

Research Article

NIRS Characterization of Paper Pulps to Predict Kappa Number

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Rice is one of the most abundant food crops in the world and its straw stands as an important source of fibres both from an economic and an environmental point of view. Pulp characterization is of special relevance in works involving alternative raw materials, since pulp properties are closely linked to the quality of the final product. One of the analytical techniques that can be used in pulp characterization is near-infrared spectroscopy (NIRS). The use of NIRS has economic and technical advantages over conventional techniques. This paper aims to discuss the convenience of using NIRS to predict Kappa number in rice straw pulps produced under different conditions. We found that the resulting Kappa number can be acceptably estimated by NIRS, as the errors obtained with that method are similar to those found for other techniques.

1. Introduction

The use of wood as the main raw material in the pulp and paper industry is related to some economic and environmental issues. Wood prices make up the largest part of the costs of cellulose pulp production. While most of the wood comes from plantation forests, this has raised some controversy due to some natural forests having been replaced by monocultures. These are two of the reasons that have fostered research into the use of alternative, nonwood raw materials in response to environmental and economic pressure. In fact, nonwood raw materials constitute the sole effective source of cellulose fibre in some regions of the world where wood is a scarce resource [1–4].

Rice for human consumption belongs commonly to species *Oryza sativa* or *Oryza glaberrima*; the latter, however, is much less widely used than the former and its production is restricted to West Africa [5]. Rice straw is an abundant nonwood raw material due to the large disposal of it which takes place during the harvest which poses serious problems to farmers. 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 valorisation. One way is by using it as animal feed; however, advocates and detractors of this use disagree on the actual protein value and the digestibility of the material [6]. Another way is by using straw ash or husk ash, which is similar in composition, to extract silicon [7]. This substance can also be obtained from the liquors of alkaline and acid treatments [8]. In any case, using rice straw to produce cellulose pulp [9] is the most attractive choice.

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 leads to a new focus on the use of alternative raw materials and the development of pulping processes which cause less environmental impact (soda, soda-anthraquinone) [10].

Pulps characterization has special relevance in studies related to the use of alternative raw materials through less polluting processes in the pulp and paper industry. Pulp properties are closely linked to the quality of the final product.

However, conventional techniques imply a high consumption of reagents and time for its realization. At the same time, the destruction of samples during the process hinders the execution of subsequent determinations that could favour the knowledge of other parameters of special interest [11].

From the 1950s, near-infrared spectroscopy (NIRS) began to get known, and its possibilities were foreseen. Previously, only MIR and FIR spectroscopy were considered useful, since they allowed for analysing individual components present in each sample [12]. NIRS began to be used in the characterization of organic compounds from the 60s and its use has been extended to the control of almost all processes in food, pharmaceuticals, textile, chemical, petrochemical, and medical industries [13, 14].

NIRS has a number of advantages over conventional techniques: it suits solids, liquids, and gases and does not require sample pretreatment; the spectral recording and analysis of routine are fast; it is nondestructive and allows for multicomponent analysis and in-line analysis, and it is inexpensive [15].

NIRS is a powerful and fast tool for the determination of the constituents of wood [16, 17]. There are precedents for the use of the near-infrared spectroscopy for the determination of yield [18] and Kappa number of pulps from hardwoods and softwoods [19, 20]. Absorption bands observed in the reflectance of the wood spectra arise from the emission of electromagnetic waves produced by the overtones and combinations of C–H, C–O, N–H, and O–H [18].

The difficulty of NIRS application lies in the nature of spectra combined with the existence of multiple peaks which overlap. Therefore, it is necessary to develop advanced chemometric techniques helping to decipher the wide range of information provided by the spectra. Instruments and software developments have allowed great advances in the applicability of the technique [21].

Multivariate calibration can be difficult to perform, and it generally requires quantitative and qualitative knowledge of the properties of the samples to be analysed. In order to extract valuable information, different chemometric techniques can be used: principal components analysis (PCA), partial least squares (PLS), and multivariate resolution of curves (MCR), to name a few.

In the pulp and paper industry, the determination of the Kappa number is a parameter of special significance, since it is an indirect method to estimate the content of residual lignin and an indicator of bleachability [22]. The aim of this study is to evaluate the potential of NIR technology as a substitute for conventional trials in the determination of the Kappa number. The influence of the variables involved in the cooking process of rice straw on Kappa number has been studied, and so has their relationship with the NIR spectra obtained.

2. Materials and Methods

2.1. Raw Material. The rice species used in this study are *Oryza sativa* (Asiatic) and *Oryza glaberrima* (African). Rice from both species was grown in the Southeast of Spain and its straw was harvested.

2.2. Pulping. Pulps were obtained by cooking rice straw in a 15 L batch cylindrical reactor that was heated by means of electrical resistances. Rice straw was placed in the reactor together with soda and anthraquinone and pulped by using a reagent concentration, temperature, cooking time, and a liquid/solid ratio as shown in Table 1. The operating conditions have been chosen based on previous works [2]. The reactor was linked through an axle to a control unit, which included a motor actuating the reactor and instruments for measurement and control of pressure and temperature. Afterwards, 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. The washed 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.

2.3. Experimental Design. Pulping processes have been modelled in various ways for the estimation of Kappa number in terms of process variables, in order to optimize the operating conditions accordingly.

Most of the existing models are kinetic equations. However, to the best of our knowledge, few researchers have used a factorial design that allows for the development of empirical models with several independent variables, to examine the Kappa number. These empirical models are preferable to the mechanistic ones, since the latter are too complex when they contain more than two independent variables.

In this work, we chose a factorial design consisting of a series of points (tests) around a central composition point (central test).

The total number of tests required for the five independent variables studied (namely, temperature (T), time (t), soda concentration (S), anthraquinone concentration (A), and liquid/solid ratio (H)) was found to be 27.

The values of the independent variables were normalized:

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

where X_n is the normalized value of temperature (T), time (t), or liquid/solid ratio (S); X is the absolute experimental value of the variable concerned; \bar{X} is the mean of the extreme values of X , and X_{\max} and X_{\min} are its maximum and minimum value, respectively. Experimental conditions and normalized values are shown in Table 1.

The experimental data were fitted to the following second order polynomial model:

$$Y = a_0 + \sum_{i=1}^n b_i X_{n,i} + \sum_{i=1}^n c_i X_{n,i}^2 + \sum_{i=1}^n b_i X_{n,i} X_{n,j}, \quad (2)$$

where $i < j$. X_n represent the normalized values of the process variables (time, temperature, concentration of reagents, etc.). The coefficients a_0 , b_i , c_i , and d_{ij} are constants to be estimated from the experimental data.

2.4. Determination of Kappa Number. Kappa number was determined in accordance with ISO 302:2004, applicable for

TABLE 1: Values of operating variables used in the design of experiments.

Experiment	T , °C	t , min	Soda, %	Anthraquinone, %	Liquid/solid ratio	X_T	X_t	X_S	X_A	X_H
1	170	60	15	0.5	6	0	0	0	0	0
2	155	30	10	1	4	-1	-1	-1	1	-1
3	155	30	10	0	8	-1	-1	-1	-1	1
4	155	30	20	1	8	-1	-1	1	1	1
5	185	60	15	0.5	6	1	0	0	0	0
6	170	60	15	1	6	0	0	0	1	0
7	170	30	15	0.5	6	0	-1	0	0	0
8	170	60	10	0.5	6	0	0	-1	0	0
9	185	30	10	1	8	1	-1	-1	1	1
10	185	30	20	1	4	1	-1	1	1	-1
11	170	60	20	0.5	6	0	0	1	0	0
12	170	90	15	0.5	6	0	1	0	0	0
13	185	30	20	0	8	1	-1	1	-1	1
14	170	60	15	0.5	8	0	0	0	0	1
15	155	60	15	0.5	6	-1	0	0	0	0
16	185	90	10	0	8	1	1	-1	-1	1
17	170	60	15	0	6	0	0	0	-1	0
18	155	90	20	0	8	-1	1	1	-1	1
19	185	90	20	0	4	1	1	1	-1	-1
20	155	90	20	1	4	-1	1	1	1	-1
21	185	90	20	1	8	1	1	1	1	1
22	155	90	10	1	8	-1	1	-1	1	1
23	185	90	10	1	4	1	1	-1	1	-1
24	155	30	20	0	4	-1	-1	1	-1	-1
25	155	90	10	0	4	-1	1	-1	-1	-1
26	170	60	15	0.5	4	0	0	0	0	-1
27	185	30	10	0	4	1	-1	-1	-1	-1

X_T , X_t , X_S , X_A , and X_H = normalized values of temperature (T), time (t), soda concentration (S), anthraquinone concentration (A), and liquid/solid ratio (H), respectively.

a wide range of values, from 1 to 100. It aims to determine the degree of delignification of pulp. It is defined as the volume (in mL) of a 0.1N solution of potassium permanganate that is consumed per gram of dry pulp. Iodometric titration was performed to measure permanganate consumption. Three repetitions were made for each test.

2.5. NIR Spectroscopy Analysis. All samples were scanned by duplicate with a Foss NIRSystems 6500 monochromator (Foss NIRSystems, Silver Spring, MD, USA) using the WinISI II 1.5 software (Infrasoft International, Port Matilda, PA, USA). This software was also used for the treatment of the spectral data obtained. The visible and NIR (VNIR) spectra (400 to 2500 nm) were collected at 2 nm intervals. Samples were placed in a rectangular cell with a $4.5 \times 5.5 \text{ cm}^2$ quartz window.

2.6. Spectral Data Analysis. Spectral data analysis and calibration equations were performed with WinISI II 1.5 software (Infrasoft International, Port Matilda, PA, USA). Data of calibration sets were subjected to spectral pretreatments combined with mathematical pretreatments. Standard normal

variate (SNV) and Multiplicative scatter correction (MSC) were used as spectral pretreatments [23].

SNV is often used on spectra where baseline and path length changes cause differences between otherwise identical spectra. Mathematically, it is identical to an autoscaling of the rows instead of the columns of the matrix.

Multiplicative scatter correction (MSC) is achieved by regressing a measured spectrum against a reference spectrum and then correcting the measured spectrum using the slope and intercept of this linear fit. This pretreatment method has proven to be effective in minimizing baseline offsets and multiplicative effect.

As for mathematical pretreatments, first and second derivatives were used to reduce baseline variation and enhance spectral features. Two preprocessing methods were evaluated: (1,4,4,1) and (2,5,5,1). The numbers in parentheses, respectively, designate the order of the derivative, the gap, the first smoothing, and the second smoothing [24].

Calibration in all cases was based on full cross-validation. Modified partial least square regression (MPLSR) [22] was used to relate spectra with the measured values of dependent variables. Multivariate regression was carried out using the partial least squares (PLS) algorithm.

The residuals obtained after the calculation of each regression term in the modified partial least squares (MPLS) regression were standardized dividing by the standard deviation before the calculation of the next regression term. According to Shenk and Westerhaus [25], the number of terms was fixed when the SECV presented a minimum value before overfitting.

The different pretreatments were characterised by calculating the standard error of cross-validation (SECV) and the coefficient of determination of cross-validation (1-VR). Two measurements of each sample were used to estimate the standard error of the reference method (ETL):

$$\text{ETL} = \sqrt{\frac{\sum (y_1 - y_2)^2}{2N}}, \quad (3)$$

where y_1 and y_2 are the values obtained for a sample and its repetition and N is the number of data pairs used to calculate the ETL.

3. Results and Discussion

Table 2 gives the results of the tests (Kappa number) as the averages of three determinations for each set of independent variables. Relative standard deviation was never higher than 5%.

We dealt with experimental data by using nonlinear regression to fit them to a polynomial model of second degree described in the experimental part (see (2)). This regression analysis is conducted considering five independent variables, these same variables to the square and its products two to two, thus neglecting higher order terms.

The statistically significant terms of the polynomial model were selected with the double standard of having a value of Snedecor's F greater than 4 and a Student's t greater than 2.0. Also, coefficients whose 95% confidence interval included 0 were discarded.

We found the following equation:

$$KN = 10.9 + 1.7X_A X_H - 2.0X_t - 2.2X_S - 2.6X_T. \quad (4)$$

As expected, time, soda concentration, and temperature were found to be the most influencing independent variables. Equation (4) also shows that there is a significant interaction between anthraquinone concentration and the liquor-to-solid ratio.

Statistical parameters of the model are shown in Table 3. This model provides a good fit of the experimental data to the polynomial model, as indicated by the values of R -multiple, R^2 , R^2 -adjusted, Student's t (given for a 95% confidence level), and Snedecor's F of the terms of (4).

According to the model, the lowest value of Kappa number that can be obtained, as long as the values of independent variables fall into the intervals considered, is 2.40. The values needed to achieve that local optimum are temperature of 185°C, time of 90 min, 20 grams of soda per 100 grams of dry pulp, 1 gram of anthraquinone per 100 grams of dry pulp, and a liquid-to-solid ratio of 4. If a brighter pulp with a lower Kappa number is desired, operating under more severe conditions is necessary.

TABLE 2: Kappa number values obtained by iodometric titration for the different operating variables of the experimental design.

X_T	X_t	X_S	X_A	X_H	Kappa number
0	0	0	0	0	9.4
-1	-1	-1	1	-1	16.5
-1	-1	-1	-1	1	16.8
-1	-1	1	1	1	16.0
1	0	0	0	0	8.8
0	0	0	1	0	9.3
0	-1	0	0	0	11.6
0	0	-1	0	0	11.7
1	-1	-1	1	1	14.8
1	-1	1	1	-1	6.7
0	0	1	0	0	8.9
0	1	0	0	0	9.2
1	-1	1	-1	1	7.1
0	0	0	0	1	9.3
-1	0	0	0	0	14.5
1	1	-1	-1	1	7.8
0	0	0	-1	0	9.5
-1	1	1	-1	1	8.1
1	1	1	-1	-1	6.4
-1	1	1	1	-1	8.0
1	1	1	1	1	6.5
-1	1	-1	1	1	15.3
1	1	-1	1	-1	7.2
-1	-1	1	-1	-1	15.1
-1	1	-1	-1	-1	16.2
0	0	0	0	-1	9.4
1	-1	-1	-1	-1	15.2

TABLE 3: Values of statistical parameters for the fitting of experimental data (Kappa number) to (4).

Fitting parameter	R -multiple	R^2	R^2 -adjusted	$t >$
Value	0.96	0.93	0.92	6.69
Equation term	$X_A X_H$	X_t	X_S	X_T
Snedecor's F	44.71	65.48	80.23	112.55

As can be seen from Figure 1, all spectral data were summarized in a few variables (PLS terms of multivariate regression) with good correlation with reference values. In the graph, the predicted values (x -axis) do not deviate in more than 8% from the reference values (y -axis).

In order to determine the relevance of the simultaneous analysis of visible and NIR (VNIR) spectroscopy with the aim to perform forecasting based only with NIRS, a set of trials were carried out using both analytic methods. The VNIR trials were carried out in a spectral region between 400 and 2500 nm and the NIR samples were processed in a spectral region between 1100 and 2500 nm, as Figure 2 shows. Figure 2(a) shows the whole near-infrared spectrum with no mathematical pretreatment, while Figure 2(b) focuses on the

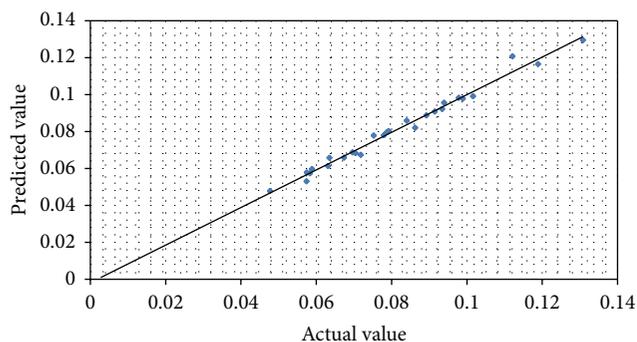
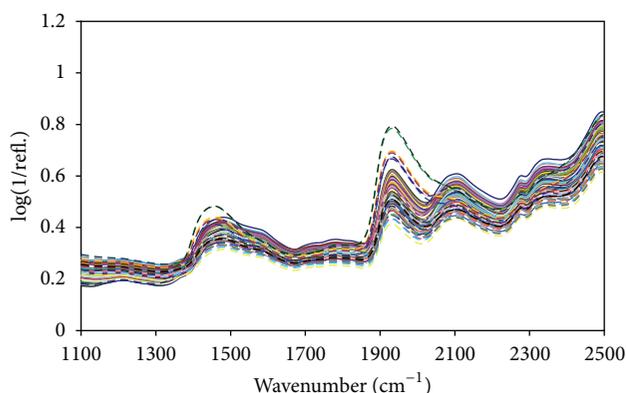
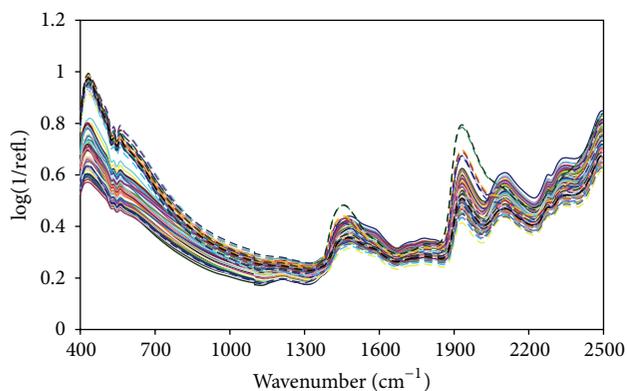


FIGURE 1: Correlation of the PLS terms with spectral data.



(a)



(b)

FIGURE 2: Near-infrared (NIR) and visible NIR (VNIR) spectra for the samples.

visible part. The whole NIR spectrum shows a peak outside of the visible region, at 450 cm^{-1} .

As it is shown in Table 4, the reference error (ETL) used in the calculation of Kappa number was 0.11. The error (as SECV) obtained by the mathematical method (1,4,4,1) in the trials carried out for NIR was lower than that obtained by the mathematical methods (2,5,5,1) for NIR. The coefficients of determination of cross-validation (measurement of the expected explained variation) obtained support the use of the NIR prediction method for the determination of Kappa index

TABLE 4: Comparison between the errors obtained by VNIR, NIR, and the standard error of the reference method (Kappa number).

Treatment	SECV	1-VR	ETL	CV (%)
1, 4, 4, 1_VNIR	0.13	0.92		
2, 5, 5, 1_VNIR	0.12	0.87		
1, 4, 4, 1_NIR	0.15	0.89	0,11	7,8
2, 5, 5, 1_NIR	0.18	0.85		

present in the raw matter studied. CV (%), the coefficient of variation, is acceptably low.

These results show that the Kappa number obtained after different cooking processes can be predicted by means of a direct measurement of rice straw pulp, using near-infrared spectroscopy.

4. Conclusions

The errors (SECV) obtained in the measurements carried out for VNIR and NIR were similar. The results obtained using a spectral scanning of VNIR and NIR do not show a significant variation between both of the systems used.

The use of NIR technology can be seen as a viable alternative method to predict Kappa number in rice straw pulp subjected to different treatments. The NIR technology also has the additional advantage of being a fast, nondestructive technique that does not need any sample pretreatment. Therefore, the cost and the environmental impact are diminished by removing the chemical reagents needed for other ways to measure Kappa number.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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