

Influence of Operating Variables and Model to Minimize the Use of Anthraquinone in the Soda-Anthraquinone Pulping of Barley Straw

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Soda-anthraquinone (soda-AQ) pulping of barley straw was used to obtain cellulosic pulps for papermaking purposes. The identified parameters, or variables to be optimized, were operating time, anthraquinone concentration, and PFI refiner revolutions, and the influence of these operating variables on pulp properties was studied. A polynomial model that reproduced the experimental results with errors less than 6% was developed. Operating variables were found (46 min of processing time, 0.4 wt.% of anthraquinone concentration, and 3000 rpm of PFI revolution) that yielded competitive pulp properties (82 °SR beating grade number, 870 mL/g of viscosity, Kappa number of 13, 77 Nm/g of tensile index, and 30% ISO brightness) at reasonable chemical and energy costs. On the other hand, this study highlights the usefulness of this polynomial model as a method to minimize the use of anthraquinone in these pulping processes and to be able to predict what the pulp properties will be. For comparison purposes, new operating conditions were found, and the pulp properties still remain at a very good level for this cereal straw.

Keywords: Barley straw; Soda pulping; Polynomial model; Simulation; Anthraquinone; Hazard potential

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INTRODUCTION

Biomass has been relevant as a source of products and energy (Ferrer *et al.* 2011a). New alternative raw materials, such as non-woody materials and residues from agricultural and forest industries, among others, are being considered since the demand for pulp to be used in papermaking cannot be fulfilled only by classic raw materials such as hard- and softwoods (Ferrer *et al.* 2011a,b; Gonzalez *et al.* 2011; Hou *et al.* 2011).

In line with this, remarkable advantages are provided by the use of non-woody raw materials (Huang *et al.* 2006; Rodriguez *et al.* 2008):

- a) deforestation and replanting can be alleviated, since wood raw materials are saved for other uses different from papermaking;
- b) the woody cellulose fiber imports can be reduced in countries where there is a lack of wood raw materials; and
- c) the increasing demand of paper that is produced through clean technologies or from non-woody materials can be helped and fulfilled.

Among all the non-woody raw materials, cereal straws are a very important source of raw material, since the world production of cereals such as wheat, barley, maize, and oats was 1695 million tons in 2012 (FAOSTAT 2012). According to these numbers, this

agricultural activity generates a large amount of residue every year since a considerable number of kilograms of straw are produced from cereals. These cereal straws are currently being used for different purposes such as organic amendment and food for cattle; however most of them are burnt in the field, which contributes to the pollution and is a fire hazard (Navaee-Ardeh *et al.* 2004; Gonzalez-Garcia *et al.* 2010; Vargas *et al.* 2012).

Barley (*Hordeum vulgare* L.) is a member of the grass family Poaceae. Several million tons of this straw are generated from this crop every year. Nowadays, barley straw usually can be used to feed animals and sometimes as mulch or even incorporated into the plowed layer. If the straw is to be used for these purposes, it must be processed after harvesting (Law and Jiang 2001; Tavakoli *et al.* 2009).

Among all the known chemical-based pulping processes, the soda pulping is the oldest and simplest, and it can be used for cooking both woody and non-woody materials (Jimenez 2006). The pulps obtained from this pulping process are characterized by the presence of short fibers. The process also generates a liquid waste called "black liquor", which contains lignin degradation products and byproducts of cellulose and hemicellulose hydrolysis. Furthermore, it has been found that adding small amounts of certain organic compounds that act as catalysts (some compounds used for this purpose are hydrazine, hydroxylamine, anthraquinone, *etc.*) can increase the speed and selectivity of the delignification process (Jimenez 2006).

Anthraquinone (AQ) is an oxidant that is often used in chemical pulping for carbohydrates stabilization and delignification improvement (Borrega *et al.* 2013). The mechanism of action of the anthraquinone process "soda-AQ" is well known: it acts as a catalyst for redox reactions which occur during cooking (Fig. 1) (Kubes *et al.* 1978; Fleming *et al.* 1979).

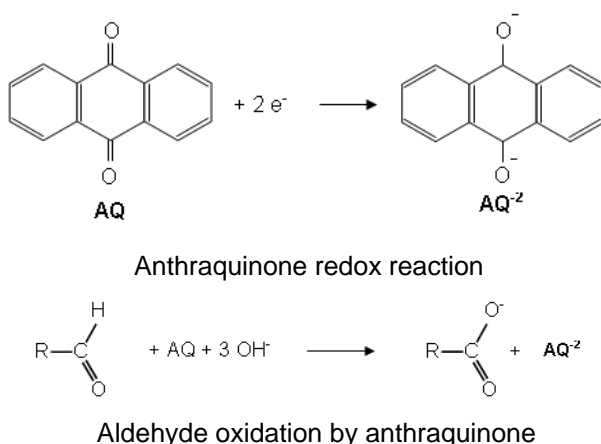


Fig. 1. Chemical reactions of anthraquinone

With the presence of anthraquinone as a chemical additive in the alkaline pulping process, the delignification rate and the preserved pulp yield can be improved. This can be mainly attributed to the redox cycle mechanism between the oxidized and reduced forms of anthraquinone, that is, AQ and anthrahydroquinone (AHQ), respectively. As shown in Fig. 1, the solubility of anthraquinone is due to its presence in the reduced form.

Electrons of the aldehyde groups from the carbohydrates in the fibers are transferred to the anthraquinone molecule and the aldehyde groups are converted into carboxyl groups (Fig. 1). This transformation causes carbohydrates to become stabilized, resulting in an increase in yield and preventing the peeling process (Löwendahl and Samuelson 1978; Chai *et al.* 2007). Because of the transfer of electrons, anthraquinone is converted into its reduced form, anthrahydroquinone. The acceleration mechanism of anthraquinone delignification involves the anthrahydroquinone attack on the transitional and reactive lignin structures (Landucci 1980).

Though there are references that report that adding small amounts of anthraquinone significantly improves the efficiency of the pulping process (Bozell *et al.* 1994), the health and environmental aspects of the use of anthraquinone are currently being considered. The European Food Safety Authority (EFSA) studied the impact of anthraquinone exposure in rats and mice over a two-year period, concluding that it could have carcinogenic effects on the liver and kidneys of laboratory animals. EFSA announced in 2012 that there is a need to know the toxicological properties (potential carcinogenic effects) of anthraquinone (European Food Safety Authority 2012). As a consequence, pulp and paper manufacturers have received attention from the authorities due to their use of this organic compound. In addition to this, the German Federal Institute for risk assessment (BfR) reconsidered the inclusion of this organic compound on its list of safe substances that may be used in food packaging. Finally, in 2012 they decided to remove it from that list. Besides this, the Confederation of European Paper Industries (CEPI) also issued an opinion on anthraquinone in 2014 in which CEPI advised paper and board manufacturers to stop using this substance in their production processes. This has led to a further debate on the costs that such a ban will entail for pulp manufacturers (Metsafibre 2014).

Although the soda pulping process has been used to cook barley straw and this redox cycle mechanism of AQ has been established in general (De Lopez *et al.* 1996), there is still a need to establish its validity in the soda pulping of straw pulps, since this cereal straw has not been that widely used for this purpose. Furthermore, there is no contribution to our knowledge related to the use of a polynomial model in order to minimize or just avoid the use of anthraquinone in the soda pulping process.

The current study deals with the soda-anthraquinone pulping process of barley straw in order to obtain cellulose-enriched pulp. The influence of operating variables (processing time, anthraquinone concentration, and PFI revolution) in the pulping process was studied by simulating the process through a polynomial model, in order to find optimum operating conditions to obtain the least degraded cellulose pulp.

On the other hand, this study was used to test this polynomial model in order to minimize the use of AQ, which is the most expensive chemical in the process and also has a carcinogenic potential, or as a method to eliminate it and be able to predict what the pulp properties will be if AQ concentration is set to zero. In other words, this polynomial model was used to determine what changes in operating variables are needed in order to offset the positive effects that could be lost if there is no AQ loading. For comparison purposes, the AQ concentration was set to zero and new operating conditions were found in order to predict the pulp properties.

The concepts from this study can also be used for other non-woody substrates pulped using the soda process. Finally, this study reveals the effects of beating (PFI revolution) on the pulp properties and how these results should be taken into account in order to scale them to the industry.

EXPERIMENTAL

Raw Material Characterization

In this work, barley straw was provided by the Ecopapel S.L. Company from cooperatives of Ecija (Seville, Spain). After harvesting this cereal straw, undesirable elements such as stones, seeds, *etc.* need to be separated through a manual screening. Once all these elements had been separated from the desirable material, the straw mentioned above was then dried until constant weight and stored in plastic bags until needed (Vargas *et al.* 2012). The chemical characterization of barley straw was determined according to the following TAPPI standards for the different components, namely: T-222 for lignin, T-203 0S-61 for α -cellulose, T-9m-54 for holocellulose, T-204 for ethanol extractives, and T-211 for ash. Hemicellulose content was estimated as the difference between holocellulose and α -cellulose contents.

Pulping

A 15-L batch cylindrical reactor that was heated by an electrical wire was used in order to cook barley straw. To ensure proper agitation, the reactor was linked to a control unit in order to control pressure and temperature (Vargas *et al.* 2012). The cooked fibers were fiberized in a wet disintegrator at 1200 rpm for 30 min and the screenings were separated by sieving through a screen of 0.14 mm mesh size. The pulp obtained was then beaten in a Sprout-Bauer refiner (Andritz Sprout Bauer Austria) and after that, was beaten on a PFI refiner from Metrotec (San Sebastian, Spain) with precise control of the number of beating revolutions used.

The cellulosic pulps from barley straw were obtained under the following sulfur-free chemical treatments: 10 % NaOH, 160 °C, 20 (-1), 40 (0) and 60 (+1) min processing time, 0 (-1), 0.3 (0) and 0.6 (+1) wt.% anthraquinone concentration, 0 (-1), 1500 (0) and 3000 (+1) PFI revolution and H = 10, where the H is the hydromodule (liquid-solid ratio). The processing conditions used were selected based on results from previous works (De Lopez *et al.* 1996; Vargas *et al.* 2012).

Pulp Characterization

As in the chemical characterization of the raw material, obtained pulps were characterized according to common standards, determining their contents of lignin, α -cellulose, and holocellulose, among others (results not shown). Furthermore, for all the experiments, the cellulosic pulps were characterized in terms of (°SR) Beating grade number (ISO 5267-1), viscosity (UNE-57-039) and Kappa number (UNE 57-034). Paper sheets with a grammage over 60 g/m² were obtained by using an Enjo-F39.71 sheet former according to UNE 57-042. Followed conditioning in accordance with UNE 57-001, the sheets were characterized in terms of tensile index (UNE 57-028) and brightness (UNE 57-062) (Rodriguez *et al.* 2011).

Experimental Design

Experimental data were fitted to the following second-order polynomial (Montgomery 1991) (Eq. 1),

$$Y_e = a_0 + a_1 X_T + a_2 X_A + a_3 X_R + a_{12} X_T X_A + a_{13} X_T X_R + a_{23} X_A X_R + a_{11} X_T^2 + a_{22} X_A^2 + a_{33} X_R^2 \quad (1)$$

where Y_e denotes the response variables [viz. beating grade number or beating degree (BG), viscosity (VI), Kappa number (KN), tensile index (TI) or brightness (BR)]; X_T , X_A and X_R are the normalized values of the operational variables (processing time – T, anthraquinone concentration – A and PFI (refiner or refining) revolution – R, respectively); and a_0 to a_{33} are constants. The values of the operational variables were normalized to values from -1 to $+1$ by using the following equation (Eq. 2),

$$X_n = \frac{2(X - \bar{X})}{X_{\max} - X_{\min}} \quad (2)$$

where X_n is the normalized value of T, A, or R; X is the actual experimental value of the variable concerned; \bar{X} is the mean of X_{\max} and X_{\min} ; and X_{\max} and X_{\min} are the maximum and minimum value, respectively, of such a variable. The normalized values for the independent variables in the 15 experiments conducted are given in Table 1.

Table 1. Values of Operational Variables and Experimental Values of the Pulp Properties Obtained by Soda-Anthraquinone Pulping of Barley Straw

Exp.	Normalized values of operational variables			Beating grade number, °SR	Viscosity, mL/g	Kappa number	Tensile index, Nm/g	Brightness, %
	X_T	X_A	X_R					
1	-1	-1	-1	28.0	749.25	25.31	53	37.34
2	-1	-1	1	72.5	678.20	20.39	70	31.83
3	-1	1	-1	25.0	796.85	20.06	51	36.25
4	-1	1	1	70.5	759.50	19.17	74	29.57
5	1	-1	-1	26.0	686.39	33.66	42	34.32
6	1	-1	1	66.5	763.97	29.24	69	30.78
7	1	1	-1	27.0	908.58	14.76	42	37.55
8	1	1	1	77.5	862.54	15.11	71	28.95
9	0	0	0	55.5	807.17	17.55	62	32.63
10	0	0	0	62.5	865.34	13.47	70	31.67
11	-1	0	0	66.5	788.14	15.20	71	33.43
12	1	0	0	63.5	823.56	18.08	65	29.56
13	0	-1	0	55.5	749.82	25.67	67	33.41
14	0	1	0	58.5	858.19	12.72	59	36.06
15	0	0	-1	49.0	877.04	15.34	51	36.89
16	0	0	1	73.5	876.96	13.87	76	32.23

RESULTS AND DISCUSSION

Raw Material Characterization

Table 2 shows the results of the chemical analysis of barley straw, various agricultural residues (empty fruit bunches (EFB), olive prunings, wheat straw, rice straw, oat straw, sugarcane bagasse, vine shoots, and cotton stalks) (Jimenez *et al.* 1990; Jimenez *et al.* 1993; Jimenez *et al.* 2006b; Ferrer *et al.* 2011a; Vargas *et al.* 2012), alternative raw materials (Jimenez *et al.* 2005; Jimenez *et al.* 2006b), and hardwoods and softwoods (Alonso 1976).

Table 2. Chemical Characterization of Various Agricultural Residues, Alternative Raw Materials, and Hardwoods and Softwoods

Raw material	Ethanol extractives, %	Ash, %	α -cellulose, %	Hemicellulose, %	Lignin, %
Barley straw	8.30	9.32	36.20	28.30	16.10
EFB (Ferrer <i>et al.</i> 2011a)	1.17	3.20	47.91	-	24.45
Olive prunings (Jimenez <i>et al.</i> 1990)	10.36	1.36	35.67	25.80	19.71
Wheat straw (Jimenez <i>et al.</i> 1990)	4.01	6.49	39.72	36.48	17.28
Rice straw (Jimenez <i>et al.</i> 2005)	1.40	15.39	-	-	25.23
Oat straw (Vargas <i>et al.</i> 2012)	6.40	7.00	37.90	37.70	16.60
Sugarcane bagasse (Jimenez <i>et al.</i> 2005)	1.73	2.10	-	-	19.80
Vine shoots (Jimenez <i>et al.</i> 2006b)	4.87	3.49	41.14	26.00	20.27
Cotton stalks (Jimenez <i>et al.</i> 2006b)	1.42	2.17	58.48	14.38	21.45
<i>Leucaena diversifolia</i> (Jimenez <i>et al.</i> 2006b)	4.44	-	40.10	-	19.09
Tagasaste (Australia) (Jimenez <i>et al.</i> 2006b)	2.17	-	47.65	-	15.71
<i>Paulownia fortunei</i> (Jimenez <i>et al.</i> 2005)	5.50	-	37.40	-	22.40
<i>Pinus pinaster</i> (Alonso 1976)	2.57	0.54	55.92	13.67	26.22
<i>Eucalyptus globulus</i> (Alonso 1976)	1.15	0.57	52.79	27.68	19.96

According to the data presented in Table 2, the following conclusions could be made:

- The content of α -cellulose in barley straw was similar to that for the olive prunings, wheat, and oat straw. However, this was lower compared to the values of α -cellulose for the cotton stalks, hardwoods and softwoods.
- The content of hemicellulose in barley straw was higher than that measured for the *Pinus pinaster* and cotton stalks. However, wheat and oat straws had higher values for hemicellulose.
- The content of lignin for the barley straw was one of the lowest as compared to other agricultural residues, alternative raw materials, hardwoods, and softwoods.
- The extractives and ash contents for the barley straw were among the highest compared to the rest of the raw materials considered in Table 2.

All these results suggest that this low-cost, widely available residual bioresource could be used as feedstock for papermaking purposes, among others, since it contains a relatively high amount of cellulose and one of the lowest amounts of lignin. Vargas and co-workers (2012) found similar results in their work (Vargas *et al.* 2012). On the other hand, barley straw could become a good substrate for fermentation to ethanol because of its high cellulose and hemicellulose content. It is well known that straw hemicellulose is a valuable source of xylose, which can be used as a feedstock for ethanol production (De Lopez *et al.* 1996). Though its lignin content is not that high, barley straw could still be used as a source for lignin. Even though, lignin, a byproduct of pulp and paper production,

is now used primarily as in-plant fuel, there are efforts to seek commercial uses of this byproduct as a chemical feedstock and convert it into useful, higher value compounds such as pulping catalysts (Bozell *et al.* 1994). The extractives are the fraction of material that cannot be classified as either carbohydrate or lignin, so it can be classified as "solvent-extractable extractives". This fraction consists primarily of resin and fatty acids and their esters, along with waxes and unsaponifiable substances (Baptista *et al.* 2006). They, together with the ash fraction, can have either negative or positive effect on pulp properties, depending on the end use applications. If one wants to improve fibrillation of the pulp by mechanical refining, then the high content of extractable materials such as fatty acids, together with lignin, could be useful since it will contribute to a higher density of anionic surface charge of semichemical fibers (Eronen 2011). Usually, fibers that are easy to beat are also easy to fibrillate, and these have anionic charges on their surface (Eronen 2011). However, these extractives probably have a negative impact on pulp color and bleachability (Baptista *et al.* 2006).

Pulping Model

Preliminary experiments were carried out, based on the results of other researchers on different raw materials, in order to define the ranges of operating variables (De Lopez *et al.* 1996; Vargas *et al.* 2012). According to this, the following ranges were chosen: processing time from 20 to 60 min, anthraquinone concentration from 0 to 0.6 %, and PFI refining revolutions from 0 to 3000 rpm. Constant conditions were maintained with respect to operating temperature (160 °C), soda charge (10 %), and the liquid/solid ratio (10:1).

In this study, the experimental results were fitted to polynomial models by multiple regression using the software Design of Experiments (DOE) PRO XL v 3.0. Other authors (De Lopez *et al.* 1996; Jimenez *et al.* 2006a) have reported polynomial models with similar approach in order to fit their experimental data; however most of these authors have used different software, which apparently are more complicated and no longer commercially available. The software used in this study is very simple and straightforward, and it supports four ways to create a design.

In this case of study, the terms possessing a P (2 tail)-value (measure of the significance of an effect) lower than 0.5 and a Tol-value (proportion of orthogonally for each effect) equal to 1 were deemed statistically significant. Equations obtained, as well as the R²-value (measure of the fit of the regression model), standard error-value (standard deviation of the response variable) and F-value (greater than 6, indicates a significant model for prediction), are the following (Eqs. 3 through 7):

Beating grade (BG):

$$\begin{aligned} \text{BG} &= 61.750 + 20.550 X_R + 2.125 X_T X_A - 11.050 X_A^2 + 1.375 X_A X_R \\ R^2 &= 0.9296 \quad \text{std. error} = 5.7065 \quad F = 36.3301 \end{aligned} \quad (3)$$

Viscosity (VI):

$$\begin{aligned} \text{VI} &= 852.55 + 27.310 X_T + 55.803 X_A - 7.694 X_R - 38.542 X_T^2 + 23.983 X_T X_A + 17.493 \\ & X_T X_R - 40.387 X_A^2 - 11.240 X_A X_R \\ R^2 &= 0.8995 \quad \text{std. error} = 32.0605 \quad F = 7.8299 \end{aligned} \quad (4)$$

Kappa number (KN):

$$\text{KN} = 14.797 + 1.072 X_T - 5.245 X_A - 1.135 X_R + 2.365 X_T^2 - 3.320 X_T X_A + 4.920 X_A^2 + 1.100 X_A X_R \quad (5)$$

$$R^2 = 0.9724 \quad \text{std. error} = 1.3968 \quad F = 40.2608$$

Tensile Index (TI):

$$\text{TI} = 65.833 - 3 X_T + 12.100 X_R + 2 X_T X_R - 6.033 X_A^2 + 1 X_A X_R \quad (6)$$

$$R^2 = 0.9380 \quad \text{Std error} = 3.3813 \quad F = 30.2730$$

Brightness (BR):

$$\text{BR} = 33.815 - 0.72600 X_T - 2.899 X_R - 0.85700 X_T^2 + 0.59375 X_T X_A - 0.77875 X_A X_R \quad (7)$$

$$R^2 = 0.8028 \quad \text{Std error} = 1.5653 \quad F = 8.1416$$

The foregoing equations predict the experimental results of the dependent variables (response variables) with errors less than 15% for the beating grade number, 4% for the viscosity, 6% for the Kappa number, 4% for the tensile index, and 5% for brightness, in most cases (85 to 90% of cases). In view of the results, the errors in predicting pulp properties by using the polynomial models were quite small in most cases (Table 3) and thus confirm the validity of the models.

Table 3. Values of the Dependent Variables as Estimated with the Polynomial Model and Deviations from Their Experimental Counterparts

Exp.	Beating grade number, °SR		Viscosity, mL/g		Kappa number		Tensile index, Nm/g		Brightness, %	
	Est. value	Dev., %	Est. value	Dev., %	Est. value	Dev., %	Est. value	Dev., %	Est. value	Dev., %
1	33.65	20.18	728.44	2.78	25.17	0.55	53.70	1.32	36.40	2.52
2	72.00	0.69	700.54	3.29	20.70	1.52	71.90	2.71	32.16	1.03
3	26.65	6.60	814.56	2.22	19.12	4.69	51.70	1.37	36.77	1.43
4	70.50	0.00	741.70	2.34	19.05	0.63	73.90	0.14	29.41	0.53
5	29.40	13.08	700.11	2.00	33.95	0.87	43.70	4.05	33.76	1.64
6	67.75	1.88	742.18	2.85	29.48	0.83	69.90	1.30	29.52	4.10
7	30.90	14.44	882.16	2.91	14.62	0.92	41.70	0.71	36.50	2.79
8	74.75	3.55	879.28	1.94	14.55	3.68	71.90	1.27	29.15	0.68
9	61.75	11.26	852.55	5.62	14.80	15.69	65.83	6.18	33.82	3.63
10	61.75	1.20	852.55	1.48	14.80	9.85	65.83	5.95	33.82	6.77
11	61.75	7.14	786.70	0.18	16.09	5.86	68.83	3.05	33.68	0.76
12	61.75	2.76	841.32	2.16	18.23	0.85	62.83	3.33	32.23	9.04
13	50.70	8.65	756.36	0.87	24.96	2.76	59.80	10.75	33.82	1.21
14	50.70	13.33	867.97	1.14	14.47	13.77	59.80	1.36	33.82	6.23
15	41.20	15.92	860.24	1.92	15.93	3.86	53.73	5.36	36.71	0.48
16	82.30	11.97	844.86	3.66	13.66	1.50	77.93	2.54	30.92	4.08

The values of the operational variables providing the best pulp properties (beating grade number, viscosity, kappa number, tensile index, and brightness) were identified by using a multiple response optimizer on the input data. Table 4 shows the optimum values of the dependent variables and those of the operational variables required to obtain them.

The polynomial equations for beating grade number, viscosity, Kappa number, tensile index, and brightness of the pulps permitted identification of operational variables

having the highest influence on pulp properties. The maximum variations in the dependent variables with changes in the operational variables over the studied range were obtained by altering one independent variable at a time while keeping all others constant (with their optimal values, Table 4). Figures 2 and 3 also show the changes presented in Table 4.

Table 4. Optimal Values of the Pulp Properties (Dependent Variables)

	Dependent variable				
	Beating degree, °SR	Viscosity, mL/g	Kappa number*	Tensile index, Nm/g	Brightness, %
Optimum (maximum or minimum*) value of the dependent variable	82.58	894	12.77	78.97	37.50
Value of processing time (min) required to obtain the optimum value of dependent variables	60	48.50	41.92	20	38.46
Value of anthraquinone concentration (wt.%) required to obtain the optimum value of dependent variables	0.35	0.59	0.44	0.32	0.6
Value of PFI revolution (rpm) required to obtain the optimum value of dependent variables	3000	0	3000	3000	0
Normalized value of processing time required to obtain the optimum value of dependent variables	+1	+0.43	+0.10	-1	-0.08
Normalized value of anthraquinone concentration required to obtain the optimum value of dependent variables	+0.17	+0.97	+0.47	+0.07	+1
Normalized value of PFI revolution required to obtain the optimum value of dependent variables	+1	-1	+1	+1	-1

According to Table 4 and Figs. 2 and 3, the following conclusion can be extracted: the PFI revolution had a greater influence on the beating grade number than the anthraquinone concentration and the processing time. Similarly, according to Table 4, the PFI revolution had a greater influence on the tensile index than the anthraquinone concentration and the processing time.

Beating (PFI revolutions) is used to enhance the bonding power of plant fibers in paper sheets, which is done by applying mechanical stress to fiber as it is milled by a device called a “beater”. During beating, the fiber wall is squeezed, kneaded, and plasticized, and the fiber surface is partly disintegrated. Mechanical shear separates parts of cellulose fibrils so that the fiber structure becomes hairy and fluffy (Sixta 2006), resulting in fiber collapse. Furthermore, fibrillar fines are produced during beating, which enhances the fiber/fiber joint strength and paper strength (*i.e.*, tensile index) (Levlin and Söderhjelm 1999).

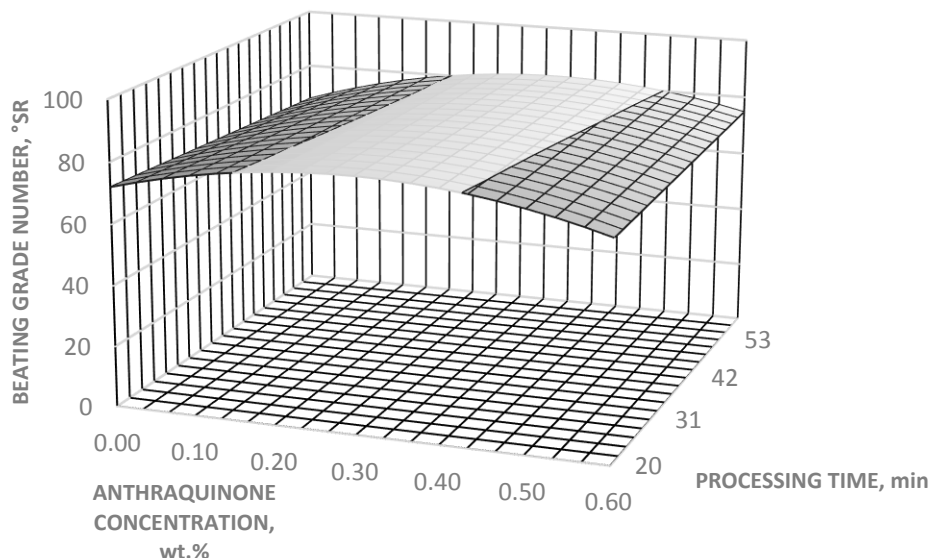


Fig. 2. Surface plot of Beating grade number in response to processing time vs. anthraquinone concentration at high PFI revolutions ($X_R = +1$ (3000 rpm))

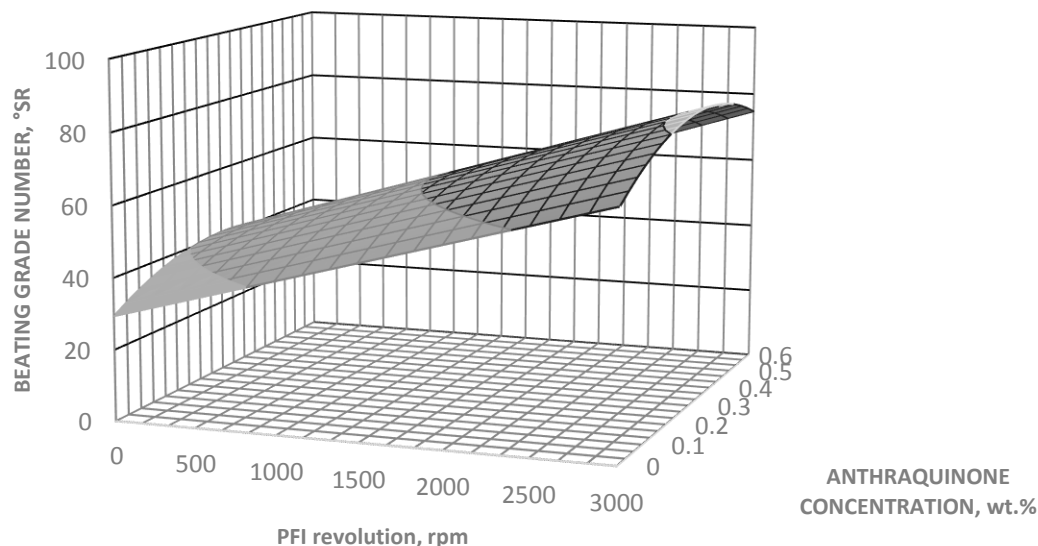


Fig. 3. Surface plot of Beating grade number in response to anthraquinone concentration vs. PFI revolutions at high processing time ($X_T = +1$ (60 min))

The major effect of beating is a drastic increase in water uptake by the fiber material. The kneaded cell wall will swell, and the fibril fur on the surface will store water by capillary forces, while the isolated cellulose fibrils aggregate to hydrogels containing huge amount of immobilized water (Ulfa *et al.* 2014). The hydrodynamic volume of the fibers is increased substantially, so that filtration in sheet forming process is severely hampered. On the other hand, beating lowers the drainage capability of pulp, and this

reduces the production rate and increases the energy consumption in papermaking process. Some paper properties are improved with beating (*i.e.*, strength properties) but others deteriorate (such as the tear strength), which increases with gentle beating but drastically decreases with more intense beating (Sixta 2006). Though the PFI revolution or beating could affect negatively the papermaking process (industrial scale), these results show the importance of beating, since it has a large influence on the pulp properties (as can be observed in Figs. 2 and 3), meaning that in the chemical pulp testing could possibly be the most important single step. This laboratory beating could simulate the industrial beating process to predict the usability of a pulp, meaning that these results obtained from the PFI could be scaled in order to select beater (disk or otherwise) conditions.

These conclusions that have been extracted can be explained by the different magnitude of the coefficients of the beating grade number (Eq. 3) and tensile index (Eq. 6). A similar explanation can be given for the remaining dependent variables. The viscosity varied more with anthraquinone concentration and less with the PFI revolution (Table 4 and Eq. 4). The Kappa number was also more influenced by the anthraquinone concentration than by the processing time and PFI revolutions (Table 4 and Eq. 5). Regarding the brightness, this property was more influenced by the PFI revolutions than by the processing time (Table 4 and Eq. 7).

The data in Table 4 can be used to select values of the operational variables providing near-optimal pulp properties while saving chemicals, energy, and investment for industrial installation by using lower values of operational variables. For this purpose, a multiple response optimizer of the input data was used, and five constraints with different weights (regarding importance) were used: to reach the maximum values for beating grade number (weight of the constraint: 15%), viscosity (weight of the constraint: 25%), tensile index (weight of the constraint: 20%), and brightness (weight of the constraint: 15%), while to reach the minimum ones for the Kappa number (weight of the constraint: 25%).

One combination leading to near-optimal properties with reduced costs is to use a processing time of 46 min, an anthraquinone concentration of 0.4 wt.%, and a PFI revolutions value of 3000. Operating under these conditions the following values for the dependent variables were obtained: beating grade number of 82 °SR, viscosity 870 mL/g, Kappa number 13, tensile index 77 Nm/g, and brightness 30% ISO; these values deviate by 0.70%, 2.70%, 1.80%, 2.50%, and 20%, respectively, from the optimum values of beating grade number, viscosity, Kappa number, tensile index, and brightness, respectively.

This combination of operating conditions corresponding to the optimum results seems to be logical based on the following reasons or explanations. First of all, and as was mentioned previously, in order to obtain good fiber fibrillation, the pulp must be beaten in a PFI mill. Indeed, the beating of chemical pulp is an essential step in improving the bonding ability of fibers, causing a variety of simultaneous changes in fibers, such as internal fibrillation, external fibrillation, fiber shortening or cutting, and fines formation (Ulfa *et al.* 2014). In other words, during the beating process, tensile index increased due to improved fiber swelling, fibrillation, flexibility, hydrogen bonding, and fiber-to-fiber bonding. However, excessive beating would result in fiber cutting, thereby leading to a decrease in tensile strength. That explains why beating revolutions above 3000 rpm should not be used in the experimental design, since it could affect the mechanical properties of the handsheets, among other properties. Regarding the processing time, it is well known that increasing the cooking time causes an increase in the values for all the considered properties, but according to this model and in order to save costs, the optimum value for

the processing time was found to be 46 min. For the anthraquinone concentration, the best set of conditions was obtained in the reaction performed at 0.4 wt.% of anthraquinone as consequence of a better compromise between cellulose preservation and lignin removal. This could be explained by the following: under alkaline conditions, peeling reactions occur as sugar units in a polymeric chain are removed one by one from the reducing ends and transformed into a carboxylic acid. This removal is accompanied by the formation of a new reducing end-group (Borrega *et al.* 2013). Despite the addition of anthraquinone to the pulping liquor to minimize peeling reactions, a significant decrease in cellulose yield still occurred. As a matter of fact, under severe extraction conditions, extensive cleavage of glycosidic bonds is observed in cellulose content meaning that the formation of new end groups increases the susceptibility of cellulose chains towards peeling in subsequent alkaline pulping processes (Borrega *et al.* 2013).

Nevertheless, this polynomial model could be used as a tool to minimize or avoid the use of anthraquinone in the pulping process while maintaining a high level of pulp properties. The following combination of conditions was tested: processing time of 46 min, an anthraquinone concentration of 0 wt.%, and a PFI revolution of 3000 rpm were studied for comparison. The idea of this simulation was to set the anthraquinone to zero concentration by keeping the rest of the operating variables at those values shown before (46 min and 3000 rpm), as this organic compound is no longer recommended for papermaking or food packaging purposes, among others, anymore because of its hazard potential and costs. Operating under these conditions the following values for the dependent variables were obtained: beating grade number 75 °SR, viscosity 763 mL/g, Kappa number 24, tensile index 71 Nm/g, and brightness 31% ISO. If we compare this set of results to the ones that were obtained by operating with the optimum conditions (46 min, 0.4 wt.% and 3000 rpm), it can be concluded that °SR, tensile index, and brightness were approximately in the same range of values; however Kappa number and viscosity were slightly lower. These results are logical and in agreement with the models, as Kappa number and viscosity were more influenced by the anthraquinone concentration, while the PFI revolutions had a greater influence on the other pulp properties (°SR, tensile index and brightness).

CONCLUSIONS

1. On the basis of these results, it can be concluded that barley straw should be considered suitable for pulp and paper production because it has acceptable contents of cellulose (36%) and hemicelluloses (28%).
2. After an optimization using a central composite design procedure, a polynomial model (Multiple Response Regression) (using temperature, anthraquinone concentration, and PFI revolution as operational variables) predicts the pulp properties in the pulping process of barley straw with errors less than 6% in all the cases except for the beating degree number which is higher (15%).
3. Barley straw pulping with 46 min of processing time, 0.4 wt.% of anthraquinone concentration, and 3000 rpm of PFI revolution is the best choice to save energy and chemicals and results in a pulp with acceptable properties.

4. On the other hand, this study demonstrated the usefulness of this model in order to minimize the use of anthraquinone in this pulping process and achieve a high quality pulp.

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