OBTAINMENT OF HEMICELLULOSE DERIVATIVES AND CELLULOSE PULP FROM WHEAT STRAW FOLLOWING COLD ALKALINE EXTRACTION

MARIA T.GARCÍA,[*]ASCENSION ALFARO,[**]JUAN C. GARCIA,[*]
MINERVA A. M.ZAMUDIO,[***]ANA B. MORALES[***] and FRANCISCO LÓPEZ[*]

[*]*PRO[2]TEC-Chemical Engineering Department, University of Huelva, Av. 3 deMarzo s/n, 21071, Huelva, Spain*
[**]*Agroforestry Department, University of Huelva, Av. 3 de Marzo s/n, 21071, Huelva, Spain*
[***]*Technological Institute of Ciudad Madero, J. Rosas y J. Ureta s/n. Col. Los Mangos, 89440, Ciudad Madero, Tamaulipas, Mexico*
✉ *Corresponding author:Ascensión Alfaro,ascension.alfaro@uhu.es*

In this work, we addressed the integral exploitation of wheat straw by fractionating its lignocellulosic components, following removal of hemicelluloses by cold alkaline extraction. The treatment provided a liquid fraction that was used to obtain hemicelluloses by alcoholic precipitation and a solid fraction that gave cellulose pulp by soda–anthraquinone delignification.The proposed processing scheme is environmentally friendly because it uses cold alkaline extraction to valorize the hemicellulose fraction of wheat straw, while facilitating its delignification, which can be thus accomplished under milder conditions. This saves raw material and energy, and provides paper sheets similarly strong to those obtained from untreated cellulose.

Keywords: biorefinery, wheat straw, hemicelluloses, cold alkaline extraction, soda-anthraquinone, pulp, paper

INTRODUCTION

Agriforest and agrifood residues, such as wheat straw, are abundant, renewable and inexpensive sources of raw materials for the obtainment of end-products with a high added value, without interfering with nutritional uses, and help reduce GHG emissions and the fossil energy demand, in industrial biorefining schemes.[1,2] Also, they allow cellulose pulp manufacturers in developed countries to maintain industrial activity despite the growing trend of delocalization to emerging countries. Conventional pulp manufacturing plants could be adapted to the biorefining production scheme by converting lignocellulosic biomass feedstocks into a wide range of valuable products (a large variety of precursor chemicals and biobased materials, energy), much like petroleum refineries in order to maintain competitiveness, and ensure economic and environmental sustainability.[3,4] Transforming cellulose manufacturing plants into integral forest biorefineries would additionally allow the production of cellulose fiber to be supplemented with that of by-products, including

fuel-grade ethanol and energy, with a view to increasing income and profits and, potentially, reducing greenhouse gas emissions.[5,6]

To this end, paper pulp production platforms should aim at obtaining cellulose-rich, scarcely degraded pulp to manufacture strong enough paper. The first fractionation step for this purpose can be pre-extraction of hemicelluloses.[7-10]At kraft pulp mills, lignin and most hemicellulose are dissolved in the black liquor during the pulp production process, and then burnt to obtain steam and electricity. This use is inefficient in biorefining terms since hemicelluloses have a lower heat value than lignin.[5]

So far, hemicelluloses have been extracted by using various pretreatments involving hydrothermal processing, alkalis, acids, hydrogen peroxide,[10,11] or steam explosion.[12] Cold alkaline extraction is especially suitable here, as it affords the exploitation of lignocelluloses with no adverse impact on the environment.[13] Hemicellulose exhibits higher solubility in alkaline conditions than in acidic ones with less degradation to

furfural substances. Also, alkali pre-extraction generally requires much milder conditions of temperature, pressure, and chemical dosage than acidic conditions.[14]

The alkali extraction of hemicellulose succeeds in separating polymeric heteropolysaccharides from the fiber source.[15] By this process, using alkali and temperatures below 40ºC, the wheat straw can be simply fractionated into alkali-soluble lignin and hemicelluloses and residue, which makes it easy to utilize them for achieving more valuable products with minimal physical and chemical changes.[16] In this work, we used wheat straw, which is produced in amounts exceeding 170 million tons each year in Europe alone.[2]

Studies on other materials, such as corn stover, revealed that an alkaline pre-extraction stage could improve the brightness and decrease the kappa number of the subsequent pulp, causing a slight loss of yield, viscosity, density, and burst strength, but an obvious improvement in tear strength. Also, pre-extraction of hemicellulose is a potential way to solve silicon problems associated with alkaline pulping of stover.[14] It was found that, for a kraft pulp from eucalyptus wood previously subjected to an alkaline pretreatment, the pulp viscosity, breaking strength, and tensile index of the handsheets were slightly improved.[17] Alkaline pre-extraction prior to soda-AQ pulping largely preserved the pulp yield, while a substantial amount of xylan could be extracted in polymeric form during the pre-treatment.[18] Additional potential advantages include the lack of a direct relationship between the xylan content and cellulose pulp yield and the fact that partial removal of xylan from lignocellulosic materials facilitates extraction of lignin without an adverse impact on paper production.[19]

Hemicellulosic derivatives extracted into the liquid phase have a number of uses, such as prebiotic xylooligosaccharides or polymers and molecules for chemical, pharmaceutical applications, natural barrier for packaging films, bioethanol, plastics, cellulosic pulp additives,[12,20] ethanol, xylitol[5,19] *etc*. Lignin obtained by delignifying the solid fraction can be used for either paper or cellulose derivatives, or biocomposites, and lignin can be converted to valuable products, such as carbon fiber and adhesives, or degassed to obtain synthesis gas.[6]

The aim of this work was to integrally exploit wheat straw by fractionating its lignocellulosic components, following cold alkaline extraction of hemicelluloses. The liquid fraction was used to extract hemicelluloses by alcoholic precipitation and the solid fraction to obtain cellulose pulp by using a soda–anthraquinone delignification scheme. To optimize the pulping process, experimental design was applied.

EXPERIMENTAL
Source and analysis of biomass

Wheat straw biomass was obtained from a plantation in Huelva (southwestern Spain). The raw material was prepared in accordance with TAPPI T-257 cm-85 and analyzed for the following parameters: 1% NaOH solubles (TAPPI T 212 om-07), hot water solubles (TAPPI T 207 cm-93), ethanol–acetone extractives (TAPPI T 204 cm-07), holocellulose[21] and ash (TAPPI T 211 om-07) contents.

α-Cellulose in the raw material (as glucan) and glucose, xylose, arabinose and acetic acid in the acid hydrolysates of the Klason lignin test were determined by high performance liquid chromatography (HPLC), as described by García *et al.*[16]

All HPLC determinations were performed in a completely randomized design with three replications (variation coefficient less than 4%).

Cold alkaline extraction of hemicellulose

The cold alkaline extraction (CAE) pretreatment conditions were selected based on previous results obtained in the study of optimum conditions for cold alkaline extraction of wheat straw hemicelluloses.[16]

The selected optimum conditions for the present study were: 100 g·L^{-1} of alkali concentration, 90 minutes and 40ºC of operation time and temperature, respectively. The solid/liquid ratio was 1/14. For this pretreatment, a 10 L stainless steel reactor from M/K Systems, Inc. (Denvers, Massachusetts 01923 USA), equipped with a recirculation pump, was used.

The excess of sodium hydroxide applied in CAE – and the alcohol used for hemicelluloses precipitation – could be reused in later cycles of the hypothetical industrial process.

As for the raw material, the liquid and solid phases obtained after cold alkaline extraction were characterized following the methodology described by García *et al.*[16] We determined the yield, lignin, glucan, xylan, araban and total hemicelluloses.

Soda-anthraquinone pulping

The solid obtained after the CAE, water, soda and anthraquinone were mixed in the desired proportions and reacted in the same reactor used for the CAE treatment. The operating conditions were as follows: 110, 125 and 140 ºC; 60, 90 and 120 minutes operating time, 2%, 5% and 8% NaOH, 0.1% anthraquinone and a liquid/solid ratio of 8 kg water per kg of raw material on a dry basis (the moisture content of the material was considered to be water). Following cooking, the pulp

was separated from the liquor by screening and disintegrated, without breaking the fibers, for 20 min in a high concentration pulper machine (Metrotec S.A.).

Characterization of the pulp and paper sheet

The pulps were determined as follows: yield (Tappi 257 cm-85), α-cellulose (Tappi 203 om-93), holocellulose,[21] lignin contents (Tappi T 222 om-98), viscosity (Tappi T230 om-94) and kappa number (Tappi T 236 cm-85).

Paper sheets were prepared with an ENJO-F-39.71 sheet machine according to TAPPI T 205 sp-06. Grammage, burst, tear and tensile indexes, Schopper-Riegler degree (ºSR) and ISO brightness were determined according to TAPPI T 220 sp-06, TAPPI T 403 om-10, TAPPI T 414 om-04, TAPPI T 494 om-06, TAPPI T 525 om-06 andISO 5267/1,respectively.

Experimental design for pulping process

In order to relate the dependent (yield, kappa number, intrinsic viscosity, holocellulose, α-cellulose, Klason lignin, soluble lignin, Shopper-Riegler degree (ºSR), ISO brightness, and tensile, burst and tear indexes) and independent variables (temperature, time and soda concentration) in the pulping process with the minimum possible number of experiment, a 2^ncentral composite factor experimental design was used, making it possible to construct a second-order polynomial. Independent variables were normalized by using the following equation:

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

(1)

where X is the absolute value of the independent variable of concern, X is the average value of the variable, and X_{max} and X_{min} are its maximum and minimum values, respectively.

The number of tests required was calculated as $N=2n+2^n+nc$, 2n being the number of points constituting the factor design, 2^n that of axial points, and nc that of central points. Under the conditions used, N = 16.

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

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

(2)

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

Scheme of experimental work

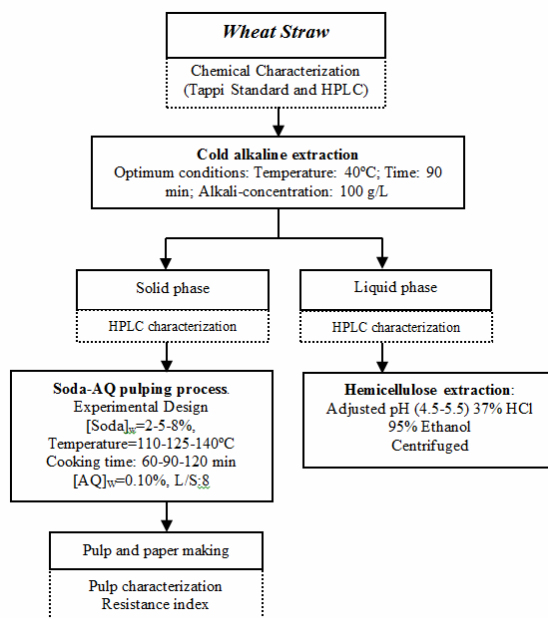Figure 1 shows the sequence of the experimental work realized.

Figure 1: Scheme of realized work

RESULTS AND DISCUSSION
Chemical properties of the raw material

In general, agricultural residues contain large amounts of soluble substances. In the particular case of the wheat straw used in this work (Table 1), the contents of soda-soluble components fell within the reported ranges for the same material.[22,23] As can be seen, the contents of wheat straw were much higher than those of widely used wood species, such as *Eucalyptus globulus* (44.5% *vs.* 12.4%).

On the other hand, the content of ethanol–acetone extractives was slightly higher than other reported values[22,23] and much higher (5.3 times) than that of eucalyptus. Among the materials listed in Table 1, only corn stover had a content of organic solvent-extractables markedly exceeding that of wheat straw.

As can be seen from Table 1, the α-cellulose content of our wheat straw (31.1%) was the lowest of all (*e.g.*, 21.8% lower than that reported by Jiménez *et al.*[23]). In our case, the α-cellulose content was determined as glucan by HPLC. This can explain the lower result than that obtained by gravimetric determination. The content of wheat straw was similar to those of rice straw (35.0%) and *Helianthus annuus* (33.8%), but lower than those of *E. globulus* and corn stover by 33.7% and 38.8%, respectively. The last material was that with the highest content of α-cellulose among those listed in Table 1 (50.7%).[14]

The Klason lignin content of the wheat straw (18.9%) was slightly higher than other wheat straw values reported (16.5%-17.3%). The content of lignin was lower by 17.7% than that for eucalyptus and higher by 57.1% than that for rice straw. Also, the content of soluble lignin for wheat straw (2.7%) was similar to that obtained by Pan *et al.*:[22] 2.5%.

Also, as can be seen in Table 1, Pan *et al.*[22] reported unusually high ash content for rice straw (around 10.0%). *Helianthus annuus* has a high content of ash (9.4%). The ash content of the wheat straw (6.7%) was high in relation to wood materials like Eucalyptus (0.6%).

Wheat straw, which contains about 35% hemicellulose (calculated as the difference between holocellulose and α-cellulose) and less than 19% Klason lignin, can provide an effective raw material for the selective separation of the hemicelluloses fraction.

In conclusion, wheat straw was found to be the most suitable raw material for pulp and paper production, as compared to other agricultural residues, such as olive tree fellings, sunflower stalks, vine shoots and cotton stalks. Wheat straw contains little lignin, intermediate amounts of α-cellulose, even though it contains large amounts of solubles and ashes.[27]

Cold alkaline extraction of hemicelluloses

Cold alkaline extraction affords the relatively selective extraction of hemicelluloses as highly pure polymers.[15]

Based on the foregoing, and on previously reported optimal results,[16] the optimum operating conditions were established as described in the Experimental section. Table 2 summarizes the results of the characterization of the liquid and solid phases obtained after cold alkaline extraction.

As can be seen, the cold alkaline extraction step was highly selective for the hemicellulosic and polyphenolic fractions of wheat straw relative to cellulose. In fact, only 7.2% of all glucan initially present in the raw material (*i.e.*, 2.2% of the amount of material) was extracted into the liquid phase. The extraction yields thus obtained were of 20.1% for hemicelluloses and 10.7% for lignin with respect to the raw material.

These results are suggestive of highly selective extraction or separation of the hemicellulose fraction relative to glucan derivatives. The selectivity of the separation is probably even higher since part of the glucose present in the liquid phase must have come from hemicellulose rather than from glucan in the raw material.[28]

Subsequent separation of hemicellulose in the liquid phase from the cold alkaline extraction by precipitation with ethanol allows 39.4% of all hemicellulose present in the raw material to be recovered. Also, the extracted-precipitated fraction contains only 10.3% lignin, which accounts for 12% of all present in the raw material.[16]

Table 1
Chemical characterization of wheat straw and other lignocellulosic materials

Determination	Wheat straw	Wheat straw, other authors[22,23]	Eucalyptus globulus[24]	Corn stover[14]	*Helianthus annuus* (sunflower stalks)[25]	Rice straw[19,26]
Hot water solubles, %	15.03	17.5[22]-12.27[23]				7.3[26]
1% NaOH solubles, %	44.50	46.0[22]-41.49[23]	12.4			57.7[26]
Ethanol-acetone extractables, %	6.32	5.3[22]-4.01[23]	1.2	7.4		0.56[26]
Holocellulose, %	66.00	76.6[22]-76.20[23]	66.9	70.1	74.2	60.0[19]-60.7[26]
α-cellulose, %	31.05	39.72[23]	46.8	50.7	33.8	35.0[19]-41.20[26]
Klason lignin, %	18.85	16.5[22]-17.28[23]	22.9	15.5	19.9	12.0[19]-21.9[26]
Soluble lignin, %	2.70	2.5[22]		1.4		
Ashes, %	6.65	9.6[22]-6.49[23]	0.6	3.8	9.4	9.2[26]

Table 2
Chemical characterization of solid and liquid phases after cold alkaline extraction (on dry basis)

Parameters	Composition (%) of solid phase with respect to raw material	Extracted (%) with respect to the polymer in raw material in liquid phase
Yield	61.1	
Lignin	8.0	56.8
Glucan	30.9	7.2
Xylan	9.4	
Araban	1.3	
Total hemicelluloses	10.7	57.5

Previous studies revealed that hemicellulose extraction increases with increasing temperature and operating time. Thus, Chen *et al.*[14] extracted 90% of xylan from solid substrates by using 10% NaOH at 65 ºC or 95 ºC for 120 min. The fact that the alkali concentration is the individual factor that most strongly influences the extraction of hemicelluloses allows obtaining large amounts of this fraction at low temperatures.[29] In this work, however, we chose to restrict hemicellulose extraction in order to ensure minimal extraction and depolymerization of glucan with a view to optimizing production of cellulose pulp and paper at a second fractionation stage.

Optimization of soda-anthraquinonepulping procedure after cold alkaline process

The solid residue was subjected to pulping and papermaking by using the normalized values of each variable listed in Table 3.

Table 3 also shows the pulping yield and total yield with provision for the cold alkaline extraction pretreatment, as well as various properties of the resulting cellulose pulp, namely: kappa number,brightness (% ISO), holocellulose content, α-cellulose content, Klasonlignin and soluble lignin.

Table 4 shows the ºSR and viscosity results for the pulp, in addition to the strength-related properties of the paper sheets obtained from the pulp.

As can be seen from Table 3, the pulp yield was high (47.4-65.0% and above 50% in 87.5% of all tests). Total yield, which included that of the cold alkaline extraction stage, amounted to 31.8-42.2% of the initial feedstock.

The pulp yields obtained are similar to previously reported values, such as that of Jiménez *et al.*,[30] who obtained 54% from untreated straw pulped at 147 ºC with a soda concentration of 11.8%. Under similar conditions (*viz.*, the most drastic in our experimental design, which included 8% NaOH, 140 ºC and 120 min), the pulp yield was 51.6% and total yield 34.6% (relative to the initial feedstock) here.

Our pulp yields are higher than those reported by Schall *et al.*,[31] who obtained 45.7-47.9% by using an alkali concentration of 10-14% as Na₂O, a temperature of 165 ºC and an operating time of 20-25 min; and those of Bajpai *et al.*,[32] who obtained 46.4-45.9% by using 11-12% NaOH. Ates *et al.*[33] found rising the NaOH concentration to 16% under similar conditions could reduce pulp yield to 37.9%.

The α-cellulose content is too high in the pulps (69.6-98.8%), indicating that there has been low degradation of this component during the alkaline extraction. Such high values were also the result of the previous removal of hemicelluloses and lignin during the cold alkaline extraction step. In fact, the pulp contained very little Klason lignin (2-10%).

Jiménez *et al.*[30] obtained pulp with 60-70% α-cellulose from untreated wheat straw, as compared to 69.6% achieved under similar pulping conditions in this work. Cold alkaline extraction dramatically reduced the content in Klason lignin: down to 2.5% relative to 10-12% under similar conditions. This high delignification will facilitate subsequent bleaching of the pulp.

For an expert reader in pulp and paper industry, many results do not fit together (holocellulose *vs.* α-cellulose; kappa number *vs.* Klason lignin), but our biorefinery scheme is not the same as a conventional kraft or soda pulping process. The material with a previous cold alkaline extraction is more susceptible to glucan degradation. This explains the significant decreases in the contents of cellulose at high temperature or alkaline concentration, compared with holocellulose contents. Something similar happens with the lignin content and the kappa index. For example, a high degradation of the glucan content can elevate the lignin content, but not necessarily the kappa index, because the kappa index includes oxidizable organic material (fractions of hemicelluloses and lignin).

The kappa number was less than 20 in more than 65% of all tests and smaller than previously reported values for untreated wheat straw delignified with soda. Thus, Schall *et al.*[31] obtained kappa numbers of 22.8-24.6 by using an active alkali concentration of 10%, a temperature of 165 ºC and a cooking time of 20-50 min, and Ates *et al.*[33]– one of 12.6 with an alkali concentration of 16% at 160 ºC.

According to Bajpai *et al.*,[32] conventional soda pulping of wheat straw to a kappa number of 28-30 requires using an alkali concentration of 11-12%. With the cold alkaline extraction pretreatment, we obtained kappa numbers as small as 6.9 under similar pulping conditions.

Table 3

Normalized operational conditions and characterization of solid phase pulp after cold alkaline extraction of hemicellulose. The percentages are referred to initial raw material

Normalized values of alkaliconcentration (X_C), temperature (X_t) and operation time (X_T)			Pulping yield (%)	Total yield (%)	Brightness ISO (%)	Kappa number	Holocellulose (%)	α-cellulose (%)	Klason lignin (%)	Soluble lignin(%)
0	0	0	57.0	38.2	50.5	13.9	93.6	91.9	2.1	1.2
0	0	0	58.2	39.0	50.9	13.5	94.0	92.1	2.0	1.1
1	1	1	51.6	34.6	54.6	6.9	94.2	69.6	2.5	0.9
1	1	-1	52.1	34.9	46.0	22.5	93.7	86.4	5.5	1.3
1	-1	1	48.9	32.8	55.5	9.8	97.1	73.7	10.0	0.9
1	-1	-1	55.6	37.3	42.7	30.6	94.6	88.3	6.4	1.3
-1	1	1	54.2	36.3	54.8	8.8	91.3	82.6	2.1	1.0
-1	1	-1	57.3	38.4	47.5	21.8	93.2	88.9	4.0	1.3
-1	-1	1	47.4	31.8	53.7	10.4	91.5	87.2	8.6	1.1
-1	-1	-1	63.0	42.2	40.3	27.3	95.7	91.7	6.7	1.4
1	0	0	56.1	37.6	48.9	14.3	95.5	79.7	5.7	1.5
-1	0	0	59.2	39.7	49,5	15.2	93.2	86.0	2.7	1.2
0	1	0	54.6	36.6	51,5	12.4	97.7	97.1	2.1	1.4
0	-1	0	55.9	37.5	50.2	14.8	99.2	98.8	5.0	1.5
0	0	1	54.6	36.6	56.6	8.4	89.8	83.3	2,0	1.2
0	0	-1	60.5	40.6	46.2	23.6	90.4	91.7	3.5	1.4

Table 4

Normalized operational conditions, ºSR and intrinsic viscosity of solid phase pulp after cold alkaline extraction of hemicelluloses and characterization of paper sheets

Normalized values of alkali concentration (X_C), temperature (X_t) and operation time (X_T)			Intrinsic viscosity (cm^3·g^{-1})	ºSR	Tensile index (N·m·g^{-1})	Tear index (mN·m^2·g^{-1})	Burst index (Kpa·m^2·g^{-1})
0	0	0	619.2	21.0	21.3	2.6	1.2
0	0	0	608.5	20.2	21.9	2.7	1.3
1	1	1	816.8	21.0	17.4	2.0	1.1
1	1	-1	925.9	16.2	27.2	2.7	1.4
1	-1	1	857.1	21.0	20.7	2.4	1.3
1	-1	-1	830.4	20.2	23.9	2.4	1.6
-1	1	1	940.4	20.8	19.5	2.4	1.0
-1	1	-1	488.2	15.0	17.5	2.3	1.0
-1	-1	1	882.5	19.0	19.4	2.7	1.1
-1	-1	-1	584.1	21.0	16.9	2.3	1.2
1	0	0	726.8	19.0	22.7	2.5	1.3
-1	0	0	683.2	19.0	18.7	2.5	1.0
0	1	0	759.7	19.1	25.4	2.6	1.5
0	-1	0	624.8	21.5	25.8	2.8	1.7
0	0	1	691.1	21.0	15.6	2.3	0.8
0	0	-1	523.2	18.5	18.3	2.3	1.1

Table 5
Equations yielded for each dependent variable (pulp and paper characterization)

Equations	r^2	F-Snedecor
(1) $Y_{PY}= 57.59 - 1.68X_C - 3.18X_T - 3.54X_t^2 + 1.44X_C \cdot X_T + 2.34X_t \cdot X_T$	0.956	44.44
(2) $Y_{TY}= 38.58 - 1.13X_C - 2.13X_T - 2.37X_t^2 + 0.96313X_C \cdot X_T + 1.57X_t \cdot X_T$	0.956	44.44
(3) $Y_{Br} = 50.96 + 1.21X_t + 5.24X_T - 1.62X_C \cdot X_C - 0.73X_C \cdot X_t - 1.28X_t \cdot X_T$	0.991	199.16
(4) $Y_{NK}= 13.61 - 2.05X_t - 8.15X_T + 1.20X_C^2 + 2.45X_T^2 - 0.79X_C \cdot X_T + 1.14X_t \cdot X_T$	0.992	23.22
(5) $Y_V= 609.798 + 57.86X_C + 83.61X_T + 96.654X_C^2 + 83.85X_t^2 - 104.12X_C \cdot X_T$	0.921	30.08
(6) $Y_{SR}= 20.21 - 1.07X_t + 1.19X_T - 0.98X_C^2 + 1.48X_t \cdot X_T$	0.916	42.25
(7) $Y_{HOL}= 94.18 + 1.03X_C - 0.81X_t + 4.03X_t^2 - 4.26X_T^2 + 1.14X_C \cdot X_T$	0.954	154.23
(8) $Y_{AC}= 92.21 - 3.87X_C - 1.51X_t - 5.06X_T - 9.45X_C^2 + 5.6X_t^2 - 4.82X_T^2 - 2.56X_C \cdot X_T$	0.992	31.89
(9) $Y_{KL}= 2.31 + 0.61X_C - 2.05X_t + 2.02X_C^2 + 1.35X_t^2 - 1.28X_t \cdot X_T$	0.941	16.79
(10) $Y_{SL}= 1.31 - 0.06X_t - 0.15X_T - 0.10X_C^2 + 0.09X_t^2 - 0.13X_T^2$	0.893	16.79
(11) $Y_{TI}= 21.32 + 1.98X_C - 1.12X_T + 3.86X_t X_t - 4.78X_T \cdot X_T - 2.16X_C \cdot X_T - 0.88X_t \cdot X_T$	0.962	38.39
(12) $T_{BI}= 1.21 + 0.13X_C - 0.09X_t - 0.11X_T + 0.31X_t \cdot X_t - 0.28X_T \cdot X_T - 0.07X_C \cdot X_T$	0.979	35.33
(13) $Y_{TeI}= 2.55 - 0.05X_t + 0.13X_t \cdot X_t - 0.29X_T \cdot X_T - 0.16X_C \cdot X_T - 0.13X_t \cdot X_T$	0.942	32.24

Pulp viscosity was influenced by the prior removal of hemicelluloses. In accordance with Chen *et al.*,[14] it could be seen that the dissolution of hemicellulose increased from 15 to 90% and the viscosity of the pulp decrease by approximately 22%. Our values ranged from 488.2 to 940.2 cm³/g. However, they exceeded 600 cm³/g in more than 80% of the tests and 700 cm³/g in 53.6%. These values are similar to those obtained by Tutus and Eroglu,[34] with 16% NaOH containing 0.1% anthraquinone, temperatures of 120-160 °C and times of 20-60 min, but no pretreatment: 600-718 cm³/g.

Because hemicelluloses were previously extracted to a great extent, the hemicellulose content of the pulp was obviously low: 0.4-20.2%, with less than 10% in 81.35% of the tests and less than 5% in 50%.

°SR ranged from 15.0 to 21.5, but it could be substantially improved by refining the pulp. In fact, refining can increase °SR by a factor of 2.2-17.7, depending on the particular material.[9]

The strength properties of the paper sheets were: tensile index(15.6-27.2 N·m·g⁻¹), tear index(2.0-2.8mN·m²·g⁻¹) and burst index(0.8-1.7 Kpa·m²·g⁻¹).

Singh *et al.*[35] previously obtained very similar strength values by using an active alkali concentration of 10% as Na₂O, 0.1% anthraquinone, a temperature of 150 °C and a cooking time of 60 min: tensile index of 19.10 Nm/g, tear index of 3.15 mN·m²·g⁻¹ and burst index of 0.75 Kpa·m²·g⁻¹.

Also, Jiménez and López[27] obtained soda pulp with a similar tensile index (20.7-23.3 N·m/g),

but higher values of the other two strength-related indices from wheat straw (tear index of 4.33-4.60 mN·m²·g⁻¹ and burst index of 2.62-3.44 Kpa·m²·g⁻¹). The operating conditions used were as follows: 6.6-9% NaOH concentration, 60 min, 147-148°C.

Obviously, refining the pulp leads to improved strength-related properties in the paper sheets obtained from wheat straw subjected to no extractive pretreatment. Thus, Ates *et al.*[33] subjected pulp obtained by cooking in 15% NaOH at 160 °C for 40 min to PFI beating for up to 3000 revolutions and found a tensile index of 78 N·m/g, a tear index of 3.58 mN·m²/g and a burst index of 4.84 kPa·m²/g. Schall, Singh and Pan and Sano,[31,35,36] also obtained substantially improved tensile index and burst index values (49-67.9 N·m/g and 2.7-5.7 kPa·m²/g, respectively) by refining the pulp. Similar improvements in strength-related properties can also be obtained with cold alkaline extraction of hemicelluloses.

On the other hand, the results of Tables 3 and 4 were modeled by using the multiple regression methodology described in the Experimental section. The ensuing models are shown in Table 5.

As can be seen from Table 5, temperature (X_T) was a major influential factor on the pulping of wheat straw, following cold alkaline extraction. Low temperatures in the selected range led to increased pulp yield (Y_{PY}) and total yield (Y_{TY}). Also, high alkali concentrations resulted in increased strength-related indices for the paper sheets.
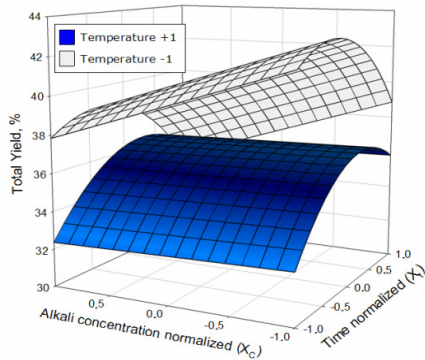
Figure 2: Variation of yield as a function of X_C, alkali concentration, and X_t, operation time, at two pulping temperature levels
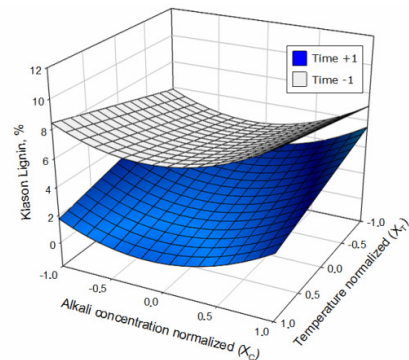

Figure 3: Variation of Klason lignin as a function of alkali concentration (X_C) and pulping temperature (X_T) at two time operation levels
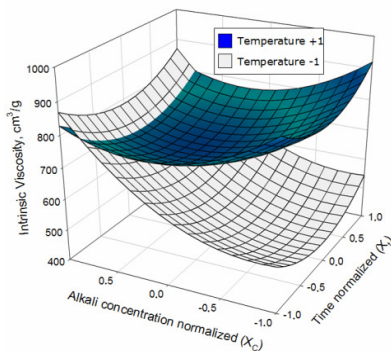

Figure 4: Variation of intrinsic viscosity as a function of alkali concentration (X_C) and operation time (X_t) at two pulping temperature levels
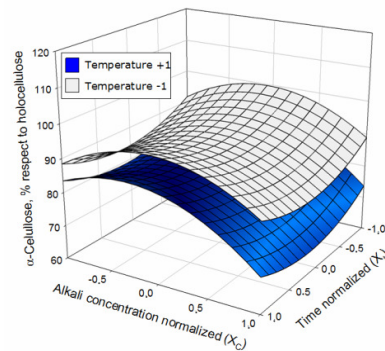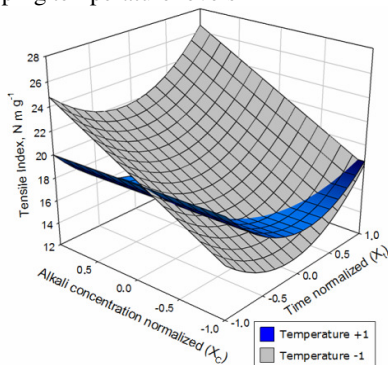

Figure 5: Variation of α-cellulose as a function of alkali concentration (X_C) and operation time (X_t) at two pulping temperature levels

Figure 6: Variation of tensile index as a function of alkali concentration (X_C) and operation time (X_t) at two pulping temperature levels
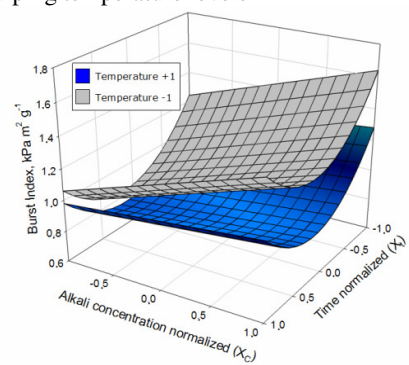

Figure 7: Variation of burst index as a function of alkali concentration (X_C) and operation time (X_t) at two pulping temperature levels

High temperatures in the operating range led to pulp with decreased soluble lignin contents and smaller kappa numbers, as well as to paper sheets with increased ºSR and brightness values, at the expense of poorer strength-related properties.

Although the operating time had little effect on virtually all dependent variables, it was adjusted in terms of the other two variables in optimizing the process. Long operating times resulted in more marked delignification of the pulp and hence in decreased contents in Klason lignin.

In order to determine the values of the independent variables in NaOH pulping (operation temperature, alkali concentration and operation time), giving the optimum values of dependent variables, the response surfaces for six dependent variables were plotted (Figs.2-7). Through the three-dimensional plot, it is very easy

and convenient to understand the interactions between two or three variables and to locate their optimum ranges. The response surfaces are shown at outliers (of the most influential variable in each case: +1 and -1) of the proposed experimental design.

As can be seen from Figure 2, yields peaked at low temperatures and also at low alkali concentrations, all with medium operating times.

The kappa number was scarcely influenced by the alkali concentration and operating time (data not shown). The lowest numbers were obtained at high temperatures. Similarly, delignification was maximal – and lignin contents the lowest – at high temperatures and long operating times (see Fig. 3).

Pulp viscosity (Fig. 4) was high at high temperatures irrespective of time and alkali concentration. At low temperatures, however, optimizing the viscosity entailed using high alkali concentrations, with little effect of temperature.

Figure 5 shows that higher α-cellulose contents are obtained when the pulping is conducted at low temperatures, with intermediate alkali concentrations and times at the end of the operating range, though time variation has a low influence on the final content of α-cellulose. The fact that the best results were obtained with values on the opposite ends of the operating ranges for the independent variables was mirrored by the strength-related properties of the paper sheets and is consistent with the above-described variation of viscosity. Thus, as can be seen from the tensile index plot of Figure 6, the highest values of tensile index are obtained at low temperatures, high concentrations of alkali and maximum or minimum operating times. The burst index (Fig. 7) and tear index (figure not shown) changed similarly as the tensile index. Thus, the optimum values were obtained at low temperatures, high alkali concentrations and times at the end of the operating range.

With longer operating time, a greater delignification is achieved, as well as higher α-cellulose content and therefore greater resistance. With low operating times, higher resistance is due to the fact that cellulose suffers less degradation during the treatment.

Using the equations in Table 5 at different values of the dependent variables allowed us to establish the optimum pulping conditions, namely: $X_T(-0.5)=117.5°C$; $X_C(0.5)=6.5\%$ and $X_t(-1)=60$ min, with which a total cellulose pulp yield of 37.3% of the initial feed stockcould be reached, with α-cellulose content of 97.0%, and which then allowed achieving a tensile index of 25.6 Nm/g, a burst index of 1.7kPa m^2/g and a tear index of 2.6 mN m^2/g.

CONCLUSION

The optimum operating conditions for the cold alkaline extraction of hemicelluloses from wheat straw were found to be: alkali concentration of 100 g/L, temperature of 40°C and operating time of 90 min. These conditions allowed 57.5% of all hemicellulose and 56.8% of all lignin to be extracted into the liquid phase.

The solid fraction provided by the pretreatment could be used to obtain cellulose pulp by soda-anthraquinone delignification. The proposed processing scheme is environmentally friendly because it can reduce the amount of soda needed by more than 50% with respect to soda pulping and can substantially decrease the operating time.

REFERENCES
[1] T. Foster-Carneiro, M. D. Berni, I. L. Dorileo and M. A. Rostagno, *Resour. Conserv. Recycl.*, **77**, 78 (2013).
[2] D. S. Ruzene, D. P. Silva, A. A. Vicente, A. R. Gonçalves and J. A. Texeira, *Appl. Biochem. Biotechnol.*, **147**, 85 (2008).
[3] M. FatihDemirbas, *Appl. Energ.*, **86**, S151 (2009).
[4] F. Carvalheiro, L. C. Duarte and F. M. Gírio, *J. Sci. Ind. Res. India*, **67**, 849 (2008).
[5] H. J. Huang, S. Ramaswamy, W. W. Al-Dajani and U. Tschirner, *Bioresour. Technol.*, **101**, 624 (2010).
[6] H. J. Huang, S. Ramaswamy, U. W. Tschirner and B. V. Ramarao, *Sep. Purif. Technol.*, **62**, 1 (2008).
[7] R. Martín-Sampedro, M. E. Eugenio, J. A. Moreno, E. Revilla and J. C. Villar, *Bioresour. Technol.*, **153**, 236 (2014).
[8] C. Vila, J. Romero, J. L. Francisco, G. Garrote and J. C. Parajó, *Bioresour. Technol.*, **102**, 5251 (2011).
[9] A. Alfaro, F. López, A. Pérez and A. Rodriguez, *Bioresour. Technol.*, **101**, 7635 (2010).

[10] A. Alfaro, A. Rivera, A. Pérez, R. Yañez, J. C. García *et al*., *Bioresour. Technol*., **100**, 440 (2009).

[11] J. M. Feria, A. Alfaro, F. López, A. Pérez, J. C. García *et al*., *Bioresour. Technol*., **103**, 381 (2012).

[12] M. Brienzo, A.F. Siqueira and A. M. F. Mialgres, *Biochem. Eng. J*., **46**, 199 (2009).

[13] F. Peng, J. L. Ren, F. Xu, J. Bian, P. Peng *et al*., *J. Agric. Food Chem*., **57**, 6305 (2009).

[14] H. Chen, H. Zang, S. Fu and A. L. Lucia, *BioResources*, **11**, 196 (2011).

[15] W. G. Glasser, W. E. Kaar, R. K. Jain and J. E. Sealey, *Cellulose*, **7**,299 (2000).

[16] J. C. García, M. J. Díaz, M.T . García, M. J. Feria, D. M. Gómez*et al*., *Biochem. Eng. J*., **71**, 127 (2013).

[17] P. F. Vena, M. P. García-Aparicio, M. Brienzo, J. F. Görgens and T. Rypstra, *J. Wood Chem. Technol*., **33**, 157 (2013).

[18] G. Schild, H. Sixta and L. Testova, *Cellulose Chem. Technol*., **44**, 35 (2010).

[19] B. C. Saha, *J. Ind. Microbiol. Biot*., **30**, 279 (2003).

[20] R. C. Sun, in "Cereal Straw as a Resource for Sustainable Biomaterials and Biofuels", Elsevier, 2010, pp. 105-117.

[21] L. E. Wise, M. Marphy and A. D'Adieco, *Paper Trade J*., **122**, 35 (1946).

[22] X. Pan, C. Arato, N. Gilkes, D. Gregg, W. Mabee *et al*., *Biotechnol. Bioeng*., **90**, 473 (2005).

[23] L. Jiménez, F. López and C. Martínez, *Process Biochem*., **29**, 595(1994).

[24] G. Garrote, M. E. Eugenio, M. J. Díaz, J. Ariza and F. López, *Bioresour. Technol*., **88**, 61 (2003).

[25] S. Caparrós, J. Ariza, F. López, J. A. Nacimiento, G. Garrote *et al*., *Bioresour. Technol*., **99**, 1368 (2008).

[26] A. Rodriguez, A. Moral, L. Serrano, J. Labidi and L. Jiménez, *Bioresour. Technol*., **99**, 2881 (2008).

[27] L. Jiménez and F. López, *Wood Sci. Technol*., **27**, 468 (1993).

[28] R. C. Sun, J. M. Lawther and W. B. Banks, *Ind. Crop. Prod*., **4**, 127 (1995).

[29] R. Sun, J. M. Fang, J. Tomkinson, Z. C. Geng and J. C. Liu, *Carbohyd. Polym*., **44**, 29 (2001).

[30] L. Jiménez, F. López and I. Sánchez, *Tappi J*.,**74**, 217 (1991).

[31] N. Schall, E. Krúger, R. Blum and M. Rübenacker, *Tappi J*., March, 35 (2009).

[32] P. Bajpai, S. H. Mishra, O. M. Mishra, S. Kumar, P. K. Bajpai *et al*., *Tappi J*., **3**, 3 (2004).

[33] S. Ates, I. Deniz, H. Kirci, C. Atik and O. T. Okan, *Turk. J. Agric. For*., **39**, 144 (2015).

[34] A.Tutus and H. Eroglu, *INPAPER International*, October-December, (2001), http://www.inpaper.com/magzines/inpaper/oct-dec-y1k/tech-1.htm

[35] S. Singh, D. Dutt and C. H. Tyag, *Bioresources*, **6**, 154 (2011).

[36] X. J. Pan and Y. Sano, *J. Wood Sci*., **45**, 319 (1999).