NONWOOD FIBERS

Organosolv pulping of wheat straw by use of methanol–water mixtures

LUIS JIMÉNEZ, FERNANDO MAESTRE, MARÍA J. DE LA TORRE, AND ILDEFONSO PÉREZ

ABSTRACT

A central composite design was used to investigate the influence of cooking conditions (time, temperature, and methanol concentration) for wheat straw with methanol–water mixtures on the properties of the pulp obtained (yield and holocellulose, α-cellulose, and lignin contents) and the pH of the resulting wastewater. A second-order polynomial model consisting of three independent process variables was found to accurately describe the organosolv pulping of wheat straw. The equations derived predict the yield, holocellulose, α-cellulose, and lignin contents of the pulp and the pH of the wastewater with multiple-R, R^2, and adjusted- R^2 values of 0.99, 0.99, and 0.99; 0.99, 0.99, and 0.98; 0.93, 0.86, and 0.81; 0.95, 0.90, and 0.87; and 0.98, 0.96, and 0.95, respectively. The process variables must be set at low values to ensure a high yield and pH. Conversely, if high holocellulose and α-cellulose contents and low lignin contents are desired, then a long cooking time, a high temperature, and a medium-to-high methanol concentration must be used.

Application:

Pulp can be obtained from agricultural residues by less-polluting methods.

THE CURRENT CHALLENGES OF THE pulp and paper industry are the achievement of affordable-quality pulp while preserving the environment by using increasingly smaller amounts of water and energy, and gradually less raw materials, and minimizing pollution from residual effluents resulting from cooking the raw materials used and from their bleaching.

Specifically, cooking the raw materials produces large amounts of highly polluting wastewater, particularly when it contains sulfur compounds (e.g., in processes using sulfite and sulfate).

On the other hand, the current annual output of pulp cannot meet demand, which is growing dramatically in developing countries and continues to rise in developed countries [by 2–3%/year in the United States, for example *(1)*). This is leading to an increasing shortage of wood raw materials and a gradual deforestation of some areas of the planet.

The above reasons have raised the need for new plants that use processes requiring modest investments to obtain quality wood products at a low cost while preserving the environment; reducing chemical, water, and energy consumption; increasing the yield of wood raw materials; and using alternative materials such as agricultural residues. This can be facilitated by the implementation of processes that use organic solvents, which are easy to reclaim and give valuable by-products *(1–3)* as well as by the use of previously unexplored raw materials.

Cereal straw abounds in many countries, such as Spain, that are short of wood resources. It makes an alternative raw material for obtaining pulp with a view to producing various types of paper and cardboard. The Spanish firm SAICA, based in Zaragoza, uses over 4×10^5 kg/day of cereal straw to make cardboard.

Regarding wheat straw, the raw material explored in this paper, Spain produces more than 7×10^9 kg/year. This residue is scattered and/or burned in the field, causing pollution and other problems that detract from environmental quality.

While the ability to obtain pulp by using organic solvents has been known for a long time, pilot plants and small-scale industrial plants exploiting them were started only recently. This has been the result of the shortage of alternatives to traditional procedures, leading to expending substantial efforts in any new processes, even if they had previously been discarded. In fact, some processes that use organic solvents are being reconsidered in response to the new economic and environmental order.

The earliest scientific references to delignification with organic solvents date from 1893, when Kason used ethanol and hydrochloric acid for that purpose. Subsequently, Aronovsky and Grotner carried out interesting work on the topic in the 1930s. Their experiments were followed by those of Brounstein in the 1950s and Kleinert in the 1970s. Since then, several authors have investigated the potential of various organic solvents for the purpose.

Prominent among the processes that use alcohols for pulping are those of Kleinert (ethanol or methanol, in the absence of a catalyst) *(2)*, Alcell (ethanol–water) *(2–4)*, MD Organocell (ethanol–soda) *(2–4)*, Organocell (methanol–soda–anthraquinone) *(3–5)*, ASAM (alkali–sulfite–anthraquinone–methanol) *(3–6)*, and ASAE (alkali–sulphite–anthraquinone–ethanol) *(7)*; that using sodium bicarbonate–ethanol–water *(8)*; and that using oxygen–alcohol

(9). Other processes based on different alcohols also worth special note are those of ester pulping *(10)*, phenol pulping *(2)*, Acetocell (acetic acid–water) *(11)*, Milox (formic acid–hydrogen peroxide) *(12)*, and Formacell (acetic acid–water–formic acid) *(13)* and those using formic acid *(14)*, glycerol *(15)*, oxygen–acetone–water *(16)*, water–glycerol–acetic acid *(17)*, and ammonia and amine bases *(2)*.

These processes have been applied with varying success to hardwood and softwood, and less frequently, to nonwood plant materials. There is only a single reference where the material used in this work, wheat straw, was treated with soda–ethanol–water following prehydrolysis with sulfuric acid *(18)*.

Pulping processes have been modeled in many ways to derive equations for estimating the quality of the resulting pulp as a function of the process variables and optimizing the operating conditions in accordance. Most such models use equations based on the kinetics of delignification to predict the extent to which it occurs; few, however, consider the effect of process variables on pulp quality and yield *(19)*.

So far, few authors have used factor design for this purpose. This modeling strategy allows the development of empirical models involving several independent variables for examining the chemical composition, pulp yield, kappa number, and degree of polymerization of pulp from various vegetables treated with organic solvents *(19–22)*. These empirical models are preferable to theoretical models that are rather complex when more than two independent variables of the pulping process are changed.

In this work, we used a central composition design to study the influence of cooking variables for wheat straw with methanol–water mixtures (i.e., the cooking time and temperature and the ethanol concentration) on the properties (yield and holocellulose, and α-cellulose and lignin contents) of the pulp and pH of the resulting wastewater.

T, °C	*t*, min	*C*, %	*Y*, %	*H*, %	α*C*, %	*L*, %	pH
−1	+1	−1	35.32	92.21	39.43	4.91	3.93
+1	+1	+1	31.53	93.49	42.25	3.71	3.79
+1	−1	−1	49.42	83.34	41.28	6.42	4.27
−1	−1	+1	67.91	80.12	37.27	8.43	4.46
+1	+1	−1	32.12	90.50	44.52	3.21	3.82
−1	+1	+1	31.99	90.52	43.91	4.13	3.78
−1	−1	−1	75.34	79.43	34.50	10.12	4.57
+1	−1	+1	43.12	86.01	38.75	5.98	4.18
0	+1	0	33.52	90.64	44.15	4.72	3.88
−1	0	0	47.91	83.54	37.15	6.72	4.32
0	0	+1	38.81	87.64	41.25	4.78	3.96
0	0	−1	40.39	84.92	35.12	7.52	4.19
+1	0	0	36.14	87.64	41.12	4.68	3.95
0	−1	0	60.12	81.34	38.23	6.52	4.39

**T* = temperature, *t* = time, *C* = methanol concentration, *Y* = yield, *H* = holocellulose, α*C* = α-cellulose, *L* = lignin

I. Conditions and results of organosolv pulping of wheat straw*

Equation	*F*	Multiple-*R*	R^2	Adj-R^2
Yield (3)	367.10	0.99	0.99	0.99
Holocellulose (4)	121.30	0.99	0.99	0.98
α-cellulose (5)	15.24	0.93	0.86	0.81
Lignin (6)	28.81	0.95	0.90	0.87
pH (7)	75.16	0.98	0.96	0.95

II. Snedecor's F, multiple-R, R^2, and adjusted- R^2 values for Eqs. 3 to 7

EXPERIMENTAL

Raw material

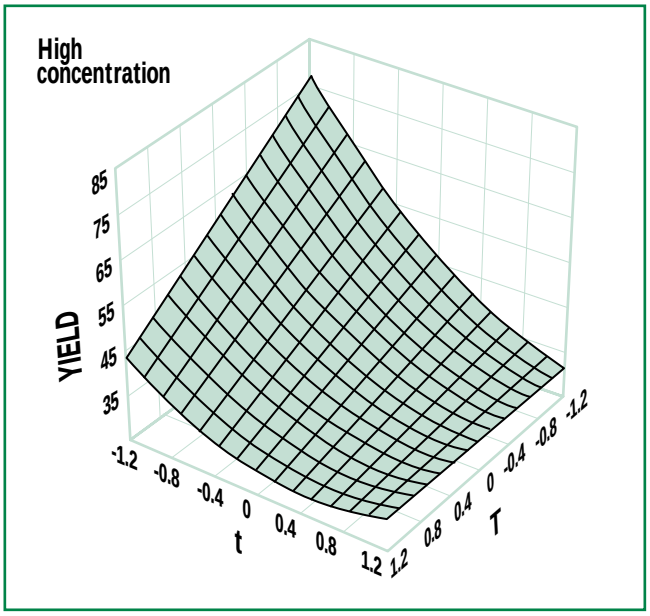
We used sun-dried wheat straw *(Triticum vulgaris)*, the composition of which was as follows: 8.52% moisture, 75.30% holocellulose, 39.67% α-cellulose, 17.73% lignin, 6.84% ash, 11.74% cold-water solubles, 13.57% hot-water solubles, 43.48% 1%-NaOH solubles, and 4.23% ethanol/benzene extractables. The deviations of these contents from their respective means were all less than 10%.

Experimental design

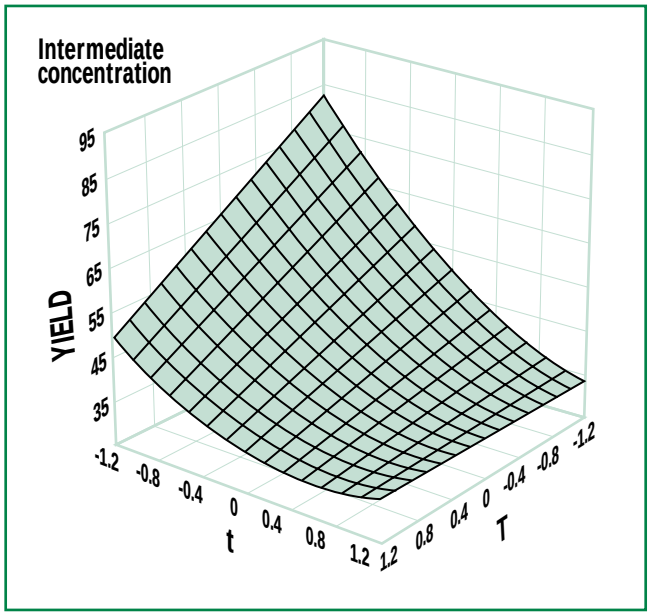
A central composite design was used to outline the composition of the experimental process conditions around a central combination. A central composite design consists of several components, i.e., a 2^n factor structure around a number of observations at a central point and additional observations on the axes to allow estimation of quadratic terms. Central composite designs meet the general requirements that every parameter in a polynomial model should be estimated from a moderate number of observations and that observations be spread fairly evenly over the experimental region of interest *(23)*. With three independent variables, 15 experiments were enough to fit a second-order polynomial model. The central combination for the experimental design was as follows: t = 75 min, T = 175°C, and [MeOH] = 65%. These three variables were varied over the ranges 30–120 min, 150–200°C, and 50–80%, respectively. The warmup time (15–20 min) was excluded form the pulping time. The liquid/solid ratio used was 40:1. The results were subjected to multiple linear regressions as implemented in the biomedical program (BMDP) new system package.

Pulping

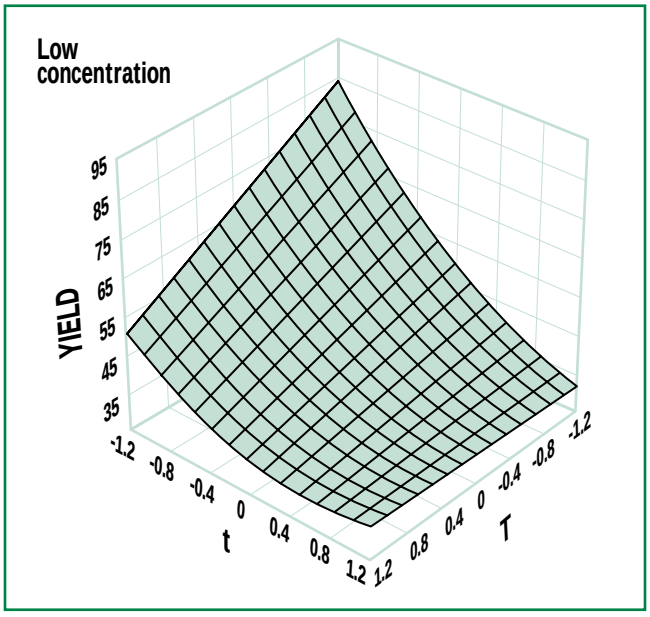
Wheat straw was pulped in methanol–water mixtures, containing no catalytic additive, in a 750-mL



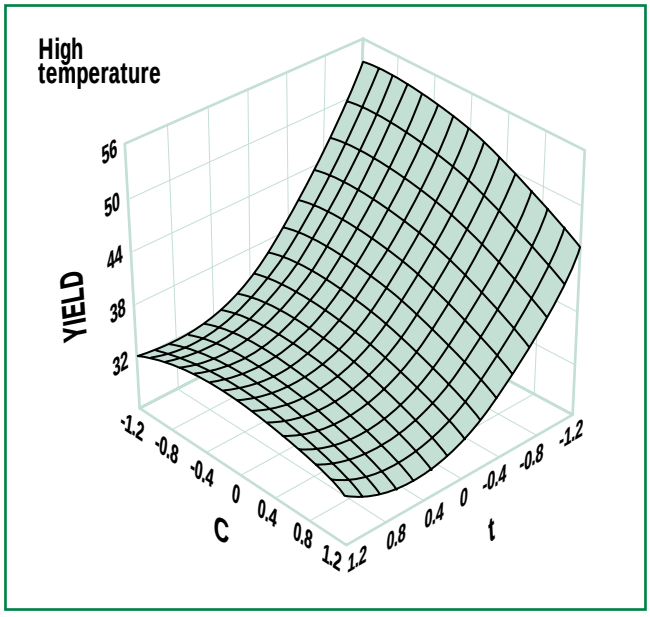
1. Variation of pulp yield with cooking time and temperature at a high, constant methanol concentration



2. Variation of pulp yield with cooking time and temperature at an intermediate, constant methanol concentration



3. Variation of pulp yield with cooking time and temperature at a low, constant methanol concentration



4. Variation of pulp yield with cooking time and methanol concentration at a high, constant temperature

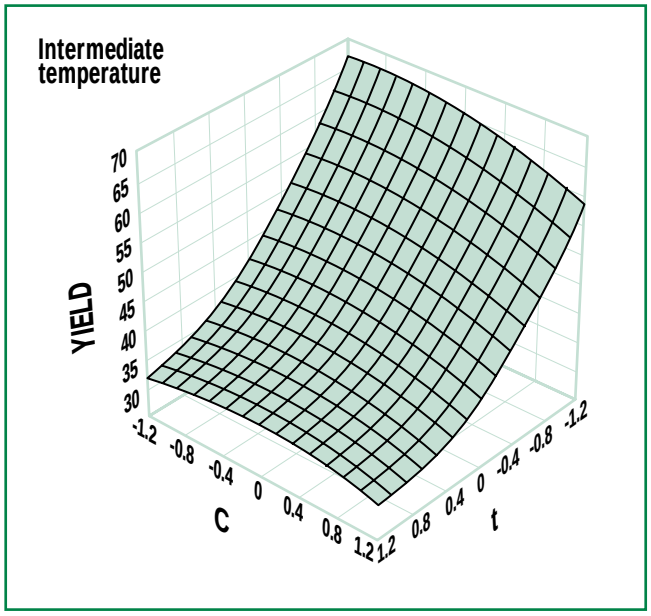
Berghof reactor. After the reactor was loaded with wheat straw and the cooking liquor, it was heated to the operating temperature, which was then maintained throughout the experiment. After cooking, the pulp was disintegrated in a laboratory blender, washed with a hot methanol–water mixture, and finally washed with hot distilled water.

Analyses

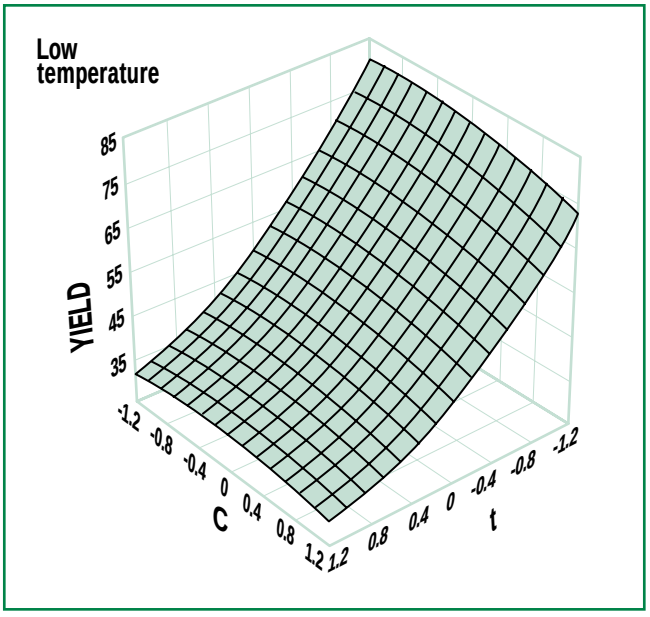
The holocellulose content in the wheat straw and pulp was determined by using the method of Wise *et al. (24).* The α-cellulose, lignin, ash, cold-water soluble, hot-water soluble, 1% NaOH soluble, and ethanol/benzene extractable contents were obtained according to the corresponding TAPPI test methods. Pulp yield was determined gravimetrically following drying at 100°C for 24 hours.

RESULTS AND DISCUSSION

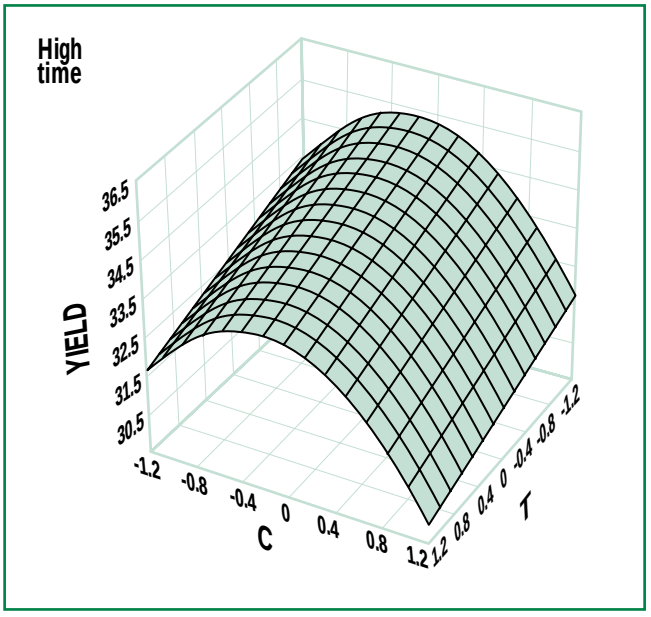
The central operating conditions (65% MeOH, 175°C, and 75 min) were used in four experiments. The results obtained in each experiment regarding yield, holocellulose, α-cellulose, and lignin in the pulp, and pH of the wastewater, differed from the mean values (42.49,



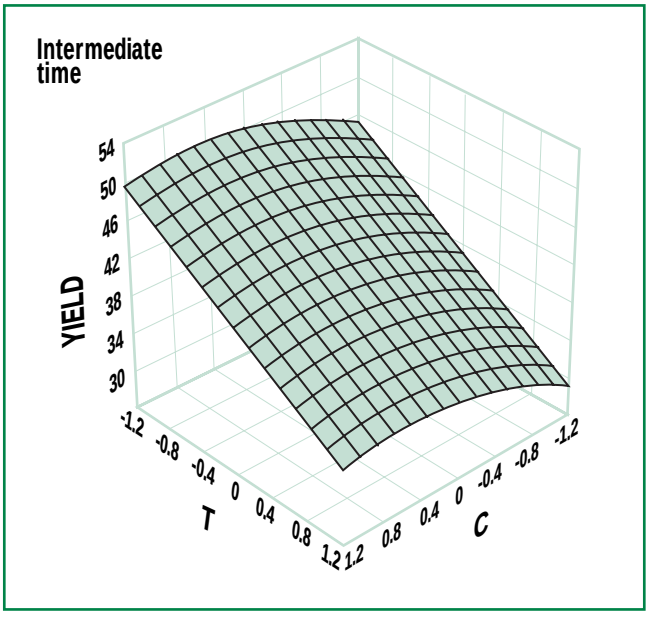
5. Variation of pulp yield with cooking time and methanol concentration at an intermediate, constant temperature



6. Variation of pulp yield with cooking time and methanol concentration at a low, constant temperature



7. Variation of pulp yield with temperature and methanol concentration at a high, constant cooking time



8. Variation of pulp yield with temperature and methanol concentration at an intermediate, constant cooking time

85.92, 38.26, 5.86, and 4.08%, respectively) by less than 5% in all instances.

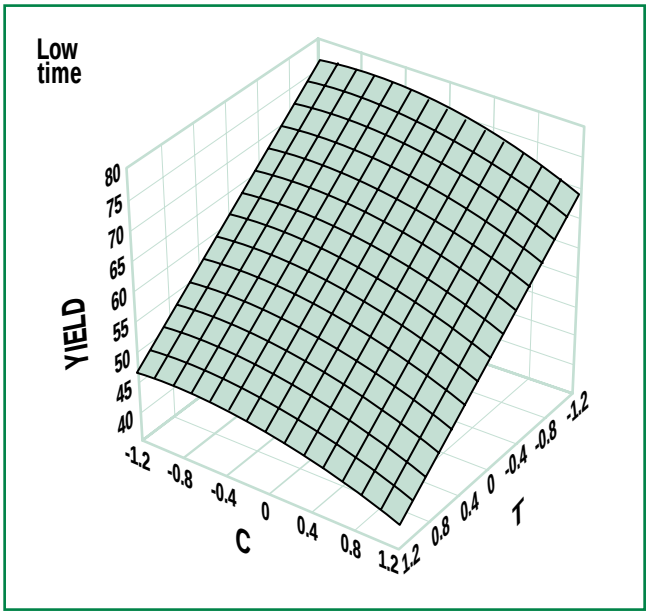
Subsequently, the proposed experimental design was used to obtain the results given in **Table I.** Experimental data were modeled by using the following second-order polynomial:

$$Y = a_0 + \sum_{i=1}^{3} b_i X_{ni} + \sum_{i=1}^{3} c_i X_{ni}^2 + \sum_{i=1;j=1}^{3} d_{ij} X_{ni} X_{nj} \quad (1)$$

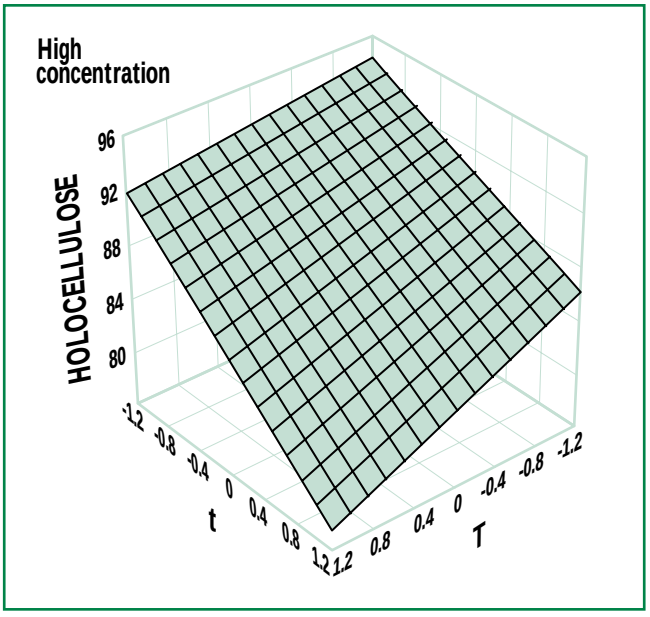
where

$$X_n = 2[(X - \bar{X})/X_{max} - X_{min})] \quad (2)$$

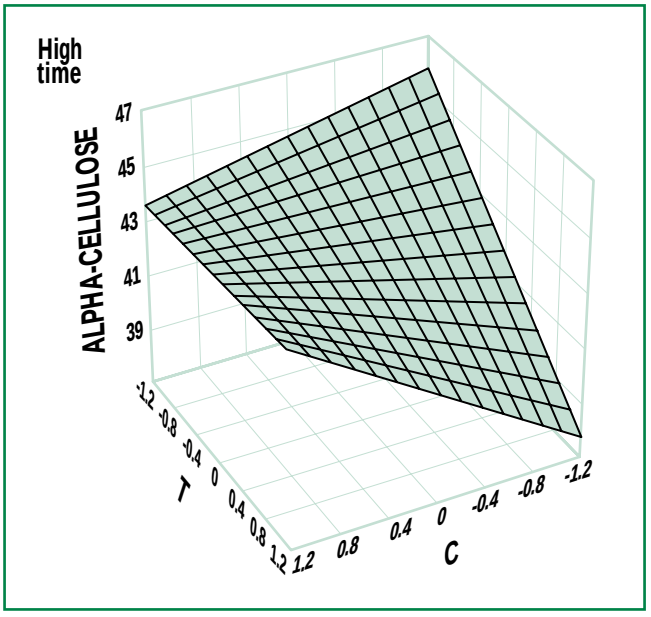
The response variable Y represents the yield, holocellulose, α-cellulose, and lignin contents of the pulp, and pH of the wastewater. The independent variables X_1 to X_3 denote the methanol concentration *(C),* temperature *(T),* and time *(t),* respectively. The independent variables were normalized from –1 to +1 by using Eq. 2 to facilitate direct comparisons of coefficients and to better understand the effects of individual variables on the response variables. Normalization of the independent variables also



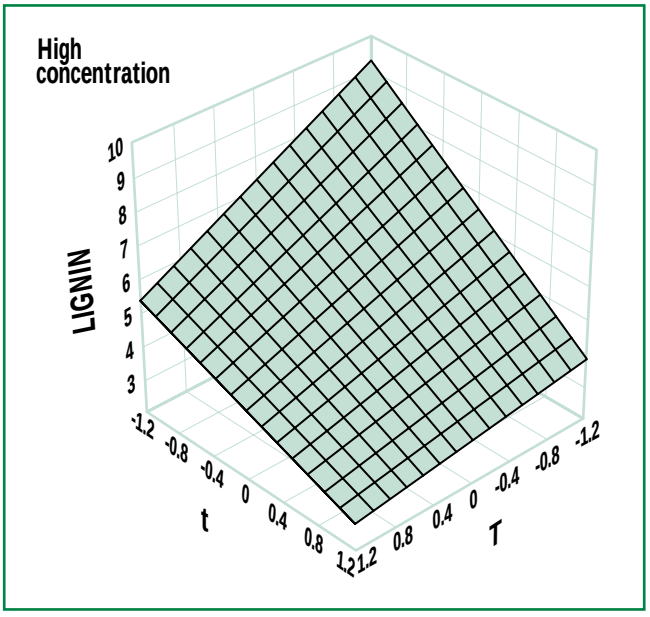
9. Variation of pulp yield with temperature and methanol concentration at a low, constant cooking time



10. Variation of holocellulose with cooking time and temperature at a high, constant methanol concentration



11. Variation of the α-cellulose with temperature and methanol concentration at a high, constant cooking time



12. Variation of lignin with cooking time and temperature at a high, constant methanol concentration

KEYWORDS
Alpha cellulose, equations, experimental design, holocellulose, lignin content, methanol, mixtures, models, organosolv pulping, pH, process variables, temperature, time, waste waters, water, wheat straw.

provides better estimates for the regression coefficients by reducing correlations between linear and quadratic interaction terms *(23)*.

The central combination is that for which all normalized independent variables are zero. Coefficients a_o, b_i, c_i, and d_{ij} are unknown regression coefficients that must be estimated from experimental data.

The multiple linear regression analysis was performed on all terms of Eq. 1 (by using the data in Table I and those for the four experiments carried out under the central operating conditions); those terms with Snedecor's F values below 4.5 were discarded by using the stepwise method.

The equations derived for the different response variables were as

follows:

$$Y_{yield} = 42.11 - 1.92C - 6.61T - 13.14t - 1.83C^2 + 5.39t^2 + 1.23Ct + 5.88Tt \quad (3)$$

$$Y_{holocellulose} = 85.85 + 0.74C + 1.52T + 4.71t + 0.96C^2 + 0.83CT - 1.07Tt \quad (4)$$

$$Y_{\alpha\text{-cellulose}} = 38.46 + 0.86C + 1.57T + 2.42t - 1.51CT + 1.97t^2 \quad (5)$$

$$Y_{lignin} = 5.85 - 0.51C - 1.03T - 1.68t + 0.50Tt \quad (6)$$

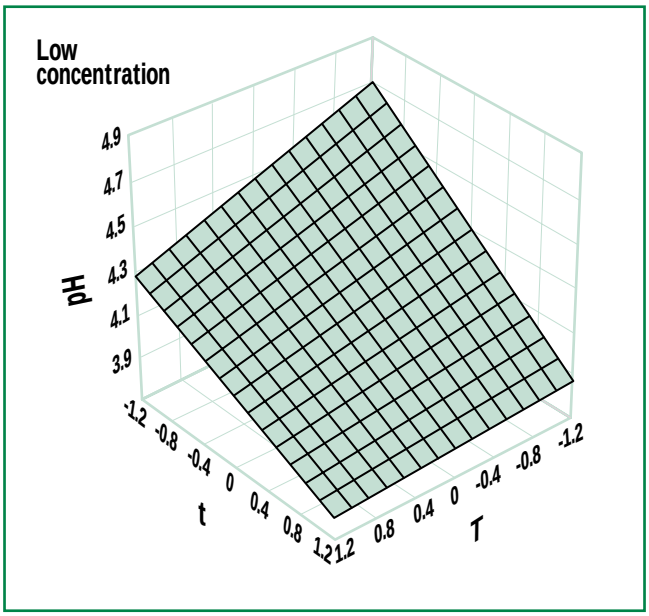
$$Y_{pH} = 4.10 - 0.06C - 0.10T - 0.27t + 0.06Tt \quad (7)$$

Snedecor's *F,* multiple-*R,* R^2, and adjusted-R^2 values for the fitting of Eqs. 3 to 7 are listed in **Table II.**

Coefficients a_0 represent the estimated response values for the central combination of operating conditions. The yield, holocellulose, α-cellulose, and lignin contents, and the pH, were found to be satisfactorily fitted by seven, six, five, four, and four exploratory variables, respectively.

There were significant interactions between the temperature and time for the yield, the holocellulose and lignin contents, and the pH. There was an additional interaction between the methanol concentration and time for the yield, and between such a concentration and the temperature for the holocellulose con-tent. On the other hand, only the methanol concentration and temperature were correlated for α-cellulose.

A comparison between the fitted values calculated from the polynomial equations and the experimental results for the different response variables revealed the experimental yield, holocellulose, and α-cellulose contents, and pH, to be predicted with errors less than 5%, and the lignin content with errors less that 15%. As can be seen from Snedecor's *F,* multiple *R,* R^2, and adjusted-R^2 values in Table II, the model fitted the experimental values for all the response variables well. The lowest values of these parameters for α-cellulose arose most likely from the high sensitivity of this dependent variable to differences in the pulping conditions that were not included in the model and to small variations in the raw material used.



13. Variation of pH of the resulting wastewater with cooking time and temperature at a low, constant methanol concentration

Figures 1–9 show the variation of yield as a function of the normalized values of two independent variables on constancy of the third independent variable. As can be seen, if a low yield (similar to that of chemical pulp) is desired, then one should use a high temperature and methanol concentration, and a long cooking time. If a high yield (similar to that of semichemical pulp) is to be obtained, then decreased values of the operating variables should be used; the methanol concentration, however, has little influence relative to the cooking temperature and time. From Figs. 1–9 and the use of Eq. 3, one can estimate the yield variation with each of the independent variables over the range considered on constancy of the other two. If the central values (65% MeOH, 175°C, and 75 min) for the two variables to be kept constant are used, then the maximum variations in the yield are obtained when the time is changed (26.28) and the minimum appears when the methanol concentration is altered (3.84). The variations with temperature (13.22) lie in between the previous two, so the yield is much more sensitive to changes in the cooking time than in the methanol concentration.

Based on Eq. 4, one should use a high methanol concentration and, judging from **Fig. 10,** also an increased cooking temperature and time for holocellulose. The variation in its content is more sensitive to changes in time (9.42) than in the methanol concentration (1.84), with the temperature in an intermediate situation (3.04).

Regarding α-cellulose, one should use an increased cooking time (Eq. 5), a high temperature, and a low methanol concentration (**Fig. 11**). The greatest changes in α-cellulose content result from variations of the cooking time (5.13), and the smallest are from alteration of the methanol concentration (1.72), the effect of cooking temperature lying between the previous two (3.14).

Regarding lignin, if a low content is obtained, then a high methanol concentration (Eq. 6) and an increased temperature and time (**Fig. 12**) should be used. Variations of the lignin content are more sensitive to changesin time (3.36) than to variations of the methanol concentration (1.02), with the temperature lying in between (2.06).

Finally, if the pH of the resulting wastewater is not to be low, then a low methanol concentration (Eq. 7) and a decreased cooking temperature and time should be used (**Fig. 13**). Changes in pH are most sensitive to variations in the cooking time (0.54) than in the methanol concentration (0.12), the temperatures having an immediate influence (0.20).

SUMMARY

Pulp making from wheat straw and methanol has two principal advantages:

- It uses a residual raw material and saves wood.
- It gives pulp properties (holocellulose and α-cellulose contents, among others) that are suitable for making paper and/or cardboard, depending on yield, which in turn is dictated by the operating variables. **TJ**

Jiménez isa professor, Maestre is Ph. D., and de la Torre is a Ph. D., at Universidad de Córdoba, Departamento de Ingeniería Química, Facultad de Ciencias, Spain. Pérez is a research assistant at Ecopapel, S.L., Ronda de San Augustin, 6, Ecija, Seville, Spain.

The authors wish to thank the firm of Ecopapel, S.L. from Ecija (Seville, Spain) for finding this research in the framework of a project aimed at obtaining cellulose paper pulp by less-polluting methods using clean technologies.

Received for review Sept. 4, 1996.
Accepted March 9, 1997.

LITERATURE CITED

1. Paszner, L. and Cho, H. J., *Tappi J.* 72(2): 135(1989).
2. Asiz, S. and Sarkanen, K., *Tappi J.* 72(3): 169(1989).
3. Lönnberg, B., Laxen, T., and Sjöholm, R., *Paperi ja Puu* 9: 575(1987).
4. Stockburger, P., *Tappi J.* 76(6): 71(1993).
5. Dahlmann, G. and Schroeter, M. C., *Tappi J.* 73(4): 237(1990).
6. Black, N. P., *Tappi J.* 74(4): 87(1991).
7. Kirci, H., Bostanci, S., and Yalinkilic, M. K., *Wood Sci. Technol.* 28(2): 89(1994).
8. Faass, G. S., Robert, R. S., and Muzzy, J. P., *Holzforschung* 43: 245(1989).
9. Deinko, I. P., Makarova, O. V., and Zarubin, M. Y., *Tappi J.* 75(9): 136(1992).
10. Asiz, S. and McDonough, T. J., *Tappi J.* 70(3): 137(1987).
11. Neumann, N. and Balser, K., *Papier* 47(10): 16(1993).
12. Poppiuslevlin, K., Mustonen, R., Huovila, T., *et al., Paperi Ja Puu* 73(2): 154(1991).
13. Saake, B., Lummitsch, S., Mormanee, R., *et al., Papier* 49(10): 1(1995).
14. Baeza, J., Urizar, S., Erismann, N. D., *et al., Bioresource Technol.* 37(1): 1(1991).
15. Kucuk, M. H. and Demirbas, A., *Cellulose Chem. Technol.* 27(6): 679(1994).
16. Delpechbarrie, F. and Robert, A., *Cellulose Chem. Technol.* 27(1): 87(1993).
17. Rutkowski, J., Mroz, W., and Perlinskasipa, K., *Cellulose Chem. Technol.* 28(6): 621(1995).
18. Papatheophanus, M. G., Koullas, D. P., and Koukios, E. G., *Cellulose Chem. Technol.* 29(1): 29(1995).
19. Tjeerdsma, B. F., Zomers, F. H. A., Wilkinson, E. C., *et al., Holzforschung* 48: 415(1994).
20. Vásquez, D., Lage, M. A., Parajó, J. C., *et al., Biores. Technol.* 40: 131(1992).
21. Parajó, J. C., Alonso, J. L., Vázquez, D., *et al., Holzforschung* 47(3): 188(1993).
22. Vásquez, G., Antorrena, G., y González, J., *Holzforschung* 49(1): 69(1995).
23. Montgomery, D. C., *Diseño y Análisis de Experimentos*, Grupo Editorial Iberoamericana, Mexico, 1991, Mexico City, 1991, pp.241–277.
24. Wise, L. D., Marphy, M., and D'Addiego, A., *Paper Trade J.* 112: 35(1946).