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Selecting The Pre-Hydrolysis Conditions For Eucalyptus Wood In A Fractional Exploitation Biorefining Scheme.

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ABSTRACT

The operating conditions for the autohydrolysis of eucalyptus wood were optimized with a view to maximizing hemicellulose extraction while preserving the integrity of glucan. The influence of the operating conditions used in the soda–anthraquinone pulping of the solid phase resulting from the autohydrolysis process was examined.

Autohydrolysis of the raw material at a liquid/solid ratio of 8 kg water/kg material at 180 ºC for 30 min was found to provide a commercially useful liquid phase containing most of the starting hemicellulose. The autohydrolysis treatment allowed the subsequent production of soda–anthraquinone cellulose pulp and paper with properties as good as or even better than those obtained without the pretreatment.

KEYWORDS

Autohydrolysis, *Eucalyptus globulus*, hemicelluloses, pulp, soda-AQ

INTRODUCTION

There is growing interest in the new processes for refining wood into cellulose, hemicellulose and lignin fractions while preserving their integrity as far as possible [1][2]. Autohydrolysis with water as the sole fractionating agent is an environmentally benign treatment that affords integral exploitation of raw materials. In fact, a mild autohydrolysis treatment efficiently converts the hemicellulose fraction of wood into a commercially valuable oligomer mixture of sugars [3-5]. Also, autohydrolysis of solid waste containing cellulose and lignin mainly affords further chemical or biotechnological transformation of the raw material with a view to obtaining a variety of marketable end-products [6] including pulp and paper.

On the other hand, in industrial production fields of paper and pulp is commonly accepted idea that the pre-extraction of pulp manufacture hemicelluloses, makes the mechanical properties of handsheets prepared with previous autohydrolysis/hot water extraction or exploded chips were slightly lower [7][8]. Fractionating wood with a preliminary hemicellulose extraction stage produces a considerably degraded solid fraction consisting largely of glucan that is useless for pulping and papermaking processes [9-11].

In studies focused on obtaining pulp and paper process is the most used Kraft. The “sulphate process” or “Kraft process” has been the predominant method for the production of pulp, due to its versatility in treating of different feedstocks, along with the high quality of the pulp and the efficient recovery of energy and chemical products. However, both the requirements for contamination control and the fact that it dissolves lignin with degraded polysaccharides can’t be recovered economically [12].

So, in the pulp and paper industry, there is much interest in develop on the concept of biorefinery, where wood is hydrolyzed prior to conventional pulping and papermaking processes and the hydrolyzate consisting of hemicellulose sugars are to be used as a feedstock for biofuels, bioplastics or other uses [13][14].

For example, in the work of Garrote et al. (2003)[15], hydrothermal processing eucalyptus wood is performed at operating temperature of 181°C, the processing time of 37.5 min and the solid water ratio

1/6 to ensure maximum recovery loss of xylan with minimum cellulose degradation fiber. Under these conditions, the loss of xylan was 22% lower than that achieved with the conditions of 196°C, 50.6 min and 1/8 solid/water ratio (these were the maximum extraction of xylan conditions).

In the work of Vila et al. (2011)[16], *Eucalyptus globulus*, wood samples were subjected to autohydrolysis extraction of hemicellulose, and the resulting solids were analyzed as substrates for kraft pulping and bleaching. At present, most pulp and paper are obtained via the kraft process, the typical conditions for which include 25% sulphidity, a 3.5 liquid/solid ratio, a temperature of 165 ºC, an operating time of 50 min and the amount of active alkali needed to obtain bleachable wood pulp and a solid residue after autohydrolysis. The hydrolysis pretreatment maximizes extraction of hemicellulose oligomers. Also, in the work of Martin-Sampedro et al. (2014) [17], hemicelluloses were extracted, either by steam explosion or by steam treatment, from *Eucalyptus globulus* wood prior to kraft pulping.

Previous studies showed the removal of hemicelluloses by autohydrolysis to allow handsheets with physical properties similar to or better than those obtained with no prior hydrolysis to be produced with the soda–anthraquinone pulping process. In work on other wood, whether it has come to corroborate the hypothesis that it is possible to make a pre-extraction of hemicellulose and get hand sheetsof physical properties comparable or even better than, those obtained in traditional soda-anthraquinone processes. In the works of García et al., (2011a) and (2011b)[18][19] with Paulownia wood, an experimental central composite design and multiple regressions were used to model the production of pulp and paper sheets of *fortune, tormentosa* and *elongate* trihybrid Paulownia clone. Also, the same experiments were carried out with the solid phase after autohydrolysis of the feedstock. The results were compared with those obtained from the solid phase remaining after autohydrolysis of the raw material in order to optimize the use of the hemicellulose and cellulose by fractionation. The solid phase obtained by autohydrolysis of Paulownia trihybridclone offers sheets of paper and cellulose, comparable in properties related to the resistance of pulp produced directly from the raw material, but using the operating conditions considerably milder and with the added advantage of the autohydrolysis treatment provides a highly recoverable liquor.

In the work with *Leucaena leucocephala* Feria et al., (2012)[20], the lignocellulosic material is subjected to a fractionation process in two steps to obtain a recoverable effluent containing derivatives of hemicellulose and a solid phase for the production of cellulose pulp, by conventional soda-anthraquinone delignification. This solid phase allows the production of cellulose pulp, under less stringent conditions of soda-anthraquinone process delignification without pretreatment and sheets of paper with better or similiar properties. Also, the first stage of autohydrolysis, allows up 46.6% of the initial hemicellulose in the feedstock to remove as xylooligomers, xylose and furfural in the liquid phase.

The primary aim of this work was to optimize the autohydrolysis conditions for eucalyptus wood with a view to maximizing extraction of hemicellulose while preserving the integrity of glucan. Secondly, this paper deals with the influence of the operating conditions used in the Soda-anthraquinone pulping of solid phase from *Eucalyptus globulus* wood autohydrolisys process (viz. soda concentration, temperature and pulping time) on the yield, kappa index, viscosity, glucan and xylan contents of the resulting pulp and tensile index of paper sheets in order to determine the best pulping conditions and compare with a conventional soda-anthraquinone pulping process.

MATERIALS AND METHODS

Characterization and storage of raw material

Eucaliptus globulus samples from local plantations (Huelva, Spain) were milled to pass an 8 mm screen, since in preliminary studies no diffusional limitations were observed by this particle, air-dried, homogenized in a single lot to avoid differences in compositions among aliquots, and stored. These experiments were made with widths of particle between 1 mm and 20 mm. There were not any problems of difussion of water or chemical reagent to the interior of the particle.

Aliquots of raw material were milled to particle size <0.5 mm and subjected to moisture and determination of extractable compounds (TAPPI T-264-om-88 and Tappi 204 cm-07), 1% NaOH soluble (Tappi 212 om-98) and to quantitative acid hydrolysis with 72% H_2SO_4 following standard methods (TAPPI T-249-em-85). The solid residue after hydrolysis was recovered by filtration and considered as Klason lignin. The compounds, glucose, xylose, arabinose and acetic acid contained in the hydrolysates were determined by HPLC. Ashes were determined by calcination (TAPPI 211 om-07). The methodology for characterization and storage of raw material is according with a previous work [25][*]

Autohydrolysis process. Pulping procedure and formation of paper sheets.

Wood chips and water were mixed in the desired proportions and reacted in a 10 L stainless steel MK-systems Inc. reactor fitted with recirculation. The operating conditions were temperature of 180ºC and operating time of 30 minutes, also, the heat-up time during autohydrolysis was 43 min and a liquid/solid ratio of 8 kg water/kg raw material. Then, the reactor was closed and simultaneously heated and actuated to assure good mixing and uniform swelling of eucalyptus chips. When the autohydrolysis time elapsed, the reactor was chilled to a temperature of 25ºC.

Cellulose pulps (from solid phase after autohydrolysis or without autohydrolysis) were obtained in the same reactor used for the hydrothermal pretreatment. Cellulose pulps were also obtained for raw materials without hydrothermal pretreatment. The reactor was then closed and simultaneously heated and actuated to assure good mixing and uniform swelling of eucalyptus chips. When the pulping time had elapsed, the reactor was chilled to a temperature of 25°C. 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, kappa number and viscosity, were determinate according to Tappi standard procedures 257, 236 and 230, respectively. Paper sheets were prepared with an ENJO-F-39.71 sheet machine according to the Tappi 205 sp-95 standard. From paper sheets, grammage (T 220 sp-96) and tensile index (Tappi 494 om-96) were determined.

Experimental design for pulping conditions. Multiple regresion model.

To be able to relate the dependent variables (yield, kappa index, viscosity, tensile index, glucan and xylan) with independent variables (NaOH concentration, temperature, and time of process) in pulping process with the minimum testing, a 2n central composite factor experimental design was used, making it possible to construct a second-order polynomial in the independent variables and the identification of statistical significance in the dependent variables. Independent variables were normalized by using the following equation,

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

where X is the absolute value of the independent variable of concern, $\overline{X}$ is the average value of the variable, and Xmax and Xmin are its maximum and minimum values, respectively. Three levels of alkali concentration (13, 17 and 21% dry wt basis), temperature (153, 163 and 173ºC) and operating time (65, 90 and 115 min) were used for the raw material without pretreatment (process NA). For the solid phase after the autohydrolysis process the following operating conditions were used: alkali concentration: 9, 13 and 17% dry wt basis, temperature: 143, 153 and 163ºC and operating time: 40, 65 and 90 min. A liquid/solid ratio of 8/1 and anthraquinone concentration of 0.1 (dry wt basis) were used in all experiments (process A).

The number of tests required was calculated as $N = 2^n + 2 \cdot n + n_C$; 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 fitted to the following second-order polynomial:

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

The independent variables used in the equations relating to both types of variables were those having a statistically significant coefficient (viz. those not exceeding a significance level of 0.05 in the student´s-test and having a 95% confidence interval excluding zero).

RESULTS AND DISCUSSION

Selection of operation conditions in autohydrolysis process and characteristics of the raw material

Our main working hypothesis was that pre-hydrolysis of the raw material allows handsheets with strength-related properties similar to those of conventional commercial paper to be obtained and a hemicellulose fraction extracted for additional exploitation, all under milder industrial operating conditions (viz., lower chemical loads and temperatures, and shorter processing times).

To this end, we used a biorefining scheme involving an autohydrolysis stage intended to extract a large portion of the hemicellulose faction and an alkaline delignification stage with a soda–anthraquinone mixture. Properly selecting the autohydrolysis conditions is crucial. Thus, using too strong conditions to extract hemicelluloses can result in excessive degradation of the main polysaccharide fraction (cellulose) and in an inadequate content in hemicellulose in the subsequently obtained cellulose pulp, both of which would detract from the quality of the paper end-product. On the other hand, too mild autohydrolysis conditions would provide a liquid fraction containing little hemicellulose for commercial use.

It is therefore very important to use appropriate operating conditions in the autohydrolysis stage of a biorefining scheme. In this work, we used a liquid/solid ratio of 8 kg water/kg raw material, a temperature of 180 ºC and an operating time of 30 min. These operating conditions for the autohydrolysis of *Eucalyptus globulus* wood were chosen from previous results of Garrote et al. (2003)[15]. These authors used an experimental design to examine the influence of process variables in the delignification of pre-hydrolysed eucalyptus wood with ethanol. The delignification conditions were as follows: an ethanol concentration of 40–70 wt%, a temperature of 145–175 ºC and a pulping time of 40–120 min. The resulting pulp yield, kappa number and viscosity were 56.8–76.9%, 53.5–100.7 and 350–741 ml g^{-1}, respectively, and comparable to those obtained by other authors [21][22] using higher temperatures (170–200 ºC), namely: 50.6–77.4% pulp yield, 7.5–91.6 kappa number and 420–1026 ml g^{-1} viscosity. The pre-hydrolysis treatment involved a liquid/solid ratio of 6/1–8/1, a temperature of 181–205 ºC —which was assumed to maximize extraction of xylose and xylo-oligomers into the liquid phase [15][23] and an operating time of 37.5–50.6 min and liquid/solid ratio between 6/1 and 8/1.

Vila et al., (2011)[16] subjected *E. globulus* wood samples to autohydrolysis extraction of hemicellulose, and the resulting solids were analyzed as substrates for kraft pulping and bleaching. In this work, the physical properties of the paper sheets reduce their rate, in one important respect, to the results of sheets of paper from wood without prior autohydrolysis. The viscosity loss caused by autohydrolysis appears as the main challenge to be addressed in the autohydrolysis-kraft delignification of eucalyptus wood. The pulp obtained from wood showed viscosities (in the range of 1468-1345 ml g^{-1}) significantly higher than those from solid residue after autohydrolysis transformation (1042-1013 ml g^{-1}). Also, in the work of Martin-Sampedro et al. (2014)[17] hemicelluloses were extracted, either by steam explosion or by steam treatment, from *Eucalyptus globulus* wood prior to kraft pulping. Results showed a similar degree of hemicelluloses extraction with both options (32-67% of pentosans), which increased with the severity of the conditions applied. Although both pre-treatments increased delignification during pulping: 12.9 kappa number for steam explosion, 22.6 kappa number for steam unexploded pulps and 40.7 kappa number for control pulps. Similar reductions in paper strength were found regardless of the type of treatment and conditions assayed, which is attributed to the increase of curled and kinked fibers.

The above-described studies have been supplemented by experiments intended to identify the most effective operating ranges for the target variables in the autohydrolysis treatment preceding delignification with a soda–anthraquinone mixture. We chose to assess stronger autohydrolysis conditions than those previously examined (particularly temperatures above 200 ºC even though they are supposed to result in increased depolymerization of polysaccharides [18][24]. One experiment involved the non-isothermal autohydrolysis of *E. globulus* wood at 180–240 ºC for times from 0 min, using a liquid/solid ratio of 8 g/g —where the greatest relative increase in xylo-oligomer concentrations was obtained at 200–220 ºC- .The greatest amounts of monomers and degradation products relative to glucose monomer (0.14 g L^{-1} glucose) were obtained at 240 ºC and the smallest at 180 ºC. The contents in the second major sugar, xylose, peaked at 220 ºC (6.47 g L^{-1} xylose) and they were minimal at 180 ºC. Obviously, the commercial value of the solid phase decreased with increasing temperature, particularly from 220 to 240 ºC as the likely result of excessive degradation of hemicelluloses into xylose and arabinose. Although this justifies using milder autohydrolysis conditions [15-17]. The temperatures used over the range 220–250 ºC in combination with operating times of 0–60 min and a liquid/solid ratio of 8 g/g. The greatest relative increase in the concentrations of xylo-oligomers and derivatives occurred at 220–235 ºC. Also, the amounts of sugars increased with increasing temperature, with monomers (glucose, xylose and arabinose) peaking at 8.87 g L^{-1} after 0 min at 220 ºC. Glucan was extracted maximally (1.51 g L^{-1}) after 0 min at 225 ºC and minimally (0 g L^{-1}) after 30 min at 220 ºC. Similarly, xylan extraction peaked after 30 min at 220 ºC and it was minimal after 60 min at 220 ºC. The value of the solid phase decreased with increasing temperature. In fact, yield peaked at low temperatures and short times, and was lowest at high temperatures irrespective of processing time (results not shown). Based on the above-described results, optimum extraction of hemicelluloses from *E. globulus* wood by isothermal autohydrolysis requires using a low temperature (220 ºC) and a medium operating time (30 min).

In any case, from the results of the isothermal and non-isothermal autohydrolysis of *E. globulus* wood at 180–250 ºC it follows that, even though high temperatures lead to increased yields, they result in considerable degradation of hemicelluloses not only to xylose but also to other products such as furfural; in addition, it causes increased degradation of the glucan main fraction, which is undesirable with a view to obtaining handsheets of adequate strength. It is therefore preferable to adopt a lower temperature such as 180 ºC for an operating time such as 30 min, which were selected for use in this work.

On the other hand, table 1 summarizes the chemical properties of E. globulus wood as determined in this work and elsewhere [25-30]. Its major fraction was that of cellulose (analyzed as glucan according to TAPPI T 203-om-93), which accounted for 42.8% or 41.0%, 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%. This composition is similar to others previously reported by [26][29]. Based on it, *Eucalyptus globulus* can be a suitable raw material for industrial production of hemicellulosic sugars, pulp and paper. For example, the liquid phase from the autohydrolysis process could be used to obtain furfural, which requires a minimum content inpentosans of 15–20% [31].

Chemical and physical characteristics of the cellulose pulp and paper sheets

The operational conditions were stablished by performing a literature review and additional experiments. Tables 2 and 3 show the normalized values of the independent variables and summarize the properties of the pulp and paper sheets obtained by using the proposed experimental designs with and without autohydrolysis (processes A and NA). Each experimental value was the average of five results for pulp properties or twelve for tensile index. Deviations from the respective means were all less than 5%.

The yields of soda–anthraquinone pulping of *Eucalyptus globulus* wood in A and NA processes were comparable if one considers that the autohydrolysed raw material was subjected to two chemical processes in order to remove lignocellulosic components. In fact, kappa numbers were very similar; thus, they ranged from 32.9 to 76.7 for NA pulp and from 33.2 to 87.9 for A pulp. These are moderate kappa values taking into account that the raw material has gone through two chemical separation processes of lignocellulosic components.

The intrinsic viscosity was generally higher in the autohydrolysis process (A) with values comprised between 575.6 cm^3 g to 926.1 cm^3 g. These viscosity values are relatively high, taking into account the raw material has subjected to separating two chemistries lignocellulosic components, while for the NA process was 485.6 cm^3 g to 769.2 cm^3 g.

The tensile index was higher for A process with ranges between 14.2 N m g^{-1} to 22.8 N m g^{-1}, being relatively good resistance values taking into account that the raw material has gone through two chemical separation processes of lignocellulosic components while with NA process was 6.5 N m g^{-1} to 17.5 N m g^{-1}. On the other hand, and compared to current commercial tensile index values paper are relatively low results for the two processes, but they note that it is not properly paper commercial properties where pulps from various sources and additives are mixed and besides, it is a cellulose pulp that has not been subjected to refining process. It is expected that a suitable refined pulp raise substantially the results shown.

Finally measurements of glucan and xylan in the solid material were much lower for the A process with 30.3% to 80.4% and 0% respectively, while for NA for glucan were recorded ranges between 38.4% to 85.2% glucan and 5.1% to 10.8% xylan.

Substituting the values of the independent variables for each dependent variable in Tables 2 and 3 into the previous polynomial expression yielded the equations of Table 4. All polynomial models thus obtained exhibited good overall fitting, 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 estimated by using the proposed equations never exceeded 10% of the former. As can be seen from Table 4, the concentration of active alkali emerged as the independent variable most strongly influencing development of kappa index and tensile index, with autohydrolysis, however, the tensile index was more markedly affected by the operation time than by the active alkali concentration. In any case, the temperature was the most influential variable on performance of the resulting cellulose pulp. Temperature was the variable that most affects performance, kappa index and the intrinsic viscosity of NA process (equations (1), (2) and (3) in Table 4). On the other hand, time processing and, to a lesser extent, temperature, were the two variables that most significantly affect the tensile index of the paper sheets.

In order to better envisage the influence of the operational variables on pulp and paper properties, and to compare the pulp and paper sheets directly obtained from the raw material (NA process) and the solid phase without autohydrolysis (A process), we constructed the hyperspaces of variation of the dependent variables via the response surfaces of Figs 1–6. The space between two response surfaces represents the whole range of values for each dependent variable —we used two extreme values, +1 and –1, for the most influential variable in each case. A combined plot of the results for the NA and A pulping processes revealed marked overlap between spaces and allowed us to identify the specific operating conditions affording production of cellulose pulp or paper with a given value of some property from the raw material (NA) or authoydrolysed solid phase (A).

Obviously, a better value of intrinsic viscosity and tensile index signifies better properties of paper sheets. Also, low values of kappa index facilitate the bleaching of pulp. And a high rate glucan and xylan in delignification process can contribute to increase the yield of the pulping process.

Overall, soda–anthraquinone delignification of *Eucalyptus globulus* with prior autohydrolysis (A) resulted in better paper properties (tensile index and kappa index). Also, yield exhibited wide ranges of overlap for the dependent variables where the pulping conditions required for the solid phase from autohydrolysis were much milder than those for the original material. The economy inherent in using a lower temperature, time or alkali concentration is thus supplemented by the obtainment of a highly valorizable liquor containing abundant sugars and oligomers [18].

The extraction of hemicelluloses has traditionally been assumed to have an adverse impact on the properties of cellulose pulp and paper obtained from the post-hydrolysis solid fraction. Such was the case with experiments on pine [32] , eucalyptus [16][33] and birch wood [34] , among other raw materials, subjected to various autohydrolysis treatments including steam treatment or steam explosion. The autohydrolysis conditions used were intended to maximize extraction of hemicelluloses for subsequent conventional pulping of the solid phase. Based on our results, however, autohydrolysis may not lead to degradation in pulp or paper properties.

Based on its response surface (figure 1), yield was the only property where the untreated raw material exceed the autohydrolyzed material—an obvious result of the latter being subject to a double fractionation process. However, the yields for processes A and NA were similar. Thus, the yield for A at an active alkali concentration of 13%, a temperature of 143 ºC and a time of 65 min was 67.2% (see eq. 1 in Table 4). Obtaining a similar yield with no autohydrolysis (NA) required using an active alkali concentration of 21.0%, a temperature of 153 ºC and a time of 115 min (i.e., a 65.5% higher concentration of alkali in addition to a higher temperature and longer operating time).

Based on the response surfaces for kappa number (figure 2), there is significant overlap at high active alkali concentrations (21% for direct delignification of the raw material and 17% with prior autohydrolysis). As can be seen from figure 2, delignification was more efficient with a previous autohydrolysis (A) step; in fact, kappa index was greater with delignification in a single step. Overall, our results are better than those obtained by Garrote et al. (2003) [15] in the autohydrolysis – organosolv delignification of Eucalyptus wood (kappa number 53.5–100.7 N m² kg^{-1}). These results are especially interesting as they suggest that autohydrolysis facilitates subsequent delignification of eucalyptus wood. Thus, the pretreatment leads to better kappa numbers with milder active alkali, temperature and time conditions.

Figure 3 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 N•m•g^{-1} even with prior autohydrolysis for a 90 min cooking time, a 9% active alkali concentration, and a pulping temperature of 163 °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 (6) and (11) in Table 4, a tensile index of ca. 20.0 N•m•g^{-1} in the A process can be obtained by using an active alkali concentration of 13%, a pulping temperature of 143 °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 Martin-Sampedro et al. (2014)[17] for unrefined eucalyptus kraft pulp obtained after hydrothermal steaming or steam explosion (i.e., 8 to16 N•m•g–1 autohydrolysis versus 21 N•m•g^{-1} control).

The tensile index results are consistent with the intrinsic viscosity results (see Fig. 4). As can be seen, the viscosity peaked above 900 mL g^{-1} at high active alkali concentrations and either end of the operating time range with A. Alkali concentrations in the lower end of the operating range still led to higher viscosity values at 163 ºC than the NA process at higher temperatures (173 ºC).

Pulping after autohydrolysis (A) led to decrease glucan contents and the absence of xylan by effect of most of the latter being removed by the pretreatment and the remainder during pulping. The solid phase obtained in the absence of autohydrolysis (NA) contained some residual xylan.

CONCLUSIONS

Autohydrolysis of *E. globulus* wood allows a liquid phase containing most hemicelluloses in the raw material to be extracted for subsequent pulping at a liquid/solid ratio of 8 kg water/kg raw material, a temperature of 180 ºC and a time of 30 min. The autohydrolysis pretreatment affords production of soda–anthraquinone pulp and paper with at least as good or even better properties (kappa index, intrinsic viscosity, glucan and xylan contents, tensile index) than those obtained in its absence, all by using less aggressive operating conditions (active alkali concentration, temperature and time).

Also, autohydrolysis allows pulp to be obtained in similar yields by using milder operating conditions. The savings inherent in using a lower temperature, time or alkali concentration are thus supplemented by the obtainment of a highly valorizable liquor containing abundant sugars and oligomers.

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Caption Figures

Figure 1 .Scheme of realized works

Figure 2. Variation of yield as a function of Xc: alkali concentration and Xt: operation time at two pulping temperature levels.

Figure 3. Variation of klason lignin as a function of alkali concentration (XC) and pulping temperature (XT) at two time operation levels.

Figure 4. Variation of intrinsic viscosity as a function of alkali concentration (XC) and time operation (Xt) at two pulping temperature levels.

Figure 5. Variation of α-cellulose as a function of alkali concentration (XC) and time operation (Xt) at two pulping temperature levels.

Figure 6. Variation of tensile index as a function of alkali concentration (XC) and time operation (Xt) at two pulping temperature levels.

Figure 7. Variation of burst index as a function of alkali concentration (XC) and time operation (Xt) at two pulping temperature levels.

Tables

Table 1: Average chemical composition for *Eucalyptus globulus* used and other bibliographic *Eucalyptus globulus* composition[1]. [1] Raw material percentages (100 kg dry matter).

	Eucalyptus globulus					
	Present study [25][*]	**Garrote and Parajó, 2002** [26]	**López et al., 2008** [27]	**Lezchynsky et al., 2009** [28]	**Rencoret et al., 2011** [29]	**Miranda et al., 2013** [30]
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**	**10.1**	**nd**	**nd**	**nd**	**nd**

Table 2. Normalized values of independent variables (*XA*: alkali concentration, *Xt* and *XT* : time and temperature of operation, respectively), chemical characterization of pulps and tensile index values of paper sheets obtained in the pulping process using the proposed experimental design. Pulping process with autohydrolysis (CA)

XT	Xt	XA	Yield (%)	Kappa Number	Viscosity (cm^3 g^{-1})	Tensile Index (Nm g^{-1}) [25][*]	Glucan	Xylan
0	0	0	55,1	69,2	737,1	18,0	39,6	0
0	0	0	56,6	67,8	755,3	18,1	38,8	0
-1	-1	-1	64,4	65,1	584,4	15,7	46,7	0
-1	-1	1	55,9	62,8	894,7	22,8	53,4	0
-1	0	0	67,2	76,2	633,9	16,7	30,3	0
-1	1	-1	64,3	87,9	575,6	11,3	33,5	0
-1	1	1	63,3	54,3	903,4	21,0	37,8	0
0	-1	0	58,7	77,5	816,4	18,2	48,7	0
0	0	-1	50,9	44,7	616,2	16,8	34,0	0
0	0	1	45,3	33,2	823,2	19,4	60,8	0
0	1	0	52,9	86,4	798,9	15,4	53,7	0
1	-1	-1	52,9	64,5	856,2	23,3	31,9	0
1	-1	1	45,1	75,9	909,1	14,2	68,2	0
1	0	0	51,9	83,9	792,2	16,6	40,5	0
1	1	-1	42,5	84,7	882,3	17,5	56,5	0
1	1	1	43,4	39,1	926,1	16,1	80,4	0

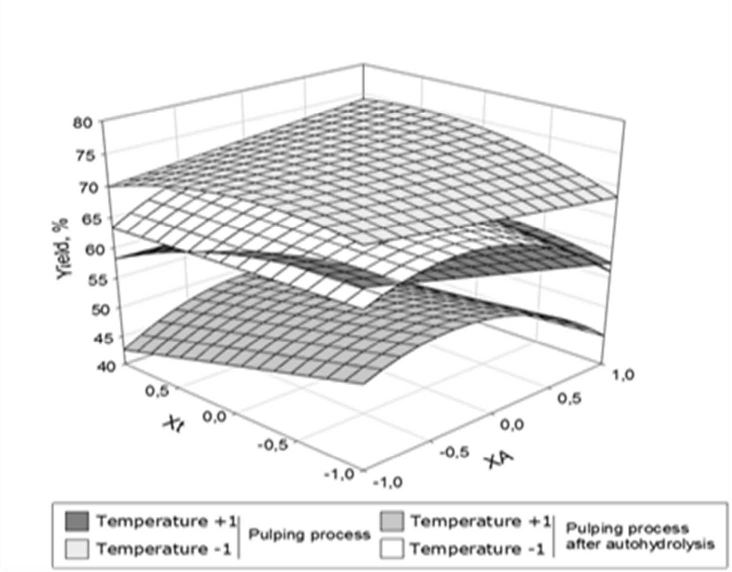
Table 3. Normalized values of independent variables (*XA*: alkali concentration, *Xt* and *XT* : time and temperature of operation, respectively), chemical characterization of pulps and physical properties of paper sheets obtained in the pulping process using the proposed experimental design. Pulping process without autohydrolysis (SA)

XT	Xt	XA	Yield (%)	Kappa Number	Viscosity ($cm^3 g^{-1}$)	Tensile Index ($Nm g^{-1}$) [25][*]	Glucan	Xylan
0	0	0	68,7	64,4	638,2	12,0	44,9	6,3
0	0	0	69,0	64,0	638,2	12,1	43,1	6,3
-1	-1	-1	73,3	65,4	568,4	17,5	49,3	10,8
-1	-1	1	69,1	60,4	723,2	6,5	54,7	8,7
-1	0	0	72,9	68,7	586,4	9,1	44,9	8,4
-1	1	-1	70,2	76,7	485,6	16,8	41,7	6,5
-1	1	1	73,7	51,9	760,3	7,0	41,8	6,6
0	-1	0	66,3	67,5	593,8	13,1	49,9	7,2
0	0	-1	70,6	67,4	579,3	11,4	38,4	5,1
0	0	1	66,9	45,2	742,9	7,0	50,5	5,9
0	1	0	65,3	65,8	624,5	15,3	50,8	5,7
1	-1	-1	68,1	71,6	697,6	8,1	50,8	8,4
1	-1	1	57,1	58,7	746,5	7,0	77,4	9,1
1	0	0	62,8	68,6	649,4	10,1	64,3	8,9
1	1	-1	57,4	74,3	634,2	14,7	68,2	6,6
1	1	1	57,6	32,9	769,2	15,7	85,2	8,4

Table 4. Equations obtained for each dependent variable of pulping process after autohydrolysis process. Dependent variables: *Yi*: yield (%); *KN*: kappa number; *Vis*: viscosity (cm3 g^{-1});TI: tensile index (Nm g^{-1}),; X: Xylan; Gl: Glucan. Independent Variables: *XA*: alkali concentration, *Xt* and *XT* : time and temperature of operation, respectively. The differences between the experimental values and those estimated using the equations never exceeded 10% of the former

Equation	**r²**	**F-Snedecor**	**Equation Nº**
Pulping process			
$Yi = 68.51 - 5.63 X_T - 0.94 X_t - 1.53 X_A - 2.70 X_t^2 - 1.47 X_TX_t - 1.24 X_TX_A + 2.36 X_tX_A$	0,98	68	**1**
$KN = 65.06 - 2.21X_t - 10.63 X_A + 4.30 X_T^2 - 8.04 X_A^2 - 3.22 X_TX_t - 3.07 X_TX_A - 6.05 X_tX_A$	0,96	35	**2**
$Vis = 621.77 + 37.30 X_T + 77.71 X_A + 48.97 X_A^2 - 30.69 X_TX_A + 25.75 X_tX_A$	0,99	240	**3**
$Glu = 44.64 + 11.37 X_T + 6.13 X_A + 9.23 X_T^2 +4.98 X_t^2 + 5.69 X_TX_t + 4.74 X_TX_A$			**4**
$X=6,36 -1,02X_A +2,46X_AX_A – 0,71X_tX_t +0,49X_TX_T +0,53X_tX_A +0,41X_TX_t$	0,95	50	**5**
$TI = 11.30 + 1.73 X_t - 2.53 X_A - 1.31 X_T^2 + 3.29 X_t^2 - 1.71 X_A^2 +1.9 X_TX_t+2.58 X_TX_A$	0,94	43	**6**
Pulping process after autohydrolysis			
$Yi_{Aut} = 55.44 – 7.94 X_T – 2.21 X_A – 1.05 X_t – 6.55 X_A^2 +4.89$	0,98	68	**7**
$KN_{Aut} = 67.7 – 8.17 X_A – 28.39 X_A^2 + 14.64 X_t^2 +12.76 X_T^2 – 11.02 X_tX_A – 3.86 X_TX_t$	0,96	35	**8**
$Vis_{Aut} = 726.32 + 77.39 X_T + 94.17 X_A + 88.41 X_t^2 – 67.66 \mathbf{X_TX_A}$	0,99	240	**9**
$Gl_{Aut} = 40.49 + 7.58 X_T + 9.78 X_A - 5.66 X_T^2 + 10.09 X_t^2 + 6.32 X_A^2 + 8.19 X_TX_t + 6.15 X_TX_A$			**10**
$TI_{Aut} = 17.60 – 1.29 X_t + 0.88 X_A – 3.41 X_TX_A + 1.29 X_tX_A$	0,94	43	**11**

Figure 1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Xt
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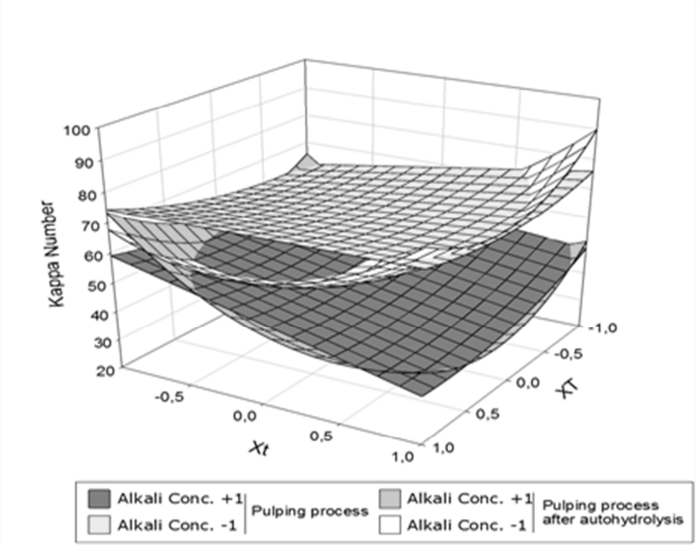
-0,5
0,0
0,5
1,0
XA
▩ Temperature +1
☐ Temperature -1
Pulping process
▨ Temperature +1
☐ Temperature -1
Pulping process after autohydrolysis

Figure 2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20
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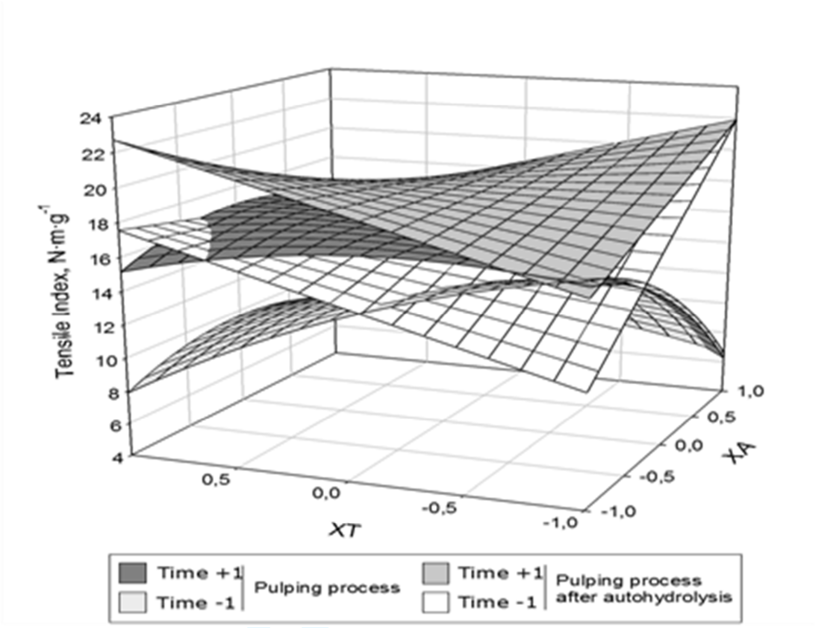
0,0
0,5
1,0
XT
Alkali Conc. +1
Alkali Conc. -1
Pulping process
Alkali Conc. +1
Alkali Conc. -1
Pulping process after autohydrolysis

Figure 3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6
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-1,0
XT
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0,5
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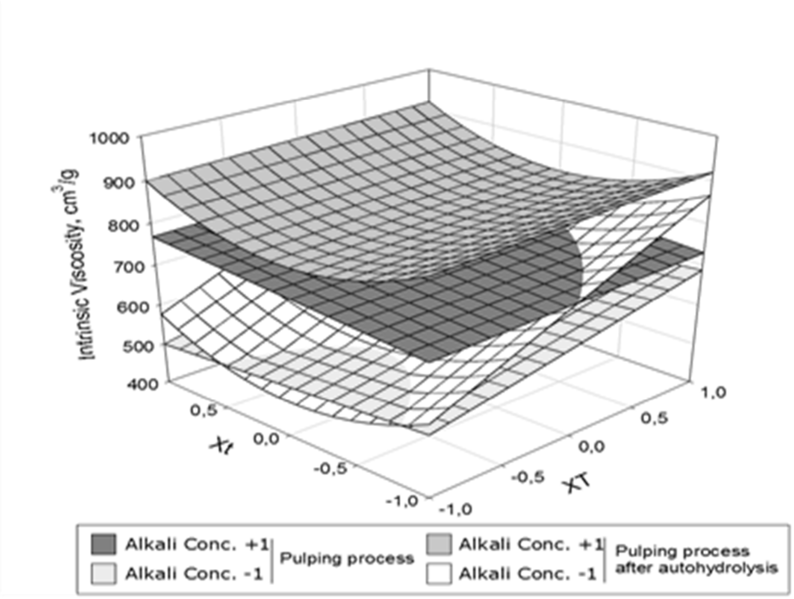
XA
Time +1
Time -1
Pulping process
Time +1
Time -1
Pulping process after autohydrolysis

Figure 4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XT
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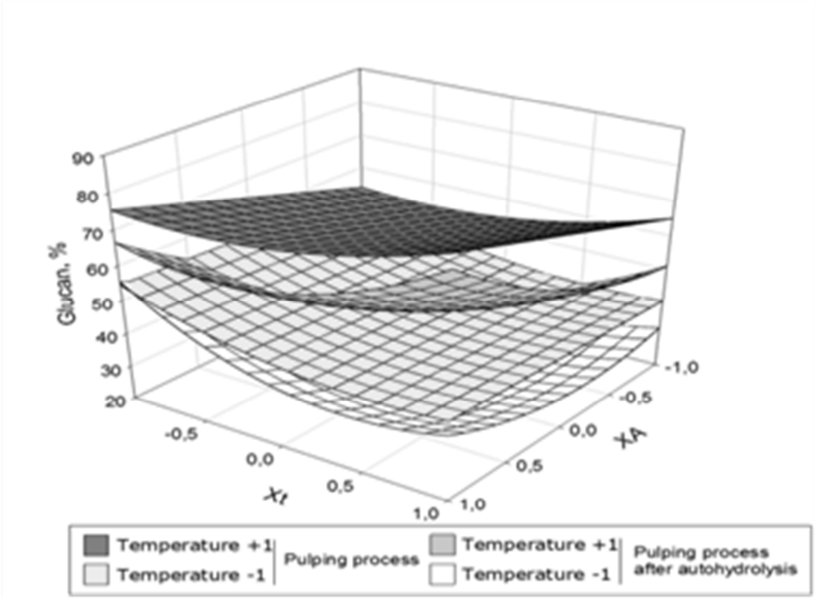
0,0
0,5
1,0
▩ Alkali Conc. +1
☐ Alkali Conc. -1
Pulping process
▨ Alkali Conc. +1
☐ Alkali Conc. -1
Pulping process after autohydrolysis

Figure 5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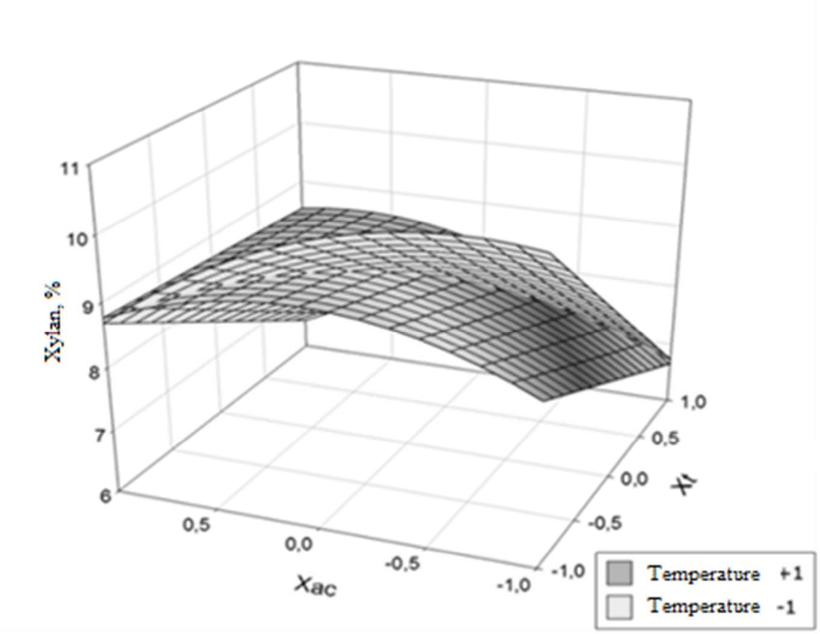
Temperature -1
Pulping process
Temperature +1
Temperature -1
Pulping process after autohydrolysis

Figure 6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Xt
Temperature +1
Temperature -1