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Organosolv pulping of olive tree trimmings by use of ethylene glycol/soda/water mixtures

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Abstract

This paper reports on the influence of independent variables in the ethylene glycol/soda pulping of olive wood trimmings (165–195°C, 30–90 min, ethylene glycol concentration 5–15%, soda concentration 2.5–7.5% and liquid/solid ratio 4–6), on the yield and Kappa index of the pulps and the strength properties (breaking length, burst index and tear index) of paper sheets. By using a central composite factorial design, equations that relate each dependent variable to the different independent variables were obtained which reproduced the experimental results for the dependent variables with errors less than 12%. Using a temperature of 184°C, ethylene glycol and soda concentrations of 15% and 7%, respectively, a liquid/solid ratio of 5:1 and a cooking time of 30 min results in yield, Kappa index, breaking length, burst index and tear index values that depart by 14.3%, 8.2%, 17.1%, 17.0% and 2.3%, respectively, from their optimum levels. These conditions result in substantial savings in power consumption and immobilised capital investments as they involve a lower temperature, a lower liquid/solid ratio, and a shorter time than the maximum values tested.

Keywords: organosolv; ethylene glycol; soda pulping; pulp; paper; strength properties; agricultural residues; olive tree.

Introduction

The current annual production of pulp falls short of the demand, which is growing very rapidly especially in developing countries, and even in some developed ones; with antecedent gradual shortage of wood raw materials and the consequent deforestation of some areas of the planet. This has aroused interest in the use of wood and non-wood agricultural residues as pulp raw materials. In Spain, olive tree trimmings are very abundant and a promising source of pulp. Spain produces a vast amount of trimming residues from olive trees (over 2 million tons each year, of which more than 60% is generated in Andalusia) (Jiménez et al. 1997a). Such residues lack specific uses, so they are generally burned on site, which increases air pollution and the risk of fire.

The pulping of raw materials to obtain cellulose pulp produces large amounts of highly polluting waste water (particularly if it contains sulphur compounds, as in the sulphite and kraft pulping processes). Although the possibility of obtaining cellulose pulp, using sulphur-free methods, has been known for some time, few such methods have been used on an industrial scale; also, many of them (particularly those based on organic solvents) have only recently started to be tested on a pilot plant scale (Jiménez et al. 1997b; Hergert 1998; Gilarranz et al. 1998).

Scarcity of effective alternatives to conventional pulping has generated substantial interest in new procedures, and even some processes that were discarded on various grounds long ago are being revisited in the light of the new economic and environmental demands. As noted earlier, the annual production of pulp falls short of the demand; this has fostered the establishment of new industrial plants requiring modest investment, lower production costs and lower environmental impact, as well as efficient use of the raw materials (by maximising yields); all this can be achieved by using sulphur-free, solvent-based pulping processes.

According to Aziz and Sarkanen (1989) and Dahlmann and Schroeter (1990), the earliest references to delignification with organic solvents date from 1983, when Klason used ethanol and hydrochloric acid to obtain pulp. In the 1930s, Aronovsky and Gortner, and Kleinert and Tayenthal conducted interesting research on this topic that was followed by the work of Brounstein in the 1950s and that of Kleinert in the 1970s (cited in Aziz and Sarkanen 1989; Dahlmann and Schroeter 1990; Jiménez et al. 1997b; Gilarranz et al. 1999); until then the prevalence of traditional chemical pulping processes had never been challenged.

Since the 1970s, however, attempts at circumventing the typical shortcomings of the traditional processes (viz., unpleasant odours, poor yields, heavy pollution, difficulties in bleaching pulp, large investments and high water, power, reagent and raw material consumption, among others) were made by modifying the existing processes first and then developing new, sulphur-free ones; the new processes, however, were also confronted with other problems such as the difficulty of recovering the reagents and their polluting nature (Cox and Worster 1971).

Since the 1980s, organic solvent-based pulping processes have been revisited as alternatives to the traditional processes. The principal advantage of processes using organic solvents was that they extracted the full

chemical potential from the raw materials; since some such processes were regarded as methods for obtaining hydrolysable cellulose, phenolic polymers of lignin and sugars, rather than as pulping methods proper (Abad et al. 1997; Montane et al. 1998; Botello et al. 1999a,b; Lehnen et al. 2001).

In the 1990s, the kraft process found no competition among chemical pulping processes; however, its severe environmental costs and the large capital investments involved in construction of green field mills prompted a search for alternative pulping processes. Among such alternatives organic solvent-based processes adhere to the currently prevailing philosophy that the raw material should not be used as a mere source of cellulose fibre but rather be fully exploited; this is referred to as "wood refinery" by analogy with petroleum crude fractionation (Judt 1990; Botello et al. 1999b). A number of processes using organic solvents have been developed since the mid-1990s for the delignification of various types of plants (Jiménez et al. 1997b, 2000; Hergert 1998).

Organic solvent-based processes have been applied with varying success to hardwoods and softwoods, and also, less frequently, to non-wood materials. The solvents most frequently used for this purpose include alcohols and low-molecular weight organic acids. The acid media provided by the reagent or produced by the delignification causes some damage to cellulose fibres and detracts from the quality of the resulting pulp; this can in principle be avoided by using a solvent such as ethylene glycol in an alkaline media.

According to Hergert (1998) and Muurinen (2000), several authors have used ethylene glycol for pulping since the 1940s. Gast et al. (1983) and Gast and Puls (1984) found this compound to be especially efficient in the pulping of birch when used in combination with aluminium sulphate or chloride. Also, Rutkowski et al. (1993) and Chaudhuri (1996) used ethylene glycol to pulp hardwood (aspen, birch and beech) and bagasse. Finally, Surna-Slusarsaka (1998) studied the origin of the losses of ethylene glycol in the pulping of hardwood.

Pulping processes have been modelled in a number of ways with a view to deriving equations for estimating the quality of the pulp as a function of the variables of the processes and identification the optimum operating conditions. Most of the models used for this purpose are mathematical schemes based on the kinetics of delignification (specifically, on its prediction). These theoretical models are rather complicated and impractical when more than two independent variables are involved. Under these conditions, it is preferable to use an empirical model based on an experimental factorial design to estimate several dependent variables for the pulp (e.g., yield, composition) in terms of several independent operational variables.

Parajó et al. (1993), Tjeerdsma et al. (1994), Vázquez et al. (1995), Vega et al. (1997), Gilarraz et al. (1998, 1999) and Jiménez et al. (1999, 2000) have applied such factorial designs to pulping processes using organic solvents. These authors used alcohols, organic acids and various other organic solvents, but none have studied ethylene glycol/soda mixtures.

In this work, we used a central composite factorial design to examine the influence of the independent cooking variables (viz. temperature, time, ethylene glycol concentration, soda concentration and liquid/solid ratio) on the pulping of olive tree wood using ethylene glycol/soda/water mixtures. The resulting yield and Kappa index of the pulps, and breaking length, burst index and tear index of the paper sheets were then predicted with a view to identifying the most suitable operating conditions.

Materials and methods

We used agricultural olive tree (*Olea europea*) trimmings as pulping raw material. Following air-drying and deleafing, olive wood trimmings were chipped on a semi-industrial wood chipper and the 5–10 mm fraction was isolated by sieving. The bark was not stripped off as it was very thin and difficult to remove; in any case, it never accounted for more than 1–2% of the overall mass. The olive wood contained 61.5% holocellulose, 35.7% α-cellulose and 19.7% lignin by dry matter weight.

Analysis of the raw material and characterisation of pulps and paper sheets

The starting materials and the products obtained from them were characterised according to the following standard methods: holocellulose (method of Wise et al. (1946)), α-cellulose (TAPPI 203 os-61), lignin (TAPPI 222) and Kappa index (TAPPI 236), breaking length (TAPPI 494), burst index (TAPPI 404) and tear index (TAPPI 414).

Pulping and sheetmaking

Pulp was obtained by using a 15-l batch cylindrical reactor that was heated by means of electrical resistance wires and linked through a rotary axle (to ensure proper agitation). The unit was controlled by a motor actuator and the required instruments for measurement and control of pressure and temperature.

The cooked olive wood was fiberised 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.

Experimental design

The tested model uses a series of points (experiments) around a central one (central experiment), and several additional points (additional experiments), to estimate the first- and second-order interaction term polynomials. This design provides the general advantage that every parameter in the mathematical model can be estimated from a fairly small number of experiments (Montgomery 1991).

The total number of experiments required for our five independent variables (temperature (T), cooking time (t), ethylene glycol concentration (E), soda concentration (S) and liquid/solid ratio (R)) was 27.

The values of the independent variables were normalised from -1 to $+1$ by using Eq. (1) in order to facilitate direct comparison of the coefficients and visualisation of the effects of the individual independent variables on the response variable:

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

where X_n is the normalised value of T, t, E, S or R; X is the

Table 1 Processing conditions used in the ethylene glycol/soda pulping of olive wood and experimental results of the characterisation of pulps and paper sheets.

X_T	X_t	X_E	X_S	X_R	Yield, %	Kappa index	Breaking length, m	Burst index, KN/g	Tear index, mNm^2/g
0	0	0	0	0	54.7	86.6	500.1	23.78	0.73
−1	−1	−1	1	−1	52.4	79.3	295.7	37.50	0.58
−1	−1	−1	−1	1	50.3	78.6	369.0	24.86	0.34
−1	−1	1	1	1	48.7	71.7	412.0	37.63	0.70
1	0	0	0	0	53.7	88.0	530.4	25.29	0.75
0	0	0	1	0	47.5	86.2	438.0	23.50	0.67
0	−1	0	0	0	55.0	75.8	451.4	23.00	0.67
0	0	−1	0	0	55.4	86.3	656.3	27.58	0.80
1	−1	−1	1	1	53.4	84.3	641.5	27.84	0.76
1	−1	1	1	−1	51.5	81.3	668.2	31.25	0.82
0	0	1	0	0	53.3	83.9	601.7	29.57	0.78
0	1	0	0	0	50.7	84.5	470.7	22.35	0.70
1	−1	1	−1	1	53.9	82.9	423.0	25.64	0.71
0	0	0	0	1	49.0	83.9	485.3	20.63	0.65
−1	0	0	0	0	50.0	78.8	287.9	27.89	0.49
1	1-	1	−1	1	53.7	89.0	457.3	21.84	0.62
0	0	0	−1	0	56.8	82.8	389.4	20.72	0.60
−1	1	1	−1	1	55.1	80.6	225.9	26.10	0.50
1	1	1	−1	−1	52.9	90.9	479.7	23.35	0.75
−1	1	1	1	−1	50.1	73.6	508.7	25.25	0.74
1	1	1	1	1	44.2	80.6	649.7	28.24	0.76
−1	1	−1	1	1	49.5	77.9	554.8	24.73	0.68
1	1	−1	1	−1	53.1	82.1	494.7	26.15	0.75
−1	−1	1	−1	−1	51.2	81.3	426.0	27.97	0.38
−1	1	−1	−1	−1	58.9	78.2	256.2	24.42	0.43
0	0	0	0	−1	54.5	86.3	486.9	20.33	0.71
1	−1	−1	−1	−1	55.5	80.9	474.0	21.45	0.68

absolute experimental value of the variable concerned; $\bar{X}$ is the mean of all the experimental values for the variable in question; and X_{max} and X_{min} are the maximum and minimum values, respectively, of such a variable.

Experimental data was fitted to the following second-order polynomial:

$$Z = a + bX_T + cX_t + dX_E + eX_S + fX_R + gX_T^2 + h\,X_t^2 + iX_E^2 + jX_S^2 + kX_R^2 + lX_TX_t + mX_TX_E + nX_TX_S + oX_TX_R + qX_tX_E + sX_tX_S + uX_tX_R + vX_EX_S + yX_EX_R + zX_SX_R \quad (2)$$

where Z denotes the response variables (yield YI, Kappa index KI, breaking length BL, burst index BI and tear index TI), X_T, X_t, X_E X_S and X_R are the normalised values of T, t, E, S and R; and letters a to z denote constants.

The normalised values for the independent variables of the 27 pulping experiments conducted, are given in Table 1.

Results and discussion

A set of four preliminary experiments was conducted under the central operating conditions, namely: 180°C, 60 min, 10% ethylene glycol concentration, 5% soda concentration and 5:1 liquid/solid ratio. The experimental results obtained in the determinations of the dependent variables differed from the mean values, shown in the first row of Table 1, by less than 5–10%. Subsequent tests, corresponding to the experimental design adopted, provided the results shown in the other rows. The operating variables were varied over the following ranges: 165–195°C, 30–90 min, 5–15% ethylene glycol concentration, 2.5–7.5% soda concentration and 4–6 liquid/solid ratio; Table 2 shows the extreme, central and normalised values of the operational variables. The time needed for the operating temperature to be reached was 4–8 min and was excluded from the pulping time; such a short time was the result of the olive wood and the ethylene glycol/soda/water mixture being preheated prior to heating in the reactor. The short time (in the region of 4–8 min) required to attain the operating temperature (165–195°C) was found to have no substantial influence on the final properties of the pulp, first because such a time was only a small fraction of the overall time, and second because, owing to the combined effects of temperature and time, the severity of the treatment was negligible during the time (4–8 min) taken to raise the temperature from about 100°C to 165 or 195°C relative to the treatment involving the operating temperature (165–195°C) and cooking times of 30–90 min (Jiménez et al. 1999).

Table 2 Absolute and normalised values of cooking variables.

	Normalised values of variables		
	−1	0	+1
Temperature, °C	165	180	195
Time, min	30	60	90
Ethylene glycol, %	5	10	15
Soda, %	2.5	5.0	7.5
Liquor/solid ratio	4	6	8

In order to compare our experimental results with those for pulp obtained using ethylene glycol containing no soda, and soda containing no ethylene glycol, we performed two tests at 180°C, using a cooking time of

Table 3 Comparison of pulping processes using ethylene glycol/soda, ethylene glycol and soda.

Pulping process	Yield, %	Kappa index	Breaking length, m	Burst index, kN/g	Tear index, mNm^2/g
Ethylene glycol/soda	54.7	86.6	500.1	23.78	0.73
Ethylene glycol	40.0	100.8	578.0	25.30	0.77
Soda	49.1	109.7	556.7	24.20	0.90

60 min and a liquid/solid ratio of 6 plus 15% soda in one test and 15% ethylene glycol in the other. The yield, Kappa index, breaking length, burst index and tear index achieved are given in Table 3, which also shows the values obtained using the same temperature, cooking time and liquid/solid ratio but mixture of 10% ethylene glycol and 5% soda (row 1 in Table 1).

As can be seen from Table 3, the highest yield was obtained in the process using ethylene glycol/soda as a result of the alkaline organic solvent preserving the integrity of cellulose fibres much more efficiently than ethylene glycol or soda alone. The lowest Kappa index was also obtained in the process using ethylene glycol/soda; however, all index values were high, so olive tree wood is an unsuitable raw material for this pulping process if the resulting pulp is to be subsequently bleached.

As regards the strength properties of the paper sheets, the parameter values were somewhat lower for the pulp obtained using ethylene glycol/soda; this disadvantage, however, was offset by the increased brightness and yield of the pulp (i.e., with an improved use of the raw material).

The BMDP software suite (Dixon 1988) was used to conduct a multiple linear regression analysis involving all terms in Eq. (2) except for those with Snedecor's F-values less than 4, which were left out using the stepwise method (Draper and Smith 1981). The following equations (accompanied by their corresponding Snedecor's F and r^2 values, and the highest p and lowest Student's t values for their terms at a confidence limit of 95%) were obtained:

$$YI = 52.4 - 1.2\,X_E - 2.1\,X_S - 1.2\,X_R - 1.3\,X_T X_t - 1.2\,X_t X_S$$
$$(F = 10.4;\ r^2 = 0.71;\ p < 0.02;\ t > 2.5) \quad (3)$$

$$IK = 84.8 + 3.3\,X_T + 1.2\,X_t - 1.6\,X_S - 4.0\,X_t^2 - 1.1\,X_t X_S - 1.6\,X_E X_S - 1.3\,X_E X_R$$
$$(F = 13.6;\ r^2 = 0.83;\ p < 0.06;\ t > 2.0) \quad (4)$$

$$BL = 484.9 + 82.6\,X_T + 64.4\,X_S - 83.2\,X_T^2 + 136.7\,X_E^2 - 78.6\,X_S^2 + 29.2\,X_t X_S - 54.4\,X_E X_R + 28.5\,X_S X_R$$
$$(F = 32.8;\ r^2 = 0.93;\ p < 0.006;\ t > 3.1) \quad (5)$$

$$BI = 23.34 - 1.41\,X_T - 1.93\,X_t + 1.03\,X_E + 2.54\,X_S + 3.11\,X_T^2 + 5.09\,X_E^2 - 1.37\,X_S^2 - 3.00\,X_R^2 + 1.30\,X_T X_t - 1.60\,X_t X_S + 1.25\,X_E X_R$$
$$(F = 35.9;\ r^2 = 0.97;\ p < 0.05;\ t > 2.1) \quad (6)$$

$$TI = 0.70 + 0.10\,X_T + 0.30\,X_E + 0.08\,X_S - 0.08\,X_T^2 + 0.09\,X_E^2 - 0.07\,X_S^2 - 0.03\,X_T X_t - 0.05\,X_T X_S$$
$$(F = 34.9;\ r^2 = 0.94;\ p < 0.009;\ t > 2.9) \quad (7)$$

The yield values calculated from Eq. (3) differ from their experimental counterparts by less than 6%.

Non-linear programming (More and Toraldo's method (1989)) was applied to Eq. (3) in order to determine the highest yield over the ranges studied for the process variables (normalised values from -1 to $+1$ for all); the maximum yield thus calculated for a low temperature, ethylene glycol concentration, soda concentration and liquid/solid ratio (-1 for all) and long cooking time ($+1$), was 59.4%.

Equation (3) allows one to estimate the variation of the yield with changes in each independent variable, over the range considered on constancy of the other variables. With constant temperature, cooking time, ethylene glycol concentration, soda concentration and liquid/solid ratio at their normalised values -1, $+1$ -1, -1 and -1, respectively, the greatest changes in yield resulted from variation of the soda concentration (6.6 units or 11.1% with respect to the maximum value) and cooking time (5.0 units or 8.4%), and the smallest ones from the ethylene glycol concentration (2.4 units or 4.0%) and liquid/solid ratio (2.4 units or 4.0%); the effect of the temperature (2.6 units or 4.4%) was between the previous two extremes. The yield was thus much more sensitive to changes in soda concentration and cooking time than to variations in ethylene glycol concentration and liquid/solid ratio. Figure 1 and similar other plots confirm these results.

The results of Table 4 were obtained by using a similar procedure applied to the other dependent variables. As can be seen, all the equations relating the dependent variables to the independent ones reproduce the experimental results with errors less than 6 to 12%.

As can be seen from Table 4, ensuring optimum values for yield, Kappa index, breaking length, burst index and tear index entails using rather different values for the independent operational variables.

As can also be seen from Table 4, the temperature and soda concentration are the two independent variables most markedly influencing the dependent variables, and the liquid/solid ratio is the least influential variable in this respect. Figures 2–5 and other, similar ones, confirm this assertion.

Efficient use of the raw material (i.e., achieving a high pulp yield) entails the use of a long cooking time and low values of the other operational variables. Under these conditions, the yield is maximal and the Kappa index is only 7.7% higher, but the values of the strength proper-

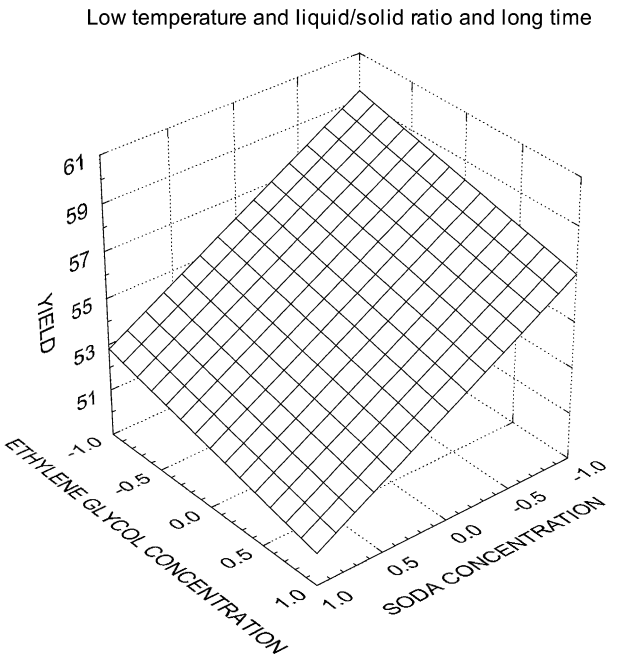

Figure 1 Variation of the pulp yield with soda concentration and ethylene glycol concentration at constant long cooking time and low temperature and liquid/solid ratio.

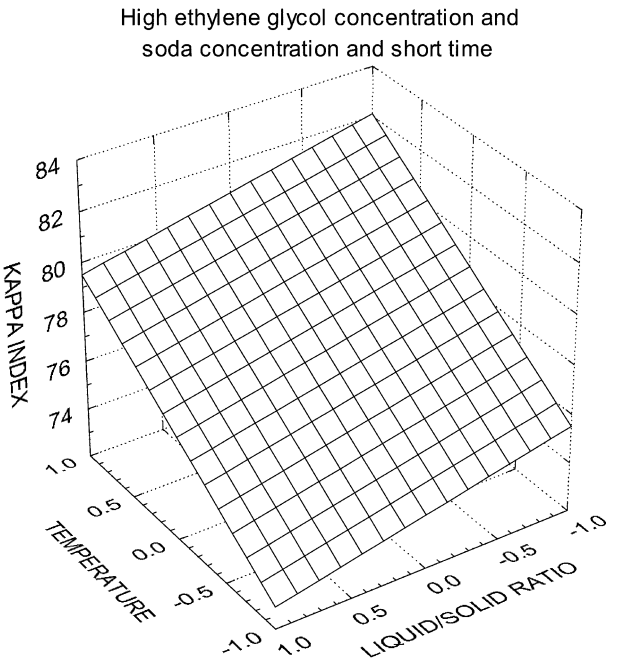

Figure 2 Variation of the Kappa index with temperature and liquid/solid ratio at constant high soda concentration and ethylene glycol concentration and short cooking time.

ties are considerably reduced (the breaking length by 65.4%, the burst index by 38.6% and the tear index by 53.4%). However, these conditions result in substantial savings in power consumption (through the use of a low heating temperature), less chemicals and lower equipment immobilised capital (through the use of a short cooking time and a low liquid/solid ratio).

Production of brighter pulp (i.e., pulp with a lower Kappa index) entails the use of high ethylene glycol and soda concentrations and liquid/solid ratio, and low temperature and short cooking time. The yield is thus reduced by 19.5% (to 47.8%, which is typical of unbleached chemical pulp), however the breaking length, burst index and tear index are also decreased by as much as 48.0%, 4.8% and 23.9%, respectively. In any case, the values of the strength properties can be restored by subjecting the pulp to an effective beating procedure.

Table 4 Optimum values of the dependent variables and variations with changes in the independent variables for the ethylene glycol/soda pulping of olive wood.

Dependent variable	% errors estimating dependent variables with respect to experimental values	Optimum value	Normalised values of the independent variables leading to optimum values of dependent variables					Maximum changes in the dependent variables (in units and percentages with respect to the optimum values, which are shown in brackets) with changes in the independent variables (from −1 to +1)				
			X_T	X_t	X_E	X_S	X_R	T	t	E	S	R
Yield	6	59.4%	−1	+1	−1	−1	−1	2.6% (4.4%)	5.0% (8.4%)	2.4% (4.0%)	6.6% (11.1%)	2.4% (4.0%)
Kappa index	5	72.9	−1	−1	+1	+1	+1	6.6 (9.1%)	4.1 (5.6%)	5.8 (8.0%)	4.2 (5.8%)	2.6 (3.6%)
Breaking length	12	743.9 m	+0.50	+1	−1	+0.78	+1	186.3 m (25.0%)	49.5 m (6.1%)	196.5 m (26.4%)	248.1 m (33.4%)	153.2 m (20.6%)
Burst index	10	40.11 kN/g	−1	−1	+1	+1	+0.21	4.41 kN/g (16.0%)	9.66 kN/g (24.1%)	6.46 kN/g (16.1%)	8.24 kN/g (20.6%)	4.38 kN/g (10.9%)
Tear index	10	0.88 mNm²/g	+0.71	−1	+1	+0.32	−	0.24 mNm²/g (27.3%)	0.04 mNm²/g (4.6%)	0.12 mNm²/g (13.6%)	0.12 mNm²/g (13.6%)	−

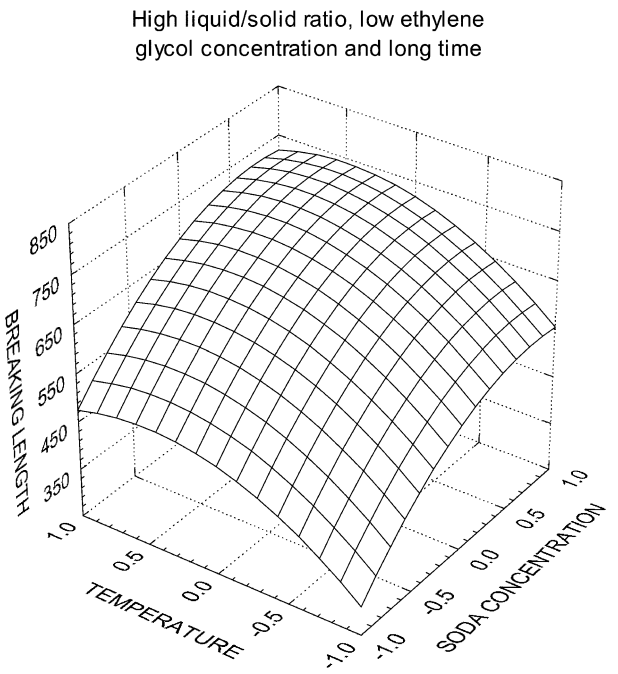

Figure 3 Variation of the breaking length with soda concentration and temperature at constant high liquid/solid ratio, long cooking time and low ethylene glycol concentration.

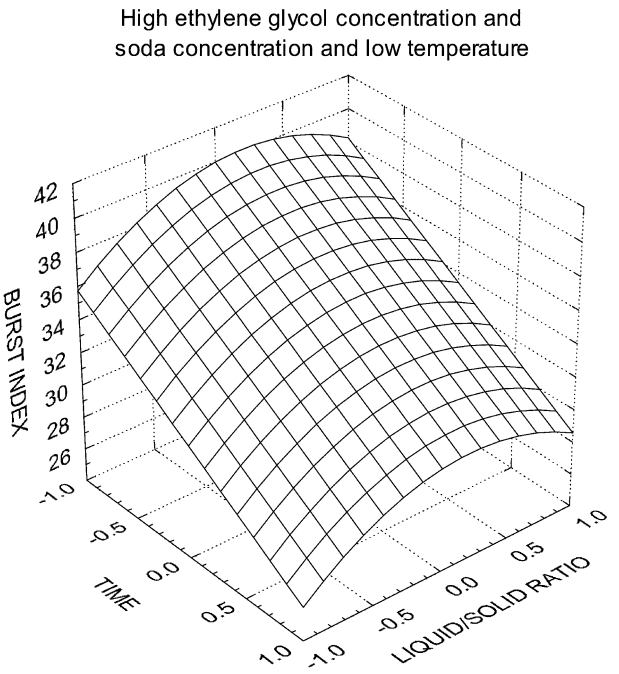

Figure 4 Variation of the burst index with cooking time and liquid/solid ratio at constant high soda concentration and ethylene glycol concentration and low temperature.

On the other hand, in order to avoid reductions by more than 15–20% in the values of the dependent variables from their optimum levels, one must use conditions in between the previous two extremes. Thus, by using a temperature of 184°C, an ethylene glycol concentration of 15%, a soda concentration of 7%, a liquid/solid ratio of 5:1 and a cooking time of 30 min, the yield, Kappa index, breaking length, burst index and tear index obtained depart by 14.3%, 8.2%, 17.1%, 17.% and 2.3%, respectively, from their optimum values. Also, these conditions result in appreciable savings in power consumption and immobilised capital costs of the equipment.

Conclusions

Pulping with mixtures of ethylene glycol and soda provides pulp with an increased yield and a lower Kappa index, in addition to somewhat poorer strength properties for the resulting paper, than those obtained with ethylene glycol or soda alone. Based on the high values obtained for the Kappa index, olive tree wood is unsuitable for use with this pulping process if the resulting pulp is to be subsequently subjected to bleaching.

By using a central composite factorial design, equations that relate each dependent variable (yield, Kappa index, breaking length, burst index, and tear index) to the different independent variables (temperature, time, ethylene glycol concentration, soda concentration and liquid/solid ratio) were obtained that reproduced the experimental results for the dependent variables with errors less than 12%.

Using a temperature of 184°C, ethylene glycol and soda concentrations of 15% and 7%, respectively, a liquid/solid ratio of 5:1 and a cooking time of 30 min results in yield, Kappa index and strength properties values that depart by 2.3% to 17.0% from their optimum levels. These conditions result in substantial savings in power consumption and immobilised capital investments as they involve a lower temperature, a lower liquid/solid ratio, and a shorter time than the maximum values tested.

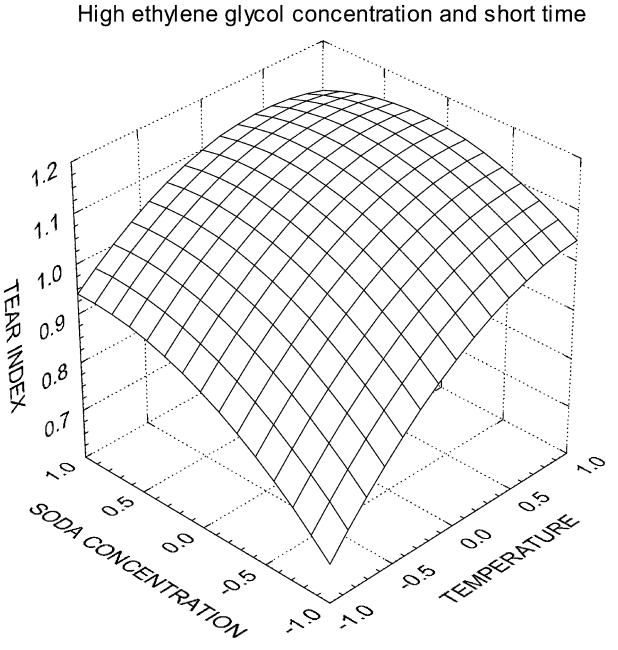

Figure 5 Variation of the tear index with temperature and soda concentration at constant high ethylene glycol concentration, short cooking time and all value of liquid/solid ratio.

Acknowledgements

The authors are grateful to Ecopapel, S.L. (Écija, Seville, Spain) and ENCE (Huelva, Spain) for their support, and to Spain's DGICyT for funding this research within the framework of Projects PPQ2000-1068-C02-01 and PPQ2001-2489-C03-01.

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Received December 16, 2002