

# ETHYLENE GLYCOL/SODA ORGANOSOLV PULPING OF OLIVE TREE TRIMMINGS

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## ABSTRACT

This paper reports on the influence of independent variables in the ethylene glycol/soda pulping of olive wood trimmings [*viz.* cooking temperature (165–195°C) and time (30–90 min), ethylene glycol concentration (5–15%), soda concentration (2.5–7.5%), and liquid/solid ratio (4/1–6/1)], on the yield and viscosity and holocellulose,  $\alpha$ -cellulose, and lignin contents of the pulps.

By using a central composite factorial design, equations that relate each dependent variable to the different independent variables were obtained that reproduced the experimental results for the dependent variables with errors less than 8%.

Obtaining pulp with maximum possible holocellulose content (78.9%),  $\alpha$ -cellulose content (61.8%), and viscosity (426.8 mL/g), in addition to the minimum possible lignin content (19.1%), entails using high ethylene glycol and soda concentrations (15% and 7.5%, respectively), a long cooking time (90 min), and a low liquid/solid ratio (4/1). A high temperature (195°C) is also required to maximize the holocellulose and  $\alpha$ -cellulose contents and viscosity, and one of 175°C to minimize that of lignin. On the other hand, the maximum yield (59.4%) is obtained by using a long cooking time (90 min) and low values of the other operating variables.

The use of intermediate operating conditions (*viz.* a temperature of 187.5°C, an ethylene glycol concentration of 15.0%, a soda concentration of 7.5%, a liquid/solid ratio of 4/1, and a cooking time of 30 min) results in a yield, holocellulose content,  $\alpha$ -cellulose content, lignin content, and viscosity values (52.2%, 76.5%, 58.8%, 20.40%, and 352.7 ml/g, respectively) that differ by only 12.1%, 3.0%, 4.9%, 6.8%, and 17.4% from the respective optimum values, all with substantial savings on power consumption and immobilized capital in commercial operations. The strength-related properties of this pulp can be improved with an appropriate refining treatment.

*Keywords:* Ethylene glycol, organosolv, soda, pulp, composition, viscosity, olive tree wood.

## INTRODUCTION

The annual production of pulp falls short of the demand, which is growing very rapidly in developing countries—and even in some developed ones. This is leading to a 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. Specifically, olive tree trimmings are highly abundant in Spain (particularly in Andalusia). In fact, 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) (Anuario de Estadística Agrario 1999; 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 cooking of raw materials to obtain cellulose pulp produces large amounts of highly polluting waste water (particularly if it contains sulfur compounds, as in the sulfite and kraft pulping processes).

Although the possibility of obtaining cellulose pulp, using sulfur-free methods, has been known for a long time, few such methods have been used on an industrial scale; also, some of them (particularly those based on organic solvents) have only recently been tested at pilot plants (ORGANOCELL,<sup>TM</sup> ALCALL,<sup>TM</sup> ACETO-SOLV).

Because of the current scarcity of low-energy and pollution-free effective alternatives to conventional pulping procedures, new procedures invariably create substantial attention, and even some 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 but using processes involving modest investments, low production costs, and environmental benignity, as well as efficient use of the raw materials (by maximizing yields). All these goals can be achieved by using some sulfur-free pulping processes.

The earliest references to delignification with organic solvents date from 1893, when Klason used ethanol and hydrochloric acid to obtain pulp. In the 1930s, Aronovsky and Grotner, 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 (Jiménez et al. 1997b); the prevalence of traditional chemical pulping processes was never challenged until then.

Since the 1970s, however, attempts at circumventing the typical shortcomings of the traditional processes (*viz.* unpleasant odors, poor yields, heavy pollution, difficult to bleach pulp, large investments, and high water, power, reagent and raw material consumption, among

others) were made by modifying the existing processes first and developing new, sulfur-free ones then. 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).

In the 1980s, organic solvent-based pulping processes were revisited as alternatives to the traditional processes. The principal advantage of processes using organic solvents was that they extracted the full potential from the raw materials; some such processes were regarded as methods for obtaining hydrolysable cellulose, phenolic polymers of lignin, and fermentable sugars rather than as pulping methods proper.

In the 1990s, the kraft process found no competition among chemical pulping processes; however, its severe environmental problems and the large investments involved promoted a search for alternative pulping processes. One such alternative is provided by organic solvent-based processes, which adhere to the currently prevailing philosophy that the raw material should not be used as a mere source of cellulose fiber but rather be fully exploited. This is referred to as "wood refinery" by analogy with petroleum crude fractionation (Judt 1990).

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; Hergert 1998; Paszner 1998).

Finally, it should be noted that contemporary pulping processes using organic solvents aim at the obtainment of pulp, lignin, sugars, and other products in order to exploit the full potential of the raw materials among others (Yawalata and Paszner, 1997; Abad et al. 1997; Montane et al. 1998; Botello et al. 1999a,b; Lehen et al. 2001).

Organic solvent-based processes have been applied with varying success to different types of hardwood and softwood, 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 medium provided by the reagent or produced by the delignification causes some dam-

age to cellulose fibers and detracts from the quality of the resulting paper sheets; this can, in principle, be avoided by using a solvent such as ethylene glycol in an alkaline medium.

Pulping processes have been modeled 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 process and identifying 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 factor 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), Gilarranz et al. (1998, 1999), and Jiménez et al. (1997c,d; 1998a,b,c; 1999a; 2000) have applied such factorial designs to pulping processes using organic solvents. They used alcohols, organic acids, and various other organic solvents, but never 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 yield, viscosity, and holocellulose,  $\alpha$ -cellulose, and lignin contents, of the pulp obtained by using mixtures of ethylene glycol, soda, and water with a view to identifying the most suitable operating conditions.

## EXPERIMENTAL

### *Raw materials*

We used the agricultural olive tree (*Olea europaea*) trimmings. 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%  $\alpha$ -cellulose, and 19.7% lignin by dry matter weight.

### *Analysis of the raw material and characterization of pulps*

The starting materials and the products obtained from them were characterized according to the following standard methods: holocellulose (Wise et al. method (1946)),  $\alpha$ -cellulose (TAPPI 203 os-61), lignin (TAPPI 222), and viscosity (ISO 5351/1).

### *Pulping*

Pulp was obtained by using a 15-L batch cylindrical reactor that 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 olive wood was cooked in the reactor. Next, the cooked material was fiberized in a wet disintegrator at 1200 rpm for 30 min, and the screenings were separated by sieving through a screen of 1-mm mesh size.

### *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 terms of a polynomial. This design meets the general requirement that every parameter in the mathematical model can be estimated from a fairly small number of experiments (Montgomery 1991).

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

The values of the independent variables were normalized from  $-1$  to  $+1$  by using Eq. (1) in order to facilitate direct comparison of the coefficients and visualization 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 normalized value of T, t, E, S, or R;  $X$  is the 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 were fitted to the following second-order polynomial:

$$\begin{aligned} Z = & a + bX_T + cX_t + dX_E + eX_S + fX_R \\ & + gX_T^2 + hX_t^2 + iX_E^2 + jX_S^2 + kX_R^2 \\ & + lX_TX_t + mX_TX_E + nX_TX_S + oX_TX_R \\ & + qX_tX_E + sX_tX_S + uX_tX_R + vX_EX_S \\ & + yX_EX_R + zX_SX_R \end{aligned} \quad (2)$$

where  $Z$  denotes the response variables [yield (YI), holocellulose (HO),  $\alpha$ -cellulose ( $\alpha$ C), lignin (LI), and viscosity (VI)],  $X_T$ ,  $X_t$ ,  $X_E$ ,  $X_S$ , and  $X_R$  are the normalized values of T, t, E, S, and R; and letters a to z denote constants.

The normalized values for the independent variables in the 27 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:

TABLE 1. Processing conditions used in the ethylene glycol/soda pulping of olive tree wood and experimental results of the characterization of pulp.

$X_T$	$X_t$	$X_E$	$X_S$	$X_R$	Yield, %	Holocellulose, %	$\alpha$ -cellulose, %	Lignin, %	Viscosity, mL/g
0	0	0	0	0	54.7	75.1	55.7	23.6	278.9
-1	-1	-1	1	-1	52.4	72.0	55.4	21.2	240.4
-1	-1	-1	-1	1	50.3	77.1	52.7	23.0	192.5
-1	-1	1	1	1	48.7	71.0	54.7	20.4	242.9
1	0	0	0	0	53.7	76.1	59.6	28.1	335.8
0	0	0	1	0	47.5	76.1	57.6	22.2	270.0
0	-1	0	0	0	55.0	76.4	54.7	23.1	258.2
0	0	-1	0	0	55.4	76.7	58.3	23.4	272.5
1	-1	-1	1	1	53.4	78.5	58.3	23.1	290.1
1	-1	1	1	-1	51.5	78.0	60.0	21.7	395.7
0	0	1	0	0	53.3	74.6	57.0	22.8	290.1
0	1	0	0	0	50.7	74.9	56.4	24.6	270.7
1	-1	1	-1	1	53.9	76.4	56.4	25.6	307.8
0	0	0	0	1	49.0	74.2	55.2	21.8	242.0
-1	0	0	0	0	50.0	74.0	53.0	24.2	213.7
1	1	-1	-1	1	53.7	72.5	58.8	26.2	340.0
0	0	0	-1	0	56.8	74.3	53.9	25.3	247.1
-1	1	1	-1	1	55.1	76.0	54.0	22.4	252.4
1	1	1	-1	-1	52.9	72.3	58.6	26.6	355.2
-1	1	1	1	-1	50.1	75.7	59.7	19.7	303.7
1	1	1	1	1	44.2	78.9	61.9	22.3	411.2
-1	1	-1	1	1	49.5	75.5	58.2	21.1	252.9
1	1	-1	1	-1	53.1	79.0	60.1	23.1	412.7
-1	-1	1	-1	-1	51.2	76.1	53.1	22.3	218.7
-1	1	-1	-1	-1	58.9	75.4	52.9	24.2	243.1
0	0	0	0	-1	54.5	76.2	57.5	23.3	256.8
1	-1	-1	-1	-1	55.5	76.1	57.3	24.8	267.5

165–195°C, 30–90 min, 5–15% ethylene glycol concentration, 2.5–7.5% soda concentration, and 4–6 liquid/solid ratio. 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 heated prior to meeting 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 initial 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., 1999b).

The BMDP software suite (Dixon 1988) was used to conduct a multiple linear regression analysis involving all terms in Eq. (2) except 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:

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

$$\begin{aligned}
 HO = & 75.5 + 0.8 X_T + 0.5 X_S - 0.8 X_T X_t \\
 & + 1.7 X_T X_S + 1.2 X_t X_S \quad (4) \\
 (F = 46.7; r^2 = 0.92; p < 0.05; t > 3.1)
 \end{aligned}$$

$$\alpha C = 56.0 + 2.1 X_T + 1.0 X_l + 1.6 X_S + 1.1 X_E^2 \quad (5)$$

(F = 36.0; r<sup>2</sup> = 0.97; p < 0.01; t > 2.7)

$$LI = 24.0 + 1.3 X_T - 0.4 X_E - 1.4 X_S + 1.9 X_T^2 - 1.2 X_E^2 - 1.7 X_R^2 \quad (6)$$

(F = 30.7; r<sup>2</sup> = 0.90; p < 0.04; t > 2.1)

$$VI = 263.7 + 53.1 X_T + 23.8 X_l + 14.8 X_E + 22.0 X_S - 9.0 X_R + 30.2 X_E^2 - 10.2 X_S X_R \quad (7)$$

(F = 43.3; r<sup>2</sup> = 0.94; p < 0.03; t > 2.3)

The pulp yields calculated from Eq. (3) reproduced the experimental results with errors observed less than 6% in all cases.

The highest possible pulp yield for the respective ranges of the independent variables of the process (normalized values of -1 to +1 for all) was calculated by using linear-non-programming (Press et al. 1992) as implemented in the method of More and Toraldo (1989). The maximum yield, 59.4%, was found to correspond to a low temperature (165°C), ethylene glycol concentration (5%), soda concentration (2.5%), and liquid/solid ratio (4/1) (normalized values of -1 in the four variables), in addition to a long cooking time (90 min) (normalized value of +1). This yield is typical of semi-chemical pulp and suggestive of more efficient use of the raw material.

The equation for pulp yield allows one to estimate its variation with changes in an independent variable over the range concerned on constancy of all other independent variables. With the temperature, cooking time, ethylene glycol concentration, soda concentration, and liquid/solid ratio at their optimum values (165°C, 90 min, 5%, 2.5%, and 4/1, respectively), the greatest variations in the yield were caused by changes in the soda concentration (6.6 units or 11.1% from the maximum value) and cooking time (5.0 units or 8.4%), and the smallest by changes in the ethylene glycol concentration (2.4 units or 4.0%), liquid/solid ratio (2.4 units or 4.0%) and temperature (2.6 units or 4.4%). Consequently, the pulp yield is more sensitive to changes in the soda concentration and cooking time than to those in the ethylene glycol concentration, liquid/solid ratio, and tempera-

Low temperature, ethylene glycol concentration and liquid/solid ratio

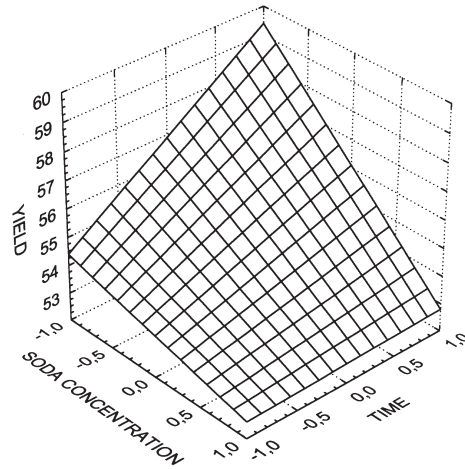


FIG. 1. Variation of pulp yield with soda concentration and time at constant low temperature, ethylene glycol concentration, and liquid/solid ratio.

ture. Response surfaces reproduced in Figs. 1–4 illustrate these effects.

The results of Table 2 were obtained by using similar reasoning with the other dependent variables. As can be seen, all the equations derived to relate the dependent variables to the independent variables reproduced the experimental results for the former with errors observed less than 8%.

As can be seen from Table 2, obtaining the optimum holocellulose (78.9%),  $\alpha$ -cellulose (61.8%), and lignin (19.1%) contents, and the best possible viscosity (426.8 ml/g) entails using high values of the ethylene glycol concentration (15%), soda concentration (15%), and cooking time (90 min), in addition to a low value for the liquid/solid ratio (4/1). A high temperature (195°C) must also be used to optimize the holocellulose content,  $\alpha$ -cellulose content, and viscosity, and a medium-to-low temperature (175°C) to ensure an optimum lignin content (19.1%).

As can also be seen from Table 2, the soda concentration and temperature are the two independent variables most strongly influencing the holocellulose,  $\alpha$ -cellulose and lignin contents, and the viscosity; and the soda concentration and



TABLE 2. Optimum values of the dependent variables and variations with changes in the independent variables for the ethylene glycol/soda pulping of olive tree wood.

Dependent variable	Percent errors made in estimating the dependent variables with respect to the experimental values	Optimum value	Normalized values of the independent variables leading to optimum values of the dependent variables						Maximum changes in the dependent variables (in units and percentages with respect to the optimum values (shown in brackets) with changes in the independent variables (from -1 to +1)					
			X <sub>T</sub>	X <sub>L</sub>	X <sub>E</sub>	X <sub>S</sub>	X <sub>R</sub>	T	t	E	S	R		
Pulp 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%)		
Holocellulose	2	78.9%	+1	+1	-	+1	-	3.4% (4.3%)	0.8% (1.0%)	-	6.8% (8.6%)	-		
α-cellulose	4	61.8%	+1	+1	+1	+1	-	4.2% (6.8%)	2.0% (3.2%)	1.1% (1.8%)	3.2% (5.2%)	-		
Lignin	6	19.1%	-0.34	-	+1	+1	-1	3.4% (17.8%)	-	1.6% (8.4%)	2.8% (14.7%)	1.7% (8.9%)		
Viscosity	8	426.8 mL/g	+1	+1	+1	+1	-1	106.2 mL/g (24.9%)	47.6 mL/g (11.2%)	46.8 mL/g (11.0%)	64.4 mL/g (15.1%)	35.4 mL/g (9.0%)		

Low ethylene glycol concentration, soda concentration and liquid/solid ratio

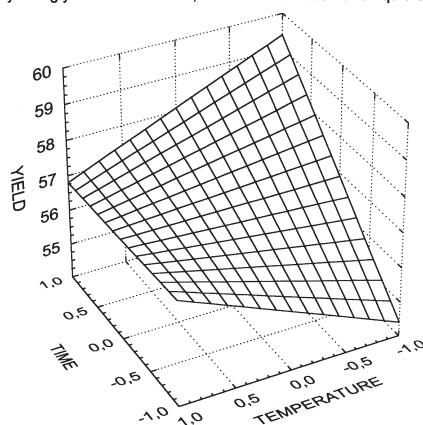


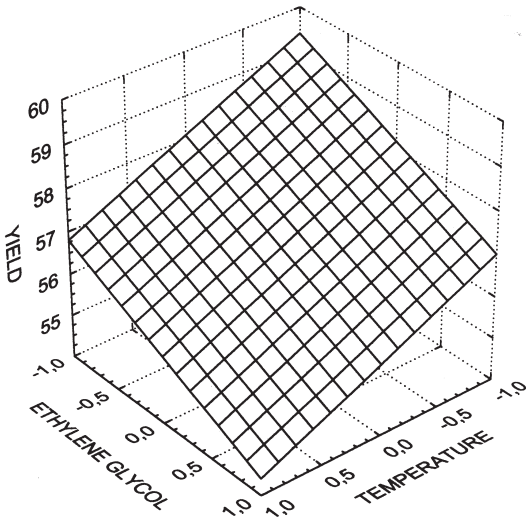
FIG. 2. Variation of pulp yield with time and temperature at constant low ethylene glycol concentration, soda concentration, and liquid/solid ratio.

time are those most markedly affecting the yield. On the other hand, the ethylene glycol concentration and liquid/solid ratio are the least influential of all variables. Figures 1–4 and other, similar ones, confirm these assertions.

Based on the results, from the corresponding equations, it follows that using a high soda concentration (7.5%) and temperature (195°C), in addition to a long time (90 min) and a low ethylene glycol concentration (5%) and liquid/solid ratio (4/1), provides optimum holocellulose (78.9%) and α-cellulose (61.8%) contents, viscosity value (397.2 ml/g) that depart by only 6.9% from the optimum level, and lignin contents (23.3%) and yields (50.2%) that differ somewhat more markedly (by 22.0% and 15.5%, respectively) from the optimum values. The unbleached yield thus achieved, 50.2%, is typical of chemical pulp. This process produces very dark pulp with a substantially decreased yield, but saves on immobilized capital (through the use of reduced amounts of liquid), reagents (ethylene glycol) and their recovery.

Obtaining brighter pulp entails using a medium temperature (180°C), high ethylene glycol (15%) and soda concentrations (7.5%), a short cooking time (30 min), and a low liquid/solid ratio (4/1). This results in holocellulose (74.8%), α-cellulose (57.7%), and lignin (19.3%) contents that depart by only

Low soda concentration and liquid/solid ratio and long time



Low soda concentration and temperature and long time

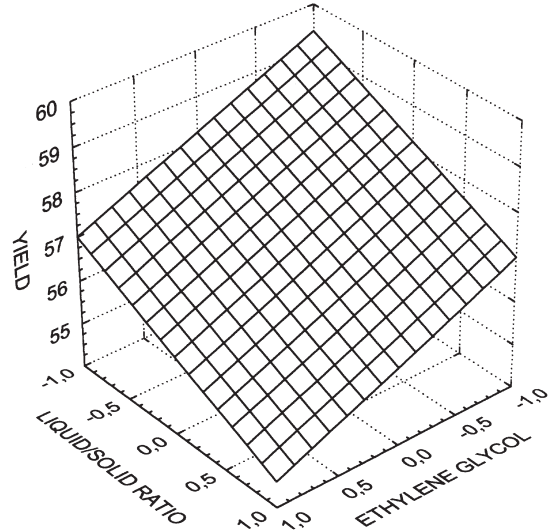


FIG. 3. Variation of pulp yield with temperature and ethylene glycol concentration at constant low soda concentration, and liquid/solid ratio, and long time.

FIG. 4. Variation of pulp yield with ethylene glycol concentration and liquid/solid ratio at constant low temperature and soda concentration, and long time.

5.2%, 6.6%, and 1.1%, respectively, from their optimum values, with a yield (51.5%) and viscosity (326.1%) that are 13.3% and 23.6% lower than the optimum values and thus give rise to poorer resistance properties. The use of less liquid (liquid/solid ratio of 4/1) for a shorter time (30 min) provides increased savings on immobilized capital, while that of a lower temperature (180°C) reduces power consumption.

Finally, using a medium-to-high temperature (187.5°C), high ethylene glycol, and soda concentrations (15.0% and 7.5%, respectively), a low solid/liquid ratio (4/1), and a short cooking time (30 min) provides a somewhat higher yield (52.2%) and improved resistance properties, without considerably reducing pulp brightness while saving on immobilized capital and power consumption. The yield (52.2%), holocellulose (76.5%),  $\alpha$ -cellulose (58.8%), lignin (20.4%) contents and viscosity (352.7 ml/g) thus obtained differ by 12.1%, 3.0%, 4.9%, 6.8%, and 17.4%, respectively, from their optimum values. Also, the viscosity/lignin content ratio is 17.2 and exceeds those obtained under the previous conditions; therefore, pulping under these conditions is more selective towards delignification and reduces damage to cellulose fibers as a result.

Finally, we should note that ethyleneglycol/soda pulp has abundant lignin and a low viscosity; as a result, it exhibits poor strength-related properties, which, however, can be improved by appropriate refining.

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