Barley Straw (*Hordeum vulgare*) as a Supplementary Raw Material for *Eucalyptus camaldulensis* and *Pinus sylvestris* Kraft Pulp in the Paper Industry

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The present study shows that barley straw (*Hordeum vulgare*) can be a supplementary raw material of softwoods and hardwoods such as *Pinus sylvestris* and *Eucalyptus camaldulensis*, respectively, for the production of cellulose and paper, reducing an agricultural residue that has no added value. Barley straw has a lower content of cellulose at 36.4% than *P. sylvestris* and *E. camaldulensis*, but it contains a lower quantity of lignin, 15.9%. After pulping with soda anthraquinone (AQ), high contents of cellulose (56.5 to 67.5%) and holocellulose (>80%) were attained. Paper sheet properties were able to reach, and even improve upon, those of wood species (*Pinus* and *Eucalyptus*) pulped with kraft. Better values of total yield (56.5%), Kappa number (8.9), and ISO brightness (36.4%), were attained for paper sheets from barley straw pulp *versus E. camaldulensis* and *P. sylvestris*, respectively, and comparable values for viscosity, tensile, and burst index were obtained.

Keywords: Barley straw; Agrifood residue; Biomass resources; Cellulose; Paper

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INTRODUCTION

Nowadays, the sustainability concept is being widely applied in all aspects of life, especially regarding biomass resources to produce energy and different types of materials such as cellulose, for paper production. Traditionally, two very well-known wood families are used in the paper industry, Pinaceae and Myrtaceae. *Pinus* and *Eucalyptus* are the most used genera because of their fast growth rate. However, demand for wood for different uses has increased considerably, and trees are felled faster than forests can recover. As a consequence, deforestation and desertification are affecting a large area of forests, becoming an important problem to face.

Because of this (deforestation and desertization), it would be interesting to use alternative sources such as non-wood biomass. In this way, straw can be suggested as a supplementary raw material to be studied in the paper industry for the production of pulp and paper and other derivatives. Usually, when cereals are harvested, straw has no added value other than animal feed. As a result, straw is generally burned, *in situ*, by farmers, releasing black smoke that contributes to air pollution. It is estimated that biomass burning produces 40% of the carbon dioxide (CO_2), 32% of the carbon monoxide (CO), 20% of the particulate matter, and 50% of the polycyclic aromatic hydrocarbons released to the environment on a global scale (Kambis and Levine 1996). It is also important to note that the production of dioxins due to incomplete burning causes the release of highly toxic and carcinogenic compounds (Lemieux *et al*. 2004; CEC 2014). On top of that, it can cause pollution of the soil as emissions of nitrous oxide from the decomposition of crop residues on cultivated soils is common; in 2012, a total of 192,581 gigagrams of CO_2 equivalents were released to the atmosphere. In particular, barley straw (*Hordeum vulgare*) could be a good option to be considered as a raw material in the pulp and paper industries, taking into account that in 2012, due to barley residues, 10^{13} grams of CO_2 equivalents were released to the atmosphere in the world (5.2% of total emissions). A total of 57.9% of these emissions were from Europe, and Spain was among the 10 top emitters in 2012 with 465.82 time 10^{10} grams of CO_2 equivalents. In addition, in 2013, the production of barley (cereal) over the world was 144 M tons; 59.3% of the production was carried out in Europe, and 10 Mtons were produced in Spain (12% of the total production of Europe). Moreover, Spain is fifth on the list of top producers of the world, preceded by Russia, Germany, France, and Canada. Barley is the fifth most produced commodity in Europe and the most produced in Spain, followed by olives, wheat, maize, and sugar beets (FAOSTAT 2014).

In a preliminary study, it was shown that the pulping of barley straw and other kinds of straws under weak conditions (100 °C, 7% NaOH oven dry matter (o.d.m), 10 liquid/solid ratio (LSR), and 150 min of cooking) results in very good paper properties for packaging products and can be used at an industrial scale (Vargas *et al*. 2012). For this reason, as a complement to the previous study, it has been considered important to study the use of barley straw under not very harsh conditions in order to produce pulp to manufacture cellulose destined for paper uses. In the present study, the aim was to find the optimal condition to produce cellulose and paper from barley straw in order to give value to this residue and transform it into a byproduct of agriculture activity, reducing the negative effects of its decomposition on the environment. Besides, the additional goal of this work was to demonstrate that in comparison to some wood species used in the paper industry such as pine and eucalyptus pulped by kraft processes, paper made from barley straw through a soda-anthraquinone (soda-AQ) process presents great potential to be an additional raw material for use by paper industries.

For this goal, the soda-anthraquinone pulping process has been studied for the previously mentioned raw material. Usually, pulping processes produce pollutant effluents, especially when sulfur compounds are used as delignificant agents, as in the kraft process. On the contrary, for the soda-anthraquinone pulping process, recovery of black liquors is well known. In that pulping process, anthraquinone produces an acceleration of the alkaline delignification as well as carbohydrate stabilization (Jiménez *et al*. 2005). Moreover, it shows advantages such as a good rate of pulp production, high yields, reduction of cooking times, and medium values of Kappa number (Sánchez *et al*. 2010).

In this work, *Hordeum vulgare* was characterized in terms of its contents in holocellulose, α-cellulose, and lignin. Also, an experimental factor design was used to examine the influence of operational variables in the soda-AQ pulping of it (*viz*. soda concentration, cooking temperature, and time) on the contents in holocellulose, α-cellulose, lignin, yield, viscosity, and kappa number of the resulting pulps, and also on the breaking length, stretch, burst index, tear index, and brightness of paper sheets made from it.

EXPERIMENTAL

Materials

Barley straw was collected from a local farm in Alcalá la Real (Jaén, Spain). The first task was to spread the bales of straw in order to homogenize the moisture of the material. Second, it was necessary to sift and perform a manual screening in order to separate undesirable elements such as stones, plastic bags, seeds, dust, and wire. After that, the straw was dried at room temperature and stored in plastic bags for proper conservation.

Methods

Raw material and pulp characterization

The chemical properties of barley straw and pulps obtained in these experiments were determined in accordance with the respective standards for the different components of ethanol extractives (TAPPI T204 cm-97 (1997), 1% NaOH solubles (TAPPI T212 om-98 (1998)), hot water solubles (TAPPI T207 cm-99 (1999)), α-cellulose (TAPPI T203 cm-99 (1999)), holocellulose (TAPPI T9m-54 (1998)), Klason lignin (TAPPI T222 om-98 (1998)), ash (TAPPI T211 om-93 (1993)), yield (gravimetrically), viscosity (TAPPI T230 om-99 (1999)), and Kappa number (TAPPI T236 om-99 (1999)).

Paper sheet properties

Paper sheets obtained from the pulping process of barley straw under different conditions were characterized according to the following standard methods: breaking length (TAPPI T494 om-96 (1996)), tensile index (TAPPI T494 om-96 (1996)), stretch index (TAPPI T494 om-96 (1996)), burst index (TAPPI T403 om-97 (1997)), tear index (TAPPI T414 om-98 (1998)), and ISO brightness (ISO 2470-2 (2008)). Five measures of brightness on both sides of each sheet were made, getting a standard deviation lower than 3 for 93% of the measurements. For the rest of the properties, two measures in ten sheets were carried out.

Pulping of raw material

Pulps from barley straw were produced using a 15-L batch cylindrical reactor that was heated by means of an electrical wire linked through a rotary axle to ensure proper agitation and to a control unit including a motor actuating the reactor, and the required instruments for measurement, control of pressure, and temperature.

The experimental conditions of work in the reactor were given by three independent variables as follows: temperature (100, 130, and 160 °C), time (90, 120, and 150 min), and soda concentration (o.d.m) (8, 11, and 14%), with a constant liquid/solid ratio of 10 and 1% of anthraquinone (o.d.m). These operating conditions were selected based on previous works and experiments in order to obtain proper values of yield, cellulose content in the pulps, and good values for the properties of the sheets. After pulping, the pulped material was washed with water, fiberized in a wet disintegrator at 1200 rpm for 30 min, and beat in a Sprout-Bauer defibrator (Germany). Finally, the screenings were separated by sieving through a 0.14 mm mesh, and the pulps were dried at room temperature and stored in bags until used.

Experimental design

As in previous works (Rodríguez *et al*. 2011), a second order factorial design was used, and the experimental data was fit to the following second-order polynomial (Eq. 1),

$$Y = a_0 + a_1X_T + a_2X_t + a_3X_S + \cdots + a_{11}X_T^2 + a_{12}X_TX_t + a_{13}X_TX_S + \ldots + a_{22}X_t^2 + a_{23}X_tX_S + \cdots + a_{33}X_S^2 \quad (1)$$

where Y denotes a characteristic or property of the pulp (pulp yield, viscosity, Kappa number) or a paper sheet property (tensile, stretch, burst or tear index, brightness), and coefficients a_0, a_1, $a_{2\ldots}$ are unknown characteristic constants estimated from the experimental data. The independent variables X_T, X_t, and X_S represent the normalized values of the pulping process: temperature, time, and soda concentration.

The independent variables are normalized from -1 to +1 according to Eq. 2:

$$X_{(T,t,S)} = 2\frac{X-\bar{X}}{X_{max}-X_{min}} \quad (2)$$

In this way, it becomes easier to compare the coefficients and the individual effects of the independent variables on the response variable, improving the estimation of regression coefficients and decreasing interrelations between lineal and quadratic terms. Using experimental data for each one of the dependent variables of the pulping process for the different experiments of the experimental design, proceeding with a multiple regression analysis by using the Biomedical Computer Programs BMDP ©Statistical Software (Dixon 1988), considering all the terms of Eq. 1 and driving out all those terms in which F-Snedecor is lower than 3, and by using the Stepwise method (Draper and Smith 1981), equations that connect the dependent and independent variables were found.

RESULTS AND DISCUSSION

Raw Material

Chemical characterization of barley straw was carried out according to the TAPPI standards, giving the results shown in Table 1. All the experiments were carried out in triplicate.

Table 1. Chemical Characterization of Barley Straw as a Raw Material *versus* Wood Species *Eucalyptus camaldulensis* and *Pinus sylvestris*

Chemical characterization	Content (%)			
	Hordeum vulgare	*Eucalyptus camaldulensis* I (Khristova *et al*. 2006)	*Eucalyptus camaldulensis* II (Dharm and Tyagi 2011)	*Pinus sylvestris* (Sable *et al*. 2012)
1% NaOH extractives	40.9±0.5	-	-	-
α-cellulose	36.4±0.1	44.1*	-	49*
Holocellulose	73.8±0.2	-	55.6	-
Klason Lignin	15.9** ±0.2	20	33.2	27.1
Ash	8.3±0.25	0.7	1.26	0.3

*****Kürschner-Hoffer cellulose
******Considered as total lignin

For *Hordeum vulgare*, the value obtained for the 1% NaOH solubles predicts average pulping yield values of around 40 to 50%. These values, not high in comparison with conventionally raw materials used in the paper industry, allowed the use of at least 50% of the total quantity of the raw material. When comparing barley straw content of cellulose and lignin to some examples of softwoods and hardwoods used in the paper industry such as pine (*Pinus sylvestris*) (Sable *et al*. 2012), and eucalyptus (*Eucalyptus camaldulensis*) (Khristova *et al*. 2006; Dharm and Tyagi 2011), lower cellulose values can be observed in barley straw composition (36.4%) compared to pine (49%) and eucalyptus I (44.1%). Despite this fact, lignin content in barley straw has the lowest value at 15.9%. This can be considered total lignin as acid soluble lignin content for untreated barley straw is lower than 1.5% (Iroba *et al*. 2014) *versus* 27.1% in the case of pine (Sable *et al*. 2012), and 20% and 33.2% for eucalyptus I (Khristova *et al*. 2006) and eucalyptus II (Dharm and Tyagi 2011), respectively. It can also be seen that holocellulose content is higher for barley straw (73.8%) than for *Eucalyptus camaldulensis* II (55.6%). Barley straw ash content is higher than that of pine and eucalyptus. It is known that a high content of ash can cause abrasion and inlay in pipes systems. However, it has been demonstrated that this raw material can be used in industrial processes without causing further problems of clogging (Vargas *et al*. 2012).

Soda Process and Polynomial Design

In this process, barley straw was subjected to pulping at given sodium hydroxide concentrations, temperatures, cooking time, and a liquid/solid ratio of 10, according to the experimental design, as shown in Table 2. These operational conditions were chosen taking into account previous works (Vargas *et al.* 2012). With this pulping process, it is possible to eliminate most of the lignin content of raw materials and further reduce degradation of hemicelluloses and cellulose (Vargas *et al*. 2012). Additional advantages of this process compared to kraft, the most used process for industrial pulping. The residual liquors are free of sulfur components; it is possible to use this process with different raw materials - wood and non-wood- as cereal straw, olive tree prunings, *etc*., obtaining good yield values and pulp and papersheets properties.

Table 2 shows the operational conditions and experimental values for chemical characterization of barley straw pulps with Soda-AQ as reagent, which differed less than 5% from their means as obtained in triplicate measures.

It can be observed that after pulping, the content of cellulose obtained had increased up to high values between 56.5% and 67.5%, reaching the maximum at the strictest conditions in experiment 2. Moreover, as can be noted from experiments 6, 10, 11, 12, and 14 in Table 2, under different pulping conditions, very similar contents of cellulose were obtained. Besides, the content of holocellulose was over 80% in all the experiments, reaching almost 93% in experiment 6. In addition, a good delignification was achieved. Lignin decreased from 15.9% to values lower than 7.8% in all experiments except for those in which soda concentration applied was the minimum (8%). Additionally, it is worthy to mention that ash content after pulping process decreased drastically. As can be seen from chemical composition after the pulping process, it seems to be that pulps must have a good chemical composition in order to manufacture paper.

In Table 3, experimental values of total yield after pulping process, and paper sheets properties from soda-AQ pulping of barley straw are shown.

Table 2. Experimental Values for Chemical Characterization

Experi-ment	Temperature (°C), Time (min), Soda conc. (%)	Normalized values (X_T, X_t, X_s)	α-celullose, (%)	Holocellulose, (%)	Klason Lignin, (%)	Ash, (%)
1	130,120,11	0, 0, 0	59.4±0.1	82.8±0.1	5.7±0.2	1.28±0.17
2	160,150,14	1, 1, 1	67.5±0.2	91.9±0.3	2.9±0.7	1.08±0.01
3	100,150,14	-1, 1, 1	59.9±0.2	85.7±0.5	6.1±0.4	1.55±0.08
4	160,150,8	1, 1, -1	60.1±0.1	86.5±0.2	11.5±0.2	2.52±0.10
5	100,150,8	-1, 1, -1	56.5±0.1	83.8±0.7	11.4±0.7	1.35±0.05
6	160,90,14	1, -1, 1	66.7±0.1	92.8±0.4	0.7±0.2	1.42±0.10
7	100,90,14	-1, -1, 1	59.5±0.2	84.0±0.5	7.8±0.2	0.99±0.43
8	160,90,8	1, -1, -1	57.8±0.2	80.9±0.1	11.2±0.5	3.07±0.01
9	100,90,8	-1, -1, -1	57.7±0.1	84.7±0.7	12.3±0.6	0.78±0.48
10	130,150,11	0, 1, 0	64.9±0.4	91.5±0.5	5.7±0.1	1.16±0.02
11	130,90,11	0, -1, 0	64.8±0.1	90.7±0.1	6.7±0.4	1.12±0.01
12	130,120,14	0, 0, 1	63.9±0.1	88.8±0.5	3.6±0.3	1.11±0.12
13	130,120,8	0, 0, -1	57.1±0.2	82.7±0.4	9.9±0.9	1.58±0.26
14	160,120,11	1, 0, 0	64.8±0.1	89.7±0.2	7.1±0.1	1.35±0.04
15	100,120,11	-1, 0, 0	59.5±0.5	86.5±0.1	7.8±0.3	1.26±0.06

Table 3. Experimental Values of the Paper Sheets Properties

Experiment	Total Yield (%)	Viscosity (mL/g)	Kappa Number	Tensile Index (Nm/g)	Stretch Index (%)	Burst Index (kN/g)	Tear Index (mNm^2/g)	ISO Brightness (%)
1	41.5	669.6 ±2.5	37.9 ±1.0	73.9 ±1.2	2.46 ±0.07	3.92 ±0.14	2.52 ±0.09	28.1 ±0.4
2	41.9	770.7 ±0.1	13.6 ±0.25	52.3 ±3.0	2.40 ±0.30	3.06 ±0.08	2.72 ±0.04	37.1 ±0.9
3	46.7	655.7 ±2.3	42.5 ±0.2	68.6 ±1.8	1.99 ±0.11	3.66 ±0.18	2.53 ±0.05	33.3 ±0.1
4	45.8	668.9 ±4.4	78.4 ±0.5	41.6 ±3.0	1.68 ±0.22	2.16 ±0.17	2.60 ±0.05	17.1 ±0.1
5	54.7	484.7 ±0.1	63.9 ±1.3	62.9 ±1.7	1.67 ±0.18	3.19 ±0.09	2.39 ±0.08	27.4 ±0.1
6	37.5	765.9 ±0.1	10.1 ±0.1	56.4 ±4.2	2.28 ±0.30	3.46 ±0.37	2.57 ±0.06	37.2 ±0.2
7	51.4	531.1 ±2.3	52.6 ±1.2	72.4 ±2.2	2.09 ±0.12	4.01 ±0.16	2.51 ±0.07	30.7 ±0.1
8	45.6	606.3 ±3.8	73.7 ±1.3	43.8 ±2.1	1.84 ±0.19	2.11 ±0.13	2.46 ±0.05	17.8 ±0.1
9	56.2	474.8 ±0.1	75.1 ±0.2	64.1 ±4.9	1.47 ±0.30	3.16 ±0.20	2.44 ±0.10	27.4 ±0.1
10	47.9	683.7 ±0.1	39.0 ±0.2	68.2 ±4.3	2.32 ±0.23	3.57 ±0.13	2.41 ±0.07	27.5 ±2.4
11	43.6	632.7 ±4.3	35.5 ±0.2	75.7 ±2.6	2.37 ±0.17	4.05 ±0.18	2.45 ±0.05	30.0 ±0.4
12	43.3	699.8 ±0.1	21.3 ±0.26	67.2 ±1.5	2.07 ±0.13	3.59 ±0.20	2.58 ±0.05	37.0 ±0.1
13	49.2	519.1 ±2.3	64.1 ±1.1	59.6 ±2.8	1.89 ±0.15	3.07 ±0.11	2.37 ±0.07	21.3 ±0.1
14	40.4	688.3 ±3.9	47.8 ±0.1	55.6 ±3.3	1.84 ±0.23	2.87 ±0.18	2.58 ±0.09	20.8 ±0.1
15	50.5	601.4 ±3.9	49.9 ±0.3	73.2 ±3.5	1.73 ±0.27	3.83 ±0.30	2.46 ±0.09	31.5 ±0.1

In the experiments that were carried out, the total yield fluctuated between 37.5% and 56.2%, corresponding this maximum to the weakest operational conditions. The highest viscosity value, 770.7 mL/g, was not achieved under the least stringent condition, but instead under the strictest one, and the lowest, 474.8 mL/g under the least stringent one. The lowest Kappa number that was obtained in the experimental design was 10.1, at the maximum temperature and soda concentration, but minimum cooking time (experiment 6). This Kappa number differs very little from the 13.6 value resulting from the most severe conditions (experiment 2). In terms of energetic efficiency, it would be better to minimize the cooking time, which may allow reduction in capital expenses. The maximum values obtained for tensile, stretch, burst, and tear indexes and ISO brightness, under different operational conditions, were 75.7 Nm/g, 2.46%, 4.05 kN/g, 2.72 mNm^2/g, and 37.2%, respectively. These are considered very good mechanical properties in handsheets.

In order to adjust the experimental data shown in Table 3, a multiple regression analysis was carried out by considering the independent variables to be temperature, cooking time, and soda concentration.

The selection of the statistically significant terms of the polynomial model was determined according to the F-Snedecor and had to be higher than 3, and a Student t-test that had to be higher than 1.75. Additionally, confidence intervals at 95% for the coefficients of each variable or parameter constant of models, did not include the zero.

The equations for the different dependent variables, in relation to pulp characteristics and the obtained paper sheets, are shown in Eqs. 3 through 10:

$$\text{Yield}= 44.78+1.35\, X_T X_t+2.45\, X_S^2-3.07\, X_S-4.83\, X_T \tag{3}$$

$$\text{Viscosity}= 655.13-37.45\, X_S^2+25.29\, X_t+66.94\, X_S+75.22\, X_T \tag{4}$$

$$\text{Kappa Number}= 39.56+3.69\, X_T X_t-6.04\, X_T+11.20\, X_T^2 -10.56\, X_S X_T-21.51\, X_S \tag{5}$$

$$\text{Tensile Index}= 72.02+1.16\, X_S X_T-1.88\, X_t-6.76\, X_T^2-7.72\, X_S^2+4.49\, X_S-9.15\, X_T \tag{6}$$

$$\text{Stretch Index}= 2.15+0.17\, X_t^2+0.11\, X_T-0.39\, X_T^2+0.23\, X_S \tag{7}$$

$$\text{Burst Index}= 3.79-0.34\, X_T^2-0.36\, X_S^2+0.41\, X_S-0.42\, X_T \tag{8}$$

$$\text{Tear Index}= 2.46+0.04\, X_T X_t+0.06\, X_T^2+0.06\, X_T+0.06\, X_S \tag{9}$$

$$\text{Brightness}= 28.28-2.03\, X_T+3.78\, X_S X_T+6.43\, X_S \tag{10}$$

where X_T, X_t, and X_S represent normalized values for temperature, time, and soda concentration, respectively.

From Eqs. 3 to 10, it can be observed that time (X_t), temperature (X_T), and soda concentration (X_S) have influence on all the dependent variables except for burst index and ISO brightness, where cooking time does not have an important effect.

The values for multiple-R, R^2, and adjusted-R^2 of the corresponding Eqs. 3 through 10, as well as the highest values for p, and the lowest for Student t-test (for a 95% of confidence interval), are shown in Table 4.

Table 4. Values of Statistical Parameters for the Equations that Relate the Considered Dependent Variables of the Paper Sheet Properties to the Operation Variables during the Pulping of *Hordeum vulgare* Straw with Soda-AQ

Equation	Multiple R	R^2	Adjusted R^2	p <	t >
Yield	0.9577	0.9172	0.8840	0.0690	2.11
Viscosity	0.9609	0.9233	0.8927	0.0492	2.24
Kappa Number	0.9898	0.9797	0.9684	0.0238	2.72
Tensile Index	0.9937	0.9875	0.9782	0.0713	2.08
Stretch Index	0.8955	0.8019	0.7227	0.1116	1.75
Burst Index	0.9513	0.9051	0.8671	0.0263	2.60
Tear Index	0.9137	0.8348	0.7687	0.0341	2.45
Brightness	0.9581	0.9180	0.8956	0.0124	2.99

p = p-value
t = Student t-test value

A good fitting of the experimental data was obtained for the calculation of all the response variables, as multiple R, R^2, adjusted R^2, p, and Student t-test (Table 4). The data achieved multiple-R and R^2 values superior to 0.90 for all the dependent variables, except for stretch index and tear index (R^2), with a Kappa number and tensile index superior to 0.96. The estimated values through the previous equations reproduced the experimental results of the considered dependent variables for the paper sheets with errors lower than 3.3% for yield and 8.56% for stretch index in 87% of the experiments; 6.1% for viscosity, 6.71% for burst index, and 9.9% for brightness in 93% of the experiments; and, finally, 2.8% for tensile index and 2.53% for tear index in all the experiments.

Equations 3 through 10 make it possible to predict results of any of the dependent values, as long as they are in the range of the normalized values. To determine the values of the independent variables that result in the optimal values for each one of the dependent variables of the pulp and paper sheets (yield, viscosity, Kappa number, tensile, stretch, burst and tear index, and brightness), a non-lineal programming, following More and Toraldo´s method (1983), was applied.

In Table 5, optimal values of dependent variables, and the corresponding required values for operation variables are shown. From results shown in the table it can be noted that by working with the minimum cooking time (90 min), the optimal values for dependent variables are reached, except for viscosity, and tear index which need 150 min to get the best results. Working at reduced times involves power efficiency as well as a higher production rate and a reduction of the costs. Soda concentration has an important effect over all the dependent variables with values of X_S close to 1, except for the tensile index of 0.24 and the burst index of 0.57, which present values closer to X_S=0 and -1, to get the optimal yield. Finally, temperature (X_T) has an essential influence over viscosity, Kappa number, tear index, and brightness.

The optimal values obtained for barley straw through soda-AQ pulping process in the present work are compared in Table 6 to those obtained in previous works for wood species also used in the paper industry, such as *Eucalyptus camaldulensis* (Khristova *et al*. 2006; Dharm and Tyagi 2011) and *Pinus sylvestris* (Sable *et al*. 2012), that have been pulped through the kraft process.

Table 5. Values of Operations Variables for Barley Straw Soda-AQ Pulping Process to Get the Optimal Values for the Dependent Variables Related to Paper Sheets

Dependent variables	Optimal value for dependent variable (maximum or minimum*)	Values of independent variables to achieve optimal values for dependent variables		
		X_T	X_t	X_S
Total Yield (%)	56.5	-1	-1	-1
Viscosity (mL/g)	785.6	1	1	0.89
Kappa Number	8.9*	0.91	-1	1
Tensile Index (Nm/g)	77.4	-0.66	-1	0.24
Stretch Index (%)	2.56	0.14	-1	1
Burst Index (kN/g)	4.03	-0.62	-0.6	0.57
Tear Index (mNm^2/g)	2.72	1	1	1
Brightness (%)	36.4	1	-0.6	1

Table 6. Experimental Values Obtained for Eucalyptus and Pine versus Barley Straw Optimal Values

	Total Yield (%)	Viscosity (mL/g)	Kappa Number	Tensile Index (Nm/g)	Stretch Index (%)	Burst Index (kN/g)	Tear Index (mNm^2/g)	Brightness (%)
E. camaldulensis I (Khristova *et al*. 2006)	44	908	24.4	79.4	n/a	4.7	8.7	25.9
E. camaldulensis II (Dharm and Tyagi 2011)	52.44	n/a	22.18	53.9	n/a	3.49	5.49	n/a
P. sylvestris (Sable *et al.* 2012)	45.9*	n/a	27.5**	33.5	1.1	1.57	n/a	n/a
Hordeum vulgare	56.5	785.6	8.9	77.4	2.56	4.03	2.72	36.4

*****Screened yield
******Estimated data from Klason lignin value
n/a: not available

From Table 6 it can be seen that total yield is found to be similar or even higher for barley straw than for eucalyptus. The screened yield of barley straw, 47.4%, is very close to the screened yield for *P. sylvestris*, 45.9%. It can be seen that if *Hordeum vulgare* viscosity is compared to the one for *E. camaldulensis* I, the value is lower, 785.6 mL/g, but still high and considered a good value. Furthermore, as an unusual behavior and due to the nature and composition of the raw material, the highest viscosity coincides with the most severe operational conditions, the maximum quantity of cellulose at 67.5%, a high quantity of holocellulose at 91.9% and low lignin content of 2.9%, would lead to better mechanical properties in the formation of paper sheets. For the Kappa number, it can be seen that a low value of 8.9 can be obtained through the soda-AQ pulping process *versus* the kraft process. It is worthy to mention that from a non-wood raw material like barley straw, a very good tensile index in paper sheets of 77.4 Nm/g has been attained, compared to *E. camaldulensis* I tensile index of 79.4 Nm/g, and higher than 53.9 and 33.5 Nm/g for *E. camaldulensis* II and *P. sylvestris*, respectively. The optimal value of burst index accomplished for barley straw of 4.03 kN/g is also comparable to that obtained for *E. camaldulensis* I at 4.70 kN/g, slightly superior to *E. camaldulensis* II , and much higher than for *P. sylvestris* at 1.57 kN/g. The best value of tear index of barley straw was the worst among the studied species. However, ISO brightness was higher at 36.4%, compared to *E. camaldulensis* I at 25.9%.

Taking into consideration that the harvested area of barley over the world was about 50 Mha in 2013, the production yield was 2.908 tons of cereal per hectare in that year. The ratio of harvested barley straw/produced cereals is 0.53 (MAGRAMA 2014), and the amount of residue per hectare was 1.541 tons. If an average yield of pulping of 50% is considered, more than 38 Mtons of pulp could be produced from this residue, thereby avoiding pollution of the atmosphere and soils and reducing the cutting of trees (up to 20% of the total produced wood pulp).

As mentioned in the previous paragraph, if an average yield of pulping of 50% is taken into account, and considering the average values of holocellulose that pulps present, around 43 g of holocellulose can be obtained from 100 g of barley straw. From this quantity of holocellulose, around 60% is alpha cellulose, which implies about 26 g of pure cellulose, with diverse applications, being hemicelluloses of commercial interest. Hemicelluloses are applicable as gels, films, coatings, adhesives, and stabilizing and viscosity-enhancing additives in food and pharmaceuticals, as well as in other industrial branches. Some of them serve as biodegradable components in composites with synthetics or pre-polymers for production of new functionalized polymeric materials (Ebringerová 2006).

CONCLUSIONS

1. Barley straw has a lower content of cellulose compared to *Pinus sylvestris* and *Eucalyptus camaldulensis*, but a lower quantity of lignin.
2. High contents of cellulose and holocellulose were attained through the soda-AQ pulping process of barley straw.
3. In order to get optimal results for paper sheets, it is necessary to apply the highest concentration of soda, except for tensile and burst index.
4. Temperature has a low influence on total yield, tensile, and burst index, while having a relevant impact on the rest of the dependent variables.
5. Paper sheet properties can equalize, and even improve upon, those for *Pinus*, and *Eucalyptus* pulped with kraft.

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REFERENCES CITED

CEC. (2014). *Burning Agricultural Waste: A Source of Dioxins*. Montreal, Canada. Commission for Environmental Cooperation. pg. 6, http://www3.cec.org, Accessed on October, 2014.

Dharm, D., and Tyagi, C. H. (2011). "Comparison of various eucalyptus species for their morphological, chemical, pulp and paper making characteristics," *Indian J. Chem. Technol*. 18, 145-151.

Dixon, W. J. (1988). *BMDP Statistical Software Manual,* University of California Press, Berkeley, California.

Draper, N., and Smith, H. (1981). *Applied Regression Analysis*, Wiley, New York.

Ebringerová, A. (2006). "Structural diversity and application potential of hemicelluloses," *Macromol. Symp*. 232, 1-12. DOI: 10.1002/masy.200551401

FAOSTAT. (2014). *Food and Agriculture Organization of the United Nations, Statistics Division*, http://Faostat3.fao.org. Accessed October, 2014.

ISO 2470-2. (2008). "Paper, board and pulps - Measurement of diffuse blue reflectance factor - Part 2: Outdoor daylight conditions (D65 brightness)," *International Organization for Standardization*, Geneva, Switzerland.

Iroba, K. L., Tabil, L. G., Sokhansanj, S., and Dumonceaux, T. (2014). "Pretreatment and fractionation of barley straw using steam explosion at low severity factor," *Biomass Bioenerg*. 66, 286-300. DOI: 10.1016/j.biombioe.2014.02.002

Jiménez, L., Torre, M. J., and Gutiérrez, J. C. (2005). "Pasteado "a la sosa"," in: *Pastas Celulósicas de Materias Primas Alternativas a las Convencionales*, L. Jiménez (ed.), Gráficas Sol, Spain, pp. 141-162.

Kambis, A.D., and Levine, J. S. (1996). "Biomass burning and the production of carbon dioxide: A numerical study," in: *Biomass burning and global change*, J. S. Levine (ed.), Massachusetts Institute of Technology, Cambridge, EU, vol. 1, pp. 170-177.

Khristova, P., Kordsachia, O., Patt, R., and Dafaalla, S. (2006). "Alkaline pulping of some eucalypts from Sudan," *Bioresour. Technol*. 97, 535-544. DOI: 10.1016/j.biortech.2005.04.006

Lemieux, P. M., Lutes, C. C., and Santoianni, D. A. (2004). "Emissions of organic air toxics from open burning: A comprehensive review," *Prog. Energy Combust. Sci.* 30, 1-32. DOI: 10.1016/j.pecs.2003.08.001

MAGRAMA (2012). "Crops areas and production," http://www.magrama.gob.es, Accessed October 2014.

More, A., and Toraldo, A. (1983). "Algorithms for bound constrained quadratic programming problems," *Numer. Math*. 55, 377-400.

Rodríguez, A., Sánchez, R., Requejo, A., and Ferrer, A. (2011). "Simulation of *Hesperaloe funifera* diethanolamine pulping by polynomial and neural fuzzy models," *Chem. Eng. Res. Des.* 89, 648-656. DOI:10.1016/j.cherd.2010.10.001

Sable, I., Grinfelds, U., Jansons, A., Vikele, L., Irbe, I., Verovkins, A., and Treimanis, A. (2012). "Comparison of the properties of wood and pulp fibers from Lodgepole pine (*Pinus contorta*) and Scots Pine (*Pinus sylvestris*)," *BioResources* 7(2), 1771-1783. DOI: 10.15376/biores.7.2.1771-1783

Sánchez, R., Rodríguez, A., Navarro, E., Conesa, J. A., and Jiménez, L. (2010). "Use of *Hesperaloe funifera* for the production of paper, and extraction of lignin for synthesis and fuel gases," *Biomass Bioenerg*. 34, 1471-1480. DOI: 10.1016/j.biombioe.2010.04.019

TAPPI T9 m-54. (1998). "Holocellulose in wood," *TAPPI Press*, Atlanta, GA.

TAPPI T203 cm-99. (1999). "Alpha-, beta- and gamma-cellulose in pulp," *TAPPI Press*, Atlanta, GA.

TAPPI T204 cm-97. (1997). "Solvent extractives of wood and pulp," *TAPPI Press*, Atlanta, GA.

TAPPI T207 cm-99. (1999). "Water solubility of wood and pulp," *TAPPI Press*, Atlanta, GA.

TAPPI T211 om-93. (1993). "Ash in wood, pulp, paper and paperboard: combustion at 525 ºC," *TAPPI Press*, Atlanta, GA.

TAPPI T212 om-98. (1998). "One percent sodium hydroxide solubility of wood and pulp," *TAPPI Press*, Atlanta, GA.

TAPPI T222 om-98. (1998). "Acid-insoluble lignin in wood and pulp," *TAPPI Press*, Atlanta, GA.

TAPPI T230 om-99. (1999). "Viscosity of pulp (capillary viscometer method)," *TAPPI Press*, Atlanta, GA.

TAPPI T236 om-99. (1999). "Kappa number of pulp," *TAPPI Press*, Atlanta, GA.

TAPPI T403 om-97. (1997). "Bursting strength of paper," *TAPPI Press*, Atlanta, GA.

TAPPI T414 om-98, (1998). "Internal tearing resistance of paper (Elmendorf type method)," *TAPPI Press*, Atlanta, GA.

TAPPI T494 om-96. (1996). "Tensile properties of paper and paperboard (using constant rate of elongation apparatus," *TAPPI Press*, Atlanta, GA.

Vargas, F., González, Z., Sánchez, R., Jiménez, L., and Rodríguez, A. (2012). "Cellulosic pulps of cereal straw as raw material for the manufacture of ecological packaging," *BioResources* 7(3), 4161-4170. DOI: 10.15376/biores.7.3.4161-4170

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