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Short communication

# relating near infrared spectra of *Oryza sativa* pulps to paper mechanical strength and brightness

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ABSTRACT

Rice straw pulps produced under different conditions were subject to near infrared (NIR) spectroscopy. At the same time, samples from those pulps were used to make handsheets, whose mechanical properties were measured. These values and those of brightness were successfully fitted to the pulping variables. Relating them to the NIR spectra, we found valid correlations for all parameters except the burst index, concluding that NIR spectroscopy could be used as an economical, timesaving and non-intrusive way to predict the mechanical strength of pulps before the paper sheet is made.



## 1. Introduction

The conventional way to remove the great amounts of straw left after the harvest of *Oryza sativa* (Asian rice) is open-field burning, which is hazardous to the environment. Different applications allow for reusing rice straw, such as the production of nanosilica (Carmona et al., 2013), energy (Yu et al., 2008), cellulosic ethanol (Castro and Roberto, 2015), and cellulosic pulp for the paper and board industry (Rodriguez et al., 2008). Since this industry is regarded as a source of pollution and bad odours (Pinkerton, 2007), it needs to invest resources in alternative raw materials and cleaner production. However, one of the most important concerns is whether sulphur-free pulping of these materials will result in mechanical properties that can compete with those of kraft pulps from hardwoods and softwoods (Moral et al., 2016).

Conventional techniques to measure mechanical properties are time-consuming and destructive. We hypothesise that near infrared spectroscopy (NIRS) can be used to predict brightness and key mechanical properties of paper sheets, saving time and preserving the sample. Among other applications with fibre-based materials, researchers have successfully tried NIRS to determine the sucrose content in sugar beet (Pan et al., 2015), to estimate the quality of hardwood pulps (Michell, 1995), to quantify carbohydrates in pulp rejects (Moral et al., 2012), and to study the composition of sweet potato (Diaz et al., 2014). Henriksen et al. (2004) proposed calibration methods to estimate two key properties of sulphite pulps, kappa number and intrinsic viscosity. Sandak et al. (2015) found variations in bands 4283, 4400, 4742 and 4808 $cm^{-1}$ as breaking length decreased by fungal degradation. Nonetheless, as far as we are concerned, no studies involve NIRS to assess the determination of mechanical properties of virgin fibres after pulping.

In this communication, the potential of NIR technology to replace conventional trials in the determination of key properties (brightness, breaking length, strength, tear index, burst index) of rice straw pulp is evaluated. We address the influence of cooking variables on said properties, using a fractional experimental design with five factors and three levels. The data sets obtained by NIRS are treated through different chemometric methods to remove systematic noise. Modified partial least square (MPLS) regression is used to relate NIR spectra to the values of the mechanical properties measured.

## 2. Materials and methods

Rice from species *Oryza sativa* was grown in the South-East of Spain, harvesting its straw. Rice straw was analysed according to TAPPI standards: T-9m54 for holocellulose, T-203 os-61 for α-cellulose, T-222 for lignin, T-211 for ashes and T-204 for extractives.

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The experimental tasks are schematised in Fig. 1. Pulping was followed by washing and screening, but we omitted these common steps in the diagram.

To predict key properties related to paper mechanical strength from the most relevant pulping variables, we proposed a central composite design (CCD). With five independent variables and three levels, the smallest amount of different experiments is 27 (Montgomery, 1991). Table 1 shows the operational conditions. $X_T$, $X_t$, $X_S$, $X_A$ and $X_H$ are the normalised values of temperature (T), time (t), soda concentration (S), anthraquinone concentration (A) and liquid/solid ratio (H), respectively. The dependent variables and the inputs were fitted to a second order polynomial equation with the BMDP package.

We used the WinISI II 1.5 software (Infrasoft International) both to obtain and to treat the spectral data. *Standard Normal Variate* (SNV) and *Multiplicative Scatter Correction* (MSC) were used for signal correction (Gemperline, 2006).

Two mathematical treatments were tested: (1,4,4,1) and (2,5,5,1), on the NIR region only and on both the visible and NIR regions (VNIR). The numbers in parentheses respectively define the order of the derivative, the gap, the first smoothing and the second smoothing (Heise and Winzen, 2002).

In order to relate the data sets from NIRS to the measured values of dependent variables, multivariate regressions were carried out using a modified partial least squares (MPLS) algorithm. The number of terms was fixed when the standard error of cross-validation (SECV) reached a value of 0.1 or higher before overfitting (Schimleck et al., 1997). SECV and the coefficient of determination of cross-validation (1-VR) were determined by an iterative algorithm, using 18 samples for the calibration and the remaining 9 samples for the prediction.

## 3. Results and discussion

### 3.1. Chemical characterisation

The holocellulose content in rice straw samples was found out to be 60.7%, more than a half of it (67,9%) being α-cellulose. These measurements were lower than those showed by other authors who analysed rice straw (Hasanjanzadeh et al., 2014). Klason lignin was determined to be 21.9%, while the percentage of ashes was 9.2%. Extractives accounted for 7.3% of the raw material.

### 3.2. Characterisation of paper sheets

Table 1 shows the measured values for the breaking length (*BL*), the stretch (*ST*), the burst index (*BI*), the tear index (*TI*) and the ISO brightness (*BR*), which are the dependent variables in Eqs. (1)–(5). The statistical parameters of these non-linear regressions are presented in Table 2. Regressions showed a strong correlation for all mechanical properties, with high values of adjusted $R^2$ (higher than 0.95), the p-value of any of the terms being always lower than 0.05, and their Student's *t* always higher than 2. For brightness, however, a good correlation could not be found.

$$BL = 2782 + 13X_tX_S - 32X^2{}_T - 34X_t + 50X_TX_S - 113X_S{}^2 - 92X_T + 225X_S \quad (1)$$

$$ST = 2.30 + 0.04X_A + 0.05X_TX_S + 0.05X_t + 0.18X^2{}_S + 0.3X_T + 0.31X_S \quad (2)$$

$$BI = 1.64 + 0.01X_A + 0.02X_AX_H + 0.02X_TX_S - 0.03X_tX_S + 0.04X_TX_t + 0.07X^2{}_S - 0.09X_t - 0.11X_T + 0.41X_S \quad (3)$$

$$TI = 0.46 - 0.01X_TX_S - 0.01X^2{}_A - 0.01X_AX_H - 0.01X_tX_S + 0.01X_A + 0.02X^2{}_S - 0.02X_t - 0.02X_T + 0.06X_S \quad (4)$$

$$BR = 57.8 - 2.6X_AX_H + 2.9X_t + 3.1X_S + 3.6X_T \quad (5)$$

Breaking length was favoured by a high reagent concentration. Too high temperatures seemed to lead to significant hydrolysis of cellulose chains, which was translated into lower values of breaking length and stretch (experiments 4, 11 and 20). For these mechanical properties, the influence of liquid-to-solid ratio was deemed insignificant. The tear and burst indices were difficult to predict, but the concentration of soda and anthraquinone clearly showed a positive effect on them. Anthraquinone protects carbohydrates from alkaline degradation, whilst soda removes lignin, improving fibre-to-fibre bonding. Brightness, as expected, was found to increase with soda concentration, temperature and time. These brightness values after pulping, always above 49%, were in the high range for unbleached pulps.

### 3.3. Near infrared spectra

Fig. 2 shows the spectra obtained for all the 27 experiments, with MSC and SNV pretreatments. The visible range (400–800 nm or $25 \times 10^3$–$12.5 \times 10^3$ $cm^{-1}$, approximately) is also presented to determine whether this prediction should be carried out with NIRS only or it is advisable to consider the whole visible and near infrared (VNIR) range.

At 1400 nm or 7100 $cm^{-1}$, a reordering of the spectra occurs. The spectrum for the experiment 16, which was in the high range, starts showing the lowest absorbance values. Likewise, the spectrum 4 was in the low range in the visible region, but has the highest absorbance values in the most part of the near infrared region. Remarkably, experiment 16 resulted in the worst breaking length and one of the highest brightness values, while experiment 4 showed very low brightness and one of the best performances in tensile tests.

These spectra are similar to those found in literature for cellulose and lignocellulosic materials (Henriksen et al., 2004; Schimleck et al., 1997). Near 1212 nm, a band assigned to the second overtone of C—H stretching in polysaccharides is found, while the first overtone is located at 1764 nm. The absorption band at 1490 nm is normally associated with interactions between O—H groups in cellulosic chains (polymeric O—H). Near 1580 nm, a change of slope can be appreciated, and it can be assigned to the O—H combination band of water. The following regions are related to C—O stretching, O—H stretching and O—H bending in cellulose and hemicellulose. The combination bands after 2200 nm, mainly assigned to C—H stretching and C—H bending, are influenced by the functional groups of lignin, due to overtones of aryl C—H bonds occurring at 2208 and 2545 nm (Workman and Weyer, 2012).

### 3.4. Potential of NIRS to predict mechanical properties of paper

The statistical parameters allowing to compare NIRS prediction with measured values are presented in Table 3. The prediction was unsuccessful for the burst index, as the coefficient of determination of cross-validation (1-VR) was 0.7 in the best case, after the