

# *Pulps from Solid Fraction of Hydrothermal Treatment of Rice Straw*

Rodríguez, A.\*; Moral, A.; Sánchez, R.; Jiménez, L.  
Chemical Engineering Department. University of Córdoba. Córdoba. Spain.

*Uso de dietanolamina para obtener pastas celulósicas de la fracción sólida de un tratamiento hidrotérmico de la paja de arroz*

*Ús de dietanolamina per obtenir pastes cel·lulòsiques de la fracció sòlida d'un tractament hidrotèrmic de la palla d'arròs*

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## RESUMEN

Se investiga el potencial del residuo sólido de un tratamiento hidrotérmico de la paja de arroz como materia prima alternativa para la producción de pastas celulósicas. Se estudia la influencia de las variables de operación en el pasteado con dietanolamina de la fracción sólida de un tratamiento hidrotérmico de la paja de arroz, sobre las propiedades de las pastas celulósicas resultantes y de las hojas de papel hechas a partir de éstas. Utilizando un diseño de experimentos de composición central y ajustando los resultados a un modelo polinómico se obtienen ecuaciones que relacionan las variables dependientes con las independientes con errores menores al 8 % en todos los casos excepto para el índice de estallido (27 %).

Las condiciones óptimas de operación que permiten ahorrar reactivos, energía para el calentamiento y capital inmovilizado resultan ser una concentración de dietanolamina del 70 %, una temperatura de 162,5°C, un tiempo de reacción de 60 minutos y una relación líquido/sólido de 8. Estas condiciones proporcionan hojas de papel con propiedades físicas que se desvían poco de las óptimas (menos del 8 % en el peor de los casos) así como valores de rendimiento y número Kappa que se desvían menos del 14 % respecto de los valores óptimos.

Se compara los resultados obtenidos en el pasteo con dietanolamina de la fracción sólida de un tratamiento hidrotérmico de la paja de arroz con los de pastas de eucalipto y pino obtenidas con reactivo Kraft y con dietanolamina, observándose que las propiedades se sitúan a medio camino entre las de eucalipto y pino.

**Palabras clave:** Paja de arroz. Dietanolamina. Alto punto de ebullición. Hidrotérmico. Pasta.

## SUMMARY

We assessed the potential of the solid residue from a hydrothermal treatment of rice straw as an alternative

raw material for obtaining cellulose pulp. To this end, we examined the influence of operational variables in the diethanolamine pulping of this material on the properties of the cellulose pulp obtained and of paper sheets made from it.

Using a central composite factor design and fitting the results to a polynomial model allowed us to establish equations relating the dependent variables to the independent ones with errors less than 8% in all cases except for burst index (27%).

The optimum conditions with a view to saving reagents, heating energy and immobilized capital were found to be a diethanolamine concentration of 70%, a temperature of 162.5 °C, a cooking time of 60 min and a liquid/solid ratio of 8. These conditions provide paper sheets with physical properties that depart by less than 8% from their optimum values, and a pulp yield and Kappa number differing by less than 14% from their best levels.

We compared the results obtained in the diethanolamine pulping of the solid fraction from the hydrothermal treatment of rice straw with those for kraft and diethanolamine pulp from eucalyptus and pine wood, and found the properties of the former to fall in between those for the latter two.

**Key words:** Rice straw. Diethanolamine. High boiling point. Hydrothermal. Pulp.

\* Corresponding author. Alejandro Rodríguez.  
Chemical Engineering Department.  
Campus de Rabanales, C-3.  
Universidad de Córdoba. Córdoba. Spain.  
Tlf: +34 957 21 85 86 Fax: +34 957 21 86 25  
E-mail: q42ropaa@uco.es

## RESUM

S'investiga el potencial del residu sòlid d'un tractament hidrotèrmic de la palla d'arròs com a matèria primera alternativa per a la producció de pastes cel·lulòsiques. S'estudia la influència de les variables d'operació en el pastament amb dietanolamina de la fracció sòlida d'un tractament hidrotèrmic de la palla d'arròs sobre les propietats de les pastes cel·lulòsiques resultants i dels fulls de paper fets a partir d'aquestes.

Utilitzant un disseny d'experiments de composició central i ajustant els resultats a un model polinòmic, s'obtenen equacions que relacionen les variables dependents amb les independents amb errors inferiors al 8% en tots els casos, excepte per a l'índex d'esclat (27%).

Les condicions òptimes d'operació que permeten estalviar reactius, energia per a l'escalfament i capital immobilitzat resulten ser una concentració de dietanolamina del 70%, una temperatura de 162,5°C, un temps de reacció de 60 minuts i una relació líquid/sòlid de 8. Aquestes condicions proporcionen fulls de paper amb propietats físiques que es desvien poc de les òptimes (menys del 8% en el pitjor dels casos), així com valors de rendiment i número Kappa que es desvien menys del 14% respecte dels valors òptims.

Es compara els resultats obtinguts amb el pastament amb dietanolamina de la fracció sòlida d'un tractament hidrotèrmic de la palla d'arròs amb els de pastes d'eucaliptus i pi obtingudes amb reactiu Kraft i amb dietanolamina, observant-se que les propietats se situen a mig camí entre les d'eucaliptus i les de pi.

**Mots clau:** Palla d'arròs. Dietanolamina. Alt punt d'ebullició. Hidrotèrmic. Pasta.

## INTRODUCTION

The advent of new information and communication technologies, and the growing use of computers in developed countries, were in its day anticipated to lead to a decreased use of paper worldwide. However, the Spanish production of writing and printing paper grew from 1.090 million tons in the year 2000 to 1.593 million tons in 2006 (FAO).

Wood species have provided 95% of all raw materials for making cellulose pulp for a little over a century. However, the production of cellulose pulp from non-wood fibre has risen dramatically in recent years: from 12 000 tons in 2003 to 850 000 tons in 2006 (FAO, 2008; EUROSTAT, 2008). In parallel, the production of pulp from wood fibre rose much less markedly: from 1.894 million tons in 2003 to 2.104 million tons in 2006 (FAO, 2008; EUROSTAT, 2008). The greater relative increase in the use of non-wood fibre has been a result of the need for alternative, non-wood raw materials raised by economic and environmental problems. In addition, non-wood raw materials are the sole effective source of cellulose fibre in some world regions. This has boosted research into the pulp making potential of non-wood raw materials such as rice straw, pauwlonia, tagasaste or abaca, among others (Navae-Ardeh *et al.*, 2004; Roliadi *et al.*, 2003; Peralta, 1996; López *et al.*, 2004; Jiménez *et al.*, 2002a, 2005).

Using non-wood fibre for pulp and paper production purposes can have major advantages such as the following:

- Valorizing some agricultural and agrifood residues, thereby increasing the profitability of agrarian holdings.

- Reducing wood and cellulose pulp imports in countries with deficient wood resources capable of producing large amounts of alternative raw materials such as agricultural residues and non-wood plants.

- Boosting consumers' interest in paper obtained with clean technologies or from recycled fibre or alternative raw materials.

Rice wood is an abundant non-wood raw material. A total area of 101 700 ha was cropped with rice in Spain in 2007; also, the Spanish production of rice that year was 713 000 ton (EUROSTAT, 2008). Therefore, the country produces a large amount of rice straw disposal of which poses serious problems to farmers. Although the straw is partly used as an agricultural amendment, most has to be disposed of. Traditionally, straw has been burnt on site, this practice generates heavy smoke frequently resulting in breathing, cardiorespiratory and allergic problems in nearby populations, and also in the release of large amounts of carbon dioxide to the environment.

However, rice straw can be processed differently in order to facilitate its valorization. One way is by using it as animal feed; however, advocates and opposers of this use disagree on the actual protein value and digestibility of the material (Srinivasan *et al.*, 1983; Misra, 1993). One other way is by using straw ash or husk ash, which is similar in composition to extract silicon (Souza *et al.*, 2000, 2002). This element can also be obtained from the liquors of alkaline (Kalapathy *et al.*, 2000) and acid treatments (Lam *et al.*, 2001). In any case, using rice straw to produce cellulose pulp (Johan *et al.*, 2005; Bhardwaj *et al.*, 2005) and the resulting liquors to obtain silicon appears to be the most attractive choice.

Also, the growing concern with the preservation of the environment in developed societies must be reconciled with the increasing demand for paper and board pulp worldwide. This has led to research being refocused on the use of alternative raw materials and the development of new pulping processes based on less polluting, more easily recovered reagents such as organic solvents. In addition, so-called organosolv processes only require modest investments in low-output industrial facilities, feature also low production costs, provide high-quality products and make highly efficient use of the raw materials; this results in high pulp yields and provides a number of by-products that ensure integral exploitation of the raw materials. Some recent studies have explored the pulping potential of various raw materials including beech, pine, olive prunings, jute and cotton (Claus *et al.*, 2004; Jahan 2001; Jahan and Farouqui, 2000, 2003; Jahan *et al.*, 2001; Jiménez *et al.*, 2002b, 2004; Sarwar *et al.*, 2002).

In this work it was studied, by means of the use of a factorial design of experiments, the influence of the operating variables of the pulping using diethanolamine (temperature, time and concentration of diethanolamine), on the yield, viscosity, Kappa index and drainage index of pulps, and the breaking length, stretch index, burst index, tensile index and brightness of the paper sheets made from pulps.

## METHODS

### Raw material

In this work a rice straw solid residual fraction of a hydrothermal treatment is used, under the following conditions: temperature of 190°C, time of 0 minutes (after reaching the 190°C) and liquid-solid relationship of 8. This solid fraction has a pulp yield of 96.78%, a content of holocellulose,  $\alpha$ -cellulose and lignin of 64.4%, 39.5% and 24.7%, respectively.

### Pulp production

Pulps were obtained by using a 15-L batch cylindrical reactor that was heated by means of electrical resistances and was linked through an axle to a control unit including a motor actuating the reactor and the required instruments for measurement and control of the pressure and temperature.

Rice straw was cooked in the reactor. Next, the cooked material was unloaded into a washer in order to remove residual cooking liquor and then fiberized in a disintegrator at 1200 rpm for 30 min, after which the pulp was beaten in a Sprout-Bauer refiner and the fiberized material passed through a screen of 0.16 mm mesh size in order to remove uncooked particles.

### Experimental design

Pulping processes have been modelled in a variety of ways with a view to establishing equations for estimating pulp quality in terms of process variables and optimizing the operating conditions accordingly. Most such models consist of kinetic expressions for estimating the extent of delignification of the raw material, but fail to consider the effect of process variables on the properties of the resulting pulp and paper.

In this work a factorial design is used that allows the development of empiric models with several independent variables, to examine the yield, Kappa index, viscosity and drainage index of the pulps as well as the breaking length, stretch, burst index, tear index and brightness of the paper sheets of the pulps obtained with diethanolamine.

The experimental 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 quadratic terms of a polynomial model. The design met the general requirement that it allowed all parameters in the mathematical model to be estimated with a relatively small number of tests (Montgomery, 2001).

The total number of tests required for the three independent variables studied [viz., temperature (T), time (t) and diethanolamine concentration (D)] was 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

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 D.

Experimental data were fitted to the following second-order polynomial

$$Y = a_0 + \sum_{i=1}^n b_i X_{ni} + \sum_{i=1}^n c_i X_{ni}^2 + \sum_{i=1, j=1}^n d_{ij} X_{ni} X_{nj} \quad i < j \quad [\text{Eq. 2}]$$

where Y denotes a characteristic or property of the pulp (yield, Kappa number, viscosity or drainage index) or paper sheets (breaking length, stretch, burst index, tear index or brightness), and coefficients  $a_0$ ,  $b_i$ ,  $c_i$  and  $d_{ij}$  are unknown characteristic constants estimated from the experimental data.

## RESULTS AND DISCUSSION

We used three different levels of each of the three independent variables considered (viz. T, t and D) to examine their influence on the characteristics of the resulting pulp (yield, Kappa number, viscosity and drainage index) and paper sheets (breaking length, stretch, burst index, tear index and brightness). Table 1 gives the values of the operational variables and their normalized levels. Table 2 show the average results for each dependent variable for the pulp and paper sheets as a obtained in each test of the experimental design.

TABLE I

Operating conditions used in the diethanolamine pulping of solid fraction from hydrothermal treatment applied to rice straw.

| Experiment | T, °C | t, min | Diethanolamine, % | XT | Xt | XD |
|------------|-------|--------|-------------------|----|----|----|
| 1          | 170   | 60     | 70                | 0  | 0  | 0  |
| 2          | 180   | 90     | 80                | 1  | 1  | 1  |
| 3          | 160   | 90     | 80                | -1 | 1  | 1  |
| 4          | 180   | 90     | 60                | 1  | 1  | -1 |
| 5          | 160   | 90     | 60                | -1 | 1  | -1 |
| 6          | 180   | 30     | 80                | 1  | -1 | 1  |
| 7          | 160   | 30     | 80                | -1 | -1 | 1  |
| 8          | 180   | 30     | 60                | 1  | -1 | -1 |
| 9          | 160   | 30     | 60                | -1 | -1 | -1 |
| 10         | 170   | 90     | 70                | 0  | 1  | 0  |
| 11         | 170   | 30     | 70                | 0  | -1 | 0  |
| 12         | 170   | 60     | 80                | 0  | 0  | 1  |
| 13         | 170   | 60     | 60                | 0  | 0  | -1 |
| 14         | 180   | 60     | 70                | 1  | 0  | 0  |
| 15         | 160   | 60     | 70                | -1 | 0  | 0  |

$X_T, X_t, X_D$  = Normalized values of temperature, time and diethanolamine concentration, respectively

**TABLE II**

**Experimental results of the characterization of pulp and paper sheets properties of the pulps obtained with diethanolamine.**

| Experiment | Yield, % | Kappa index | Viscosity, mL/g | Drainage index, °SR | Breaking length, m | Stretch index, % | Burst index, kN/g | Tear index, mNm <sup>2</sup> /g | Brightness, % |
|------------|----------|-------------|-----------------|---------------------|--------------------|------------------|-------------------|---------------------------------|---------------|
| 1          | 64.3     | 59.1        | 735             | 19.0                | 2187               | 2.66             | 1.11              | 0.40                            | 40.2          |
| 2          | 54.7     | 53.8        | 677             | 19.0                | 1080               | 1.67             | 0.23              | 0.41                            | 42.2          |
| 3          | 59.1     | 54.2        | 702             | 18.0                | 1085               | 1.70             | 0.24              | 0.39                            | 40.5          |
| 4          | 69.9     | 62.7        | 770             | 24.5                | 1125               | 1.78             | 0.25              | 0.38                            | 39.5          |
| 5          | 76.2     | 65.8        | 795             | 22.0                | 1203               | 1.84             | 0.27              | 0.42                            | 38.0          |
| 6          | 55.8     | 53.9        | 680             | 18.5                | 1208               | 1.85             | 0.36              | 0.41                            | 41.4          |
| 7          | 59.4     | 54.5        | 704             | 18.0                | 1208               | 1.85             | 0.31              | 0.41                            | 40.4          |
| 8          | 70.0     | 63.1        | 772             | 23.0                | 1212               | 1.90             | 0.43              | 0.40                            | 39.5          |
| 9          | 76.4     | 67.0        | 797             | 22.0                | 1420               | 2.06             | 0.62              | 0.39                            | 37.0          |
| 10         | 64.1     | 58.8        | 733             | 20.0                | 1595               | 2.12             | 0.72              | 0.41                            | 40.4          |
| 11         | 64.5     | 59.2        | 739             | 19.0                | 1708               | 2.29             | 0.74              | 0.41                            | 39.9          |
| 12         | 57.1     | 54.0        | 690             | 18.0                | 1764               | 2.31             | 0.85              | 0.38                            | 40.9          |
| 13         | 73.1     | 64.3        | 783             | 22.5                | 1897               | 2.44             | 0.87              | 0.39                            | 39.2          |
| 14         | 62.7     | 58.7        | 723             | 20.0                | 1982               | 2.50             | 0.94              | 0.41                            | 40.4          |
| 15         | 66.0     | 59.5        | 750             | 19.0                | 2303               | 2.72             | 1.01              | 0.42                            | 39.8          |

A multiple regression analysis of the experimental data of Table 2 for each independent variable of the pulping process as obtained in the different tests of the experimental design was used to establish equations relating the dependent variables to the independent ones with a confidence interval of 95% (Draper and Smith, 1998). The analysis was performed with the software BMDP<sup>®</sup> (Dixon, 1988), initially using all terms in equation [2] and then suppressing those with Snedecor's *F* and Student's *t* values smaller than 4 and 2, respectively. The statistics for each equation are shown in brackets.

$$YI = 64.3 + 0.8X_D^2 + 0.6X_T X_D - 2.4X_T - 8.0X_D \quad [\text{Eq. 3}]$$

(multiple-R=0.99; R<sup>2</sup>=0.99; fitted-R<sup>2</sup>=0.99; p<0.009; t>3.21)

$$KA = 59.2 - 0.2X_t + 0.7X_T X_D - 0.9X_T - 5.3X_D \quad [\text{Eq. 4}]$$

(multiple-R=0.99; R<sup>2</sup>=0.99; fitted-R<sup>2</sup>=0.99; p<0.063; t>2.09)

$$VI = 737 - 2X_t - 13X_T - 46X_D \quad [\text{Eq. 5}]$$

(multiple-R=0.99; R<sup>2</sup>=0.99; fitted-R<sup>2</sup>=0.99; p<0.001; t>4.60)

$$SR = 19.4 + 0.3X_T X_t - 0.3X_T X_D + 0.3X_t + 0.6X_T + 1.2X_D^2 - 2.3X_D \quad [\text{Eq. 6}]$$

(multiple-R=0.99; R<sup>2</sup>=0.99; fitted-R<sup>2</sup>=0.98; p<0.055; t>2.24)

$$BL = 2188 - 52X_D - 61X_T - 67X_t - 402X_D^2 - 582X_t^2 \quad [\text{Eq. 7}]$$

(multiple-R=0.99; R<sup>2</sup>=0.98; fitted-R<sup>2</sup>=0.97; p<0.064; t>2.11)

$$ST = 2.67 + 0.07X_T^2 - 0.05X_T + 0.06X_D - 0.08X_t - 0.3X_D^2 - 0.5X_t^2 \quad [\text{Eq. 8}]$$

(multiple-R=0.99; R<sup>2</sup>=0.99; fitted-R<sup>2</sup>=0.98; p<0.043; t>2.40)

$$BI = 1.11 - 0.05X_D - 0.14X_T^2 - 0.08X_t - 0.25X_D^2 - 0.39X_t^2 \quad [\text{Eq. 9}]$$

(multiple-R=0.98; R<sup>2</sup>=0.96; fitted-R<sup>2</sup>=0.94; p<0.087; t>1.92)

$$TI = 0.40 + 0.01X_T X_D + 0.01X_T^2 - 0.01X_D^2 \quad [\text{Eq. 10}]$$

(multiple-R=0.71; R<sup>2</sup>=0.50; fitted-R<sup>2</sup>=0.37; p<0.089; t>1.87)

$$BR = 40.0 + 0.7X_T + 1.2X_D \quad [\text{Eq. 11}]$$

(multiple-R=0.95; R<sup>2</sup>=0.90; fitted-R<sup>2</sup>=0.88; p<0.000; t>5.25)

In these expressions, YI, KA, VI, SR, BL, ST, BI, TI and BR denote yield, Kappa number, viscosity, drainage index, breaking length, stretch, burst index, tear index and brightness, respectively; and X<sub>T</sub>, X<sub>t</sub> and X<sub>D</sub> the normalized values of T, t and D, respectively.

The previous equations reproduced the experimental results of the dependent variables with errors less than 2, 2, 1, 3, 8, 3, 27, 5 and 3% for yield, Kappa number, viscosity, drainage index, breaking length, stretch, burst index, tear index and brightness, respectively. It can be observed that the equation found for the burst index [eq. 9] does not seem to be adapted to predict the experimental results.

The experimental results fitted the polynomial model used quite well, as reflected in the statistics multiple-R, R<sup>2</sup>, fitted-R<sup>2</sup>, *p*, Student's *t* and Snedecor's *F*. As it can be observed, the burst index equation doesn't seem to be adapted to predict the experimental results because the errors made in the estimates are high as well as to the values of multiple-R, R<sup>2</sup>, fitted-R<sup>2</sup>.

The multiple programming method of More and Toraldo (1989) was used to identify the specific values of the independent variables providing the optimum levels of the dependent variables for the pulp and paper sheets (Table 3). Equation (3) allows one to predict the variation of pulp yield with each independent variable on constancy of all others. Thus, the highest yield change (22.47%) would be obtained by varying the diethanolamine concentration at constant temperature and soda concentration (normalized value -1 for both). On the other hand, changing the temperature can be expected to alter pulp yield by 7.88% at most. Figure 1 shows these estimations in graphical form.

Table 3 shows the results obtained by using the above-described procedure with the different dependent variables. As can be seen, obtaining the optimum Kappa number and brightness entails using high temperature, time and diethanolamine concentration values (1 for the three); however, pulp brightness is not influenced by the treatment time. On the other hand, obtaining the optimum vis-

**TABLE III**

Values of the independent variables providing the optimum levels of the dependent variables for the pulp and paper sheets.

| Dependent variable              | Optimum value of the dependent variable (maximum or minimum*) | Values of the independent variables to obtain optimum values for the dependent variables. |                |                | Maxim variations in the dependent variables (in brackets % error vs optimum values). |                  |                              |
|---------------------------------|---|---|----------------|----------------|--|------------------|------------------------------|
|                                 |   | X <sub>r</sub>  | X <sub>t</sub> | X <sub>o</sub> | Temperature  | Time             | Diethanolamine concentration |
| Yield, %                        | 76.1<br>55.4*   | -1<br>1   | -<br>-         | -1<br>1        | 70.1<br>(7.88%)  | -                | 59.0<br>(22.47%)             |
| Kappa index                     | 53.6  | 1   | 1              | 1              | 53.9<br>(0.56%)  | 54.1<br>(0.93%)  | 62.6<br>(17.79%)             |
| Viscosity, mL/g                 | 798   | -1  | -1             | -1             | 772<br>(3.26%)   | 795<br>(0.38%)   | 705<br>(11.65%)              |
| Drainage index, °SR             | 24.4  | 1   | 1              | -1             | 22<br>(9.84%)  | 23.2<br>(4.91%)  | 19.2<br>(21.31%)             |
| Breaking length, m              | 2250  | -1  | -0.1           | -0.1           | 2128<br>(5.42%)  | 1601<br>(28.84%) | 1796<br>(20.18%)             |
| Stretch index, %                | 2.70  | -0.35   | -0.1           | -0.1           | 2.57<br>(4.81%)  | 2.14<br>(20.74%) | 2.33<br>(13.70%)             |
| Burst index, kN/g               | 1.12  | 0   | -0.1           | -0.1           | 0.98<br>(12.5%)  | 0.65<br>(41.96%) | 0.81<br>(27.68%)             |
| Tear index, mNm <sup>2</sup> /g | 0.42  | ±1  | -              | ±0.2           | 0.40<br>(4.76%)  | -                | 0.39<br>(7.14%)              |
| Brightness, %                   | 41.8  | 1   | -              | 1              | 40.4<br>(3.34%)  | -                | 41.8<br>(5.74%)              |

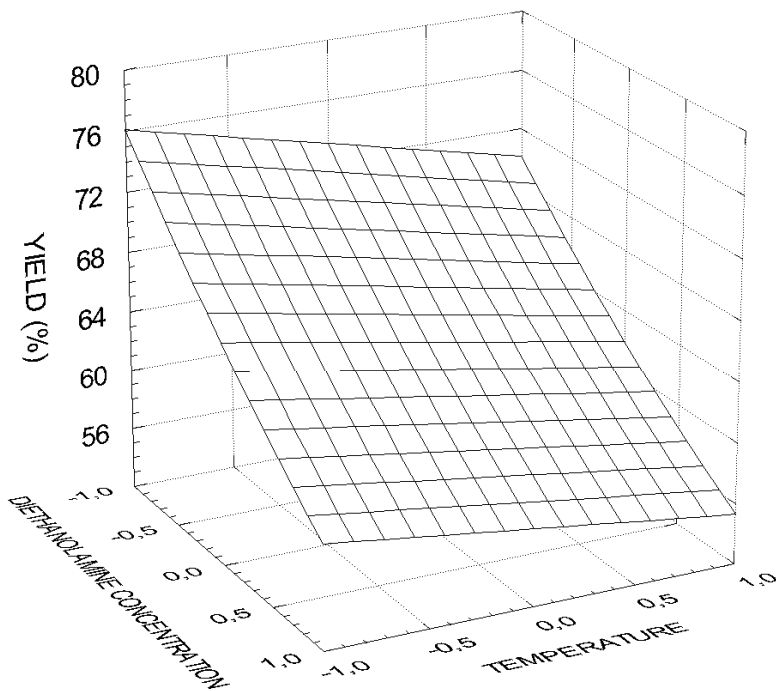


Figure 1. Variation of the pulp yield with diethanolamine concentration and temperature.

osity entails using low values (+1) for the three variables. Finally, ensuring optimal breaking length, stretch and burst index entails using a medium time and diethanolamine con-

centration in addition to a different temperature level for each property.

Equations (3) to (11) can be used to simulate the outcome of using non-optimal values for the operational values (Table 4) in order to obtain pulp and paper sheets with near-optimal values while saving energy, reagents and immobilized capital for industrial facilities by effect of using a lower temperature, time and diethanolamine concentration than those required for optimal results. We found the following combinations to be effective alternatives:

- (a) A medium time (60 min) and diethanolamine concentration (70%) with a low temperature (160 °C).
- (b) A low temperature (160 °C) and time (30 min) with a medium diethanolamine concentration (70%).
- (c) A low temperature (160 °C), medium-low time (45 min) and medium diethanolamine concentration (70%).
- (d) A medium-low temperature (162.5 °C), and a medium time (60 min) and diethanolamine concentration (70%).
- (e) A medium-low temperature (162.5 °C) and time (45 min) with a medium diethanolamine concentration (70%).
- (f) A medium-high temperature (177.5 °C), medium-low time (45 min) and medium diethanolamine concentration (70%).

As can be seen from Table 4, the conditions in (d) appear to be the most suitable as they involve a medium-low temperature (162.5 °C), and a medium time (60 min) and diethanolamine concentration (70%). In fact,

they should provide paper sheets departing by 8% at most from their optimum values while saving reagents, heating energy and immobilized capital for industrial facilities. In addition, the resulting pulp yield and Kappa number should differ by less than 14% from their optimum values.

Table 5 shows the results obtained in the characterization of diethanolamine pulp and paper sheets from *Eucalyptus globulus*, *Pinus pinaster* and a solid residue from the hydrothermal treatment of rice straw at 190 °C for 0 min after the target temperature was reached and a liquid/solid ratio of 8. The three raw materials were processed under the same conditions, namely: a 70% diethanolamine concentration at 162.5 °C for 60 min. The table also gives the results of the characterization of two pulp samples and paper sheets from *E. globulus* and *P. pinaster* obtained by kraft pulping under temperature, time, active alkali and sulphidity conditions similar to those used at an industrial level. The results allow us to draw the following conclusions.

- The pulp yield and beating grade of the pulp obtained by diethanolamine pulping of the solid fraction from a hydrothermal treatment of the rice straw exceeds those for the other pulp types.
- The Kappa number of the rice pulp is greater than those for kraft pulp from eucalyptus and pine, but smaller than those for diethanolamine pulp from these two materials.
- The viscosity of the rice pulp is lower than that of kraft pulp from eucalyptus, but higher than those of the other types of pulp.
- The breaking length of paper sheets obtained from the rice pulp is lower than that for kraft paper from pine, similar to those for kraft and diethanolamine paper from eucalyptus, and higher than that for diethanolamine paper from pine.
- The stretch and burst index of the rice paper are higher than those for all other types of paper except that from kraft pine pulp.

**TABLE IV**

Values of the dependent variables related to pulps and the obtained paper sheets in the pulping with diethanolamine of the solid fraction of the hydrothermal treatment of the rice straw, when operating under the conditions that are specified.

| Dependent variable              | Optimum value of the dependent variable | Value of the dependent variable |      |      |      |      |      |
|---------------------------------|---|---------------------------------|------|------|------|------|------|
|                                 |   | A                               | B    | C    | D    | E    | F    |
| Yield, %                        | 76.1                                    | 66.7                            | 66.7 | 66.7 | 66.1 | 66.1 | 62.5 |
| Kappa index                     | 53.6                                    | 60.1                            | 60.4 | 60.2 | 59.9 | 60.0 | 58.7 |
| Viscosity, mL/g                 | 798                                     | 724                             | 751  | 750  | 746  | 747  | 728  |
| Drainage index, °SR             | 24.4                                    | 18.8                            | 18.8 | 18.8 | 19.0 | 18.9 | 19.6 |
| Breaking length, m              | 2250                                    | 2249                            | 1734 | 2137 | 2233 | 2121 | 2030 |
| Stretch index, %                | 2.70                                    | 2.66                            | 2.27 | 2.58 | 2.68 | 2.60 | 2.53 |
| Burst index, kN/g               | 1.12                                    | 0.98                            | 0.66 | 0.92 | 1.04 | 0.98 | 0.98 |
| Tear index, mNm <sup>2</sup> /g | 0.42                                    | 0.42                            | 0.42 | 0.42 | 0.41 | 0.41 | 0.41 |
| Brightness, %                   | 41.8                                    | 39.2                            | 39.2 | 39.2 | 39.4 | 39.4 | 40.5 |

**TABLE V**

Comparison of the properties of the pulps obtained with diethanolamine and of the corresponding paper sheets, of rice straw and of the solid fraction of a hydrothermal treatment.

| Dependent variable              | Pulp with diethanolamine* of solid fraction of rice strawhydrothermal treatment | <i>Eucalyptus globulus</i> Kraft** | <i>Pinus pinaster</i> Kraft** | <i>Eucalyptus globulus</i> diethanolamine* | <i>Pinus pinaster</i> diethanolamine* |
|---------------------------------|---|------------------------------------|-------------------------------|--|---------------------------------------|
| Yield, %                        | 66.1  | 51.5                               | 40.9                          | 55.3                                       | 38.4                                  |
| Drainage index, °SR             | 19.0  | 12.3                               | 12.8                          | 11.5                                       | 13                                    |
| Kappa index                     | 59.9  | 15.5                               | 28.0                          | 87.6                                       | 176.6                                 |
| Viscosity, mL/g                 | 746   | 832                                | 575                           | 259  | 135                                   |
| Breaking length, m              | 2233  | 2399                               | 3878                          | 2504                                       | 1771                                  |
| Stretch index, %                | 2.68  | 0.70                               | 2.87                          | 0.71                                       | 0.89                                  |
| Burst index, kN/g               | 1.04  | 0.22                               | 3.23                          | 0.19                                       | 0.55                                  |
| Tear index, mNm <sup>2</sup> /g | 0.41  | 0.24                               | 1.32                          | 0.24                                       | 0.55                                  |
| Brightness, %                   | 39.4  | 59.4                               | 54.9                          | 46.2                                       | 42.3                                  |

\* = 70% diethanolamine, 162.5°C, 60 minutes and 8 liquid-solid ratio. \*\*= 16% active alkali 25% sulphidity, 170°C, 40 minutes and 4 liquid-solid ratio. \*\*\*= 20% active alkali 30% sulphidity, 170°C, 40 minutes and 4 liquid-solid ratio.

- The tear index of the rice paper is higher than those for kraft and diethanolamine paper from eucalyptus, but lower than those for kraft and diethanolamine paper from pine.
- The brightness of the rice pulp is lower than those of all other types of pulp.

## CONCLUSIONS

Based on the results of the chemical properties of pulps and paper sheets made from it, diethanolamine pulping of solid fraction residual of a hydrothermal treatment of rice straw provides an effective choice with a view to valorizing the agricultural residues produced by rice crops. In fact, pulp and paper sheets from solid fraction residual of a hydrothermal treatment of rice straw possess acceptable properties relative to *Eucalyptus globulus* and *Pine pinaster* pulps obtained with Kraft reagent and diethanolamine. Rice straw therefore constitute an effective alternative pulping raw material in as much as they provide pulp and paper sheets with acceptable properties and allow an agricultural residue from a major economic activity (*viz.* rice production) to be exploited.

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