replicate determinations and deviations from the mean were all less than 5%.

**Table 3.** Normalized Values of the Process Variables and Characterization ofPulp Obtained by Autohydrolysis + Kraft Pulping in Accordance with theExperimental Design

Exp.	(t)	(T)	Yield (%)	Kappa Number	Ethanol- Extractives (%)	Glucan (%)	Xylan (%)	Manose (%)	Viscosity (cm <sup>3.</sup> .g <sup>-1</sup> )
1	1	1	32.6	4.9	0.68	32.2	0.29	0.05	603
2	1	-1	40.4	9.5	0.29	38.2	1.88	0.08	1019
3	-1	1	40.5	8.7	0.14	37.7	1.40	0.06	938
4	-1	-1	46.6	13.7	0.58	38.3	4.83	0.09	1033
5	1	0	37.3	6.1	0.76	35.1	0.56	0.04	801
6	-1	0	44.4	10.9	0.7	38.2	2.82	0.09	1005
7	0	1	35.5	6.1	0.45	34.8 0.39		0.04	745
8	0	-1	42.2	10.7	0.44	38.1	3.35	0.09	1048
9	0	0	39.2	7.6	0.67	36.4	1.33	0.04	887
10	0	0	39.1	7.5	0.66	36.2	1.25	0.08	901
Ref.	-	-	48.5	17.1	0.02	38.7	6.02	0.10	1017

The polynomial models relating the dependent variables to the independent variables (Table 4) were obtained by fitting the non-linear regression models of Eq. 2 to

the data of Table 3. Fitting was invariably very good ( $R^2 > 0.96$ ; Snedecor's F > 100). The residuals between the experimental values of the dependent variables and their estimates from Eq. 4 were also very good, in fact, all differences (residuals) were less than 5% of the range spanned by each dependent variable.

	Equation	R²	F- Snedecor	
(1)	<b>Y</b> = 39.28 - 3.530 <i>X</i> t - 3.44 <i>X</i> T + 1.40 <i>X</i> t <i>X</i> t - 0.57 <i>X</i> T <i>X</i> T - 0.40 <i>X</i> t <i>X</i> T	0.99	641.71	
(2)	K = 7.64 - 2.10Xt - 2.37XT + 0.85XtXt + 0.73XTXT	0.99	320.23	
(3)	<b>V</b> = 898.0 – 92.16 <i>X</i> t – 135.66 <i>X</i> T – 80.25 <i>X</i> t <i>X</i> T	0.99	305.09	
(4)	<b>G =</b> 36.52 – 1.46 <i>X</i> t – 1.64 <i>X</i> T – 1.35 <i>X</i> t <i>X</i> T	0.98	295.01	
(5)	E = 0.69 + 0.05Xt - 0.26XTXT + 0.20XtXT	0.97	102.36	
(6)	<b>X</b> = 1.34 – 1.05 <i>X</i> t – 1.33 <i>X</i> T + 0.30 <i>X</i> t <i>X</i> t + 0.48 <i>X</i> T <i>X</i> T + 0.46 <i>X</i> t <i>X</i> T	0.98	145.08	

**Table 4.** Polynomial Models for the Dependent Variables of the Autohydrolysis +

 Pulping Process

Dependent variables: Yield (Y, %), Kappa number (K), intrinsic viscosity (V, cm<sup>3</sup>.g<sup>-1</sup>), glucan (G, %), ethanol extractives (E, %), and xylan (X, %); Independent variables: Temperature ( $X_T$ ) and time ( $X_t$ ); Normalized values for the independent variables were used in equations from Table 3

The kraft pulping yields obtained for *E. urograndis* wood with autohydrolysis were lower than those obtained with the reference pulp. This was because the raw material was subjected to two processes to remove the hemicellulose components. In fact, the Kappa numbers were low for the autohydrolysed raw material than that of the reference pulp.

This observation was consistent with the widespread belief in the paper industry that the pulp should contain a certain amount of hemicellulose, whose content influences the quality of the resulting paper. In fact, more lignin, and a high proportion of hemicellulose were lost in the pulping liquor during conventional industrial processes (Cruz et al. 2012). The most labile fraction, the hemicellulose-lignin complex (containing approximately 15 to 25% of all lignin and 40% of all hemicellulose) was rapidly removed early in the process (Cenunez 2018; Villar 2018). The reference kraft pulp contained approximately 6.02% xylan. This amount was equivalent to 26.6% of all xylan present in the raw material, which was therefore 73.4% extracted into the autohydrolysis liquor. Additionally, based on the total content of hemicelluloses, approximately 16.3% (or 25% as the difference from the glucan content) was extracted 82.1% to 88.3% into the liquor. One of the hypotheses (Hypothesis 1) for this work was that removing hemicelluloses early by autohydrolysis would not have any adverse effect on the hemicellulose content of the final pulp to detract from the strength-related properties in the resulting paper sheets. Another hypothesis (Hypothesis 2) was based on the previous one, and was that the autohydrolysis treatment would provide a valorizable liquor containing a substantial amount of hemicelluloses.

A total of 10 preliminary tests under the temperature and time conditions of Table 3 provided solid phase yields from 75.5% to 95.7% and hemicelluloses contents as the combination of araban, galactan, xylan, and mannose contents from 3% to 13.1%. Therefore, hemicelluloses were extracted to the extent of 86.1% to 90.9% with a

hemicellulose content of 16.3% in the raw material and 21.7% to 49.0% (25% based on difference between holocellulose and glucan). The hemicellulose extraction in the autohydrolysis liquors in tests 4, 6, and 8 were those whose samples were closest to the reference pulp in xylan content (Table 3) and hence was chosen for subsequent bleaching and beating. This sample had 21.7% to 32.5% initial hemicellulose content (16.3% is the hemicellulose content in the raw material) or 49.0% to 56.0% (with one of (25%, based on difference between holocellulose and glucan in raw material)

If Hypothesis 1 were to be fulfilled, a given hemicellulose or xylan content of the pulp would exist above which the strength-related properties of the resulting paper would not be substantially better. Based on Eq. 6 in Table 4, the xylan content at experimental isothermal conditions at 170 °C, and 160 °C for 15 min, respectively— corresponded to the kraft pulp samples with the highest xylan contents (82.6%, 44.7%, and 52.3%, respectively, of that in the reference pulp). In other words, based on the combined yield of autohydrolysis and delignification, 79.0%, 89.1%, and 87.9%, respectively, of xylan initially present in the raw material (11%) was dissolved versus 73.4% in the reference pulping process. The proportion of dissolved hemicelluloses ranged from 85.8% to 90.7% in test 4, 92.7% to 95.2% in test 6, and 91.8% to 94.7% in test 8 with an initial content of 16.3% (or 25% if expressed as the difference between holocellulose and glucan). By contrast, the hemicelluloses in the reference raw material were dissolved to the extent of 82.1% to 88.3%. The previous experimental points (4, 6, and 8) were used for the subsequent bleaching and refinability tests. The increased hemicellulose contents of the pulp samples obtained under the corresponding operating conditions coincided with the highest viscosity values in the studied operating ranges.

In regards to other pulp properties shown in Table 3 or modelled in Table 4, the autohydrolysis treatment was especially influential on the Kappa number, which ranged from 4.92 under the strongest operating conditions to 13.7 under the mildest, and also on the pulp yield, which was 32.6% and 46.6%, respectively.

To better envision the influence of the operational variables on the chemical properties, and to directly compare with the result obtained from reference pulp, the response surface plots (Figs. 1 to 4) were constructed.



**Fig. 1.** Variation of solid yield after kraft pulping as a function of temperature (XT) and operation time (Xt) in the pre-autohydrolysis process

As shown in Fig. 1, the solid yield changed corresponding to the Kappa number. Thus, it was markedly influenced by temperature and time in the higher ranges of the operating conditions (*viz.*, 180 °C and 30 min); also, their interaction term in Eq. 1 in Table 4 was statistically significant, but minimally relative to the other coefficients for the model. Using temperatures in the lower range, and times in the central and high ranges, was predicted to provide yields of 40.4%, and hence 16.7% lower than those for the reference pulp.

As shown in Fig. 2, the Kappa number decreased with increasing severity of the operating conditions, which, based on the previous conclusion, should lead to a significant loss of pulp viscosity. However, the interaction term for the two variables in Eq. 2 in Table 4 was not statistically significant. Additionally, the predicted Kappa numbers for temperatures in the lower range (160 °C) and times in the higher range (15 min to 30 min) were 9.5 and 10.5, respectively, which were considerably greater than the calculated values for the higher ranges of both variables (4.7). However the Kappa numbers were substantially (44.5% to 38.7%) smaller than those for the reference pulp with an identical level of viscosity. In fact, the predicted value was 1022 cm<sup>3</sup>.g<sup>-1</sup> and not significantly different from that of the reference pulp (1017 cm<sup>3</sup>.g<sup>-1</sup>).



**Fig. 2.** Variation of Kappa number after kraft pulping as a function of temperature (XT) and operation time (Xt) in the pre-autohydrolysis process

Figure 3 shows the response surface plot for intrinsic viscosity. As shown, an increased autohydrolysis temperature and time had an adverse effect on the pulp viscosity. However, the effect was a result of the synergistic combination of the two independent variables. Thus, the results were approximately 50% smaller under the strongest autohydrolysis conditions (*viz.*, 180 °C and 30 min). The response surface effect was consistent with Eq. 3 in Table 4, where the quadratic terms for the independent variables were not significant but that for their interaction was significant. Additionally, with temperatures close to the lower range, the operating time had virtually no effect on the viscosity. In fact, using temperatures in the lower range resulted in no decrease in viscosity relative to the reference pulp. As a rule, temperatures and time slightly exceeding the central ranges for the two variables (170 °C and 15 min) reduced viscosity by no more than 15% to 20% relative to the highest level calculated with the model (1048 cm<sup>3</sup>.g<sup>-1</sup>), which would result in the treated pulp being comparable to or even slightly better than the reference pulp in terms of viscosity.



**Fig. 3.** Variation of intrinsic viscosity after kraft pulping as a function of temperature (XT) and operation time (Xt) in the pre-autohydrolysis process

Because the pulp was to be bleached after autohydrolysis, the operating conditions used should simultaneously ensure maximal viscosity and yield. Based on Figs. 1 and 3, the pulp yield and viscosity could be increased to some extent by using temperatures in the lower range (160 °C) and times in the central range (15 min), albeit with a slightly greater Kappa number. These conditions should provide a pulp yield of 42.2%, a viscosity of 1034 cm<sup>3</sup>.g<sup>-1</sup>, and a Kappa number of 10.7, which were 13.1% lower, only 1.6% higher, and 37.3% smaller —and thus better—than the respective values for the reference pulp. The yield loss relative to the reference pulp under these conditions (6.33%) was largely (45.3%) ascribed to the difference in xylan content between the reference pulp (Table 3) and that calculated from Eq. 6 in Table 4.



**Fig. 4.** Variation of glucan content after kraft pulping as a function of temperature (XT) and operation time (Xt) in the pre-autohydrolysis process

The hemicellulosic derivatives lost to the liquor could be separately valorized with a biorefining scheme. Under these operating conditions, the autohydrolysis process was highly selective towards extraction of the hemicellulose fraction. Model 4 in Table 4 predicted a glucan content of 38.2%, which was only 1.3% lower than that of the reference pulp. The autohydrolysis treatment is usually highly selective for hemicelluloses; thus, based on the values in Table 3, and on those calculated by using model 4 in Table 4, the glucan content decreased 17.1% at most. By contrast, the hemicelluloses were extracted 17.6% to 96.7% depending on the particular operating conditions. As shown in Fig. 4, the glucan was scarcely dissolved at temperatures in the higher operating range. Additionally, the content in the other extracted substances was negligible (0.2% to 0.8%) and the xylan contents were consistent with the above-described numerical analysis.

# **Bleaching Process**

The pulp samples obtained under the autohydrolysis conditions in tests 4, 6, and 8 in Table 1, and of the central experimental point (test 9), were bleached as described in the pulping and bleaching section. These specific samples were chosen for the reasons stated in the previous section. The samples obtained in tests 8 and 9 were subjected to an O-D-(EP)-D bleaching sequence under the conditions previously described in the Materials and Methods section, but used a lower temperature (95 °C instead of 80 °C) and shorter times (30 min instead of 120 min) because of a very small Kappa number (7.6 to 10.7).

The samples obtained in the higher yields (tests 4 and 6) were also chosen for bleaching. Such samples had increased Kappa numbers and slightly greater viscosity. The results obtained after each stage of the bleaching sequence are shown in Table 5.

Expt.		Unbleached pulp	0	D	(EP)	D(a)	D(b)	D(b)	D(int)
Ref	Kappa Number	17.1	8.2	-	2.2	-	-	-	1.1
	Brightness (%)		54.6	70.8	86.4	90.7	90.9	91.3	91.0
	Viscosity (cm <sup>3</sup> .g <sup>-1</sup> )	1017	-	-	-	-	-	-	693
4	Kappa Number	13.7	7.8	-	1.4	-	-	-	0.6
	Brightness (%)	-	55.0	72.8	87.4	90.6	91.4	92.1	91.0
	Viscosity (cm <sup>3</sup> .g <sup>-1</sup> )	1033	-	-	-	-	-	-	711
6	Kappa Number	12.4	5.9	-	0.9	-	-	-	0.2
	Brightness (%)	-	60.5	77.5	88.1	90.5	91.3	91.5	91.0
	Viscosity (cm <sup>3</sup> .g <sup>-1</sup> )	1005	-	-	-	-	-	-	630
8	Kappa Number	10.7	5.6	-	1.2	-	-	-	0.6
	Brightness (%)	-	59.4	78.6	88.6	90.2	90.4	91.1	91.0
	Viscosity (cm <sup>3</sup> .g <sup>-1</sup> )	1048	-	-	-	-	-	-	729
9	Kappa Number	7.6	3.3	-	0.9	-	-	-	0.2
	Brightness (%)	-	62.2	76.7	87.0	90.7	91.7	91.8	91.0
	Viscosity (cm <sup>3</sup> .g <sup>-1</sup> )	887	-	-	-	-	-	-	505

 Table 5. Results of the Bleaching Process

The results indicated that the brightness values were all similar to those of the reference pulp but the Kappa numbers were smaller —in any case, the Kappa number for the bleached reference pulp was only 1.1. The viscosity values were similar to or only slightly higher than those for the reference pulp —by exception, the viscosity of the pulp

obtained under conditions falling in the central ranges of both independent variables was 27.1% lower than that of the reference pulp.

#### Physical Characteristics of Cellulosic Pulps and Paper Sheets Obtained

Obtaining paper sheets with the desired physical properties entails beating the pulp to an appropriate extent. A refinability parameter was used in this context to assess the amount of energy required by a pulp sample to reach a pre-set value of some property that is usually the degree of drainage (CSF) or drainage resistance as measured in Schopper– Riegler degrees (°SR). The refinability is strongly influenced by the hemicellulose content of pulp. Thus, hemicelluloses in the fibre walls reduce the amount of energy required to obtain a given level of a strength-related property by helping fibres to absorb water and connect to one another. Foelkel (2009) found an increased xylan content in brown pulp to facilitate refining and thus reduce energy use.

Under these premises, Hypothesis 1 was checked by assessing the strength-related properties in paper sheets obtained from pulp beaten to a variable extent in terms of energy. The pulp samples used for this purpose were chosen from tests 4, 6, and 9.

As shown in Figs. 5 through 7, the tensile, tear, and burst indices for the reference pulp were 50.3 N·m·g<sup>-1</sup> to 89.8 N·m·g<sup>-1</sup>, 6.1 mN·m<sup>2</sup>·g<sup>-1</sup> to 9.7 mN·m<sup>2</sup>·g<sup>-1</sup>, and 1.6 kPa·m<sup>2</sup>·g<sup>-1</sup> to 5.3 kPa·m<sup>2</sup>·g<sup>-1</sup>, respectively. These values were similar to the values for the samples previously autohydrolysed at T = 160 °C and t = 0 min (test 4) or T = 160 °C and t = 15 min (test 8). In addition, the xylan content of both autohydrolysed samples was more than 50% of that of the reference pulp. The previous strength-related properties were somewhat less favourable in the paper sheets obtained from the pulp autohydrolysed at T =170 °C and t = 0 min (test 8). Thus, the xylan content of the pulp amounted to only 44.7% of that of the reference pulp. In addition, at the above xylan content level, the paper properties failed to further improve with beating of the pulp. In fact, the strength of paper sheets from the pulp obtained in test 8 evolved with the beating as those of the sheets from test 4 and, at a given beating level, were even better than those for the reference pulp (results not shown).



Fig. 5. Variation of the tensile index as a function of the energy consumption



Fig. 6. Variation of the tear index as a function of the energy consumption



Fig. 7. Variation of the burst index as a function of the energy consumption

Based on the substantially decreased tensile index resulting from the reduced xylan content, autohydrolysed pulp from *E. urograndis* can be useful for producing a soft paper variety such as tissue paper. The tear index of paper is known to be adversely affected by the strong beating of the pulp *via* strong structural damage in fibres, diminishing their length (Hartler 1997; Silva and Oliveira 2000). Based on the results from this study, no further increase in tear index was observed beyond 22 °SR to 25 °SR with the selected pulp samples.

This study examined not only the typical strength-related properties of paper, but also other properties especially appreciated in tissue paper and other bulky, porous types of paper such as specific bulk volume and light scatter coefficient. Figures 8 and 9 show the curves for the specific elastic modulus (MOE) and deformation energy (TEA), respectively. The elastic modulus is a measure of the resistance of a material to deformation when subjected to an effort with an increasing load per mass unit. Paper initially exhibits a linear behaviour (elastic region) that eventually becomes plastic (plastic region) before tearing at the maximum load it can bear (Moreira 2006). The elastic modulus is inversely proportional to paper softness (Karlsson 2006). In this work, the modulus was similar for the reference pulp and for the pulp obtained in test 4 (8.08 MN·m·kg<sup>-1</sup> to 7.23 MN·m·kg<sup>-1</sup> *versus* 8.12 MN·m·kg<sup>-1</sup> to 7.24 MN·m·kg<sup>-1</sup>). The modulus for the pulp samples from tests 6 and 8 (Fig. 8) was lower (7.36 MN·m·kg<sup>-1</sup> to 6.66 MN·m·kg<sup>-1</sup> and 7.20 MN·m·kg<sup>-1</sup> to 6.40 MN·m·kg<sup>-1</sup>, respectively), which was consistent with their lower xylan contents and made them suitable for tissue paper production.



Fig. 8. Variation of the MOE as a function of the energy consumption



Fig. 9. Variation of the TEA as a function of the energy consumption

Similar conclusions can be drawn from the deformation energy results in the form of TEA, which represents the work performed by a paper specimen in response to a tensile effort leading to tear. Therefore, the TEA value is a measure of the ability of paper to absorb energy under increasing loads (Silva and Oliveira 2000). As with the elastic modulus, the TEA value was slightly better for the samples from tests 6 and 8 than for the reference pulp (see Fig. 9). Thus, the TEA was initially  $23.0 \text{ J} \cdot \text{m}^{-2}$  for the reference pulp and  $17.1 \text{ J} \cdot \text{m}^{-2}$  for that from test 8. However, more strongly beaten samples differed little in this respect ( $132.9 \text{ J} \cdot \text{m}^{-2}$  to  $143 \text{ J} \cdot \text{m}^{-2}$ ).

Figure 10 shows the variation of the apparent specific volume "bulk" with the extent of beating. As shown, the volume decreased with an increasing number of PFI revolutions (Howard and Bichard 1992), it also changed little with the hemicellulose content of the pulp. Thickness, which is directly dependent on the apparent specific volume, also exhibited no appreciable change (results not shown); overall, it started at 1.67 cm<sup>3</sup>.g<sup>-1</sup> to 1.89 cm<sup>3</sup>.g<sup>-1</sup> and decreased with increased beating to values from 1.15 cm<sup>3</sup>.g<sup>-1</sup> to 1.25 cm<sup>3</sup>.g<sup>-1</sup>.



Fig. 10. Variation of the apparent specific volume as a function of the energy consumption



Fig. 11. Variation of the light dispersion coefficient as a function of the energy consumption

As shown in Fig. 11, the light scattering coefficient for the paper sheets was influenced by the xylan content. The maximum values at the highest degree of beating were those for the pulp samples with the lowest xylan contents. This result was ascribed to the influence of xylan on interfibre links (the presence of more xylan resulted in a smaller fibre–air interface and low light scatter).

In theory, the optical differences among the paper sheets can be ascribed to differences in interfibre links, and to the presence of a number of refractive surfaces and light scattering particles (Carpim *et al.* 1987). Thus, a decreased xylan content should detract from interfibre links and lead to increased light scattering. This was the case here even though the difference between the coefficients for the reference pulp and that from test 6 —the pulp with the lowest xylan content— was fairly small (37.7 *versus* 42.1). In other words, the final values were similar for all pulp samples and ranged from 21.2 to 24.7, irrespective of beating level.

# CONCLUSIONS

- 1. Based on its chemical composition, *Eucalyptus urograndis* was a suitable raw material for obtaining hemicellulose derivatives and cellulose pulp under a two-stage biorefining scheme. A combination of kraft pulping, an autohydrolysis pretreatment, and an ECF bleaching sequence [OD(EP)D] afforded a pulp from depithed *E. urograndis* wood that could be used as dissolving pulp, irrespective of its Kappa number.
- 2. Using temperatures and times in the central ranges of the autohydrolysis operating conditions afforded relatively selective extraction of hemicelluloses in the autohydrolysis liquor while providing kraft pulp with a high enough xylan content to avoid viscosity losses relative to a reference kraft pulp obtained under identical pulping conditions. Additionally, subjecting the pulp to an O-D-(EP)-D bleaching sequence provided brightness and Kappa number values consistent with those for dissolving-grade pulp. Brightness was on par with that for the reference pulp and the Kappa number was even smaller.
- 3. The properties of the paper sheets obtained by beating *E. urograndis* pulp were similar to or even better than those obtained from the reference kraft pulp. In summary, autohydrolysis prior to kraft pulping not only preserves or even improves strength-related paper properties relative to a conventional kraft process but also provides a valorizable liquor with a high content in hemicellulose derivatives.

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# **REFERENCES CITED**

- Adom, F. K. (2012). The Potential of Industrial Waste and Agricultural Feedstock Towards Sustainable Biofuels Production: Techno-economic and Environmental Impact Perspectives, Ph.D. Dissertation, Michigan Technological University, Houghton, Michigan. https://digitalcommons.mtu.edu/etds/619
- Barba, C., Montané, D., Rinaudo, M., and Farriol, X. (2002). "Synthesis and characterization of carboxymethylcelluloses (CMC) from non-wood fibers I. Accessibility of cellulose fibers and CMC synthesis," *Cellulose* 9(3-4), 319-326. DOI: 10.1023/A:1021184509189
- Barzyc, D., Page, D. H., and Ragauskas, A. (1997). "Carboxilic acid groups and fibre bonding," in: *Fundamental Research Symposium*, Volume 11, Cambridge, UK, pp. 893-907.
- Bhaskaran, T. A., and Von Koeppen, A. (1970). "The degradation of wood carbohydrates during sulphate pulping," *Holzforschung* 24(1), 14-19. DOI: 10.1515/hfsg.1970.24.1.14
- Carpim, M. A., Barrichello, L. E., Claudio, D. S., Junior, E., and Dias, R. L. (1987). "As influências do número de fibras por grama nas propriedades óticas do papel [The influence of the number of fibers per gram on the optical properties of the paper]," in: *Congresso Anual Da ABTCP [ABTCP Annual Congress]*, São Paulo, Brazil, pp. 183-205.
- Cenunez (2018). "Transformations of wood during P. Q," Carlos Eduardo Nuñez, (http://www.cenunez.com.ar/archivos/65-), Accessed 11 March 2019.
- Chambost, V., McNutt, J., and Stuart, P. R. (2008). "Guided tour: Implementing the forest biorefinery (FBR) at existing pulp and paper mills," *Pulp. Pap. Can.* 109, 19-27.
- Cheng, K. K., Cai, B. Y., Zhang, J. A., Ling, H. Z., Zhou, Y. J., Ge, J. P., and Xu, J. M. (2008). "Sugarcane bagasse hemicelluloses hydrolysate for ethanol production by acid recovery process," *Biochem Eng J* 38, 105-109. DOI: 10.1016/j.bej.2007.07.012
- Chirat, C., Lachenal, D., and Sanglard, M. (2012). "Extraction of xylans from hardwood chips prior to kraft cooking," *Process. Biochem.* 47(3), 381-385. DOI: 10.1016/j.procbio.2011.12.024
- Christov, L. P., Akhtar, M., and Prior, B. A. (1998). "The potential of bisulfite pulping in dissolving pulp production," *Enzyme. Microb. Tech.* 23(1-2), 70-74. DOI: 10.1016/S0141-0229(98)00017-9
- Clark, J. H. (2007). "Green chemistry for the second generation biorefinery Sustainable chemical manufacturing based on biomass," J. Chem. Technol. Biot. 82(7), 603-609. DOI: 10.1002/jctb.1710
- Cruz, A., Lara, M. C. M., Miguel, J. T., Rama, A. M., and Molina, M. J. (2012). "Method for kraft cooking of lignocellulose material with low-sulphide alkaline dyes in the production of pulp with direct incorporation of dihydroxyanthracene disodium salt into the digester," Patent No. WO/2012/168513.
- Da Silva Morais, A. P., Sansígolo, C. A., and De Oliveira Neto, M. (2016). "Effects of autohydrolysis of *Eucalyptus urograndis* and *Eucalyptus grandis* on influence of chemical components and crystallinity index," *Bioresource Technol*. 214, 623-628. DOI: 10.1016/j.biortech.2016.04.124
- Dong, D., and Fricke, A. L. (1996). "Investigation of pulping effect on pulp yield and the lignin content of black liquor with a central composite kraft pulping design," *Holzforschung* 50(1), 75-84. DOI: 10.1515/hfsg.1996.50.1.75

- Duarte, G. V., Ramarao, B. V., Amidon, T. E., and Ferreira, P. T. (2010). "Properties of Eucalyptus globulus fiber after hot water extraction," in: XXI Encontro Nacional da Tecnicelpa/VI CIADICYP [XXI Tecnicelpa VI National Meeting VI Iberoamerican Congress on Pulp and Paper Research (CIADICYP 2010)], Lisbon, Portugal.
- Ferreira, P. J., Carvalho, M. G., Martins, A. A., and Figueiredo, M. M. (1998). "Efeito das variáveis de cozimento kraft na refinação de pastas de *E. globulus* nacional Avaliação das propriedades papeleiras [Effect of kraft cooking variables on the refining of *E. globulus* national pulps Evaluation of paper properties]," in: *Conferência Internacional de Engenharia Química 7 [International Conference on Chemical Engineering 7*], Lisboa, Portugal, pp. 353-360.
- Foelkel, C. E. B. (2009). "Propriedades papeleiras das árvores, madeiras e fibras celulósicas dos eucaliptos [Paper properties of eucalyptus trees, woods and cellulosic fibers]," Eucalyptus Online Book & Newsletter, (http://www.eucalyptus.com.br/eucaliptos/PT14\_PropPapeleiras.pdF), Accessed 18 March 2019.
- García, J. C., López, F., Pérez, A., Pelach, M. A., Mutjé, P., Barberá, L., and Colodette, J. L. (2010). "Initiating ECF bleaching sequences of eucalyptus kraft pulps with Z/D and Z/E stages," *Holzforschung* 64(1), 1-6. DOI: 10.1515/hf.2010.008
- García, M. T., García, J. C., Feria, M. J., Gómez, D. M., López, F., and Díaz, M. J. (2013). "Furfural production from *Eucalyptus globulus*: Optimizing by using neural fuzzy models," *Chem. Eng. J.* 221, 185-192. DOI: 10.1016/j.cej.2013.01.099
- Garrote, G., and Parajó, J. C. (2002). "Non-isothermal autohydrolysis of *Eucalyptus* wood," *Wood. Sci. Technol.* 36(2), 111–123. DOI: 10.1007/s00226-001-0132-2
- Hartler, N. (1997). "Present and future of kraft pulping," *Nord. Pulp. Paper. Res. J.* 12(2), 115-118. DOI: 10.3183/NPPRJ-1997-12-02-p115-118
- Hess, J. R., Wright, C. T., and Kenney, K. L. (2007). "Cellulosic biomass feedstocks and logistics for ethanol production," *Biofuel. Bioprod. Bior.* 1(3), 181-190. DOI: 10.1002/bbb.26
- Howard, R., and Bichard, W. (1992). "The basic effects of recycling on pulp properties," *Mater. Res. Soc. Symp. P.* 266, 195-214. DOI: 10.1557/PROC-266-195
- Jahan, M. S. (2009). "Studies on the effect of prehydrolysis and amine in cooking liquor on producing dissolving pulp from jute (*Corchorus capsularis*)," Wood. Sci. Technol. 43(3–4), 213-224. DOI: 10.1007/s00226-008-0213-6
- Kamm, B., and Kamm, M. (2007). "The concept of a biorefinery Production of platform chemicals and final products," *Chem. Eng. Technol.* 79, 592-603. DOI: 10.1002/cite.200700005
- Kamm, B., Schoenicke, P., and Kamm, M. (2009). "Biorefining of green biomass Technical and energetic considerations," *Clean-Soil Air Water* 37(1), 27–30. DOI: 10.1002/clen.200800122
- Karlsson, H. (2006). *Fibre Guide: Fibre Analysis and Process Applications in the Pulp and Paper Industry: A Handbook*, Lorentzen and Wettre, Sweden.
- Köhnke, T., and Gatenholm, P. (2007). "Modification of cellulose fibres by controlled xylan adsorption and its effect on softwood pulp properties," in: 14<sup>th</sup> International Symposium on Wood, Fibre and Pulping Chemistry, Durban, South Africa.
- Laine, J., and Hynynen, R. (1997). "The effect of surface chemical composition and charge on the fiber and paper properties of unbleached Kraft pulps," in: *Fundamental Research Symposium*, Volume 11, 2<sup>nd</sup> Edition, pp. 859-891, Cambridge, UK.

- Loaiza, J. M., López, F., García, M. T., Fernández, O., Díaz, M. J., and Garcia, J. C. (2016). "Selecting the pre-hydroloysis conditions for *Eucalyptus* wood in a fractional exploitation biorefining scheme," *J. Wood. Chem. Technol.* 36(3), 211-223. DOI: 10.1080/02773813.2015.1112402
- López, F., Alfaro, A., Caparrós, S., García, M. M., Pérez, A., and Garrote, G. (2008).
  "Aprovechamiento energético e integrado por fraccionamiento de biomasa lignocelulósica forestal y agroindustrial [Energy use and integrated by fractionation of lignocellulosic forest biomass and agroindustrial]," *CIDEU Newsletter* 5, 17–29.
- Martín-Sampedro, R., Revilla, E., Martín, J. A., Eugenio, M. E., and Villar, J. C. (2010). "Evaluation of steam explosion as a pretreatment prior to kraft pulping of Eucalyptus globulus wood," in: XXI Encontro Nacional da Tecnicelpa/VI CIADICYP [XXI Tecnicelpa VI National Meeting VI Iberoamerican Congress on Pulp and Paper Research (CIADICYP 2010)], Lisbon, Portugal.
- Mendes, C. V. T., Rocha, J. M. S., Sousa, G. D. A., and Carvalho, G. V. S. (2011). "Extraction of hemicelluloses prior to kraft cooking: A step for an integrated biorefinery in the pulp mill," *O Papel* 72(9), 79-83.
- Moreira, E. (2006). Efeito da Lixiviação Ácida de Cavacos de Eucalipto no Processo Kraft [Effect of Acid Leaching of Eucalyptus Chips in the Kraft Process], Dissertação de Mestrado [Master's Thesis], Universidade Federal de Viçosa, Viçosa, Brazil.
- Oliveira, R. C., and Sabioni, L. (2002). "Recuperação da qualidade de papéis de eucalipto no processo de reciclagem [Recovering the quality of eucalyptus paper in the recycling process]," *Rev. Árvore* 26(1), 107-119.
- Ragauskas, A. J., Williams, C. K., Davison, B. H., Britovsek, G., Cairney, J., Eckert, C. A., Frederick, Jr., W. J., Hallett, J. P., Leak, D. J., Liotta, C. L., *et al.* (2006). "The path forward for biofuels and biomaterials," *Science* 311(5760), 484-489. DOI: 10.1126/science.1114736
- Sanders, J. P. M., Annevelink, B., and Van Der Hoeven, D. (2009). "The development of biocommodities and the role of North West European ports in biomass chains," *Biofuel. Bioprod. Bior.* 3(3), 395-409. DOI: 10.1002/bbb.146
- Santos, S. R. (2005). Influência da Qualidade da Madeira de Híbridos de Eucalyptus grandis x Eucalyptus urophylla e do Processo Kraft de Polpação na Qualidade da Polpa Branqueada [Influence of the Wood Quality of Eucalyptus grandis Hybrids x Eucalyptus urophylla and the Kraft Pulping Process on the Quality of Bleached Pulp], Dissertação de Mestrado [Master's Thesis], Escola Superior de Agricultura "Luiz de Queiroz", USP, Piracicaba, São Paulo, Brazil.
- Saukkonen, E., Kautto, J., Rauvanto, I., and Backfolk, K. (2012). "Characteristics of prehydrolysis Kraft pulp fibers from Scots pine," *Holzforschung* 66(7), 801-808. DOI: 10.1515/hf-2011-0158
- SCAN-CM 40:94 (1993). "Size distribution," Scandinavian Pulp, Paper and Board Testing Committee, Stockholm, Sweden.
- Silva, R. P., and Oliveira, R. C. (2000). "Efeito da ação do refino e da reciclagem nas propriedades dos papéis de eucalipto e pinus [Effect of refining and recycling on the properties of eucalyptus and pine]," *Rev. Árvore* 24(3), 349-360.
- TAPPI T200 sp-01 (2002). "Laboratory beating of pulp (Valley beater method)," TAPPI Press, Atlanta, GA.
- TAPPI T204 cm-07 (2007). "Solvent extractives of wood and pulp," TAPPI Press, Atlanta, GA.

- TAPPI T205 sp-02 (2014). "Forming handsheets for physical test of pulp," TAPPI Press, Atlanta, GA.
- TAPPI T222 om-11 (2011). "Acid-insoluble lignin in wood and pulp," TAPPI Press, Atlanta, GA.
- TAPPI T230 om-99 (1999) "Viscosity of pulp (capillary viscometer method)," TAPPI Press, Atlanta, GA.
- TAPPI T236 cm-85 (1996). "Kappa number of pulp," TAPPI Press, Atlanta, GA.
- TAPPI T248 sp-08 (2008). "Laboratory beating of pulp (PFI mill method)," TAPPI Press, Atlanta, GA.
- TAPPI T249 cm-09 (2009). "Carbohydrate composition of extractive-free wood and wood pulp by gas-liquid chromatography," TAPPI Press, Atlanta, GA.
- TAPPI T257 cm-85 (1999). "Sampling and preparing wood for analysis," TAPPI Press, Atlanta, GA.
- TAPPI T264 cm-07 (2007). "Preparation of wood for chemical analysis," TAPPI Press, Atlanta, GA.
- Testova, L., Chong, S. L., Tenkanen, M., and Sixta, H. (2011). "Autohydrolysis of birch Wood," *Holzforschung* 65(4), 535-542. DOI: 10.1515/hf.2011.073
- Vila, C., Romero, J., Francisco, J. L., Garrote, G., and Parajó, J. C. (2011). "Extractive value from *Eucalyptus* wood before kraft pulping: Effects of hemicelluloses solubilization on pulp properties," *Bioresource Technol.* 102(8), 5251–5254. DOI: 10.1016/j.biortech.2011.02.002
- Vila, C., Romero, J., Francisco, J. L., Santos, V., and Parajó, J. C. (2012). "On the recovery of hemicellulose before kraft pulping," *BioResources* 7(3), 4179-4189. DOI: 10.15376/biores.7.3.4179-4189
- Villar, J. C. (2018). "Pastedo kraft," (http://www.inia.es/gcontrec/pub/6\_Kraft\_1227267134593.pps), Accessed 12 May 2018.
- Wallis, A., Wearne, R., and Wright, P. (1996). "Chemical analysis of polysaccharides in plantation eucalypt woods and pulps," *Appita J.* 49(1), 258-262.
- Warberg, L., and Annergren, G. (1997). "Physicochemical characterization of papermaking fibres," in: *The Fundamentals of Papermaking Materials*, C. F. Baker (ed.), Pira International, Cambridge, UK, pp. 1-82.
- Wise, L. E., Marphy, M. A., and Adieco, D. (1946). "Chlorite holocellulose, its fractionation and bearing on summative wood analysis and on studies on the hemicelluloses," *Paper Trade J.* 122(2), 35-46.
- Yahyazadeh, A. (2011). "Extraction and investigation of furfural in tea leaves and comparing with furfural in rice hull," *J. Pharmacol. Res.* 4(12), 4338-4339.

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