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SODA-AQ PULPING OF *PAULOWNIA* WOOD AFTER HYDROLYSIS TREATMENT

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A trihybrid clone of *Paulownia fortunei x tormentosa x elongata* was used for pulp and paper production using the soda-anthraquinone (AQ) process, comparing the results with those from *Paulownia fortunei*. An autohydrolysis process had been previously carried out on this raw material. A composite central experimental design and a multiple regression were used for modeling and optimizing the process. A valuable liquid phase could be obtained from the autohydrolysis process of *Paulownia*, trying to minimize cellulose degradation for pulp and paper production. A compromise to maximize the glucan and minimize the xylan contents in the postautohydrolysis solid phase could be achieved at 187.5ºC and 15 minutes. A suitable cellulosic pulp with kappa number ranging from 12.2 to 69.2 and ISO brightness from 18.2 to 30.6% presented better results than those from other studies. Regarding handsheets physical properties (tensile index 37.3 N·m/g) and viscosity (848 cm^3/g), significant improvements could be obtained when compared with previous results of a similar process using *Paulownia fortunei* or *Paulownia elongata*.

Keywords: Paulownia; Autohydrolysis; Soda-AQ pulp; Paper; Biorefinery

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INTRODUCTION

Hemicellulose, the second most common polysaccharide in nature, constitutes approximately 20 to 35% of lignocellulosic biomass. Effective utilization of biomass, hitherto underutilized, is gaining tremendous importance for the production of energy, fuels, cellulosic pulp, paper, and chemicals (Lee et al. 2008). Hemicelluloses, such as xylans, have been acid-hydrolyzed to xylose, which subsequently is cyclodehydrated to produce furfural. Furfural is the key derivative of xylose with a broad spectrum of industrial applications. About 250,000 tons of furfural, probably the only unsaturated, large volume, organic chemical, are prepared from carbohydrate sources annually (McKillip 2000; Zeittsch 2000).

Before the hemicellulose fraction of wood can be used as a substrate for the production of chemicals, it must be pre-treated to separate it from the confines of the exterior lignin wrapper and the cellulose component interspersed in the cellulose framework (Wyman, 2003). The lignocellulosic biomass must be pre-treated under optimal conditions (such operation time and temperature) to minimize the degradation of

xylose and glucan or glucose into undesirable products. Hemicellulose is reported to be more easily hydrolyzable than cellulose (glucan) fractions (Lee 2008).

Autohydrolysis, a process that treats lignocellulosic materials in a chemical-free, water-only media, provides a simple, low-cost, and environmental friendly pretreatment technology (Garrote et al. 2004; Tan et al. 2008) to obtain hemicelluloses. This process has recently been evaluated for the autohydrolysis of two woody legumes species (Alfaro et al. 2009), *Paulownia fortunei* (Caparrós et al. 2007a and 2008) and *Miscanthus x giganteus* (El Hage et al. 2010) prior to a subsequent organosolv pulping or organosolv delignification.

However, conditions known to promote lignin depolymerization also cause degradation of hemicelluloses and celluloses sugars into furfural, 5-OH-methylfurfural, and carboxilic acid (Thomsen, et al. 2009). To circumvent this drawback, two-stage pretreatments are generally considered to be the best option: a first step is performed at low severity to hydrolyse the hemicelluloses, and the second step, where the solid material from the first step is treated again, at higher severity. It has been demonstrated that, after autohydrolysis, alkaline pulping (kraft process) of hardwood is accelerated, and solubility of lignin in a subsequent extraction with aqueous alkali or organic solvent is increased (Sixta 2006).

The *Paulownia* genus has attracted considerable attention as a dedicated energy crop. Because it has modest water requirements, *Paulownia* has aroused interest as an industrial raw material, despite its difficult growth in marginal areas (Jiménez et al. 2005; Olson and Carpenter 1985). The genus encompasses nine different species, most of which exhibit very fast growth, such that it can be harvested after only 15 years planting to obtain products with a substantial added value (Kalaycioglu et al. 2005). *Paulownia* plants possess a high biomass production and resprouting potential: up to 50 tons/ha/yr, which is among the highest reported figures (especially in relation to annual crops (Sánchez 2003). Also, they exhibit fast growth and can produce as much biomass in one year as several other species (Chirko et al. 1996). Under favourable conditions, an intensive plantation of 2000 trees/ha can yield up to 150 to 300 tons of wood per year only 5 to 7 years after planting (Chirko 1993). As shown in this work, such a high biomass production can be further increased by using hybrids of some varieties. Thus, the *Paulownia fortunei–Paulownia tormentosa* clone used by Ayan et al. (2006) grew up to 76.2 cm within one year after direct seeding.

The genus *Paulownia* has lately been introduced and naturalized in a number of countries including the USA, and been a subject of study as regards adaptation to soil and survival of diverse varieties in some areas (Bergmann 2003; Johnson et al. 2003; Ayan et al. 2006).

There have been few references to industrial uses of *Paulownia*. There are, however, a number of agronomic, genetic, and health-related studies about this genus. Worth special note among them are those suggesting the potential advantages of its use in energy crops by virtue of its favourable energy input/output ratio and biomass production (Lu 2006; Wang, and Shogren 1992). Other suggested uses for *Paulownia* included veneer or plywood, furniture, handicrafts, tools, musical instruments, particleboard, and charcoal, and there also have been various attempts to generate energy from *Paulownia* chips (Curley 1993; Ede et al. 1997; Kalaycioglu et al. 2005; Cheng 1983a-c). One of

them is its use as a source for pulp. The most suitable variety of *Paulownia* for this purpose is *Paulownia fortunei* (Rai et al. 2000), characterized by a fast development and a uniform and regular growth (Curley 1993). Also, this plant could be susceptible to produce xylo-oligomers under a hydrolytic process, as well as provide a low degraded lignocellulosic residue to the pulping process, which is justified by some *Paulownia* characteristics, such as its growth and physicochemical properties (Caparrós et al. 2007a; 2008).

In this work, a tri-hybrid clone of *Paulownia fortunei x tormentosa x elongata* was used for pulp production and papermaking by use a soda-anthraquinone (AQ) process and compared with results from *Paulownia fortunei*. Previously, an autohydrolysis process was carried out on the raw material. A composite central experimental design and a multiple regression were used for modeling and optimizing the process.

EXPERIMENTAL

Raw Material: Provision and Characterization

A trihybrid variety of *Paulownia elongata x fortunei x tormentosa* clone obtained by in vitro replication was used for field experients. The material was harvested after three years of growth in plantations used to exploit biomass crops in Extremadura (southwestern Spain). The material was supplied by the firm Vicedex Europa. *Paulownia* wood trimming samples were milled to pass a 5-mm screen, because no diffusional limitations were observed for this particle size in the preliminary studies. Samples were air-dried, homogenized in a single lot (to avoid differences in composition among aliquots), and stored in a dry site.

Aliquots from the homogenized wood (without compounds extractives ethanol) were subjected to moisture determination (drying at 105 ºC to constant weight), quantitative acid hydrolysis with 5 mL of 72% sulfuric acid for an hour (TAPPI T 222 om-02 "Acid-insoluble lignin in wood"), and quantitative posthydrolysis with 4% sulfuric acid at 121 ºC and 2 atm during 60 min in order to ensure quantitative conversion of oligomers into monomers (Garrote et al. 2003).

Before High-performance liquid chromatography (HPLC) analysis, the solid residue from posthydrolysis was recovered by filtration and considered as Klason lignin. The monosaccharides and acetic acid contained in hydrolysates were determined by HPLC in order to estimate (after corrections for stoichiometry and sugar decomposition) the contents in cellulose (as glucan), hemicelluloses (xylan + araban), and acetyl groups. Chromatographic determination was performed using an Agilent 1100 HPLC equipped with an ion-exchange resin BioRad Aminex HPX-87H column under the following conditions: mobile phase, $0.005 \ mol \cdot L^{-1}$ of sulphuric acid; flow rate, $0.6 \ mL \cdot min^{-1}$; and column temperature, 50°C. The volume injected was 20 μL. The holocellulose was determined according the method of Wise et al. (1946).

Experimental Design for Autohydrolysis Process, Monosaccharides and Oligosaccharides Determination

Wood chips and water were mixed in the desired proportions and reacted in a 2 L stainless steel Parr reactor fitted with double four-blade turbine impellers. The vessels were heated up to maximum temperatures with external electric heaters. Process temperature was automatically controlled via an internal cooling coil equipped with circuit-opening electrovalves, which was used to cool the reactor after the highest temperature and operating time were reached.

At the end of treatment, the solid residue was recovered by filtration and washed with distilled water for gravimetric yield determination. An aliquot of liquors was filtered through 0.45 µm membranes and used for direct HPLC determination of monosaccharides and acetic acid. A second aliquot of liquors (25 mL) was subjected to quantitative posthydrolysis (with 4% sulfuric acid at 121 ºC and 2 atm during 60 min) before HPLC analysis. Operating conditions in the HPLC are described in previous section for raw material. The increase in the concentrations of monosaccharides and acetic acid caused by posthydrolysis measured the concentrations of oligomers and acetyl groups bound to oligosaccharides (García et al. 2010).

To be able to relate the dependent (glucose, xilose, arabinose, and acetyl groups contents) and independent (temperature and time of process) variables in autohydrolysis 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,

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

where X is the absolute value of the independent variable of concern, $\overline{X}$ is the average value of the variable, and X_{max} and X_{min} are its maximum and minimum values, respectively. Three levels of temperature (165ºC, 180ºC, and 195 ºC) and time (0, 15, and 30 min) were used in the autohydrolysis experiments. The liquid/solid ratio was 12/L in all experiments.

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, $N = 10$.

The experimental results were fitted to the following second-order polynomial:

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

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).

Experimental Design for Pulping Conditions. Characterization of Cellulosic Pulp and Paper Sheets

The solid phase after autohydrolysis and water were mixed in the desired proportions and reacted in a 10 L stainless steel MK-systems Inc. reactor fitted with recirculation for obtaining cellulose pulps. The reactor was then closed and simultaneously heated (4.68 ºC/min heating rate) and actuated to assure good mixing and uniform swelling of *Paulownia* hydrolized-chips. When the pulping time had elapsed, the reactor was chilled to a temperature of 25ºC.

Following cooking, the pulp was separated from the liquor and disintegrated, without breaking the fibers, during 10 min at 2000 rpm. Pulping yield (TAPPI T 257-02 "Sampling and preparing wood for analysis'), kappa number (TAPPI T 236 om-06 "Kappa number of pulp"), viscosity (TAPPI T 230 om-04 "Viscosity of pulp [capillary viscometer method]"), ethanol-benzene extractives (TAPPI T 204 cm-97 "Solvent extractives of wood and pulp'), α-cellulose (TAPPI T 203 cm-99 "Alpha-, beta- and gamma-cellulose in pulp'), and soluble lignin, and soluble lignin (Goldschmid 1971) were determined (TAPPI 2007). Methods for holocellulose and Klason lignin determination were described in the previous section for raw material.

Paper sheets were prepared with an ENJO-F-39.71 sheet machine according to the TAPPI T 205 sp-02 "Forming handsheets for physical tests of pulp"). The laboratory handsheets were conditioned at a temperature of 23 ºC and relative humidity of 50% and tested for grammage (TAPPI T 220 sp-01 "Physical testing of pulp handsheets"), burst index (TAPPI T 403 om-02 "Bursting strength of paper"), tear index (TAPPI T 414 om-04 "Internal tearing resistance of paper [Elmendorf-type method]"), tensile index (TAPPI T 494 om-01" Tensile breaking properties of paper and paperboard [using constant rate of elongation apparatus]"), Shopper-Riegler degree (TAPPI 227 om-99 "Freeness of pulp [Canadian standard method]"), Gurley porosity (TAPPI T 536 om-02 "Resistance of paper to passage of air [high-pressure Gurley method]"), and ISO brightness (TAPPI T 525 om-06 "Diffuse brightness of paper, paperboard and pulp [d/0 degree]") (TAPPI, 2007).

To be able to relate the dependent variables (yield, kappa number, viscosity, ethanol-benzene extractives, holocellulose, α-cellulose, Klason lignin, soluble lignin, Shopper-Riegler degree, ISO brightness, tensile index, burst index, tear index, and Gurley porosity) with independent variables (NaOH concentration, temperature, and time of process) in pulping process with the minimum testing, the same experimental design for autohydrolysis process was applied.

Three levels of alkali concentration as NaOH (14, 17, and 20% dry weight (wt.) basis), temperature (155, 163, and 171 ºC), and operating time (60, 90, and 120 min) were used for the solid phase after autohydrolysis. A liquid/solid bath ratio of 12/1 and AQ concentration of 0.1 (dry wt. basis) were used in all experiments.

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 t-test and having a 95% confidence interval excluding zero).

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RESULTS AND DISCUSSION

Raw Material Characteristics

Previous results and results from other authors for chemical characterization of *Paulownia fortunei*, *Paulownia tormentosa*, and a tri-hybrid clone of *Paulownia fortunei x tormentosa x elongata* (it is the clone used in this work) are shown in Table 1. Also results of other raw materials included *Eucaliptus globulus* as reference species.

Table 1. Chemical Composition of *Paulownia* and Other Pulp Raw Materials*

	Paulownia fortunei			*Paulownia tormentosa*		*Paulownia elongata*	*Eucalyptus globulus*	*Misca-nthus*	*Ken af*	*Asp en*	*Paulownia fortunei x tormentosa x elongata*
	1	2	3	4	5	6	7	8	9	10	11
Holocellulose	56.9	70.9	69.6	78.8	n.d.	75.7	66.9	n.d.	n.d.	n.d.	65.2 (71.4)*
Klason lignin	27.2	22.4	28.0	22.1	20.9	20.5	22.9	n.d.	19.3	19.3	27.8
Glucan	34.2	37.4	n.d.	48.3	40.7	43.6 (α-cellulose)	46.8-53.4	39.5	36.3	36.3	44.0
Xylan	18.3	n.d.	n.d.	n.d.	n.d.		14.2-16.6	19	22.7	22.7	15.7
Araban	1.1	n.d.	n.d.	n.d.	n.d.		0.4-0.54	1.8	0.6	0.6	1.1
Acetyl groups	3.3	n.d.	n.d.	n.d.	n.d.		3.56	n.d.	n.d.	n.d.	4.4
Ethanol benzene extractives	5.46	n.d.	n.d.	n.d.	n.d.		2.09	n.d.	n.d.	n.d.	4.6
Ash	n.d.	n.d.	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.	n.d.	0.9

*Percentages on dry basis.
[1]Caparros et al. 2008; [2]Jimenez et al. 2005; [3]Rai et al. 2000; Kalaycioglu 2005; Olson and Carpenter 1985; [6]Ates et al. 2008; [7]Garrote et al. 2003; [8]Ververis et al. 2004; [9]De Vrije et al. 2002; [10]Ebringerová & H. 2000; [11]García et al. 2010; * the method of Wise et al. (1946)

The content of ethanol-benzene extractive compounds in *Paulownia fortunei* was 5.46%, higher than those found for *Eucalyptus globulus* wood, with a value of 2.09% (Caparrós et al. 2007a, 2008). These compounds could cause problems related to pitch. Pitch deposits in the manufacturing of pulp represent a complex phenomenon, which has increased in recent years (Del Río et al. 2000) and could cause problems by adhering to machinery and reducing the quality of pulp (Gutiérrez et al. 2003). The cellulose content in *Paulownia* tri-hybrid (García et al. 2010), is 6.0% to 17.6% (expressed as glucan), which is lower than those found for *Eucalyptus globulus*, but higher (22.2% to 14.9%) than those found for *Paulownia fortunei*, whereas lignin content was 17.6% to 28.2%, higher than that of *Eucalyptus*. The *Paulownia* hybrid *fortunei x tormentosa x elongata*, used in this work, was harvested after 3 years of growth and produced more than 50 tons of biomass per hectare per year (Vicedex 2008). Its content in acetyl groups was the highest among the raw materials in Table 1, which is suggestive of an increased amenability to autohydrolysis. In fact, the acetyl/xylan ratio was 25% higher than in *Eucalyptus* wood. The mean fiber length was 0.97 (0.52) mm with a minimum of 0.5 mm and a maximum of 2.9 mm. This is a fiber length similar to hardwoods such as *Eucalyptus globulus*.

The holocellulose content was similar to that of eucalyptus and lower than that of *Paulownia fortunei* and *Paulownia elongata*; these previously reported values, however,

were determined with the method of Wise et al. (1946) and for *Paulownia* hybrid as a combination of monomers and oligomers. Lignin values are slight higher and xylan, araban and acetyl groups values are similar than that found for the others materials. The holocellulose content was higher to that of *Paulownia fortunei or* eucalyptus (66.9%) and lower than that of *Paulownia tormentosa* and *Paulownia elongate*. The ash content was lower than those found for other species of *Paulownia* and other energy crops. A low ash and silicon content is preferable because silicon entering alkaline pulping processes will cause problems in the chemical recovery line at the pulp mill. In *Paulownia fortunei* x *tormentose* x *elongata,* ash percent was low (0.9 %). Then the amount of solid waste after combustion will be lower, and the yield of the boiler will not be affected.

Autohydrolysis Process Modeling and Optimization

Several experiments involving isothermal autohydrolysis were carried out in order to study the effect of the process on the xylo-olygomers production and cellulose degradation. Based on previous experiences with *Paulownia fortunei* and other lignocellulosic materials (Caparrós et al. 2007a, 2007b, 2008; Alfaro et al. 2009), the operations were carried out at temperatures and times of process indicated in the experimental design. In Table 2 the variations with the temperature and time of the different analyzed compounds (glucan, xylan, araban, and acetyl groups) of the solid phase are shown. The results were modelled by using the above-described multiple regression methodology. The ensuing models are shown in Table 2.

Table 2. Values of Independent Variables and Composition of the Solid Fractions Obtained in the Autohydrolysis Process

Normalized values of Temperature (X_T) and Operating Time (X_t)		Glucan, %	Xylan, %	Araban, %	Acetyl groups, %
0	0	44.0/99.9	5.0/31.5	0.4/35.3	1.3/14.4
0	0	43.5/99.0	4.7/30.1	0.3/32.1	1.3/14.3
1	1	43.3/98.4	6.3/40.4	0.5/44.0	1.2/13.3
1	-1	43.7/99.2	6.9/43.8	0.5/50.2	1.3/15.0
-1	1	44.4/100.8	3.0/19.3	0.4/33.2	1.1/12.8
-1	-1	41.5/94.3	13.1/83.5	0.6/58.5	1.4/15.8
1	0	43.2/98.1	3.6/22.9	0.5/43.1	1.3/14.5
-1	0	42.5/96.6	6.0/38.4	0.5/44.8	1.3/14.4
0	1	44.3/100.6	4.7/29.8	0.3/27.5	1.2/13.1
0	-1	42.8/97.3	9.4/59.6	0.4/39.9	1.4/15.3
Equation				R^2	F-Snedecor
$Y_{GLS} = 43.65 + 0.66 X_T - 0.30 X_t - 0.57 X_t X_t - 0.81 X_T X_t$				0.91	24
$Y_{XYS} = 4.83 - 2.55 X_T - 0.89 X_t + 2.41 X_T X_{T=} + 2.39 X_T X_t$				0.99	164
$Y_{ARS} = 0.35 + 0.13 X_t - 0.08 X_T + 0.05 X_T X_t$				0.96	75
$Y_{AGS} = 1.27 - 0.10 X_T - 0.02 X_t + 0.03 X_T X_t$				0.99	360

Y_{GLS}, Y_{XYS}, Y_{ARS} and Y_{AGS} denote glucan, araban, xylan, and acetyl groups contents in solid phase after autohydrolysis respect initial raw material (dry basis).
X_T and X_t denotes normalized autohydrolysis temperature and time, respectively.
The differences between the experimental values and those estimated by using the previous equations never exceeded 10% of the former (5% for Y_{XYS}).
* Using the proposed experimental design (relative to the initial raw material –dry mass-)/ (relative to the content in each polymer fraction of the raw material) and equations obtained for each dependent variable of solid phase after autohydrolysis

The variations of sugar content in the liquid phase were 0.9-1.0, 0.5-4.47, 0.1-0.6, and 0.06-0.3 % of glucose, xylose, arabinose, and acetyl groups, respectively (García et al. 2010).

The discussion that follows focuses on the following assumption: autohydrolysis of the *Paulownia fortunei x elongata x tormentosa* clone provides an industrially useful liquid phase by virtue of its contents in xylose, xylo-oligomers, and various other compounds, the optimum processing conditions for which are those minimizing cellulose degradation in order to facilitate its subsequent exploitation specifically, as cellulose fibre for pulp and paper production.

In fact, the glucan content in the liquid phase after autohydrolysis was slightly affected in the range of variation of independent variables studied (García et al. 2010). The Y_{GLS} term in Table 2 only was varied between 41.5% and 44.4%. This is an interval between the 94.5% and 100.8% of glucan content in the initial raw material.

In order to determine the values of the independent variables in autohydrolysis (operation temperature and time) giving the optimum values of dependent variables (glucan and xylan contents in solid phase post-autohydrolysis), the response surfaces for each dependent variable were plotted (Figs. 1 and 2).

A compromise between maximizing the glucan content and minimizing the xylan content in the solid phase postautohydrolysis can be found at intermediate operating times and operating temperatures between intermediate and high within the operating range studied. This effect can be observed in Figs. 1 and 2. Minimizing xylan content in solid phase post-autohydrolysis can be accompanied by a higher rate of extraction of xylose and xylo-oligomers that can be obtained in the liquid phase post-autohydrolysis.
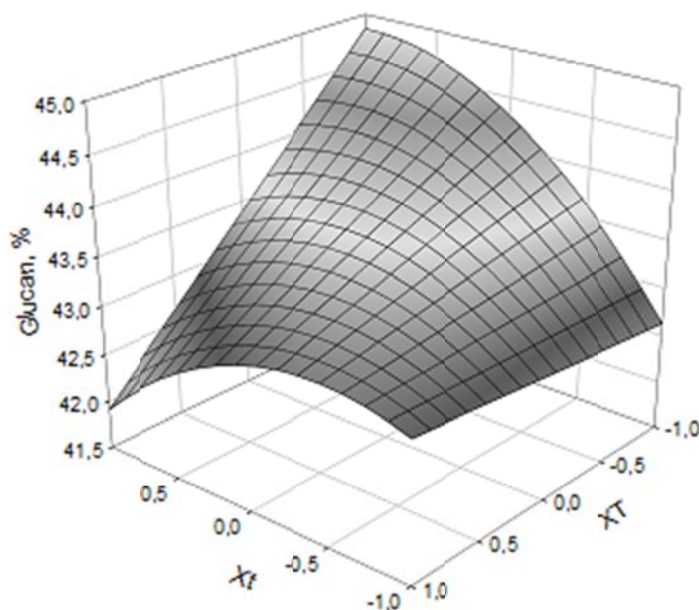

Fig. 1. Variation of glucan as a function of temperature and time of autohydrolysis process
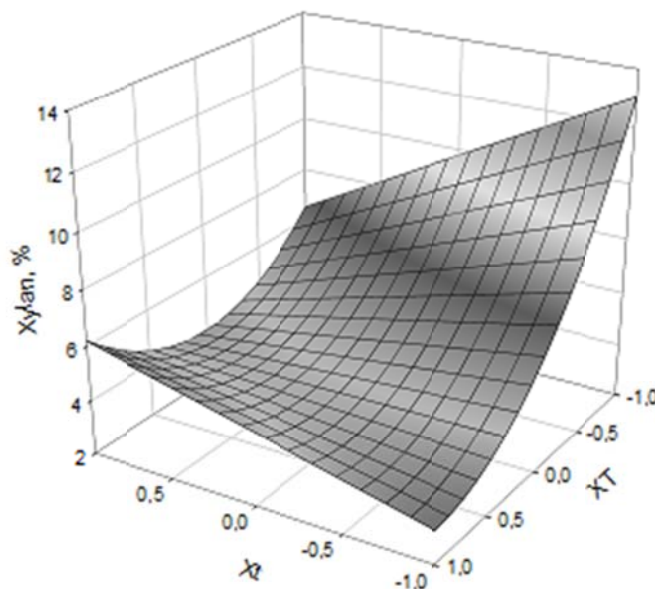
Fig. 2. Variation of xylan as a function of temperature and time of autohydrolysis process

In fact, previous works involving analysis and optimization of the extraction of sugars and oligomers in the liquid phase of the autohydrolysis process of tri-hybrid clone of *Paulownia fortunei x tormentosa x elongata* (García et al. 2010), operating conditions of: temperature 187 °C and operation time 15 min. were proposed as optimal conditions for proper extraction of xylose and xilooligomers. In accordance with the above and observing Figs. 1 and 2, operating conditions of time: 0 and temperature: 0.5 (points of experimental design) were selected. In these conditions a suitable solid phase for studying and optimizing the process of production of pulp and paper (by a soda-AQ process) was obtained.

NaOH-antraquinone Pulping Process of *Paulownia fortunei* x *tormentosa* x *elongata* after autohydrolysis

Paulownia can be considered as a promising plantation grown pulp wood (Rai et al. 2000; Ates et al. 2008). In this work, the solid fraction from autohydrolysis was delignified by using a NaOH-antraquinone pulping process, and the process was modeled and optimized using a linear multiple regression polynomial model and a factorial experimental design. Tables 3 and 4 show the results for the experimental points proposed in the experimental design. Variations with the soda concentration and temperature and time process of the different properties of pulp and paper sheets (yield, kappa number, viscosity, ethanol-benzene extractives, hollocelulose contents, α-cellulose contents, Klason lignin, soluble lignin, Shopper-Riegler degree, ISO brightness, tensile index, burst index, tear index, and Gurley porosity), are shown. The results were modeled by using the above-described multiple regression methodology. The resulting models are shown in Table 5.

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Table 3. Normalized Values of Independent Variables (X_A: Alkali concentration, X_t and X_T: time and temperature of operation) and Chemical Characterization of Pulps Obtained in the Pulping Process using the Proposed Experimental Design (% over dry basis).

Normalized values of independent variables: X_A, X_t, X_T	Yield, %	Kappa number	Viscosity, cm^3/g	Ethanol-benzene extractives, %	Holocellulose, %	α-cellulose, %	Klason Lignin, %	Soluble lignin, % (*100)
0 0 0	50.0	35.4	702	1.9	89.0	84.3	7.0	0.494
0 0 0	49.1	35.6	685	2.0	89.5	84.2	7.4	0.498
+1 +1 +1	46.8	12.2	631	2.0	94.7	89.1	12.0	0.571
+1 +1 -1	50.3	23.0	830	1.4	91.1	90.6	15.7	0.387
+1 −1 +1	47.3	16.4	774	1.2	92.8	84.6	10.2	0.415
+1 -1 -1	45.3	38.0	848	1.4	89.9	83.5	14.2	0.508
-1 +1 +1	54.6	55.0	737	2.2	89.2	82.4	14.2	0.420
-1 +1 -1	55.9	55.1	766	1.5	87.5	82.6	10.0	0.510
-1 −1 +1	59.3	59.1	707	2.0	87.0	81.8	17.2	0.464
-1 -1 -1	56.8	68.3	642	1.9	83.7	79.0	13.3	0.514
+1 0 0	49.6	21.4	730	2.5	93.9	88.4	9.1	0.540
-1 0 0	57.4	69.1	670	3.0	86.6	82.7	11.3	0.568
0 +1 0	46.8	21.7	743	1.3	91.4	85.8	10.7	0.510
0 −1 0	44.2	32.3	743	1.3	89.9	82.7	9.5	0.458
0 0 +1	50.9	32.8	674	1.4	87.1	83.4	7.1	0.425
0 0 -1	52.2	47.2	725	1.3	86.1	82.2	8.2	0.484

Table 4. Normalized Values of Independent Variables and Physical Characterization of Pulps and Paper Sheets Obtained in the Pulping Process Using the Proposed the Experimental Design

Normalized values of independent variables: X_A, X_t, X_T	Shopper Riegler degree, °SR	ISO Brightness, %	Tensile index, N m/g	Burst index, kPa·m^2/kg	Tear index, mN m^2/g	Gurley porosity, s/100 mL
0 0 0	21.9	27.0	29.5	0.99	1.70	28.1
0 0 0	22.0	26.3	30.3	1.08	1.81	33.9
+1 +1 +1	22.5	24.3	33.3	1.35	1.52	60.0
+1 +1 -1	21.0	29.5	30.4	1.07	1.55	53.7
+1 −1 +1	22.5	22.3	19.5	1.27	2.28	25.5
+1 -1 -1	18.5	25.0	22.9	0.81	1.59	17.9
-1 +1 +1	17.5	20.9	14.7	0.59	1.48	9.0
-1 +1 -1	15.5	21.7	13.4	0.45	1.30	5.0
-1 −1 +1	15.0	20.7	12.6	0.41	1.26	4.3
-1 -1 -1	14.0	19.7	12.9	0.20	0.86	1.7
+1 0 0	19.5	22.1	35.5	1.52	1.98	50.5
-1 0 0	12.5	18.2	19.1	0.66	1.34	12.1
0 +1 0	22.5	30.6	31.6	1.19	1.79	34.0
0 −1 0	22.5	27.4	25.8	1.04	1.75	28.0
0 0 +1	23.5	25.9	23.5	0.86	1.69	29.0
0 0 -1	23.0	27.2	21.5	0.80	1.53	21.0

Table 5. Equations Obtained for each Dependent Variable of Pulping Process

No Eq.	Equation	r^2	F-Snedecor
1	Y_{Yield} = 49.39 − 4.47 X_A + 4.19 $X_A X_A$ − 3.81 $X_t X_t$ + 2.24 $X_T X_T$ + 1.26 $X_A X_t$ − 1.16 $X_t X_T$	0.96	67
2	Y_{Kappa} = 35.61 − 19.54 X_A − 4.72 X_t − 5.63 X_T + 9.62 $X_A X_A$ − 8.65 $X_t X_t$ + 4.32 $X_T X_T$ − 2.91 $X_A X_T$ + 2.48 $X_t X_T$	0.98	79
3	$Y_{Viscosity}$ = 700.0 + 29.7 X_A − 25.6 X_T + 42.7 $X_t X_t$ − 38.6 $X_A X_t$ − 34.6 $X_A X_T$ − 23.4 $X_t X_T$	0.89	21
4	Y_{ABE} = 1.88 − 0.22 X_A + 0.12 X_T + 0.87 $X_A X_A$ − 0.54 $X_t X_t$ − 0.51 $X_T X_T$ + 0.11 $X_A X_T$ + 0.18 $X_t X_T$	0.95	43
5	$Y_{Holocellulose}$ = 89.14 + 2.86 X_A + 1.05 X_t + 1.26 X_T + 1.21 $X_A X_A$ + 1.60 $X_t X_t$ − 2.49 $X_T X_T$	0.93	36
6	$Y_{\alpha\text{-cellulose}}$ = 84.21 + 2.76 X_A + 1.89 X_t + 0.34 X_T + 1.40 $X_A X_A$ − 1.41 $X_T X_T$ + 0.93 $X_A X_t$ − 0.37 $X_A X_T$ − 0.72 $X_t X_T$	0.99	226
7	Y_{SR} = 22.0 + 3.0 X_A + 0.7 X_t + 0.9 X_T − 5.5 $X_A X_A$ + 1.7 $X_T X_T$	0.95	53
8	Y_{KL} = 7.32 − 0.48 X_A + 3.05 $X_A X_A$ + 2.93 $X_t X_t$ + 1.21 $X_A X_t$ − 1.98 $X_A X_T$	0.96	77
9	Y_{BR} = 26.50 + 2.20 X_A + 1.19 X_t − 0.90 X_T − 6.19 $X_A X_A$ + 2.66 $X_t X_t$ + 0.54 $X_A X_t$ − 1.01 $X_A X_T$ − 0.54 $X_t X_T$	0.99	139
10	Y_{TI} = 29.40 + 6.89 X_A + 2.97 X_t − 2.30 $X_A X_A$ − 7.09 $X_T X_T$ + 2.35 $X_A X_T$ + 0.99 $X_t X_T$	0.98	120
11	Y_{BI} = 1.08 + 0.37 X_A + 0.09 X_t + 0.12 X_T − 0.30 $X_T X_T$	0.95	72
12	Y_{Tel} = 1.77 + 0.27 X_A + 0.14 X_T − 0.12 $X_A X_A$ − 0.17 $X_T X_T$ − 0.18 $X_A X_t$ − 0.12 $X_t X_T$	0.94	39
13	Y_{GP} = 31.10 + 17.50 X_A + 8.48 X_t + 2.81 X_T − 8.34 $X_T X_T$ + 7.73 $X_A X_t$	0.96	75

Y_{ABE}: ethanol-benzene extractives (%), Y_{SR}: Shopper Riegler degree (ºSR), Y_{KL}: Klason Lignin in pulp (%), Y_{BR}: ISO Brightness (%), Y_{TI}, Y_{BI}, Y_{Tel}: Tensile index (N m/g), Burst index (MPa m²/kg) and Tear index (mN m²/g) respectively, and Y_{GP}: Gurley Porosity (s/100mL).
The differences between the experimental values and those extimated by using the previous equations never exceeded 10% of the former.

Yields of pulping process were between 44.2% and 59.3%. By observing the statistically significant terms in Eq. 1 of Table 5, the strong dependence of yield on the concentration of active alkali in the pulping process can be concluded. Yields were significantly higher than those obtained in a similar soda-AQ-ethanol process but with the variety *Paulownia fortunei* with yields between 32% and 47.2%.

Variations were obtained in kappa number between 12.2 and 69.2 (Table 3) or 10.3 and 73.3 (equation 2 in Table 5), substantially lower than those reported by Caparros et al. (2007a), ranging between 40.5 and 74.1 or 40.0 and 71.4 (prediction of neurofuzzy models, Caparros et al. 2007a) and even lower than results of kappa number of cellulose pulp obtained from a kraft process (23 to 25) from *Paulownia fortunei* (Rai et al. 2000) or results of Ates et al. (2008) for processes kraft-AQ, soda-AQ and ethanol on *Paulownia elongata*, whose kappa number was of 28.2, 27.8, and 42.1, respectively. In previous studies of delignification with soda-AQ of solid fraction of post-autohydrolysis the

following operating variables were set: AQ concentration (0.1%), operating time (90 min), operating temperature (160 ºC), ratio of liquid/solid (12/1), and the soda concentration varied between 8 and 23%, the kappa number obtained ranged between 14.4 and 160.3, and the kappa number of cellulose pulp obtained in the same operating conditions, with a soda concentration of 23% but without prior autohydrolysis was 33.6 (Garcia et al. 2010).

In a manner consistent with the variation of the kappa number, the contents of Klason lignin and ISO brightness depended mainly on the dependent variable: soda concentration (eqs. 2, 8 and 9 in Table 5) and varied between 7.0% and 17.2% (Table 3) for the case of lignin and in the case of the ISO brightness 18.2% and 30.6% (Table 4) or 17.9% and 30.6% (Eq. 9 in Table 5). These brightness values were better than those obtained by Caparros et al. (2008) for *Paulownia fortune*, ranging between 16.5% and 29.5% (experimental) or between 17.3% and 30.2% (predicted) and similar to those obtained by Ates et al. (2008) on *Paulownia elongata* to kraft-AQ processes (21.8%), soda-AQ (24.0%), and ethanol (32.9%).

Table 6. Viscosity and Other Properties of Paper Sheets of Tri-hybrid *Paulownia fortunei* x *tormentosa* x *elongata* and other Varieties Reported by Other Authors

	Paulownia fortunei, Rai et al. 2000	*Paulownia fortunei*, Caparrós et al. 2007a, 2008		*Paulownia elongata*, Ates et al. 2008			*Paulownia fortunei* x *tormentosa* x *elongata*	
	These pulps were beaten in a Lampem mill	experimental	predicted	kraft-AQ	soda-AQ	Ethanol	experimental	predicted
Viscosity, cm^3/g		255-703	266-718	706	643	763	631-848	639-848
Tensile index, N·m/g	99.84-106.12	16.97-28.87	17.17-29.08	16.6	15.3	25.9	12.61-35.47	6.8-37.3
Burst index, $kPa·m^2/g$	5.50-6.47	0.60-1.22	0.56-1.17	1.15	1.09	0.90	0.20-1.35	0.20-1.55
Tear index, $mN·m^2/g$	2.49-2.67	0.85-1.23	0.85-1.20	2.10	1.96	3.36	0.86-2.28	0.77-2.20

The soluble lignin (Table 3) was hardly affected by the different conditions in the pulping process and moved at a very low range of values between 0.0042% and 0.0057%. Regarding the set of physical properties of paper sheets and viscosity, we can see a significant improvement in paper properties obtained by soda-AQ process of the solid phase obtained after autohydrolysis process of the clone *Paulownia* tri-hybrid (*elongata x fortunei x tormentosa*) compared with previous results of a similar process over *Palownia fortunei* or *Paulownia elongata* (Table 6).

The highest ranks of the values predicted by the models in Table 5 for the viscosity are 15.3% higher than the values predicted by Caparros et al. (2008). Something similar can be argued about the physical properties of paper sheets. The highest values predicted for the tensile index, burst index, and tear index were 22.0%, 24.5%, and 45.5%, which were higher than those predicted by Caparrós et al. (2007a and 2008) for the same rates, respectively. They were also higher than the values obtained by Ates et al. (2008): between 30.6% and 59.0% for tensile index and between 25.8% and 41.9% for burst index and also higher than the tear index of paper sheets obtained from *Paulownia elongata* by kraft-AQ and soda-AQ process but lower than those obtained by the ethanol process. Rai et al. (2000) obtained higher values of the physical properties of paper sheets but refined pulps, which makes it not comparable, but it gives an idea of the potential of these pulps to obtain sheets having very good characteristics.

CONCLUSIONS

1. A valuable liquid phase could be obtained from an autohydrolysis process of *Paulownia fortunei x tormentosa x elongata* while minimizing cellulose degradation in order to facilitate its subsequent exploitation specifically as cellulose fibre for pulp and paper production. A compromise between maximizing the glucan content and minimizing the xylan content in the solid phase after autohydrolysis can be found at 187.5ºC and 15 min.
2. A suitable cellulosic pulp with kappa number between 12.2 and 69.2 and ISO brightness between 18.2% and 30.6%, which is higher than results of kappa number obtained from other authors, can be obtained. Regarding the set of physical properties of paper sheets and viscosity, we can see a significant improvement in paper properties obtained by soda-AQ process of the solid phase obtained after an autohydrolysis process of the clone *Paulownia* tri-hybrid (*elongata x fortunei x tormentosa*) compared with previous results of a similar process over *Palownia fortunei* or *Paulownia elongata*.

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