ETHANOL-SODA PULPING OF SUGARCANE BAGASSE AND STRAW

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The bagasse and straw of sugar cane correspond to the most important sugar industry wastes, and about 97 million tons of each are generated annually in Brazil. The bagasse and straw are lignocellulosic materials with potential for pulp production, especially when integrated in biorefinery processes. This paper presents the optimization of the pulping of bagasse and straw by using the soda/ethanol process conducted in a factorial experimental central composite design, with three independent variables (temperature, reaction time and concentration of ethanol in the cooking liquor) in three levels (minimum, intermediate and maximum). It was kept fixed relative to liquor/material (14/1 L/kg) and loads of soda for 15 and 10% bagasse and straw, respectively. The bagasse was more suitable to the pulp production than straw. The optimized conditions of temperature, time and concentration of ethanol for the pulp production of bagasse and straw with kappa number 12 ± 0.3 were, respectively, 195 °C-90 minutes-25% ethanol and 195 °C-150 minutes-25% ethanol.

Keywords: Sugarcane, bagasse, straw, chemical characterization, ethanol-soda pulping

INTRODUCTION

The way to a sustainable development and resource renewability includes the searching of new resources of products, where lignocellulosic biomass draws attention as an economical and renewable source of energy with other chemicals. The fact is that in order to make integral use of vegetable species, fractionation is necessary, thus providing a wide range of products in a similar way oil refineries do, following a scheme that could be summarised in the following sentence: "The biorefinery of tree: from pulp and paper to chemical products and energy".[1,2]

Bagasse is the residue of sugarcane (*Saccharum officinarum L.*) after being squeezed out and submitted to the sugar extraction process. The bagasse and straw of sugarcane are the main subproducts generated by the alcohol industry, Brazil being the major sugarcane producer in the world, with 719.1 million tonnes produced in 2010, around 43% of the world production for this year, which was approximately 1.69 x 10^3 million tonnes.[3] Each processed sugarcane tonne generates about 140 kg of bagasse and 140 kg of straw on a dry weight basis.[4] This way, about 80 million tonnes of bagasse and 80 million tonnes of straw are generated from 8.4 million hectares of land.[5] About 90% of the bagasse is burnt within the ethanol and sugar mills to produce steam/energy.[6]

About 10% of the leftover bagasse is available at very low cost for producing second-generation biofuels and bioproducts. The straw is currently burnt in the fields, but new environmental legislation makes this practice illegal starting with the year 2014, according Law number 11241 and the Green Ethanol protocol, for the Sao Paulo state; the largest producer of sugarcane in Brazil.[7]

On the other hand, sugarcane bagasse and straw are two lignocellulosic materials with potential for pulp production, especially when integrated into biorefinery processes.[8-13]

Both bagasse and straw present suitable chemical compositions, with a high carbohydrate content (51-78%) and low cost, which are relevant

factors for pulp production and other industrial uses.[14-19]

This study aimed at characterizing chemically, physically and morphologically bagasse and straw of the most important sugarcane variety planted in Brazil, and investigating the ethanol/soda process for pulping such material, with the objective to maximize the glucan and xylan retention in the cellulosic pulp. Therefore, this study aimed to determine, through the use of a factorial experimental central composite design, the optimum conditions for ethanol-soda pulping of sugarcane bagasse and straw, to produce quality pulp.

EXPERIMENTAL

Biomass samples

About 100 kg of bagasse and 100 kg of straw of 5 month old *Saccharum officinarum* plantation were obtained from the Ridesa Experimental station located in Minas Gerais State. The sugarcane bagasse was obtained after chipping and pressing of the sugarcane stalk. The sugarcane straw was collected in the field and fragmented in a shredder. The small pieces of bagasse and straw were then stored in a cold and dry room.

Methods

Chemical, physical and morphological characterization

The chemical characterization of the bagasse and straw was carried out in triplicate, according to TAPPI standard procedures on 40/60 mesh sawdust. The moisture content was determined according to TAPPI T 664 om-88.[20] The following procedures were used: total extractives content (TAPPI T 264 cm-97), acid soluble lignin,[21] Klason lignin[22] and total lignin, lignin syringyl/vanillin (S/V) ratio,[23] carbohydrates,[24] acetyl groups,[25] and uronic acids,[26] ash (TAPPI 211 om 93) and insolubles in HCl (TAPPI T 244 om-93). The physical and morphological analyses were done on the fragmented bagasse and straw. The basic density was carried out according to TAPPI T-258 procedure.[20] The morphological analyses (fiber length and width, lumen diameter and wall thickness) were done on 100 fibers.

Ethanol/soda pulping

Ethanol/soda pulping was carried out in a PARR 4843 reactor (2 L) on 50 g of bagasse/straw. The effects of ethanol concentration (25, 45 and 65%), NaOH charge (10 and 15% w/w), reaction time (90, 120 and 150 min) and temperature (175, 185 and 195 ºC) were evaluated at the initial liquor-biomass ratio (14 L kg^{-1}). The white liquors were prepared in the laboratory with NaOH 20% and ethanol 96%.

After cooking, the reactor was cooled and the pulp disintegrated to 800 rpm for 4 minutes in the presence of white liquor (consistency 1.25%). The pulp was washed with 1 liter of the same white liquor twice and, finally washed with water. The pulp was disintegrated again to 800 rpm for 20 minutes. The pulp was defiberized (consistency 0.5%) in a Sprout-Waldron refiner with a disc gap of 0.05 mm in order to isolate the uncooked material. The kappa number was determined according to TAPPI 236 cm-85. The yield was determined gravimetrically and the carbohydrates content by High-Performance Anion-Exchange Chromatography (HPAEC).[24] The glucan and xylan retention was calculated by the equation below (Eq. 1):

$$CarbR = [(X_i \times Yield)/x_i] \quad (1)$$

where: *CarbR* is the pulp carbohydrate retention (glucan or xylan); X_i is the pulp carbohydrate content (glucan or xylan in pulp with extractives); *Yield* is the cooking yield; and x_i the raw material carbohydrate content (glucan or xylan on the extractive-containing sawdust).

Paper sheets preparation and tensile strength measurements were done according to TAPPI 205 sp-95 and TAPPI 494 om-96, respectively.

Experimental design

A 2^n central composite experimental design that enabled the construction of second-order polynomial in the independent variables and the identification of statistical significance in the variables was used. This allowed relating the dependent (yield, kappa number, glucan and xylan retention and carbohydrates content) and independent (temperature, ethanol concentration, NaOH charge and time process) variables of the ethanol/soda pulping process with a minimum number of experiments.

Independent variables were normalized by using the following equation:

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

where: X is the absolute value of the independent variable concern, $\overline{X}$ is the average value of the variables, and X_{max} and X_{min} are the maximum and minimum values, respectively. The independent variables used were the temperature (175, 185 and 195 ºC), reaction time (90, 120 and 150 min) and ethanol concentration (25, 45 and 65%). The liquor-biomass ratio used was 14 L kg^{-1} (dry weight basis).

The number of different experiments was estimated by the following equation (Eq. 3):

$$N = 2^n + 2 \cdot n + n_c;\ 2^n \quad (3)$$

where: n is the number of trials done, K is the number of independent variables used (if $K < 5$; $p = 0$, if $K > 5$, $p = 1$), and n_c is the number of repetitions of the central point (in this work it equals 2). Fifteen different trials were performed following the central composite factor experimental design, with an additional repetition on the central point. The results generating second-order polynomial models[27] (Eq. 4):

$$Y = a_o + \sum_{i=1}^{n} b_i X_{ni} + \sum_{i=1}^{n} c_i X_{ni}^2 + \sum_{i=1;\, j=1}^{n} d_i X_{ni} X_{nj} \quad (i < j) \qquad (4)$$

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

RESULTS AND DISCUSSION

Bagasse and straw characterization

Table 1 shows the chemical characterization of sugarcane bagasse and straw. The straw contains more ash and silica than the bagasse. The silica is responsible for 62.3 and 73.0% of the ash content for bagasse and straw, respectively. High ash contents in bagasse and straw have been reported by other researchers. Both materials presented high extractives content as reported elsewhere.[14-16,18] The bagasse contains more total lignin than the straw, but the latter contains more soluble lignin. Bagasse and straw presented similar carbohydrate content (75.2 and 75.5%, respectively). Both bagasse and straw are rich in xylans (24.8 and 26.0%, respectively). The other sugars and acids (galactans, mannans, arabinans, acetyl groups and uronic acids) were present in low concentration in both materials, with less than 4%. Other studies[15,18] revealed similar carbohydrate composition of bagasse and straw to the ones reported in Table 1.

The contents of glucans and xylans in sawdust, based on extractive free material, were 41.8 and 24.8% for bagasse and 41.4 and 26.0% for straw, respectively. The contents of glucans and xylans in sawdust, based on extractive containing material, were 35.8 and 21.2% for bagasse and 36.1 and 22.7% for straw, respectively.

The lignin S/V ratios were 51/49% and 31/69% for bagasse and straw, respectively. The higher lignin S/V ratio on bagasse makes it more amenable for chemical deconstruction.[28]

The basic density values of bagasse (131 kg m^{-3}) and straw (173 kg m^{-3}) were quite low, if compared, for example, with eucalyptus wood.

The bagasse fiber width and lumen diameters (Table 2) were a little larger than those of straw, whereas the fiber length and wall thickness values were slightly smaller. In general, the fiber morphology of bagasse and straw is somewhat similar to those of many hardwoods, thus being qualified as short fibered materials.

Ethanol/soda pulping

Sugarcane bagasse

The sugarcane bagasse presented glucan and xylan content in sawdust, based on extractive containing material, of 35.8 and 21.2%, respectively. Fifteen different cookings were performed following the central composite factor experimental design.

Table 1
Chemical composition of sugarcane bagasse and straw on extractive free material

Analyses, %	Bagasse	Straw
Ash	2.31 ± 0.02 [a]	7.91 ± 0.02 [a]
Silica	1.44 ± 0.01 [a]	5.77 ± 0.05 [a]
Extractives [b]	15.0 ± 0.28 [a]	12.2 ± 0.29 [a]
Klason lignin [c]	19.5 ± 0.11 [a]	14.0 ± 0.28 [a]
Acid soluble lignin [c]	1.87 ± 0.06 [a]	2.17 ± 0.09 [a]
Total lignin [c]	21.4 ± 0.08 [a]	16.2 ± 0.34 [a]
Glucans [c]	41.8 ± 0.91 [a]	41.4 ± 1.33 [a]
Xylans [c]	24.8 ± 0.23 [a]	26.0 ± 0.24 [a]
Galactans [c]	0.87 ± 0.13 [a]	0.93 ± 0.07 [a]
Mannans [c]	0.93 ± 0.13 [a]	0.30 ± 0.11 [a]
Arabinans [c]	2.27 ± 0.24 [a]	3.90 ± 0.11 [a]
Uronic acids [c]	1.48 ± 0.06 [a]	1.30 ± 0.02 [a]
Acetyl [c]	3.04 ± 0.02 [a]	1.65 ± 0.01 [a]
Total Carb.[cd]	75.2 ± 1.71 [a]	75.5 ± 1.89 [a]

[a] Average for 2-3 samples plus estimated 95% confidence interval
[b] ethanol/toluene (1:2) ethanol hot water
[c] based on extractive free material
[d] includes glucans, xylans, galactans, mannans, arabinans, uronic acids and acetyl groups

Table 2
Morphological analysis results

Average dimensions	Bagasse	Straw
Fiber length, mm	1.59	1.61
Fiber width, µm	23.01	20.20
Lumen diameter, µm	13.34	10.02
Wall thickness, µm	4.84	5.09

Table 3
Values of independent variables for bagasse pulp: kappa number, yield, glucan content, xylan conten, glucan retention, xylan retention and tensile strength

Normalized values of temp. (XT), reaction time (Xt) and ethanol conc. (XC)	Kappa number	Yield (%)	Glucan content (%)	Xylan content (%)	Glucan retention (%)	Xylan retention (%)	Tensile strength (kNm/kg)
0 0 0	9.26	48.11	50.60	20.75	67.98	47.02	6.5
0 0 0	9.18	48.17	50.40	20.85	67.80	47.31	6.4
1 1 1	11.37	45.45	51.47	20.92	65.33	44.79	3.7
1 1 -1	10.35	42.91	55.91	19.40	67.00	39.21	6.4
1 -1 1	11.31	46.80	51.51	21.76	67.32	47.97	4.4
1 -1 -1	12.34	45.03	54.96	19.72	69.11	41.83	7.8
-1 1 1	15.20	50.80	47.85	23.70	67.88	56.71	3.2
-1 1 -1	13.03	47.88	51.31	21.06	68.60	47.50	10.2
-1 -1 1	14.66	50.74	47.95	22.79	67.94	54.47	2.6
-1 -1 -1	13.46	49.21	50.73	20.80	69.71	48.21	7.9
1 0 0	7.64	46.46	53.09	21.09	68.88	46.15	5.9
-1 0 0	10.93	50.60	49.15	22.50	69.45	53.63	6.5
0 1 0	8.33	47.10	51.30	20.93	67.47	46.43	5.9
0 -1 0	9.18	48.85	50.60	21.30	69.03	49.01	6.5
0 0 1	13.42	48.16	48.58	20.97	65.33	47.57	2.7
0 0 -1	12.45	46.14	51.97	19.02	66.96	41.34	8.5

The cooking performance was analyzed against the independent variables, namely: ethanol concentration (25, 45 and 65%), reaction time (90, 120 and 150 min) and temperature (175, 185 and 195 ºC).

Table 3 shows the results of kappa number, yield, glucan content, xylan content, glucan retention, xylan retention and tensile index. The first column shows the different combinations of normalized independent variables to temperature, reaction time and ethanol concentration. Glucan and xylan contents were determined in the bagasse pulp and the glucan and xylan retention were estimated considering the pulping yield, the glucan/xylan content in the sawdust of the raw material and the glucan/xylan content in the bagasse pulp after pulping process (based on extractive containing material). The difference between the two replicates of the central point was less than 2%.

The second-order models (Table 5) were obtained considering normalized independent variables, the values -1, 0 and +1 being assigned for each variable for the minimum, intermediate and maximum indexes, respectively. The results obtained for these parameters derived from the adjusted models, and the deviations for these parameters from their respective means were all less than 15% and the coefficient of determination of the models was above 95%. Response surfaces were made and these were used to analyze the factor design results obtained with the normalized independent variables. Analyzing the models, it is possible to perceive linear terms, quadratic terms and also interactions between independent variables with different coefficient values and signals (positive/negative). The variable force is determined by the coefficient value and can present positive or negative influence on the dependent variable. However, analyzing the variable force visually is possible only regarding linear terms.

Identifying the independent variables with the strongest and weakest influence on the dependent variables in equations 5-11 is not so easy, since the models contain quadratic terms and other

factors involving interactions between two independent variables. Then, to analyze the influence of each variable on the model, it was necessary to use a variation figure as a tool (Figure 1). Ethanol concentration was the variable with the strongest influence on kappa number, xylan content, glucan retention and tensile strength. Temperature was the variable with the strongest influence on yield, glucan content and xylan retention. In order to determine the values of the independent variables giving the optimum values of dependent variables, the response surfaces for each dependent variable were plotted at two extreme levels of the independent variables most strongly influencing each (Figure 1) and the other two variables were plotted at the axes.

Table 4
Values of the independent variables to the straw pulp: kappa number, yield, glucan content, xylan conten, glucan retention, xylan retention and tensile strength

Normalized values of temp. (XT), reaction time (Xt) and ethanol conc. (XC)	Kappa number	Yield (%)	Glucan content (%)	Xylan content (%)	Glucan retention (%)	Xylan retention (%)	Tensile strength (kNm/kg)
0 0 0	11.00	42.38	48.30	20.50	56.70	38.27	2.80
0 0 0	10.92	43.12	48.10	20.70	57.45	38.65	2.90
1 1 1	17.34	42.83	44.00	20.52	52.20	38.31	3.07
1 1 -1	12.34	36.14	52.29	15.85	52.35	29.59	2.75
1 -1 1	17.26	43.40	44.83	21.25	53.90	39.67	2.62
1 -1 -1	13.54	35.81	53.30	16.03	52.87	29.93	2.52
-1 1 1	19.76	45.60	43.48	21.73	54.92	40.57	2.41
-1 1 -1	13.51	39.41	49.21	16.46	53.72	30.73	3.02
-1 -1 1	19.17	45.22	43.62	21.87	54.64	40.83	1.85
-1 -1 -1	15.06	40.00	50.00	17.20	55.40	32.11	2.78
1 0 0	10.33	42.30	48.09	19.74	56.35	36.85	3.36
-1 0 0	11.98	44.38	46.41	20.73	57.05	38.70	3.15
0 1 0	11.00	42.18	48.27	20.30	56.40	37.90	2.90
0 -1 0	11.29	41.77	49.50	20.80	57.27	38.83	2.60
0 0 1	18.07	44.50	44.30	21.84	54.61	40.77	2.17
0 0 -1	13.40	38.20	51.49	16.68	54.49	31.14	2.71

Table 5
Equations yielded for each dependent variable (sugar cane bagasse)

	Equations	R^2	F
5	$KN = 9.20 + 3.83\ X_C X_C - 1.43\ X_T + 0.43\ X_C - 0.42\ X_T X_C + 0.38\ X_t X_C - 0.34\ X_t X_t - 0.27\ X_t - 0.26\ X_T X_t$	0.9948	168.4
6	$YI = 48.11 - 2.26\ X_T + 1.08\ X_C - 1.05\ X_C X_C - 0.65\ X_t + 0.33\ X_T X_T - 0.28\ X_T X_t + 0.28\ Xt X_C$	0.9950	226.5
7	$GU = 50.43 + 1.91\ X_T - 1.65\ X_C + 0.69\ X_t X_t + 0.49\ X_T X_T - 0.34\ X_T X_C + 0.23\ X_t$	0.9894	139.4
8	$XY = 20.81 + 1.01\ X_C + 0.98\ X_T X_T - 0.82\ X_C X_C - 0.80\ X_T + 0.30\ X_t X_t - 0.29\ X_T X_t$	0.9807	76.37
9	$GUR = 67.96 - 1.59\ X_C X_C + 1.43\ X_T X_T - 0.76\ X_C - 0.68\ X_t - 0.59\ X_T - 0.37\ X_T X_t$	0.9568	33.19
10	$XYR = 47.32 - 4.06\ X_T + 3.34\ X_C + 2.82\ X_T X_T - 2.61\ X_C X_C - 0.92\ X_T X_t - 0.69\ X_t$	0.9815	79.38
11	$TS = 6.28 - 2.42\ X_C + 0.78\ X_T X_C - 0.63\ X_T X_t - 0.54\ X_C X_C$	0.9668	80.19

Where: KN denotes kappa number, YI the yield (%), GU the glucan content (%), XY the xylan content (%), GUR the glucan retention (%), XYR the xylan retention (%), TS the tensile strength (kNm/kg) and X_T, X_t and X_C the value normalized of temperature, reaction time and ethanol concentration, respectively. The differences between the experimental values and those estimated by using the previous equation never exceeded 15% of the former

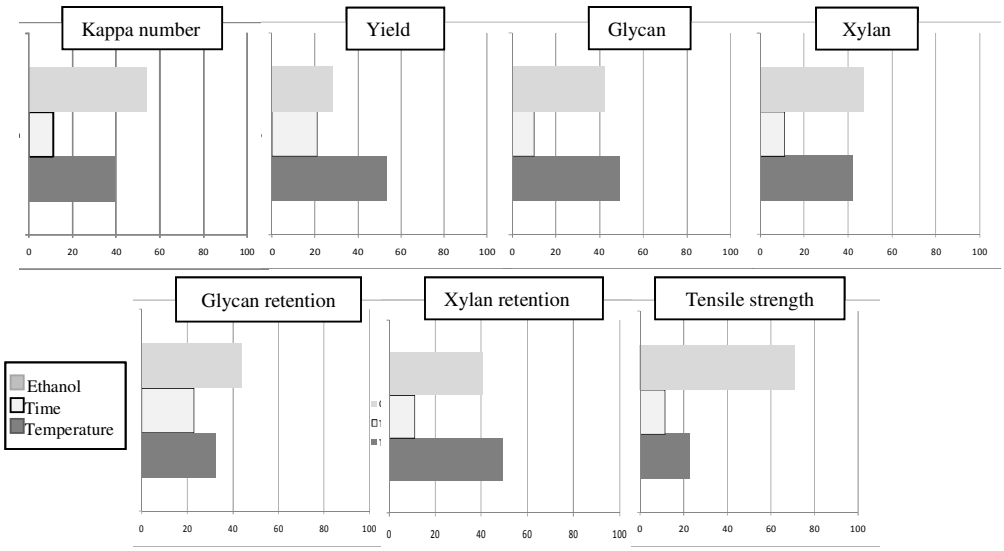

Figure 1: Variation of dependent variables as a function of normalized independent variable

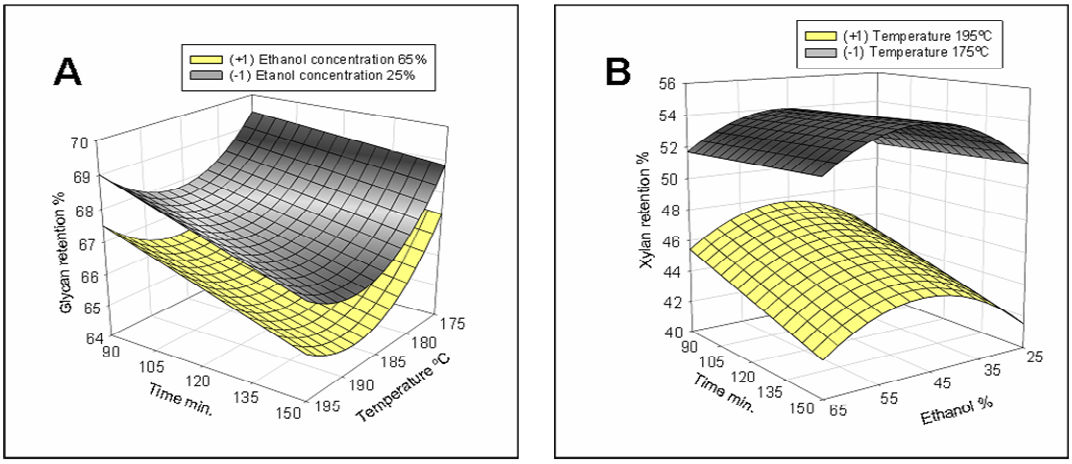

Figure 2: Effect of time, temperature and ethanol concentration on pulp glucans (A) and xylans (B) retention after ethanol/soda cooking of sugar cane bagasse

The kappa number, yield, glucan content and xylan content determination were fundamental to the development of this work, however the objective was to maximize the glucans and xylans retention, thus, only these response surfaces will be presented.

Figure 2 shows the glucans (A) and xylans (B) retained in the bagasse pulp after cooking, as estimated by the models. Glucans and xylans retention increased with decreasing reaction time. Minimal glucans retention was achieved at 185 ºC temperature, while similar glucans retention values were achieved at 175 and 195 ºC. Xylans retention was maximum at the lowest temperature (175 ºC). Maximum glucans retention was obtained at the lowest ethanol concentration (25%), but maximum xylans retention was attained at intermediate ethanol concentration in the white liquor (45%). Maximum glucans and xylans retention values were obtained at the lowest retention times (90 min). Thus, at a 15% NaOH charge, the optimum ethanol/soda cooking conditions for bagasse to achieve a kappa number of ~12 and to maximize glucans and xylan retention were 25% ethanol, 195 ºC and 90 min. Under these conditions, the glucans and xylans remaining in the pulp after cooking were of 69.0 and 41.7%, respectively.

Sugarcane straw

The sugarcane straw presented glucan and xylan content in sawdust, based on extractive containing material, of 36.1 and 22.7%, respectively. Fifteen different cookings were performed, following the central composite factor experimental design. The cooking performance was analyzed against the independent variables, namely: ethanol concentration (25, 45 and 65%), reaction time (90, 120 and 150 min) and temperature (175, 185 and 195 ºC).

Table 4 shows the results of kappa number, yield, glucan content, xylan content, glucan retention, xylan retention and tensile index. The first column shows the different combinations of normalized independent variables to temperature, reaction time and ethanol concentration. The difference between the two replicates of the central point was less than 4%.

The second-order models (Table 6) were obtained as in the previous case. The results obtained for these parameters derived from the adjusted models, the deviations for these parameters from their respective means were all less than 15%, and the coefficient of determination of the models was above 91%. Response surfaces were made and used to analyze the factor design results obtained with the normalized independent variables.

As in the previous model, identifying the independent variables with the strongest and weakest influence on the dependent variables in equations 12-18 is not so easy, since the models contain quadratic terms and other factors involving interactions between two independent variables. Then, to analyze the influence of each variable on the model, it was necessary to use a variation figure as a tool (Figure 3). Ethanol concentration was the variable with the strongest influence for all the models analyzed (kappa number, yield, xylan content, glucan content, glucan retention, xylan retention and tensile strength).

In order to determine the values of the independent variables giving the optimum values of dependent variables, the response surfaces for each dependent variable were plotted at two extreme levels of the independent variables most strongly influencing each (Figure 3) and the other two variables were plotted at the axes. The response surfaces of glucan retention was plotted with the temperature (variable with the strongest influence) in order to improve the dependent variable behaviour, because the ethanol concentration (variable with the strongest influence) appears as a quadratic term in the glucan retention model, thus, its response surface with the normalized variables -1 and +1 were the same. The kappa number, yield, glucan content and xylan content determination were fundamental to the development of this work, however, the aim was to maximize the glucans and xylans retention, therefore, only these response surfaces will be presented.

Table 6
Equations yielded for each dependent variable (sugar cane straw)

	Equations	R^2	F
12	$KN = 11.05 + 4.70\ X_C X_C + 2.38\ X_C - 0.87\ X_T + 0.43\ XtXC + 0.24\ X_t X_t - 0.21\ X_T X_C - 0.21\ X_t$	0.9984	732.4
13	$YI = 42.78 + 3.20\ X_C - 1.45\ X_C X_C - 1.41\ X_T - 0.82\ X_t X_t + 0.54\ X_T X_T + 0.36\ X_T X_C$	0.9914	171.4
14	$GU = 48.26 + 0.92\ X_T - 3.69\ X_C - 0.92\ X_T X_T - 0.63\ X_T X_C + 0.60\ X_t X_t - 0.49\ X_t - 0.39\ X_C X_C$	0.9964	313.2
15	$XY = 20.59 + 2.50\ X_C - 1.35\ X_C X_C - 0.46\ X_T - 0.37\ X_T X_T - 0.23\ X_t$	0.9972	701.4
16	$GUR = 58.87 - 2.96\ X_C X_C - 0.81\ X_T - 0.45\ X_t$	0.9197	45.82
17	$XYR = 38.43 + 4.67\ X_C - 2.51\ X_C X_C - 0.86\ X_T - 0.69\ X_T X_T - 0.43\ X_t$	0.9972	703.4
18	$TS = 2.88 - 0.46\ X_C X_C + 0.36\ X_T X_T + 0.25\ X_T X_C + 0.18\ X_t - 0.17\ X_C - 0.15\ X_t X_t + 0.11\ X_T + 0.07\ X_t X_C$	0.9805	44.05

Where: KN denotes kappa number, YI the yield (%), GU the glucan content (%), XY the xylan content (%), GUR the glucan retention (%), XYR the xylan retention (%), TS the tensile strength (kNm/kg) and X_T, X_t and X_C the value normalized of temperature, reaction time and ethanol concentration, respectively. The differences between the experimental values and those estimated by using the previous equation never exceeded 15% of the former

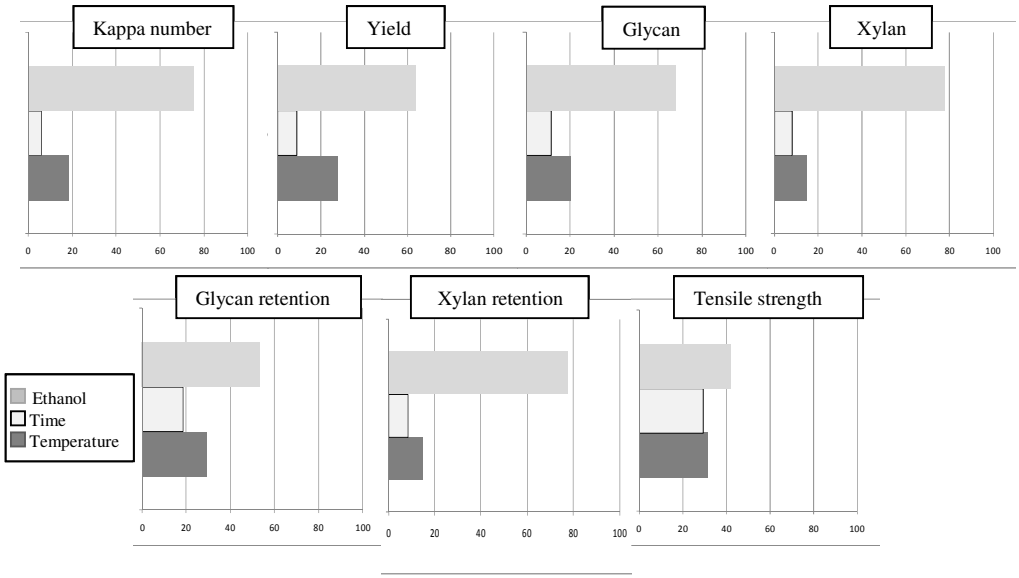

Figure 3: Variation of dependent variables as a function of normalized independent variable

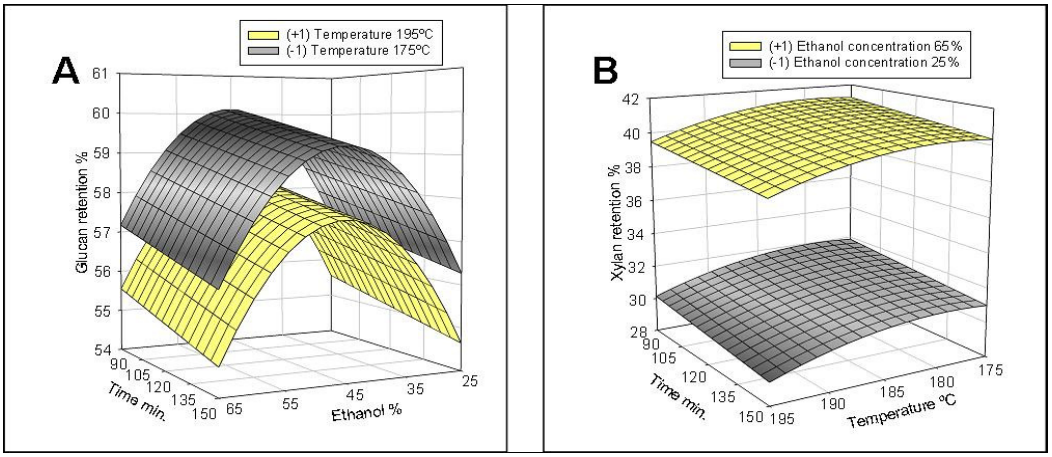

Figure 4: Time, temperature and ethanol concentration effect on pulp glucans (A) and xylans (B) retention after ethanol/soda cooking of sugar cane straw

Figure 4 shows the glucans (A) and xylans (B) retention in the straw pulp after cooking as estimated by the models. The glucans and xylans retention values were higher at lower temperature (175 ºC) and reaction times (90 min). However, the highest xylan retention was achieved at the highest ethanol concentration (65%), while glucans retention was maximized at the intermediate ethanol concentration (45%) in the white liquor. Thus, at a 10% NaOH charge, the optimum ethanol/soda cooking conditions of sugarcane straw bagasse to achieve a kappa number of ~12 and to maximize glucans and xylan retention were 45% ethanol, 175 ºC and 90 min. Under these conditions, the glucans and xylans remaining in the straw pulp after cooking were of 60.1 and 39.0%, respectively.

Comparison between sugarcane bagasse and straw cooking and pulp

Under the optimized pulping conditions for bagasse (25% ethanol, 195 ºC and 90 min) and straw (45% ethanol, 175 ºC and 90 min), the main brown pulp characteristics presented in Table 7 were achieved. At a similar kappa number (~12), the bagasse pulp presented a higher yield (45.3%) than the straw pulp (43.9%). Bagasse pulp presented higher glucan and xylan retention (69.0

and 41.7%, respectively) than the straw pulp (60.1 and 39.0%, respectively). The tensile strength of the pulp derived from the bagasse was much superior to the one of the straw. This large difference is not so easy to explain considering that the morphologies of the bagasse and straw fibers were somewhat similar (Table 2). It is not unlikely that the straw pulp might contain a large fraction of parenchyma cells that may have remained in the pulp after cooking, thus negatively affecting tensile strength.

Table 7
Cooking results for the optimized conditions

Cooking results	Bagasse	Straw
Kappa number	12.2	12.4
Yield, %	45.3	43.9
Glucan retention, %	69.0	60.1
Xylan retention, %	41.7	39.0
Tensile strength, kNm/kg	8.0	2.8

CONCLUSION

Sugar cane bagasse and sugar cane straw are two lignocellulosic materials that present adequate chemical composition to be used in the pulp and paper industry. They present a great amount of xylose and glucose in their composition, which can be favourable to the pulp production with a view to improving pulp quality. However, sugar cane bagasse and straw show high amounts of extractives, ashes, and silica, characteristics that are undesirable to the pulp production.

The basic density and fiber morphology of sugar cane bagasse and straw are somewhat similar. Both materials can be characterized as having short fibers.

The ethanol/soda process is adequate to the pulp production of sugar cane bagasse and straw. In general, the bagasse and straw pulp present low kappa number, yield under 50% and low tensile strength. Glucan and xylan retention in the pulp is higher for sugar cane bagasse than for sugar cane straw. Also, the pulp tensile strength is higher for the sugar cane bagasse.

The optimum ethanol/soda cooking conditions to achieve a kappa number of 12 were: 15% NaOH, 25% ethanol, 195 ºC and 90 min for bagasse and 10% NaOH, 45% ethanol, 175 ºC and 90 min reaction time for straw, respectively.

Under the optimum conditions for each biomass, cooking yields at kappa number 12 were of 45 and 44% for the bagasse and straw, respectively. The tensile strength of the bagasse pulp (8.0 kNm kg^{-1}) was better than that of the straw pulp (2.8 kNm kg^{-1}) under the optimum conditions.

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REFERENCES

[1] A. Alfaro, A. Pérez, J. C. García, F. López, M. A. M. Zamudio *et al*., *Cellulose Chem. Technol*., **43**, 293 (2009).
[2] M. J. Feria, F. López, J. C. García, A. Pérez, M. A. M. Zamudio *et al*., *Biomass Bioenerg*., **35**, 2224 (2011).
[3] K. Hofsetz and M. A. Silva, *Biomass Bioenerg*., **46**, 564 (2012).
[4] E. D. Larson, R. H. Williams, M. Regis and L. V. Leal, *Energy Sustain. Dev*., **5**, 54 (2001).
[5] Conab. Companhia nacional de abastecimento. http://www.conab.gov.br/OlalaCMS/uploads/arquivos/11_12_08_11_00_54_08.pdf. 2012, Brasilia, D.F.
[6] I. Macedo, *Biomass Bioenerg*., **14**, 77 (1998).
[7] D. A. Aguiar, B. F. T. Rudorff, W. F. Silva, M. Adami and M. P. Mello, *Remote Sens*., **3**, 2682 (2011).
[8] H. M. Baudel, C. Zaror and C. A. M. de Abreu, *Ind. Crop. Prod*., **21**, 309 (2005).

[9] M. Brienzo, A. F. Siqueira and A. M. F. Milagres, *Biochem. Eng. J.*, **46**, 199 (2009).
[10] A. Correa do Lago, A. Bonomi, O. Cavalett, M. Pereira da Cunha and M. A. Pinheiro, *Biomass Bioenerg.*, **46**, 5 (2012).
[11] Y. Hamzeh, A. Ashori, Z. Khorasani, A. Abdulkhani and A. Abyaz, *Ind. Crop. Prod.*, **43**, 365 (2013)
[12] J. B. D. Peterson, *Int. Sugar. J.*, **108**, 177 (2006).
[13] S. Caparros, J. Ariza, D. Hernanz and M. J. Díaz, *Ind. Eng. Chem. Res.*, **45**, 2940 (2006).
[14] R. Banerjee and A. Pandey, *Int. Sugar. J.*, **104**, 64 (2002).
[15] L. Canilha, V. T. O. Santos, G. J. M. Rocha, J. B. A. E. Silva, M. Giulietti, *et al.*, *J. Ind. Microbiol. Biotechnol.*, **38**, 1467 (2011).
[16] L. V. A. Gurgel, K. Marabezi, L. A. Ramos and A. A. D. Curvelo, *Ind. Crop. Prod.*, **36**, 560 (2012).
[17] L. E. D. E. Paula, P. F. Trugilho, A. Napoli and M. L. Bianchi, *Cerne*, **17**, 237 (2011).
[18] C. R. Soccol, L. P. D. Vandenberghe, A. B. P. Medeiros, S. G. Karp, M. Buckeridge, *et al.*, *Bioresource Technol.*, **101**, 4820 (2010).
[19] E. Virmond, R. F. De Sena, W. Albrecht, C. A. Althoff, R. F. P. M. Moreira *et al.*, *Waste Manage.*, **32**, 1952 (2012).
[20] Tappi Standard Methods, www.tappi.org; 2013.
[21] K. V. Sarkanen and H. L. Hergert (Eds.), in "Lignins: Occurrence, Formation, Structure and Reactions", Wiley Interscience, New York, USA, 1971, pp. 43.
[22] J. L. Gomide and B. J. Demuner, *O Papel*, **47**, 36 (1986).
[23] C. W. Dence and S. Y. Lin, in "Introduction in Methods in Lignin Chemistry". Springer, Heidelberg, 1992, pp. 1.
[24] A. Ferraz, J. Baeza, J. Rodriguez and J. Freer, *Bioresource Technol.*, **74**, 201 (2000).
[25] R. Solar, F. Kacik and I. Melcer, *Nord. Pulp Pap. Res. J.*, **2**, 139 (1987).
[26] R. W. Scott, *Anal. Chem.*, **51**, 936 (1979).
[27] J. C. Garcia, M. A. M. Zamudio, A. Perez, F. Lopez and J. Colodette, *Environ. Prog. Sustain. Energ.*, **30**, 92 (2011).
[28] J. L. Gomide, J. L. Colodette, R. C. Oliveira and C. M. Silva, *Rev. Árvore*, **29**, 129 (2005).