CELLULOSE CHEMISTRY AND TECHNOLOGY

ORANGE TREE PRUNINGS AS RAW MATERIAL FOR CELLULOSE PRODUCTION BY THE KRAFT PROCESS

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The aim of this work was to study the influence of operational variables in the orange tree pruning kraft pulping, such as temperature (155-185 ºC), processing time (40-90 min) and active alkali concentration (10-16%) at constant values of liquid solid ratio, anthraquinone and sulfidity concentration of 8:1, 1% and 20%, respectively, on the pulp yield, lignin content, Kappa number and viscosity of the pulps and the tensile index, burst index, tear index and brightness of the paper sheets. The experimental data obtained were used to estimate the parameters or constants in the equation for the neural fuzzy model. The predictions for the yield, Kappa number, lignin content, viscosity, tensile index, burst index, tear index and brightness differ by less than 9, 8, 21, 14, 17, 21, 9, and 6% from their respective experimental values.

Keywords: orange tree prunings, kraft pulp, neural fuzzy model

INTRODUCTION

The rational use of natural resources should be a priority in the policies aiming at supporting what is known as sustainable development. The epitome of rational use is the comprehensive utilization of these resources. Thus, when it comes to food crops, attention should be focused not only on obtaining actual food (fruit, vegetables, cereals, etc), but also on the product or by-product that can be initially considered as waste. Currently, most of the production costs of food crops leave little room for manoeuvre to farmers, forcing governments to subsidize this activity. In this context, it would be interesting to take advantage of the waste that these activities generate to obtain economic, as well as environmental benefits.

Orange tree prunings consist of lignocellulosic material resulting from the felling operation. The Spanish production of oranges is of about 6,500,000 t/year, Andalusia contributing with more than 20%. Considering that the relationship "prune/fruit" can be of 0.8, the production of prunings can exceed 5,000,000 t/year.[1,2]

Orange tree prunings and crop residues, in general, must be disposed of for various reasons, such as pollution, pests, interference with soil cultivation, occupation of large areas etc. Thus, it is interesting to try to exploit different fractions of waste, since in this way, there may be benefits by reducing disposal costs.

The use of orange tree prunings can be done in two general ways: by separating components by fractionation, to be used separately, or transforming them without prior separation, by physical-chemical processes (combustion, pyrolysis, gasification and liquefaction) or biochemical processes (bioalcohol and biogas production).[1-3]

In separation processes, it is most important to isolate the cellulose fibers for paper production. In this field, in recent years, there has been great concern for the integrated utilization of raw materials called biorefinery, consisting of the splitting of the various components of lignocellulosic materials to use them all, not only some of them, as in the production of paper using traditional processes (such as the kraft process), which recover only a part of cellulose. Thus, fractionation processes are carried out along with heat treatments in a water medium (hydrothermal processes), which may lead to different products (food additives, drugs, sugar, ethanol, xylitol, furfural etc.), and pulping processes, which apart from obtaining pulp can separate lignin, which can be transformed into various chemicals (resins, polyurethanes, acrylates, epoxies, composites, etc.).[4-9] This will improve performance and overall process economics.

The use of lignocellulosic residual materials, such as orange tree prunings for the production of paper pulp, is supported by the increasing consumption of this product. In fact, despite the development of the internet and of the information technologies, which predicted a decline in the consumption of paper, it grew by over 10% in the last 20 years of the last century,[10] and 30% of the paper currently consumed accounts for functions associated with the new trends in information technologies, which did not exist ten years ago.[11] Moreover, while 90% of the raw materials for paper production are hardwood and softwood, in recent years the increase in the production of pulp from wood has been of approximately 5%, compared to 10% or more for the non-wood pulp, such as crop residues.[12] In recent years, there has been greater awareness in the use of materials from alternative fibers, leading to a supply problem, as well as high deforestation and replanting, which can alter the ecological balance and promote climate change.

The aim of this study was to evaluate the optimal use of orange tree prunings, subjected to a kraft pulping process, and to observe the influence of operating variables on the properties of the pulps and the corresponding paper sheets.

EXPERIMENTAL

Raw material

Orange tree prunings, obtained directly from an orange tree forest, were separated into two fractions by manual handling, grinding and sieving, with the following characteristics: a) main fraction – wood consisting of stems with the diameter above 1 cm, b) residual fraction, consisting of leaves and stems with the diameter below 1 cm.

Pulping and preparing the sheets

Pulp was obtained by using a 15-L batch cylindrical reactor, which was heated by means of electrical wires and was linked through a rotary axle (to ensure proper agitation) to a control unit including a motor actuating the reactor and the required instruments for measurement and control of pressure and temperature.

The main fraction of the orange tree prunins was pulped in the reactor under the following conditions: kraft reagent concentrations – active alkali concentration of 10-16% o.d.m., 20% sulphidity and anthraquinone concentration of 1% (o.d.m.), temperature of 155-185 ºC, time of 40-90 min and liquid/solid ratio value of 8. Then, the cooked material was fiberized in a wet desintegrator at 1200 rpm for 30 min and the screenings were separated by sieving through a screen of 1 mm mesh size.

Paper sheets were prepared on an ENJO-F-39.71 sheet machine, according to the TAPPI 220 standard method.[13]

Characterization of the pulp and paper sheets

The products (pulp and paper) obtained from the raw material were characterized according to the following standard methods: yield (gravimetrically), viscosity (Tappi T230-om-94), Kappa number (Tappi T236-om-85), lignin content (Tappi T222), breaking length (Tappi T494-om-96), burst index (Tappi T403-om-97), tear index (Tappi T414-om-98) and brightness (Tappi T525-om-92).

Experimental design

The experimental factorial design used consisted of a series of points (tests) around a central composition point (central test) and several additional points (additional tests) that were used to estimate the constants or parameters of a neural fuzzy model. The design met the general requirement of allowing to estimate all parameters in the mathematical model with a relatively small number of tests.[14]

The experimental design used is defined by three parameters:[15] number of variables, k; constant p, which takes the values 0 for k<5 and 1 for k≥5; and number of central points, n_c. These parameters originate three sets of points:

- 2^{k-p} points constituting a factorial design
- 2*k axial points
- n_c central points.

The total number of points (experiments) shall be given by the following expression:

$$n = 2^{k-p} + 2 * k + n_c$$

The total number of tests required for the three independent variables studied [*viz.* temperature (T), time (t) and active alkali concentration (S)], were found to be 15.

The values of the independent variables were normalized to -1, 0 or +1 by using equation (1) in order to facilitate the direct comparison of coefficients and expose the individual effects of the independent variables on each dependent variable:

$$X_n = 2\frac{X - \bar{X}}{X_{max} - X_{min}} \quad \text{(Eq. 1)}$$

where X_n is the normalized value of T, t or S.

The relationships between the dependent variables (*viz.* lignin content, pulp yield, Kappa number, viscosity, tensile index, burst index, tear index and brightness) and the independent (operational) variables were established by using a fuzzy neural model. This type of model combines the advantages of fuzzy logic systems[16] and neural networks,[17] and provides a powerful prediction tool based on the following equation[18] with three independent variables, the use of a singleton defuzzifier (a constant parameter) and a linear membership function for the independent variables:

$$Y_e = \frac{\sum_{l=1}^{8} c_l \left[\prod_{i=1}^{4} x_{ij} \right]_{j=1}^{2}}{\sum_{l=1}^{8} \left[\prod_{i=1}^{4} x_{ij} \right]_{j=1}^{2}} \qquad \text{(Eq. 2)}$$

where Y_e is the estimated value of the property to be modelled and c_l the defuzzifier of a fuzzy rule, x_i denoting the values of temperature (T), time (t) and active alkali concentration (S), and j being 1 or 2 in the equations:

$$x_{i1} = 1 - \frac{1}{\left(x_{high} - x_{low}\right)}\left(x - x_{low}\right)$$

$$\text{(Eq. 3)}$$

$$x_{i2} = \frac{1}{\left(x_{high} - x_{low}\right)}\left(x - x_{low}\right)$$

where x_{high} and x_{low} are the extreme values of each variable.

With three independent variables, one can establish the following 8 fuzzy rules (R_i) based on the extreme (high and low) values of such variables:

R_1: low T, low t and low S
R_2: low T, low t and high S
....
R_7: high T, high t and low S
R_8: high T, high t and high S

With a Gaussian membership function with three levels (low, medium and high) for one of the variables and a linear membership function with two levels (low and high) for the other two, Eq. 2 would contain 12 terms in the numerator and another 12 in the denominator. The Gaussian membership function would be of the form:

$$x_i = \exp\left(-0.5\left(\frac{x - x_c}{L}\right)^2\right) \qquad \text{(Eq. 4)}$$

where x is the absolute value of the variable concerned; x_c – its minimum, central or maximum value; and L – the width of its Gaussian distribution.

The parameters and constants in the previous equation were estimated by using the ANFIS© (Adaptive Neural Fuzzy Inference System) Edit tool in the Matlab v. 6.5 software suite.

RESULTS AND DISCUSSION

Kraft pulping

The kraft process is one of the most widely used cooking processes in chemical pulping.[19] In this type of process, the raw material is treated with an alkaline solution consisting of sodium hydroxide and sodium sulfide at high temperatures to dissolve the lignin in a high percentage. Hence, the fibers of the raw material are mainly composed of cellulose and hemicelluloses. Thus, a satisfactory delignification, high yield, and high viscosity are provided.[20-23]

The kraft process is usually used with conifers and hardwoods, although there are several works that use alternative raw materials.[24-27] Several authors have proposed changes to the kraft process. So, according to Luthe *et al.*,[28] the use of polysulfides in the pretreatment improves the pulping yield by 1.5 to 3.5%. Gustafsson *et al.*[29] proposed a pretreatment with polysulfides in alkaline medium (0-2.5 molar sodium hydroxide), achieving significant improvements in the pulp viscosity with a low Kappa number. Wang *et al.*[30] proposed the addition of anthraquinone to the green liquor, obtaining 2% yield increases and substantial reagent (23-26%) and energy savings.

To our knowledge, no work has been reported on the kraft pulping of orange tree prunings. Based on some of the studies cited before and after a few previous experiments, the following pulping conditions were chosen: temperature 155-185 ºC, time 40-90 minutes, active alkali concentration 10-16%. In all experiments, a liquid/solid ratio of 8:1, 20% sulfidity and anthraquinone concentration of 1% were used.

Table 1 shows the experimental values of the pulp and paper sheet properties, which differed by less than 5% from their means obtained by triplicate measurements. From the discussion below, it will be noted that the results listed in Table 1 fit the neural fuzzy models.

Neural fuzzy models

The experimental data from Table 1 have been fitted to the neural fuzzy model equation to estimate the parameters or constants of this equation with linear functions belonging to two different levels (high and low) for two of the operation variables, and a function of three Gaussian membership levels (high, medium, low) for another operation variable (Tables 2 and 3).

The estimated values of the dependent variables provided by the neural fuzzy models and the corresponding errors with respect to the experimental values (Table 1) are shown in Tables 4 and 5.

Table 1
Experimental values of the pulps and paper sheets properties obtained by kraft pulping of orange tree prunings

Operational conditions: temperature (ºC), time (min) and active alkali concentration (%)	Lignin, %	Yield, %	Kappa number	Viscosity, mL/g	Brightness, %ISO	Tensile index, Nm/g	Burst index, kN/g	Tear index, mNm^2/g
170 ºC, 65´, 13%	10.12	42.2	76.18	846	16.68	15.86	0.621	1.118
185 ºC, 90´, 16%	11.13	37.4	53.02	650	19.18	21.75	0.876	1.205
155 ºC, 90´, 16%	12.51	39.5	57.73	666	21.85	19.20	0.777	1.156
185 ºC, 90´, 10%	14.57	43.7	120.72	727	11.81	10.18	0.401	0.962
155 ºC, 90´, 10%	11.79	50.2	118.51	380	17.66	22.14	0.914	1.464
185 ºC, 40´, 16%	8.58	39.8	54.06	702	22.13	21.59	0.811	1.151
155 ºC, 40´, 16%	15.61	46.2	61.08	736	22.69	20.28	0.687	1.244
185 ºC, 40´, 10%	15.69	44.2	121.16	593	13.30	14.55	0.577	1.174
155 ºC, 40´, 10%	18.71	54.9	114.23	267	20.29	18.33	0.760	1.335
170 ºC, 90´, 13%	11.04	44.6	72.08	837	16.88	19.84	0.781	1.212
170 ºC, 40´, 13%	11.24	49.4	79.03	765	18.57	19.58	0.741	1.220
170 ºC, 65´, 16%	9.64	43.6	49.36	809	20.72	24.96	0.888	1.300
170 ºC, 65´, 10%	15.22	49.9	113.99	510	15.33	16.02	0.619	1.204
185 ºC, 65´, 13%	12.77	42.8	92.68	826	14.29	16.66	0.531	1.061
155 ºC, 65´, 13%	11.97	48.6	85.47	541	20.26	15.00	0.532	1.190

As can be seen, the predictions for the yield, Kappa number, lignin content, viscosity, tensile index, burst index, tear index and brightness differ by less than 9, 8, 21, 14, 17, 21, 9, and 6% from their respective experimental values.

Table 2
Values of the constants c_i in the neural fuzzy model for the pulp properties and the R^2 value

Rule	T, °C	t, min	S, %	Dependent variables			
				Yield, %	Kappa number	Lignin content, %	Viscosity, mL/g
1	155	40	10	55.1	113.9	19.36	253
2	155	40	16	46.3	60.5	15.56	745
3	155	90	10	50.4	118.9	12.03	363
4	155	90	16	39.4	57.3	12.29	673
5	170	40	10	51.4	112.1		
6	170	40	16	45.4	48.3		
7	170	90	10	46.6	104.7		
8	170	90	16	40.3	40.5		
9	185	40	10	43.9	123	16.10	570
10	185	40	16	39.6	54.5	8.04	703
11	185	90	10	43.7	122.9	14.89	702
12	185	90	16	34.4	53.9	10.72	648
9	155	40	13			10.88	642
10	155	90	13			10.57	697
11	185	40	13			11.70	837
12	185	90	10			12.14	895
R^2				0.94	0.99	0.93	0.92

T, t, and S = Temperature, time and active alkali concentration, respectively

Table 3
Values of the constants c_i in the neural fuzzy model for the paper sheets properties and the R^2 value

Rule	T, °C	t, min	S, %	Dependent variables			
				Tensile index, Nm/g	Burst index, kN/g	Tear index, mNm^2/g	Brightness, ISO %
1	155	40	10	19.1	0.786	1.323	20.4
2	155	40	16	20.6	0.691	1.221	22.6
3	155	65	10	12.1	0.487	1.163	18.1
4	155	65	16	21.1	0.750	1.257	23.1
5	155	90	10	23.2	0.952	1.465	17.6
6	155	90	16	19.5	0.788	1.132	21.8
7	185	40	10	15.0	0.589	1.161	13.4
8	185	40	16	21.8	0.819	1.128	22.4
9	185	65	10	13.7	0.472	1.020	11.5
10	185	65	16	24.0	0.796	1.155	17.2
11	185	90	10	12.1	0.402	0.940	11.8
12	185	90	16	22.1	0.891	1.190	19.3
R^2				0.84	0.84	0.89	0.98

T, t, and S = Temperature, time and active alkali concentration, respectively

Table 4
Estimated values of the dependent variables related with pulps, using neural fuzzy models, and errors versus the experimental values (in brackets)

Experiment	T, ºC	t, min	S, %	Yield, %	Kappa number	Lignin content, %	Viscosity, mL/g
1	170	65	13	45.8 (8.43)	77.7 (1.99)	11.58 (14.43)	752 (11.04)
2	185	90	16	37.6 (0.39)	53.1 (0.11)	10.80 (2.94)	667 (2.56)
3	155	90	16	39.5 (0.01)	56.3 (2.45)	12.19 (2.56)	675 (1.27)
4	185	90	10	43.9 (0.34)	121.9 (0.94)	14.73 (1.10)	716 (1.46)
5	155	90	10	50.2 (0.03)	118.1 (0.36)	11.95 (1.31)	389 (2.32)
6	185	40	16	39.9 (0.38)	54.2 (0.18)	8.26 (3.77)	713 (1.52)
7	155	40	16	46.2 (0.02)	59.8 (2.11)	15.29 (2.06)	737 (0.15)
8	185	40	10	44.3 (0.34)	122.4 (1.00)	15.84 (0.98)	590 (0.44)
9	155	40	10	54.9 (0.03)	113.8 (0.38)	18.87 (0.84)	282 (5.72)
10	170	90	13	43.4 (2.72)	74.3 (3.14)	11.48 (3.99)	779 (6.96)
11	170	40	13	48.2 (2.46)	81.1 (2.56)	11.68 (3.91)	726 (5.19)
12	170	65	16	42.6 (2.29)	45.7 (7.34)	11.63 (20.68)	698 (13.76)
13	170	65	10	48.9 (1.99)	109.7 (3.80)	15.35 (0.83)	494 (9.47)
14	185	65	13	41.4 (3.29)	87.9 (5.20)	11.98 (6.19)	847 (2.54)
15	155	65	13	47.7 (1.91)	87.0 (1.79)	11.18 (6.59)	657 (13.89)

T, t, and S = Temperature, time and active alkali concentration, respectively

The neural fuzzy models were validated using the values achieved in two additional pulping experiments (columns 1 and 2 in Table 6). Table 6 also presents the corresponding values of the properties of the pulps and paper sheets calculated using the neural fuzzy models proposed, as well as the errors in the predictions (columns 3 and 4). The low values of these errors, as well as the high coefficients of regression (R^2), certify the accuracy of the proposed models.

A neural fuzzy model affords a physical interpretation of the constants (parameters) inasmuch as these represent the mean values of the target properties (dependent variables) under the conditions defined by the specific fuzzy rule used. For example, with low levels of temperature, time and active alkali concentration a yield of 55.1% is expected (rule 1 in Table 2), which coincides with the value of the corresponding parameter in the neural fuzzy equation.

Also, neural fuzzy models allow the influence of each operational variable on the target properties to be assessed. This can be easily illustrated with the results for yield. The parameter values of the model for estimating this property are shown in Table 2. As can be seen, the lowest yields were obtained at high levels of temperature, time and active alkali concentration.

Applying rules 1 and 2 from Table 2 reveals that, with low levels of the operational variables (rule 1), increasing the active alkali concentration (rule 2) decreases yield (from 55.1 to 46.3%). Likewise, a comparison of rules 1 and 3 reveals that, at low temperature and active alkali concentration levels, increasing the pulping time decreases yield from 55.1 to 50.4%.

Table 5
Estimated values of dependent variables related to paper sheets, using neural fuzzy models, and errors versus experimental values (in brackets)

Experiment	T, ºC	t, min	S, %	Tensile index, Nm/g	Burst index, kN/g	Tear index, mNm^2/g	Brightness, %
1	170	65	13	17.9 (12.82)	0.639 (2.89)	1.154 (3.22)	17.6 (5.58)
2	185	90	16	22.2 (1.93)	0.885 (1.07)	1.188 (1.44)	19.2 (0.02)
3	155	90	16	19.6 (2.20)	0.786 (1.17)	1.139 (1.46)	21.8 (0.00)
4	185	90	10	12.2 (3.47)	0.406 (1.25)	0.945 (1.76)	11.8 (0.06)
5	155	90	10	22.6 (1.91)	0.924 (1.06)	1.447 (1.16)	17.7 (0.02)
6	185	40	16	22.0 (1.72)	0.818 (0.89)	1.130 (1.82)	22.1 (0.25)
7	155	40	16	20.7 (1.83)	0.694 (1.03)	1.223 (1.72)	22.6 (0.22)
8	185	40	10	14.9 (2.51)	0.582 (0.90)	1.153 (1.85)	13.2 (0.43)
9	155	40	10	18.7 (2.00)	0.768 (1.00)	1.314 (1.62)	20.2 (0.27)
10	170	90	13	19.1 (3.59)	0.750 (3.95)	1.180 (2.70)	17.6 (4.39)
11	170	40	13	19.1 (2.65)	0.716 (3.38)	1.205 (1.25)	19.5 (5.27)
12	170	65	16	22.4 (10.36)	0.776 (12.65)	1.202 (7.53)	20.3 (2.00)
13	170	65	10	13.4 (16.24)	0.502 (18.94)	1.106 (8.16)	14.9 (2.71)
14	185	65	13	18.7 (12.40)	0.638 (20.24)	1.089 (2.67)	14.6 (2.35)
15	155	65	13	17.1 (13.78)	0.639 (20.23)	1.218 (2.39)	20.6 (1.65)

T, t, and S = Temperature, time and active alkali concentration, respectively

Table 6
Additional experiments for validation of neural fuzzy models

Parameter	1	2	3	4
T, ºC	162.5	177.5	162.5	177.5
t, min	52.5	77.5	52.5	77.5
S, %	11.5	14.5	11.5	14.5
Yield, % (error %)	48.8	42.9	50.1 (2.7)	41.3 (3.8)
Kappa number (error %)	89.7	62.3	97.8 (9.0)	64.9 (4.2)
Lignin content, % (error %)	14.23	10.61	14.08 (1.1)	11.26 (6.1)
Viscosity, mL/g (error %)	657	791	547 (16.8)	754 (4.7)
Tensile index, Nm/g (error %)	16.9	21.15	16.8 (0.4)	20.3 (4.1)
Burst index,kN/g (error %)	0.61	0.65	0.64 (4.9)	0.75 (15.4)
Tear index, mNm^2/g (error %)	1.21	1.23	1.21 (0.0)	1.15 (6.5)
Brightness, % (error %)	17.6	19.1	18.7 (6.3)	17.8 (6.8)

T, t, y S = Temperature, time and active alkali concentration

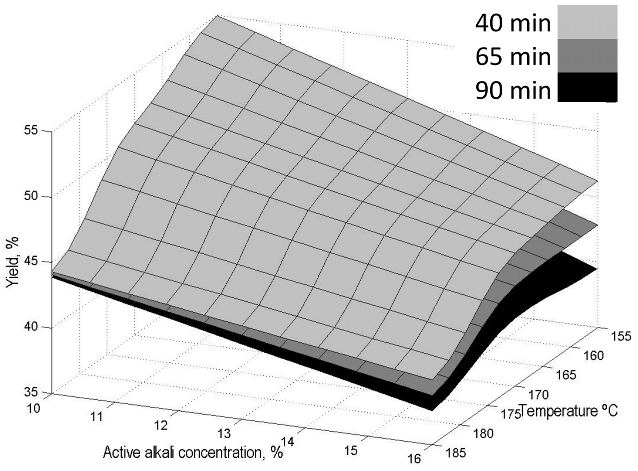

Figure 1: Yield variation at three constant values of time

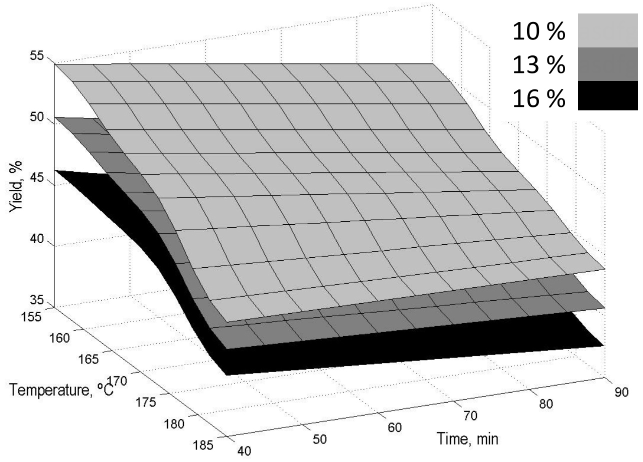

Figure 2: Yield variation at three constant values of active alkali

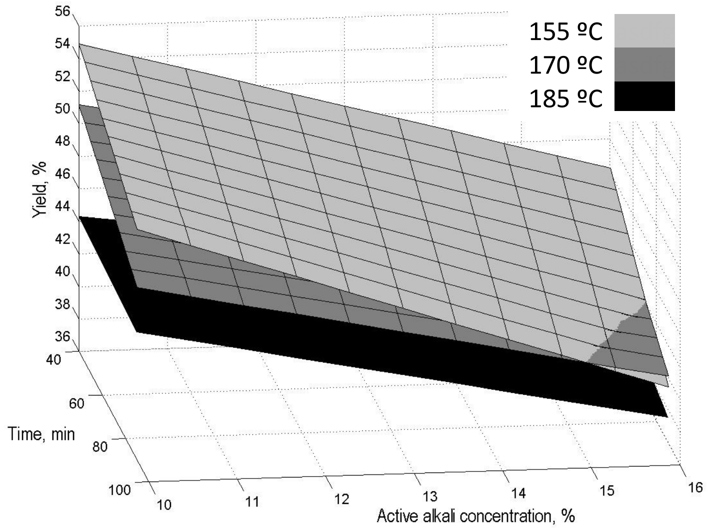

Figure 3: Yield variation at three constant values of temperature

Finally, increasing the temperature (rules 1 and 9) decreases pulp yield from 55.1% to 43.9%. Figures 1-3 show the variation of yield with the active alkali concentration vs temperature (Fig. 1), temperature vs time (Fig. 2) and time vs active alkali concentration (Fig. 3). Based on the foregoing, temperature is the most influential independent variable, and time the least.

Virtually, one can freely combine two rules with identical levels for two variables and a different one for the third to assess the influence of the last on each target property.

CONCLUSION

Due to the experimental results obtained it is possible to conclude that orange tree prunings are a suitable raw material for the production of cellulose pulp by the kraft process. The cellulosic pulps obtained can be used as reinforcement with other cellulosic fibers.

The use of orange tree prunings as raw material for obtaining cellulosic pulps is an alternative of economic interest to farmers.

The results achieved in this study permit to conclude that the applied neural fuzzy model is a convenient mathematical tool to estimate the optimal values of operation.

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