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Determination of Mechanical and Optical Properties of Eucalyptus Kraft Pulp by NIR Spectrometry and Multivariate Calibration

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Abstract: Multivariate data analysis and NIR spectrometry were used to determine the mechanical and optical properties of eucalyptus kraft pulps with different chemical compositions and refined to different levels. Tear (TrID), tensile (TsID), burst (BuID), and bending (BeID) indexes and elastic modulus (EM), stretch (ST), and breaking length (BL) were the mechanical properties measured. Measurement of beating degree (SR) was also achieved. Light scattering (LS) and light absorption (LA) coefficients were the optical properties measured. Mechanical and optical properties were modeled using NIR spectra obtained on pulp hand sheets by diffuse reflectance and application of the partial least squares (PLS) method. Models with two to seven PLS components and very good predictive ability were established after testing the first-derivative, Kubelka-Munk, or a combination of both as pre-processing techniques. Models were validated by using cross-validation methodology and a comparison of measurements

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using conventional methods for new samples. The predictive models can reduce time in traditional measurements in the pulp and paper industry and are suitable for direct application using “at-line” conditions. As an additional benefit, improvements in process monitoring and paper quality can be achieved.

Keywords: Eucalyptus, chemical pulping, refining, strength, PLS

INTRODUCTION

Pulp and paper are complex materials formed by components located in specific domains and with diverse chemical, morphological, and physico-chemical properties. As a consequence, a large number of process and product variables should be monitored to achieve quality and performance standards. Process monitoring and quality control are time consuming and expensive activities in pulp and paper mills because in most cases each property measured requires a specific instrument, sample preparation, and conditioning. A routine characterization of mechanical and optical properties of paper products can take several hours if traditional methods are used. In contrast, the development of “at-line” and “on-line” methods using spectrometry and multivariate calibration has increased in the recent years, offering alternatives of fast and reliable measurements at low cost.^[1–3]

Near infrared spectrometry (NIR) has emerged as a versatile and attractive technique either for “at-line” or “on-line” methods.^[4–7] The main advantages of NIR are the minimal sample pre-treatment required, its non-destructive character, and the fast and easy applicability for many different materials.^[5,8] The combination of NIR and fiber optic technology for process monitoring is also one of the most attractive and promising features for “on-line” application of this technique. However, breakthroughs in this area are still dependent on development of proper sensors and sampling devices. On the other side, the usual drawbacks of NIR measurements such as the presence of overlapping peaks in the spectral data, non-linearity between apparent absorbancy and concentration, specificity of calibrations, and sensitivity to matrix effects have been contoured by application of linear transforms and multivariate calibration. Pre-processing of spectra using Kubelka-Munk transform, multiplicative scatter correction, first and second derivatives, and orthogonal signal correction were reported to improve non-linearity and matrix effects.^[9–12] Multivariate calibration methods using classical least squares (CLS), multiple linear regression (MLR), principal components regression (PCR), and partial least squares (PLS) were shown to be suitable for a large number of applications.^[13–16]

Investigations using NIR and multivariate calibration for predictions of the chemical composition of wood and pulp have been extensively reported.^[17–21] In addition to the differences in chemical composition, NIR spectroscopy has proved to be sensitive to structural changes of cellulose and intermolecular

interactions between cellulose, hemicelluloses, and lignin.^[22,23] Thus, NIR spectrometry can also be suitable to detect changes in mechanical properties because they are directly related to the intra- and intermolecular interactions present in the pulp materials. The prediction of mechanical properties of pulps has usually been done by NIR reflectance measurements on milled samples in order to reduce matrix effects.^[24,25] In contrast, this approach impairs determination of optical properties such as light scattering and on-line measurements. Applications of NIR for on-line determinations of kappa number,^[26] total organic carbon, carbohydrates and lignin content in cooking liquor,^[27] and total alkali in white and green liquor^[28] were recently attempted. In this work, we present a combination of NIR and multivariate calibration models for prediction of mechanical and optical properties of eucalyptus pulps refined to different levels. The matrix effects in spectral acquisition were compensated for by an integrating sphere used in the diffuse reflectance measurements of pulp hand sheets. The NIR method was suggested to be applied as “at-line” in a routine laboratory in a pulp or paper mill.

MATERIALS AND METHODS

Wood and Pulps

Wood of *Eucalyptus grandis* trees, eight years old, was used to make chips employing an industrial chipper. Chip fractions in the width range of 2–5 mm and length range of 16–45 mm were selected for kraft pulping using a bar and hole chip classifier. Seven kraft pulp samples were prepared in a 20-L laboratory digester using active alkali of 12, 14, 16, 18, 20, 22, and 24% as Na₂O, respectively. The reactor conditions, the same in all experiments, were: pulping temperature $165 \pm 2^\circ\text{C}$, heating rate $2.8 \pm 0.1^\circ\text{C}/\text{min}$, sulfidity $21 \pm 0.1\%$ as Na₂O, liquor-to-wood ratio of 4:1, H factor of 400 ± 20 and 1000.0 g of chips (o.d.). After pulping the unbleached pulps were washed with tap water until the pH of the filtrate was around 6.8 to simulate industrial conditions. Samples were identified according to the active alkali used in pulping as F12, F14, F16, F18, F20, F22, and F24.

Kappa Number and Intrinsic Viscosity of Pulps

Kappa number and intrinsic viscosity (IV) were determined according to TAPPI T 236:85 and SCAN C15-16:62, respectively.

Mechanical and Optical Properties

Pulps were refined in a Papirindustriens Forsknings Institutt (PFI) mill using 1500, 3000, 4500, and 6000 revolutions according to ISO 5264-2. All

mechanical properties were measured on pulp hand sheets prepared with a Rapid Köthen apparatus using deionized water and properly conditioned at a temperature of $23 \pm 1^\circ\text{C}$ and relative humidity of $50 \pm 2\%$. Tear (TrID), burst (BuID), and tensile (TsID) indices were determined according to ISO 5270. Elastic modulus (EM) was determined according to ISO 1924-2 and bending index (BeID) according to ISO 2493. Stretch (ST) and breaking length (BL) were measured according to ISO 1924-2. Refining degree as indicated by Schopper-Riegler drainability was measured according to ISO 5267-1. Light scattering and light absorption were measured using a DATACOLOR 3000 spectrometer according to TAPPI T 220 om-88. At least 10 handsheets were analyzed for each mechanical property. The hand sheets were identified according to the number of PFI revolutions used in refining as A (0), B (1500), C (3000), D (4500), and E (6000). The analytical variations were determined by calculation of coefficient of variation (CV) for each property. Measured CVs ranged up to 14%.

Diffuse Reflectance Near Infrared Spectrometry

NIR spectra were obtained using a Perkin Elmer Lambda 19 spectrometer equipped with a 60-mm integrating sphere, coated with BaSO_4 . A scanning rate of 120 nm/s and a resolution of 1 nm were used in the range of 900–2200 nm for pulp hand sheets. The original NIR spectra were converted to Kubelka-Munk and first derivative modes using the software Perkin Elmer Spectrum One.

Multivariate Data Analysis

Partial least squares (PLS) in combination with a non-iterative PLS (NIPALS) algorithm was used for model building and calculation of model parameters, respectively.^[15] In this method, dependent variables such as mechanical and optical properties and refining response were grouped in different **Y** blocks, one for each dependent variable, whereas the spectra or independent variables were grouped in an **X** block. The **X** and **Y** blocks were decomposed using NIPALS to a sum of outer products of vectors called scores (t) and loadings (p). An additional set of vectors termed weights (w) was also calculated in order to improve the relation between the two blocks. NIPALS used t , p and w to calculate a vector of “inner relationship” coefficients which related **X** and **Y** block scores. Residuals for **X** and **Y** blocks and regression coefficients (b) were also calculated for each PLS component.^[15] The calculated t , p , w , and b were saved for each PLS component. The number of PLS components in each PLS model was determined by cross validation methodology, which calculates the lack of prediction accuracy, called prediction residual error sum of squares (PRESS). The number of PLS components

that yielded the lowest PRESS was used for model building. The PLS calibration model was used for prediction of mechanical and optical properties and refining response by decomposing the independent block **X** and building up a new dependent **Y** block. A set of 5 samples obtained and characterized in a similar way as the calibration set was used for comparing conventional analytical methods and prediction using NIR and multivariate calibration models. Multivariate calibration and prediction were performed using MATLAB 6.0 (release 12.1) software.

RESULTS AND DISCUSSION

Physicochemical, Mechanical, and Optical Properties of Pulps

Pulps with different characteristics were obtained by changing the active alkali in pulping (Table 1). The kappa numbers covered a broad range of commercial pulps, that is, packaging, printing and writing, and tissue papers. The intrinsic viscosity (IV) values showed that increasing the active alkali in pulping significantly degraded the cellulose.

The laboratory pulps were refined using a PFI mill and the Schopper-Riegler drainability was measured to indicate the degree of refining achieved. Scatter plots of the mechanical and optical properties as a function of Schopper-Riegler drainability are presented in Figure 1. Refining improved all mechanical properties measured, with exception of bending index. These specific effects of refining are usually observed for kraft pulps from eucalyptus.^[29,30] In general, pulps less degraded in pulping had higher levels of mechanical properties and required less refining to achieve optimum strength levels. Refining also affected the optical properties; however, a clear tendency was not observed. NIR spectra were measured in one selected hand sheet of each pulp sample.

NIR Spectrometry and Pre-Processing of NIR Spectra

The NIR spectra of pulp F14 before and after refining are presented in Figure 2A. Characteristic bands of OH of water (1930 nm), OH of alcohol (1490 nm), and OH of phenol (2100 nm), and other overlapping peaks were

Table 1. Kappa number (KP) and intrinsic viscosity (IV) of kraft pulps obtained in laboratory pulping using different active alkali levels. IV as $\text{cm}^3 \text{g}^{-1}$

	F12	F14	F16	F18	F20	F22	F24
KP	23.7	21.9	17.2	15.5	14.6	11.9	11.6
IV	1152	1121	976	915	830	684	656

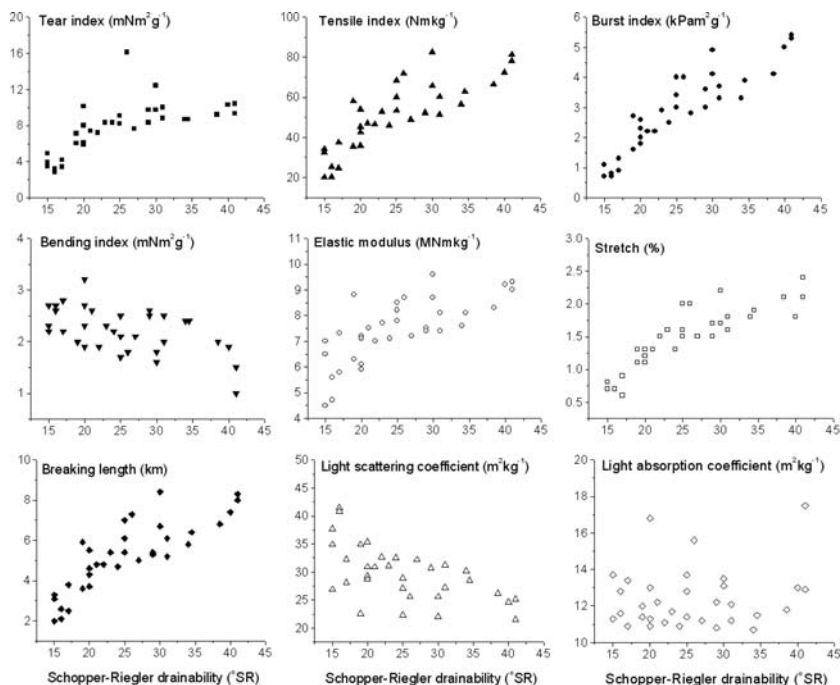


Figure 1. Scatter plot of mechanical and optical properties of unrefined and refined pulps as function of Schopper-Riegler drainability.

observed at different intensities. Refining changed the peak intensity, but no new peaks were observed in the spectra of refined samples. The original NIR spectra were pre-processed using Kubelka-Munk (KM) (Figure 2B), first derivative (D1) (Figure 2B), and a combination of KM and D1 (KM-D1). This mathematical pre-processing was performed to linearize the spectral intensity with the mechanical and optical properties investigated. Pulping and refining generate changes at the molecular level either by dissolution of carbohydrates or lignin or aggregation of nanostructured components such as cellulose fibrils. NIR spectrometry is sensitive to the chemical modifications which occur;^[5] however, it should be mentioned that the selection of the best linearization method is a trial and error procedure.

PLS Calibration and Prediction

The KM, D1, and KM-D1 NIR spectra were grouped in three different matrices **X** (33, 1301) according to the pre-processing method used and mechanical and optical properties data were grouped in individual matrices **Y** (33, 1). The matrices **X** and **Y** were mean-centred. In the PLS method, the matrices **X** were attributed as predictor and the **Y** matrices as predicted.

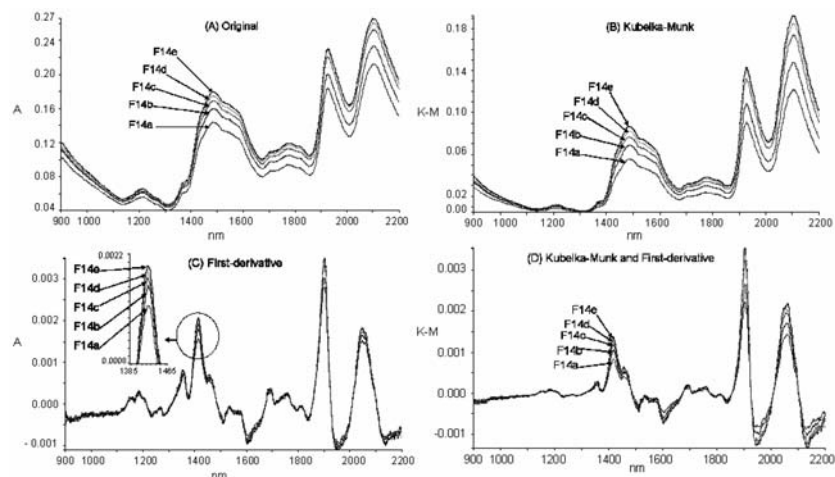


Figure 2. NIR spectra of sample F14 refined at zero (a), 1500 (b), 3000 (c), 4500 (d), and 6000 (e) PFI revolutions. The original spectra (A) were treated using Kubelka-Munk (B), first-derivative (C), and a combination of Kubelka-Munk and first-derivative (D) methods.

The leaving-one-out cross-validation method was used to calculate the PRESS and to establish the number of PLS components for each model using KM, D1, and KM-D1-treated spectra. The generated models were evaluated through the root-mean-square-error of calibration (RMSEC), root-mean-square-error of cross validation (RMSECV), and plots of measured versus predicted values and leverage versus studentized residuals.^[16] Only models that yielded the lowest RMSECV were selected; these are presented in Table 2.

Table 2. Selected PLS models for mechanical and optical properties and refining response of eucalypt kraft pulps

Model	Pre-processing	PLS		
		components	RMSEC	RMSECV
Tear index	D1	6	0.11	0.96
Tensile index	D1	6	0.36	3.64
Burst index	D1	6	0.03	0.30
Bending index	D1	5	0.09	0.28
Elastic modulus	D1	4	0.27	0.49
Stretch	D1	2	0.12	0.13
Breaking length	D1	6	0.04	0.38
Light scattering	D1	5	1.78	2.20
Light absorption	D1	6	0.10	1.20
Drainability	D1	6	0.35	3.39

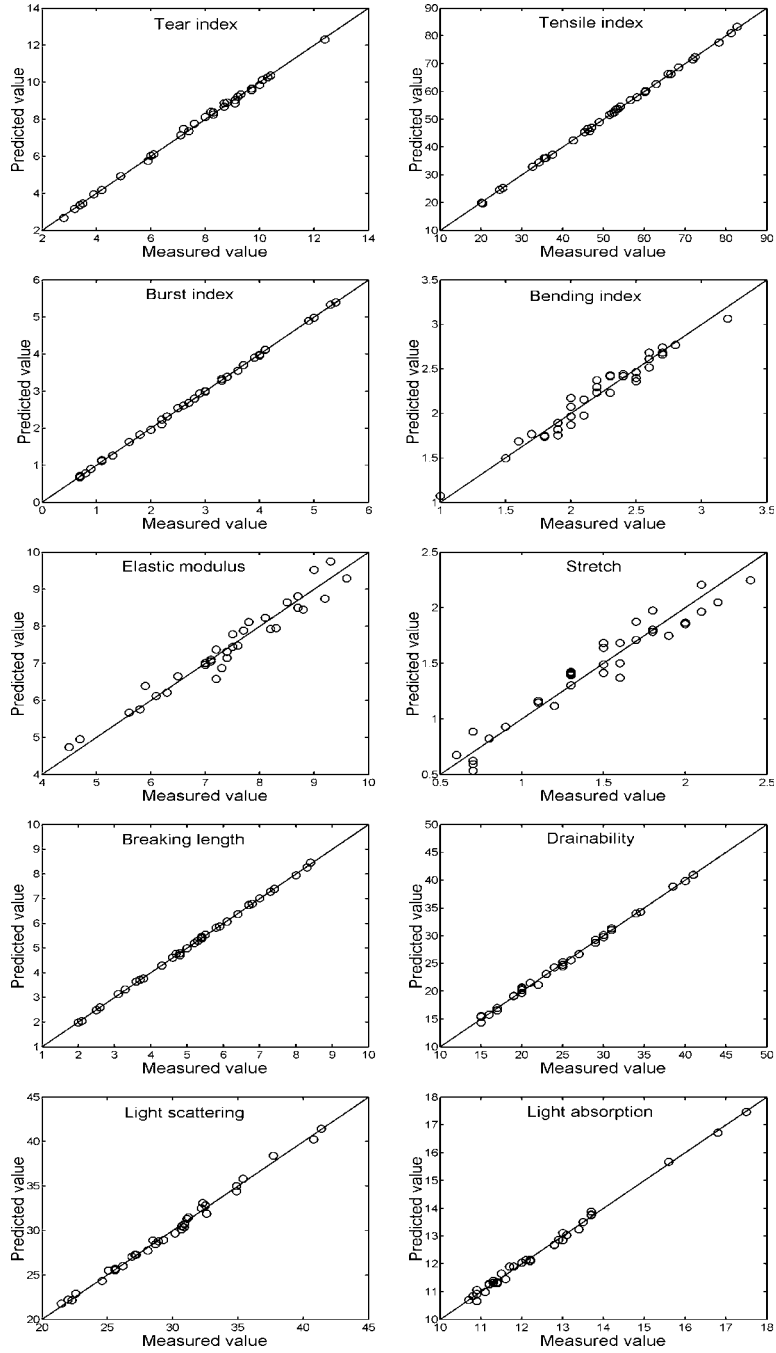


Figure 3. Measured versus predicted values for models to estimate mechanical and optical properties and beating response (as indicated by Schopper-Riegler drainability).

The measured value versus the predicted value plots for each mechanical and optical property are presented in Figure 3. According to these plots and the RMSEC values (Table 2), all the calibration models had very good predictive ability. However, the RMSECV was in some cases 10 times higher than the RMSEC value, indicating that the prediction ability for new samples tend to be poorer than for the calibration set. In order to verify this role, we selected 5 samples obtained in different pulping and refining experiments and used conventional methods for determination of their mechanical and optical properties, and refining response. After that, the results obtained were compared with determinations using NIR spectra and the calibration models on the same samples.

Determination of Mechanical, Optical Properties, and Refining Response in New Samples

The ability of the models developed using NIR spectrometry and multivariate data analysis to determine the pulp properties is presented in Table 3. Results were very similar to those obtained by conventional methods; however, the NIR method was much faster. Models for mechanical properties had excellent predictive ability for new samples and can be easily applied in “at-line” conditions in pulp and paper mills. Sample conditioning was used in all cases here and was the time consuming step in this method. In case of application using at line measurements, the pulp and paper samples can be conditioned in small scale units reducing investments in quality control facilities. In case of “on-line” conditions, particularly for paper and pulp sheets, a proper sensor can be developed. Models for optical properties and beating response (as Schopper-Riegler drainability) had acceptable predictive ability, with better results for refined samples. This might have been due to matrix effects^[5] that could not be contoured for unrefined samples by the utilization of the integrating sphere in spectral acquisition or application of pre-processing methods. However, this is a not serious limitation for quality control measurements.

CONCLUSIONS

NIR spectrometry and multivariate data analysis were used for determination of beating response and mechanical and optical properties of eucalyptus kraft pulps. The models developed had excellent predictive ability of all mechanical properties, including measurements of new different samples. Their utilization is recommended for immediate applications in “at-line” conditions. Beating response and optical properties had good predictive ability for refined samples and their application is also recommended. Further developments

Table 3. Determination of mechanical and optical properties of unrefined (a) and refined (d,e) pulps using conventional and spectrometric methods. Pulpes were obtained using 15 (F15) and 17% (F17) active alkali in pulping and refined using 4500 (d) and 6000 (e) PFI revolutions. Average (SD) of ten measurements

Property	Method	F15a	F15d	F15e	F17a	F17d
Tear index ($\text{mNm}^2 \text{g}^{-1}$)	Conv.	4.0 (0.4)	9.0 (1.2)	10.4 (1.2)	4.1 (0.5)	9.9 (0.9)
	NIR	3.7	10.3	10.7	3.7	8.8
Tensile index (Nm kg^{-1})	Conv.	26.2 (2.2)	68.9 (4.2)	73.7 (3.6)	30 (1.4)	60.0 (3.2)
	NIR	28.6	76	81.7	28.5	66.3
Burst index ($\text{kPam}^2 \text{g}^{-1}$)	Conv.	1.0 (0.1)	4.7 (0.2)	5.2 (0.3)	0.9 (0.1)	3.9 (0.4)
	NIR	0.9	4.9	5.2	0.8	4.1
Bending index ($\text{mNm}^2 \text{g}^{-1}$)	Conv.	2.4 (0.4)	2.5 (0.2)	2.3 (0.1)	3.0 (0.2)	2.0 (0.1)
	NIR	2.3	1.6	1.3	2.6	1.8
Elastic modulus ($\text{MNm}^2 \text{kg}^{-1}$)	Conv.	5.8 (0.5)	8.6 (0.5)	9.1 (0.7)	6.7 (0.4)	8.0 (0.5)
	NIR	5.9	8.9	9.7	6.0	8.7
Stretch (%)	Conv.	0.7 (0.1)	1.9 (0.1)	1.7 (0.3)	0.8 (0.1)	1.6 (0.2)
	NIR	0.6	1.9	2.2	0.6	1.8
Breaking length (km)	Conv.	2.7 (0.2)	6.8 (0.3)	7.2 (0.5)	3.1 (0.2)	5.9 (0.4)
	NIR	2.7	7.6	8.3	2.8	6.7
Light scattering ($\text{m}^2 \text{kg}^{-1}$)	Conv.	36.2 (0.2)	23.6 (0.2)	21.4 (0.2)	38 (0.3)	26.6 (0.2)
	NIR	34	24.4	22	34.5	26.3
Light absorption ($\text{m}^2 \text{kg}^{-1}$)	Conv.	16 (0.1)	14.2 (0.1)	13.2 (0.1)	14.4 (0.1)	12.9 (0.1)
	NIR	14.1	14.5	14.5	12.5	13.0
Drainability (OSR)	Conv.	15 (1)	29 (2)	40 (3)	16 (1)	32 (2)
	NIR	12	35	35	12	33

of proper sensors and sampling devices can make the NIR methods applicable for “on-line” conditions. Presently, with very low investment, NIR spectrometry can be an attractive alternative to substitute the routine control laboratories in pulp and paper mills and improve process monitoring and product quality.

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