INFLUENCE OF OPERATING CONDITIONS IN SODIUM HYDROXIDE AND ANTHRAQUINONE PULPING ON THE MORPHOLOGY OF CELLULOSE FIBERS OF TAGASASTE

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This paper discusses the potential for improving paper characteristics by controlling fiber properties. To this end, we examined the most salient changes in tagasastefibers as a function of the operating conditions during their soda–anthraquinone cooking. Using high anthraquinone concentrations and medium cooking times provided paper with good strength-related properties. These operating conditions were compatible with those required to obtain the best values of the properties dependent on fiber morphology. Thus, obtaining the optimum fiber length would require to use short cooking times or medium times if a medium alkali concentration is used. A high anthraquinone concentration in combination with a high soda concentration and temperature would provide the best conditions for maximizing the number of fibers obtained. A high soda concentration additionally reduces coarseness and increases the number of fibers; also, medium and high temperatures avoid excessive curling and kinking, increase the number of fibers and decrease coarseness.

Keyword: tagasaste, soda anthraquinone pulping, fiber morphology

INTRODUCTION

Tree species constitute the primary source of virgin cellulose fibers for pulp making; in fact, they account for 89.3% of all plant raw materials used to obtain paper pulp.[1]However, the increasing shortage of raw materials, the limited geographical distribution of some plants and the availability of more rapidly renewed, sustainable sources has increasingly fostered the use of alternative, residual raw materials, as well as the growth of non-food crops in agricultural or forest soils. The alternative plants include tagasaste (*Chamaecytisusproliferus*), a fast-growing bushy legume used to reclaim degraded soil, which has additionally proved useful for industrial and papermaking processes.[2,3]

Although the kraft process is the most widely used in the production of cellulose pulp, some alkaline processes, such as that based on a soda–anthraquinone mixture, are simpler, more environmentally friendly – they use no sulphur-containing compounds[4-7]– and productive as they provide useful by-products and allow the easy recovery of reagents, which in turn allows factories to operate with smaller-sized plants.[5]

Also, energy efficiency is increasingly in the researchers' focus. Thus, some authors have proposed gassifying the effluents from pulpmaking processes (black liquors) as an alternative to the traditional energy and product recovery procedure of the kraft process.[6]At present, the alternative process provides about 3.3 GJ per ton of pulp or 2 tons of wood (versus the typical 7.9 GJ of a gassifier).[8,9]Regenerating Na_2S used in the kraft process is time-consuming and hampered by the low efficiency and selectivity of H_2S recovery by adsorption/desorption.[10]

In this situation, the soda–anthraquinone process has emerged as an interesting choice for the future, especially if its greatest problem, viz. the low bleachability of its pulp,[11]is overcome by, for example, extending the oxygen delignification step.[6]

The primary objective of both delignification processes is to obtain a suspension of individual cellulose fibers. Fibers are the building bricks of paper. The properties of the papermaking fibers have a significant effect on the fracture properties of paper and determine the achievable quality of paper.[12-14]Although the chemical composition of the fiber wall is also important, it is the morphology of fibersthat dictates the papermaking potential of a given plant species. The most influential morphological characteristics of fibers in this respect are length (arithmetic and weighted mean lengths), wall thickness, luminal width and weight per unit length. The morphological properties of fibers account for at least 80% of their papermaking potential. It is well documented in the literature that fiber length and coarseness have a large impact on paper properties, such as tensile index, tear index and light scattering effect.[13,15,16]Other properties, such as fiber curl and kink, have been shown to affect tensile index, tear index and burst index.[17-19]

Also, the quality of the final product (the paper) depends on the raw material used, the pulping, beating and bleaching methods and also on the conditions of the paper sheet formation. Duringthe pulping process, about 50% of the raw material mass dissolves and the strength potential of the fibers decreases twice, because pulping usually takes place at high temperatures and pressures.[20]Examining fiber changes during the pulping process can be useful with a view to maximizing the quality of a paper end-product.[21]Mills are becoming more aware not only of fiber characteristics and of the way they impact product quality, but also of how their processing affects the fiber. By measuring fiber characteristics, the paper maker is able to troubleshoot and determine which parts of the process cause the most fiberdamage.[22]

This paper discusses the potential for improving paper characteristics by controlling fiber properties. Examining fiber changes during the pulping process can be useful with a view to maximizing the quality of a paper end-product.

EXPERIMENTAL

Raw material, pulping procedure, formation and characterization of paper sheets

We used pruned portions of bushes of tagasaste [*Chamaecytisusproliferus* (L.F.) ssppalmensis] for soda–anthraquinone cooking.Pulps were obtained using a batch digester wrapped and electrically heated jacket with rotary agitation.

The sequence of steps of the soda pulping process was as follows: following cooking (cooking conditions are described more fully in the next section), the pulp was filtered and washed with abundant water on a screening tray, defiberized to 1.5% consistency and passed through a Sprout-Waldrom refiner operating at 0.5% pulp consistency and using a disk spacing of 0.1 mm. The uncooked material was removed by passing through a Steiner filter of 0.4 mm mesh size, and water – by centrifugation. Paper sheets were obtained by using an ENJO-F-39.71 sheet former, according to Tappi T 205 sp-95.

Paper sheets characterization involved the following parameters: tensile index (Tappi T-494om-96), tear index (Tappi T-414 om-98) and burst index (Tappi T-403 om-97).

Experimental design for pulping conditions

In order to be able to relate the dependent and independent variables with the minimum number of experiments, a 2^n central composite factor design was used, which enabled the construction of second-order polynomials in the independent variables and the identification of statistical significance in the variables.[23,24]The polynomial model used was of the following type:

$$Z = a_0 + \sum_{i=1}^{n} b_i X_{ni} + \sum_{i=1;\, j=1}^{n} d_i X_{ni} X_{nj} \quad (\mathrm{i} < \mathrm{j}) \qquad \text{(Eq. 1)}$$

where Z and X_{ni} denote dependent and normalized independent variables, respectively, and a_0, b_i, c_i and d_{ij} are unknown constants obtained from the experimental data.

Independent variables were normalized by using the following equation:

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

were X is the absolute value of the independent variable concerned, $\overline{X}$ is the average value of the variable and $X_{\max}$ and $X_{\min}$ are its maximum and minimum values, respectively. The temperature, pulping time, active alkali concentration, antraquinone concentration and liquid/solid ratio used in the different experiments of the factorial design were 175, 185 and 195ºC; 30, 60 and 90 minutes; 12, 16 and 20% (o.d.b. –on dry basis); 0, 0.05 and 0.1% (o.d.b.); and 4:1, 8:1 and 12:1, respectively.

The independent variables used in the equations relating to both types of variables were those having a statistically significant coefficient (viz. those not exceeding a significance level of 0.05 in Student's t-test and having a 95% confidence interval excluding zero). The difference between experimental and estimated values does not exceed 10%-15%.

Morphological characterization of fibers

Fibers were characterized with a MORFI LB-01 automated optical fiberanalyzer,[25-30] which includes a measuring cell connected to a computer for accurate, precise measurement of various morphological properties of fibers and fines by analysing images for a cellulose pulp suspension. Each pulp sample was analysed for number of fibers per gram of pulp, arithmetic and weighted mean fiber lengths, fiber width, coarseness, mean kink angle, proportion of kinked fibers, curl and proportion of surface fines.

Number of fibers

The objects present in the pulp whose dimensions are too small for them to be considered as fibers (by default a length less than 200 microns and/or width less than 5 microns) were considered fine elements.[31]

MORFI analyzer reports fines as percentage of fiber on length weighted basis. This is the sum of the fines length divided by the total length of fibers and fines in the sample.[32]

Fiber length

The arithmetic and weighted mean fiber lengths were calculated from Eqs. 3 and 4, respectively. The MORFI analyzer provides both means in an automatic and highly accurate manner.

$$L_A = \frac{\sum_i n_i l_i}{\sum_i n_i} \quad \text{(Eq. 3)}$$

$$L_P = \frac{\sum_i n_i l_i^2}{\sum_i n_i l_i} \quad \text{(Eq. 4)}$$

where L_A and L_W are the arithmetic and weighted mean fiber lengths (mm), respectively, and n_i is the number of fibers having a specific length l_i. Equation 2 is more commonly used since its results are better correlated with paper properties and less dependent on the proportion of fines.[28, 33]

Coarseness

Coarseness is defined as the fiber mass per unit length, in mg/m, and is obtained by dividing the pulp mass into the overall fiber length. In practice, it is calculated from Eq. 5:

$$C = \frac{m}{nl_n} \quad \text{(Eq. 5)}$$

where C denotes coarseness, m fiber dry mass(mg), n the total number of fibers in the mass m and ln the arithmetic mean fiber length. The MORFI fiberanalyzer directly calculates fiber coarseness, in mg/m.

Fiber curl

Fiber curl, which represents the percent deviation from linearity of the longitudinal axis of a fiber, was calculated as a percent index from Eq. 6:

$$IC_T = \left[\frac{l}{L} - 1\right] \times 100 \quad \text{(Eq. 6)}$$

where IC_T is the percent curl, l the fiber contour length (mm) and L the projected length of the fiber ends (mm). Therefore, curl represents the relative increase in length of a fiber that is straightened without stretching.[25] Based on Eq. 6, fiber curl is 0% when $L = l$, (i.e. in a totally straight fiber).

The MORFI fiberanalyzer estimates fiber curl by classifying fibers according to curl, in order to calculate the mean percent fiber curl for the pulp.

In this work, the fiber kink angle, the proportion of kinked fibers and the mean fiber width were also determined.[26,34,35]

RESULTS AND DISCUSSION

The normalized values of independent variables, morphological fiber properties and strength properties of the paper sheets obtained in the pulping process by using the proposed experimental design are shown in Table 1a and 1b, respectively. The results allowed the dependent variables to be modelled in terms of the second-order polynomials of Table 2.

The mean length of tagasastefibers is 0.70 mm[3], but can range from 0.55 to 0.79 mm depending on origin.[36] Like eucalyptus (fiber length = 1 mm), which is highly appreciated by the papermaking industry, tagasaste is therefore a short-fiber plant.Fiber length strongly influences paper formation (microuniformity).[37,38] Soda pulping of tagasastefibers reduces their length by 18.4-28.6% (viz. to 0.5-0.571 mm) depending on the particular conditions.LA in Table 4 reveals a strong dependence of the linear and, especially, quadratic terms of the processing time and alkali concentration, based on which it is advisable to use medium alkali concentrations and short operation times – note the negative sign of the coefficient for the X_t term. A similar conclusion can be drawn from equation LW (weighted average length), with a substantially significant X_t term and, again, a negative $X_C X_C$ term.

Fiber width in tagasaste pulp ranged from 22.3 to 26.9 μm, which exceeds the values for organosolv pulp from olive prunings (20.94 μm) and kraft pulp from eucalyptus (18.8 μm),[39]

therefore, tagasaste pulp should be easier to refine than the latter two.

The width of a fiber is related to its specific surface area[28]and changes by effect of the outer wall breaking and causing the exposed conduits in the secondary wall to swell. An increased width facilitates paper formation and increases cohesion.

Model W in Table 2 shows a negative linear effect of all variables except the solid/liquid ratio, which is especially marked for the alkali concentration. The number of fibers measured in the tests ranged from 10754 to 26714 x 10^6/g. These values exceed those for eucalyptus kraft pulp (10659 and 7759 x 10^6, respectively).[39]As a rule, a high fiber yield in pulp from leafy plants results in improved paper conformation and leads to better formation, smoothness, quire and opacity.[20]By contrast, the proportion of fines in pulp from conifers is decreased by strong operating conditions (4.61-5.68%), possibly as a result of the intrinsic structure of the wood, which is simpler and contains more abundant (ca. 90%), longer fibers.[20,40]

In our tests, the strongest pulping conditions provided pulp with an increased number of fibers and also an increased proportion of fines, the fines consisting of non-fiber components such as vessels, radial cells, parenchyma and pieces of broken fibers, which detracted from uniformity and strength-related properties in the pulp. Only the linear term for the solid/liquid ratio, X_H, had a positive effect. As a rule, pulp containing an increased number of fibers exhibits decreased fiber length, width and coarseness.[31]Coarseness influences sheet uniformity via the number of contacts among fibers. This affects the structural, strength-related and optical properties of paper sheets.[37]

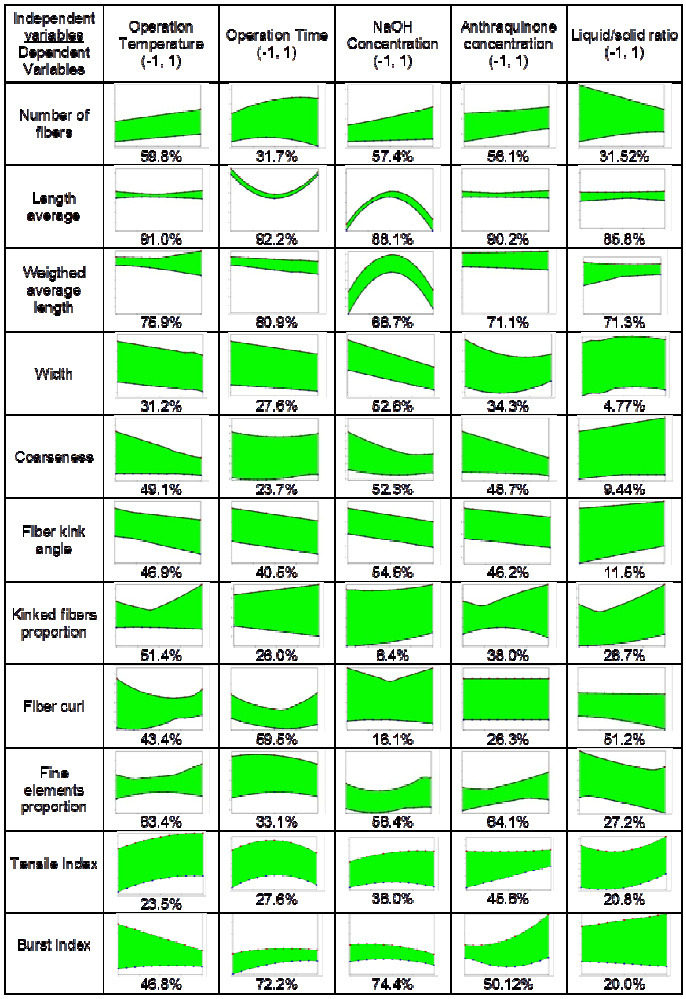

Figure 1: Variation of dependent variables as a function of normalized independent variables

Table 1a
Morphological fiber properties

Normalized values of pulping conditions					Fibersnumber, million/g	Length fiber average, mm	Weighted average length, mm	Width, μm	Coarseness, mg/m	Curl, %	Kink angle, °	Kinked fibers proportion, %	Fine elements proportion, %
T	H	t	C	A									
-1	-1	-1	+1	-1	13441	0.431	0.571	24.35	0.120	5.20	130	18.60	3.92
-1	+1	-1	+1	+1	14135	0.404	0.546	24.60	0.121	4.70	131	16.00	5.90
+1	+1	-1	-1	+1	15447	0.406	0.555	24.50	0.110	4.95	130	17.00	6.27
+1	+1	-1	+1	-1	16453	0.405	0.549	23.40	0.104	4.70	131	17.50	6.95
+1	+1	+1	-1	-1	14572	0.389	0.545	25.45	0.122	5.15	130	17.00	6.95
+1	0	0	0	0	22015	0.386	0.532	23.15	0.081	4.70	129	15.40	8.28
0	0	-1	0	0	16919	0.391	0.527	24.36	0.105	4.80	130	15.03	6.66
0	0	0	+1	0	24045	0.363	0.507	23.00	0.079	4.50	129	14.15	10.03
-1	-1	-1	-1	+1	16941	0.380	0.527	25.20	0.107	4.60	130	14.05	7.37
0	0	0	0	+1	21737	0.359	0.515	24.20	0.088	4.65	129	13.55	10.48
+1	-1	-1	+1	+1	26022	0.367	0.512	22.65	0.072	4.65	127	14.95	19.31
-1	0	0	0	0	17115	0.387	0.535	24.60	0.105	4.75	131	14.85	6.65
+1	-1	+1	+1	-1	26714	0.359	0.500	22.30	0.072	4.95	127	15.65	9.15
0	+1	0	0	0	20890	0.372	0.528	24.00	0.089	4.50	130	13.90	9.57
-1	+1	-1	-1	-1	18148	0.354	0.509	26.95	0.237	4.65	131	13.50	9.25
+1	-1	-1	-1	-1	15600	0.381	0.525	25.10	0.116	4.70	131	13.90	7.17
0	0	0	0	-1	17686	0.393	0.546	25.20	0.099	4.60	131	13.75	6.27
0	0	0	0	0	19449	0.389	0.541	23.65	0.091	4.60	129	14.35	8.34
-1	-1	+1	+1	+1	23218	0.366	0.504	23.35	0.081	5.05	128	15.55	9.95
-1	+1	+1	-1	+1	16870	0.373	0.525	25.85	0.109	4.60	130	13.20	8.32
-1	-1	+1	-1	-1	10754	0.369	0.517	26.20	0.174	4.75	131	14.60	7.84
+1	-1	+1	-1	+1	20169	0.367	0.511	24.05	0.093	4.90	128	14.55	10.11
0	0	0	-1	0	15403	0.372	0.524	25.35	0.120	4.70	131	15.35	8.29
+1	+1	+1	+1	+1	23502	0.376	0.519	23.15	0.078	5.05	127	21.05	8.75
0	0	+1	0	0	18833	0.394	0.538	24.00	0.093	4.70	129	14.40	6.30
0	-1	0	0	0	21450	0.397	0.543	23.00	0.081	4.90	128	15.65	7.32
-1	+1	+1	+1	-1	16705	0.383	0.522	22.95	0.108	4.60	129	14.70	8.14

T: temperature, H: liquid/solid rate, t: cooking time, C: active alkali concentration, A: anthraquinone concentration

Table 1b
Strength properties of paper sheets

Normalized values of pulping conditions					Tensile Index (kN m/kg)	Tear Index (N m^2/kg)	Burst Index (MPa m^2/kg)
T	H	t	C	A			
-1	-1	-1	+1	-1	4.9	19.4	1.2
-1	+1	-1	+1	+1	11.4	27.1	1.5
+1	+1	-1	-1	+1	8.0	29.2	1.5
+1	+1	-1	+1	-1	20.9	28.4	1.5
+1	+1	+1	-1	-1	6.3	22.2	1.6
+1	0	0	0	0	13.3	33.1	1.7
0	0	-1	0	0	10.9	29.0	1.5
0	0	0	+1	0	14.4	30.8	1.7
-1	-1	-1	-1	+1	11.0	30.8	3.7
0	0	0	0	+1	17.2	34.2	1.9
+1	-1	-1	+1	+1	14.9	28.2	1.6
-1	0	0	0	0	13.9	29.4	1.6
+1	-1	+1	+1	-1	9.9	26.1	1.9
0	+1	0	0	0	18.3	34.6	1.9
-1	+1	-1	-1	-1	8.4	27.3	1.8
+1	-1	-1	-1	-1	8.6	25.7	2.1
0	0	0	0	-1	14.0	29.7	4.1
0	0	0	0	0	14.6	33.0	5.8
-1	-1	+1	+1	+1	13.3	28.8	3.3
-1	+1	+1	-1	+1	11.7	31.9	5.7
-1	-1	+1	-1	-1	5.0	21.8	1.8
+1	-1	+1	-1	+1	13.5	30.8	1.9
0	0	0	-1	0	12.5	28,3	1.8
+1	+1	+1	+1	+1	13.6	29.7	1.9
0	0	+1	0	0	11.8	25.0	1.6
0	-1	0	0	0	16.4	28.5	1.7
-1	+1	+1	+1	-1	12.4	29.8	2.2

N-E: number of experiment, T: temperature,H: liquid/solid ratio, t: cooking time, C: active alkaliconcentration,A: anthraquinone concentration

Table 2
Equations yielded for each dependent variable (morphological characteristics)

Eq.	Equation	r^2	F
1	**NF** = 19978.80+1697.50 X_T – 831.86 X_H + 867.64 X_t + 2161.59 X_C + 1408.72 X_A – 2099.50 X_t^2 – 1088.78 X_TX_H + 1545.66X_TX_C – 1424.09X_HX_C – 821.97X_HX_A + 1654.34X_tX_C	0.95	45.32
2	**LA** = 0.386 – 0.007X_t + 0.005X_C + 0.011X_tX_t – 0.015X_CX_C + 0.009X_TX_H - 0.009X_TX_C + 0.005X_HX_A - 0.005X_tX_C- 0.005X_CX_A	0.87	21.11
3	**LW** = 0.536+0.006X_H – 0.009X_t – 0.003X_A – 0.008X_CX_C + 0.009X_TX_H – 0.007X_TX_C + 0.003X_HX_t + 0.005X_HX_A - 0.007X_tX_C- 0.005X_CX_A	0.96	65.21
4	**W** = 24.05 – 0.57X_T + 0.27X_H – 0.20X_t – 1.02X_C – 0.24X_A - 0.51X_HX_H + 0.85X_A^2 + 0.11X_TX_t + 0.11X_HX_A - 0.18X_t + 0.13X_tX_A + 0.29X_CX_A	0.98	109.91
5	**C** = 0.091 – 0.017X_T + 0.009X_H – 0.009X_t – 0.019X_C – 0.017X_A + 0.011 X_t^2 + 0.011X_C^2 + 0.005X_TX_t + 0.005X_TX_C + 0.009X_TX_A - 0.009X_HX_t – 0.003X_tX_A+ 0.011X_CX_A	0.98	102.81
6	**KA** = 129.37 – 0.613X_T + 0.502X_H - 0.525X_t – 0.564X_C - 0.370X_A + 0.216X_TX_H	0.92	55.12
7	**KP** = 14.321 + 0.634X_T + 0.460X_H + 0.963X_C + 0.835X_T^2 + 0.604 X_H^2 + 0.579 X_C^2 - 0.639X_A^2 + 1.148 X_TX_H + 0.529X_TX_t - 0.207X_TX_C + 0.348X_TX_A + 0.479X_HX_A+ 0.529X_TX_t – 0.207X_TX_C + 0.348X_TX_A + 0.479X_HX_A - 0.207X_TX_C + 0.348X_TX_A+ 0.479X_HX_A	0.95	47.85
8	**CU** = 4.623 + 0.026X_T - 0.053X_H + 0.028X_t + 0.111 X_T^2 + 0.094X_t^2 + 0.011 X_TX_H + 0.083 X_TX_t - 0.072 X_TX_C - 0.066X_HX_C	0.94	44.31
9	**FP** = 7.744+ 0.745X_T - 0.865X_H + 0.583X_C+1.081X_A– 0.999 X_t^2+1.683 X_C^2 – 1.345 X_TX_H - 0.782 X_TX_t + 1.293X_TX_C + 0.875X_TX_C – 0.683X_HX_C – 1.297X_HX_A+ 0.934X_CX_A	0.97	57.18
10	**TI** = 15.065+1.075 X_T + 0.758X_H + 1.699X_C + 1.355X_A – 1.434 X_T^2 + 2.381 X_H^2 – 3.618 X_t^2 – 1.553 X_C^2 – 0.482 X_TX_H –0.988 X_TX_t + 1.069 X_TX_C – 0.776 X_TX_A - 0.438 X_HX_t + 1.197X_HX_C – 1.730X_HX_A + 0.996X_tX_A- 0.677X_CX_A	0.97	50.52
11	**BI =** 2.011-0.439 X_T + 0.321X_t – 0.290X_C + 0.460 X_A – 0.376 X_t^2 - 0.386 X_C^2 + 0.959 X_A^2 – 0.133 X_TX_H – 0.258 X_TX_t +0.288 X_TX_C – 0.475 X_TX_A + 0.300 X_HX_t - 0.133 X_HX_C + 0.218X_tX_A – 0.263X_CX_A	0.97	50.52
12	**TEI=**31.842+0.302 X_T + 0.932X_H + 0.292X_t + 2.234 X_A + 1.456 X_H^2 – 4.499 X_t^2 – 1.499 X_C^2 – 1.036 X_TX_H – 0.654 X_TX_t +0.703 X_TX_C – 0.303 X_TX_A + 0.692 X_HX_C -0.964 X_HX_A + 1.093X_tX_C + 0.427X_tX_A-0.988 X_CX_A	0.97	65.68

Where NF: Number of fibers (million/gram), LA: Medium length arithmetic (mm), LW: Medium length weighted (mm), W: Width (μm), C: Coarseness (mg/m), KA: Fiber kink angle (°), KP: Kinked fibers proportion (%), CU: Fiber curl (%), FP: Fine elements proportion (%), TI: Tensile Index (kN m/kg), BI= Burst Index (MPa m^2/kg), TEI: Tear Index (Nm^2/kg) and X_T, X_t, X_C, X_A and X_H the normalized values of the pulping temperature, time, soda concentration, anthraquinone concentration and liquid/solid relation, respectively. r^2 is the multiple regression coefficient and F is the Snedecor's F

Our maximum and minimum values for coarseness were markedly different (viz. 0.072 and 0.237 mg/m, respectively). The highest value is comparable to those for other materials, such as organosolv pulp from olive prunings (0.272 mg/m) and kraft pulp from eucalyptus pulp (0.224 mg/m).[39] As with the number of fibers and their width, all independent variables except the solid/liquid ratio had a negative linear effect on coarseness. Curl ranged from 4.5 to 5.2% and the proportion of kinked fibers from 13.2 to 21.05%. The mean kink angle was 129. Fibers usually curl by effect of stretching and bending during pulping, mixing and refining.

As can be seen in Table 1b, the mean tensile index, tear index and burst index had values of 12.25 kN m/kg, 28.61 N m^2/kg and 2.23 MPa m^2/kg, respectively. The tear index was higher than those for other materials, such as soda-pulped switchgrass stems, with 7.6 N m^2/kg. On the other hand, the tensile index and burst index were both lower than those for this material [69 kN m/kg and 3.8 MPa m^2/kg,[41] respectively]. It should be noted, however, that switchgrass stems typically have a fiber length of 1 mm and also that they were pulped under different conditions.

Identifying the independent variables with the strongest and weakest influence on the dependent variables in equations in Table 2 is not so easy since the former contain quadratic terms and other factors involving interactions between two independent variables. In order to facilitate interpretation of the results, Fig. 1 shows the percent relative weight of each independent variable on the variation of each dependent variable. The methodology used is described in detail elsewhere.[2,3]

All independent variables had a strong influence; also, all had a similar effect on some dependent variables, such as the arithmetic and weighted average lengths. Only a few dependent variables (viz. coarseness, fiber curl and the proportion of fines) were especially influenced by three of the independent variables. The temperature had a marked effect on fiber morphology (particularly fiber length, surface fines and number of fibers). The operation time was the individual variable most strongly influencing the average fiber length, followed by fiber curl and kink angle. Finally, the NaOH concentration was especially influential on the average fiber length, followed by the number of fibers and surface fines.

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 variable most strongly influencing each of them and a fixed value of the two least influential variables.

The effect of the solid/liquid ratio – a high value that should be used based on model NF in Table 2 – was not apparent, however.

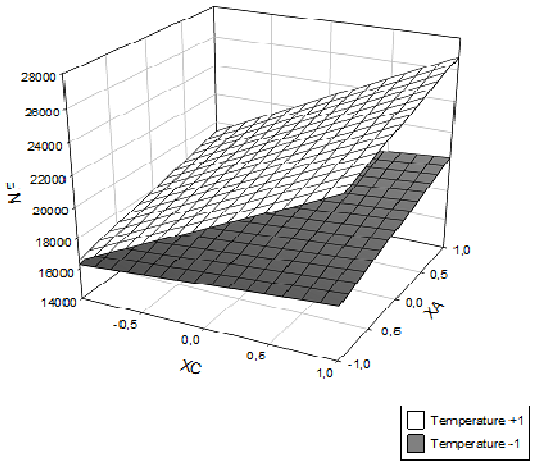

Figure 2: Variation of number of fibers as a function of soda and anthraquinone concentration at two pulping temperature levels, NF: Number of fibers (million/gram); XC and XA: the normalized values of soda and anthraquinone concentration, respectively

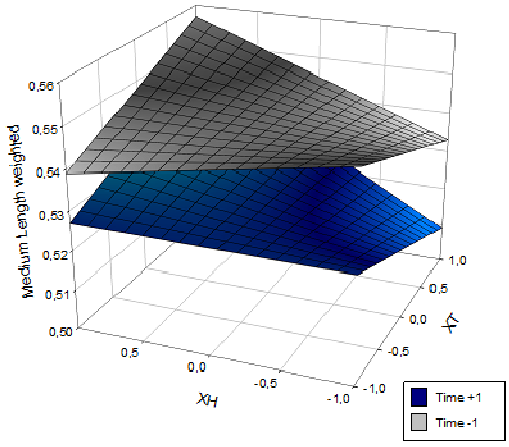

Figure 3: Variation of medium length weighted as a function of liquid/solid relation and temperature at two levels of pulping time; X_T, and X_H: the normalized values of pulping temperature, and liquid/solid relation, respectively

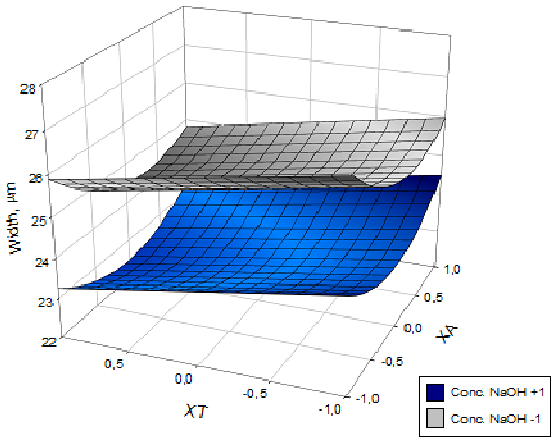

Figure 4: Variation of width as a function of temperature and soda concentration at two soda concentration levels; XT and XA: the normalized values of pulping temperature and anthraquinone concentration, respectively

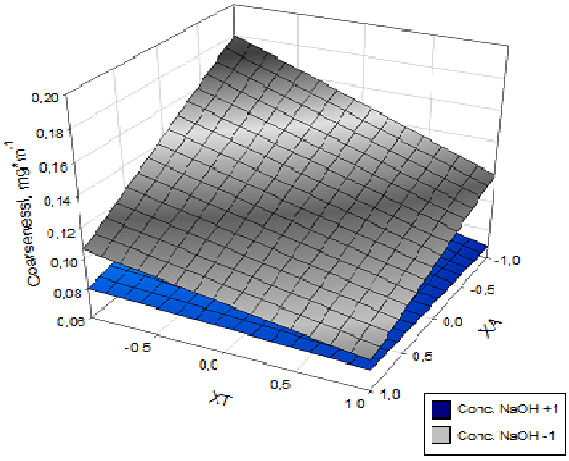

Figure 5: Variation of coarseness as a function of temperature and anthraquinone concentration at two concentration soda levels;XT and XA: the normalized values of pulping temperature and anthraquinone concentration, respectively

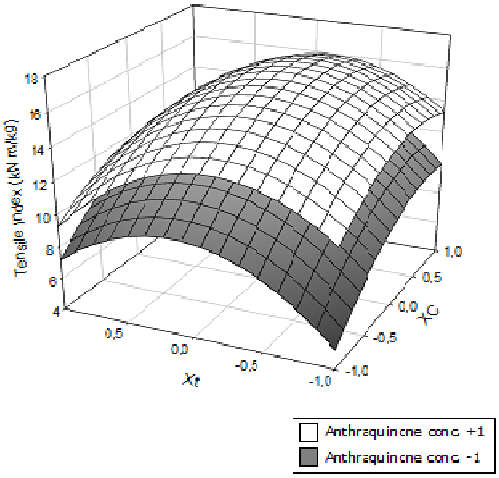

Figure 6: Variation of tensile index as a function of soda concentration and time at two anthraquinone concentration levels;X_t, and X_C:the normalized values of time and soda concentration, respectively

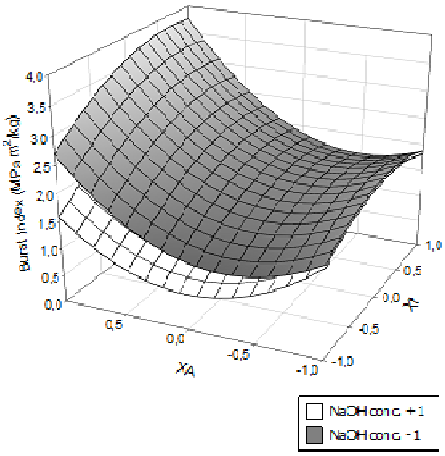

Figure 7: Variation of burst index as a function of time and soda concentration at two soda concentration levels;X_t, and X_A:the normalized values of time and anthraquinone concentration, respectively

Based on Fig. 3, obtaining the optimum fiber length entails using short cooking times, consistent with the inference from equations LA and LW, in Table 2. Using a medium soda concentration, and a high solid/liquid ratio and temperature, is also advisable. As a rule, a high processing temperature leads to increased fiber lengths.[42]

As can be seen from Fig. 4, the greatest fiber widths can be obtained with a low active alkali concentration, and also a low temperature and anthraquinone concentration.

The conditions leading to the optimum coarseness (Fig. 5) include a high active alkali concentration and, as with fiber width, a low temperature and anthraquinone concentration.

Optimizing fiber curl entails using a short cooking time in addition to a medium–high temperature (figure not shown).

Identifying the optimum value of each independent variable requires considering those morphological properties of the fibers leading to the greatest possible paper strength. It should be noted, however, that paper strength is influenced not only by fiber morphology, but also by interfiber bonding. This is consistent with the fact that the first test in Tables 1a and 1b, which provided the greatest weighted average length (0.571 µm), was also that providing the smallest strength.

Strength development in paper sheets (Figs. 6-8) was especially favourable at high

anthraquinone concentrations and medium operation times. The active alkali concentration influenced the development of burst index and should therefore be adjusted to low values in the operating range. All other independent variables were considerably less influential.

Using a high anthraquinone concentration and medium operation times to obtain paper with good strength-related properties is compatible with the conditions required to optimize the properties dependent on fiber morphology. Thus, optimizing fiber length requires using low operation times – or medium values with an intermediate alkali concentration –, the other variables having little influence on this dependent variable. A high anthraquinone concentration in combination with a high temperature and soda concentration lead to an increased number of fibers, the opposite conditions resulting in the best possible coarseness. An increased coarseness is known to detract from paper strength,[38] thus, a low coarseness increases the tensile index, but reduces the tear index through its effect on interfiber bonding.[15] Medium–low coarseness is therefore usually the goal in order to increase the tensile index without an excessive reduction in tear index; this requires using a high soda concentration and temperature in the cooking process. The anthraquinone concentration is less influential on the development of coarseness. Finally, fiber width varies similarly as coarseness.

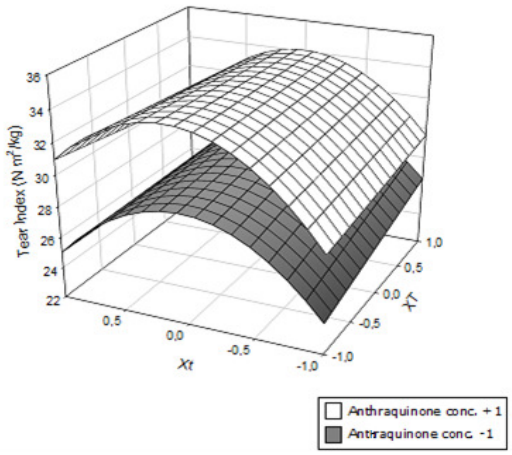

Figure 8: Variation of tear index as a function of temperature and time at two anthraquinone concentration levels.X_T and X_t the normalized values of the pulping temperature and time, respectively

Pulp with a high curl and kink provides paper with a high tear index and a decreased tensile index and burst index.[43]It is therefore advisable to aim at medium-low values of these variables, which can be obtained by using a medium–high temperature whatever the operating time and solid/liquid ratio. Finally, a short operation time leads to a low fiber curl.

CONCLUSION

Using a high anthraquinone concentration and a medium operation time in the soda–anthraquinone cooking of tagasaste wood provides paper with good strength-related properties. These operating conditions are compatible with those leading to the best properties influenced by fiber morphology. Optimizing fiber length entails using a short operation time – or a medium value in combination with a medium alkali concentration – , whatever the values of the other variables. A high anthraquinone concentration in conjunction with a high temperature and soda concentration constitute the best conditions for obtaining large numbers of fibers.Finally, a high soda concentration also results in a low coarseness and a large number of fibers, and a medium or high temperature avoids excessive curl and kink, while increasing the number of fibers and reducing their coarseness.

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REFERENCES

[1] A. Alfaro, PhD Thesis, University of Huelva, Spain, 2005.
[2] F. López, A. Alfaro, M.M. García, M J. Díaz, A. M. Caleroand J. Ariza, *Chem. Eng. Res. Des.*, **82**, 1029(2004).
[3] M.J. Díaz, A. Alfaro, M.M. García,M.E. Eugenio, J. Ariza and F. López, *Ind. Eng. Chem. Res.*, **43**, 1875 (2004).
[4] S. González García, M. Teresa Moreira, G.Artal, L. Maldonado and G. Feijoo, *J. Clean Prod.*, **18**, 137 (2010).
[5] A. García,M. González, R. Llano-Ponte and J.Labidi, *Procs. ESCAPE-20*, Naples, 6-9 June, 2010, pp. 115-120.
[6] R.C. Francis, T.S. Bolton, N. Abdoulmoumine, N. Lavrykova andS.K. Bose, *Bioresource Technol.*, **99**, 8453 (2008).
[7] P. Khristova, O. Kordsachia, R. Patt, I. Kararand T. Khider, *Ind. Crop. Prod.*, **23**, 131 (2006).
[8] E.D. Larson and D.L. Raymond, *Tappi J.*, **80**, 50 (1997).
[9] M.N. Mansour, R.R. Chandran and L.Rockvam, *Procs. Tappi Pulping Conference*,Tappi Press,San Diego, CA, 2002, pp. 1431-1450.
[10] C.A. Brown, R. Leary, J.P. Corogand, Z. Abdullah, *Procs.CHEMREC International Chemistry Recovery Conference*, Charleston, 7-10 June, 2004, pp. 1089-1093.
[11] S.K. Bose, S. Omori, D.Kanungo, R.C. Francis and H.N. Shin, *J. Wood Chem. Technol.*, **29**, 214(2009).
[12] L. Pulkkinen, K. Ala-Kaila and J. Aittamaa, *Chem. Eng. Proc. Int.*, **45**,546 (2006).
[13] E. Retulainen, *Pap. Puu*, **78**,187(1996).
[14] R. A. Horn, "Morphology of pulp fiber from hardwoods and influence on paper strength", USDA Forest Service, WI, USA, Research paper FPL312, 1 (1978).
[15] R. S. Seth, *Procs. Materials Research Society Symposium*, San Francisco, 16-17 April, 1990, pp. 143-161.
[16] R. S. Seth, *Procs. Materials Research Society Symposium*, San Francisco, 25-29 April, 2011, pp.125-141.
[17] A. Hakanen and N. Hartler, *Paper and Timber*, **77**, 339(1995).
[18] U. B. Mohlinand, C. Alfredsson, *Nordic Pulp Pap. Res. J.*, **4**, 172 (1990).
[19] O. Joutsimo, R. Wathénand, T. Tamminen, *Pap. Puu*, **87**, 392 (2005).
[20] J.A. García Hortal,"Fibraspapeleras"("Papermaking Fibers"), Barcelona, Edicions UPC, 2007.
[21] F. El-Hosseinyand, D. Anderson, *Tappi J.*, **82**, 202 (1999).
[22] P. Sutton, C. Joss and B. Crossely, *Procs. TAPPI Pulping/Process and Product Quality Conference*, Boston, 5-8 November, 2000, pp. 369-377.
[23] S. Aknazarova and V. Kafarov, "Experimental Optimization in Chemistry and Chemical Engineering", Mir Publisher, Moscow, 1982.
[24] D.C. Montgomery, "Diseño y Análisis de Experimentos", ("Design and Analysis of Experiments"), Editorial Iberoamericana, México, 1991.
[25] G. Robertson, J. Olson, P. Allen, B. Chan and R. Seth, *Tappi J.*, **82**, 93 (1999).
[26] R.J. Trepanier, *Tappi J.*, **81**,152 (1998).
[27] TECHPAP. MORFI LB-01Analizer, User Manual, 2011.
[28] M.G. Carvalho, P.J. Ferreira, A.A. Martins and M.M. Figueiredo, *Tappi J.*, **80**,137 (1997).
[29] A. Bartl, B. Mihalyiand I. Marini, *Chem. Biochem. Eng.*, **18**, 21 (2004).
[30] M. Turunen, C. LeNy, T. Tienvieri and J. Niinimaki, *Appita J.*, **58**, 28 (2005).
[31] B. Surma-Slusarska and D. Danielewicz, *Fibres Text. East Eur.*, **11**, 78 (2003).
[32] D. Guay, N.R.Sutherland, W. Rantanen, N. Malandri, A. Stephens *et al.*, *Procs. 2005 TAPPI Practical Papermaking Conference*, Milwaukee, 23-26May, 2005, pp.413-442.
[33] J. Clark, "Pulp Technology and Treatment for Paper",2nd ed., Miller Freeman, San Francisco, 1985, Chapter 17.
[34] R.P. Kibblewhite, *Tappi J.*, **57**,120(1974).
[35] R.P. Kibblewhiteand D. Brookes, *Appita J.*, **28**, 227 (1975).
[36] M.M. García, F. López, A. Alfaro,J. Ariza and R. Tapias, *Bioresource Technol.*, **99**, 3451 (2008).
[37] R.J. Kerekes and C.J. Schell, *Tappi J.*, **78**, 133 (1995).
[38] B.K. Via, M. Stine, T.F. Shupe, C. So and L. Groom, *IAWA J.*, **25**,401 (2004).
[39] J.C. García, P. Mutjé, M. Pèlach and L. Jiménez, *Procs. III CIADICYP 2004*, Córdoba, 10-12 November, 2004, pp. 372-376.
[40] H. Wisur, L.A. Sjàberg and P. Ahlgren, *Ind. Crop. Prod.*, **2**, 39 (1993).
[41] K.N. Law, B.V. Kokta and C.B. Mao, *Bioresource Technol.*, **77**, 1 (2001).
[42] P. Mutje, M.A. Pelach, F.Vilaseca, J.C. Garcia and L. Jimenez, *Bioresource Technol.*, **96**, 1125 (2005).
[43] Y.V. Sood, P. C. Pande, S. Tyagi, I. Payra, Nisha and A. G. Kulkarni, *J. Sci. Ind. Res.*, **64**, 299 (2005).