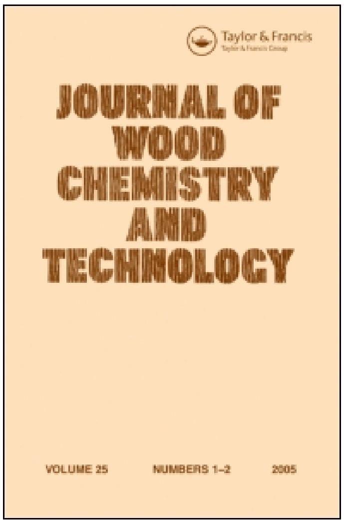

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Estimating Glucan, Xylan, and Methylglucuronic Acids in Kraft Pulps of *Eucalyptus globulus* Using FT-NIR Spectroscopy and Multivariate Analysis

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Abstract: Fourier transform near infrared (FT-NIR) associated with multivariate analysis was used to estimate glucan, xylan, 4-*O*-Methyl-α-D-glucuronic acid (MeGlcA) content, and pulp yield in kraft pulps of *Eucalyptus globulus* Labill. Several models were applied to correlate chemical composition in samples with the NIR spectral data by means of principal components regression (PCR) or partial least square (PLS) algorithms. Calibration models were built and validated by using all the spectral data and cross-validation methodology. The r_c^2 values for the best calibration models for quantification of glucan, xylan, MeGlcA contents and pulp yield were between 0.71–0.92. The model was validated using a set of external samples. The amount of glucan (64–77%), xylan (12–18%), and MeGlcA (204–363 mmol kg pulp^{-1}) in pulps were predicted with a root mean square error of prediction (RMSEP) of 0.91%, 0.46%, and 15.21% for glucan, xylan, and MeGlcA, respectively. Pulp yield (in the range of 46–70%) was also predicted with good accuracy with a RMSEP of 1.63%. These results suggest that glucan, xylan, MeGlcA composition, and pulp yield in kraft pulps of *E. globulus* can be adequately estimated by NIR spectroscopy for laboratory or industrial applications. NIR predictions can also provide useful and cost-effective tools for the rapid screening of large numbers of samples.

Keywords: *Eucalyptus globulus*, FT-NIR, glucan, kraft pulp yield, multivariate analysis, uronic acids, xylan

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INTRODUCTION

Approximately two-thirds of wood biomass consists in carbohydrates, where cellulose and hemicelluloses are the main polysaccharides involved in woody tissue formation. Pectins, oligosaccharides, and monosaccharides are other carbohydrates found in lower amounts in wood cell wall.[1] Cellulose is a linear polymer of (β-1,4)-D-glucopyranose with an average degree of polymerization of approximately 10,000. Hemicelluloses are rather small macromolecules of approximately 150–200 sugar units (primarily D-mannose, D-xylose, D-glucose, L-arabinose, D-galactose, and 4-O-Methyl-α-D-glucuronic acid). The hemicellulose compositions in hardwoods and softwoods are quite different: hardwoods contain primarily glucuronoxylans, whereas softwoods contain mainly galactoglucomannans.[1,2]

Cellulosic pulp is the main product obtained from the chemical conversion of wood and is mainly used for paper and paperboard products. Softwoods are the principal source for papermaking fibers, although at present there is also a worldwide interest in hardwood fibers due to their specific characteristics. *Eucalyptus* spp. is an important source for short fiber cellulosic pulp and well known for their properties that can produce high quality printing/writing papers, and tissue products.[3,4] Specifically, *Eucalyptus globulus* Labill is planted in temperate latitudes such as Portugal, Spain, Australia[4,5] and Chile, representing approximately 25% of the raw material used for pulp production by the Chilean industry.

The profitability of kraft pulp production is well understood, where pulp yield and chemical composition are key variables. Kraft pulp yield is traditionally assessed by cooking wood chips in an alkaline solution at elevated temperature and pressure to dissolve lignin and separate fibers.[4] The analysis of the pulp components (cellulose, non-cellulosic polysaccharides, and residual lignin) traditionally involved time-consuming laboratory wet chemical techniques such as acid hydrolysis and kappa number determination.[4,6,7] Furthermore, these methods are laborious and expensive, restricting the number of samples that may be processed in short time periods or during industrial processing. Thus, to improve laboratory and industrial characterization of the product, more rapid and cost-effective methods are required to rapidly estimate pulp yield and composition.[8]

Fourier transform infra-red (FT-IR) spectroscopy methods in combination with multivariate analysis is a very useful and powerful technique that has been used to determine wood properties, composition, and to follow structural wood changes during chemical, physical, or biological processes.[6,9–17] In contrast with conventional wood analysis methods, this technique requires a small sample size and short analysis time, offering a low-cost measurement alternative. The main applications of FT-NIR in determining wood and wood products characteristics were recently reviewed.[18] FT-NIR analysis has been traditionally used to predict wood density, pulp yield,[3,11,19,20] and cellulose content.[21] Some previous work on the application of NIR to eucalypts species

(*E. globulus, E. nitens*, and*E. grandis*) were focused on developing NIR models to quantify pulp yield, pulp properties, and pulp composition.[3–4,10,22–26] We have recently showed that FT-NIR associated with multivariate analysis can be used as an accurate method to estimate kappa number, hexenuronic acids, and lignin content in kraft pulps of *E. globulus*.[27]

For NIR and multivariate analysis (PCR: principal components regression and PLS: partial least square regression), it is necessary to have a large number of samples with a wide range of known properties for calibration and cross-validation, and an additional set of samples for external validation. The aim of this article is to use FT-NIR spectroscopy associated with multivariate analysis (PCR and PLS) to generate calibration models to estimate glucan, xylan, and MeGlcA composition of *Eucalyptus globulus* kraft pulps obtained in different pulping conditions. Pulp yield prediction models were also developed. Calibration validity was evaluated by predicting the properties of a new set of samples by cross-validation and external validation procedures.

EXPERIMENTAL

Kraft Pulping

Kraft pulping was performed by cooking industrial-size wood chips (2.5 × 1.5 × 0.2 cm) from 10–12-year-old *E. globulus* provided by a local pulp mill. Wood chips were air-dried and stored in dry conditions before use. The samples were cooked in a 1000-mL Parr reactor (Parr Instrument Co., Moline, IL, USA) loaded with 50 g of wood chips (dry basis) and a liquor:wood ratio of 5:1 (v w^{-1}). The cooking liquor composition was 12%, 15%, and 20% active alkali, and 25% sulfidity (both calculated on dry wood basis and expressed as Na_2O equivalents). The reactor was heated at 1.6°C min^{-1} and pulping experiments were performed at two temperatures, 155°C and 165°C. Cooking time was varied from 15 to 300 min. A total of 135 kraft pulps were prepared as a result of the combination of the different pulping conditions used. After cooking, pulps were disintegrated in a TAPPI laboratory blender, thoroughly washed with tap water and centrifuged. Total pulp yield was determined based on the weight of the pulp divided by wood chips weight (both on dry basis) multiplied by 100%.

Chemical Analysis of *E. globulus* Wood Chips and Kraft Pulps

Milled wood samples were extracted with ethanol/toluene following the TAPPI method 204 cm-97. Wood and pulp samples were characterized for their carbohydrate composition (glucan and xylan) using the methodology described by Ferraz et al.[6] In a test tube, 300 mg of extractive-free milled wood was weighed and 3 mL of 72% (w w^{-1}) H_2SO_4 was added. The hydrolysis was carried out in a water bath at 30°C for 1 h with stirring every 10 min. Later, the acid was diluted to 3% (w w^{-1}) with 79 mL of distilled water and the mixture transferred to a 250-mL Erlenmeyer flask and autoclaved for 1 h at 121°C. The residual material was cooled and filtered through a sintered glass filter number 3. The concentration of monomeric sugars in the soluble fraction was determined by HPLC using a Aminex HTX-87H column at 45°C, eluted at 0.6 mL min^{-1} with 5 mM H_2SO_4 and with a refractive index detector. Glucose and xylose were used as external calibration standards. The factors used to convert sugar monomers to anhydromonomers were 0.90 for glucose to glucan and 0.88 for xylose to xylan. These factors were calculated based on water addition to polysaccharides during acid hydrolysis.[28] All chemical determinations were done in triplicate for each pulp. Analytical error for carbohydrates and lignin determinations were lower than 4% and 1%, respectively.

4-*O*-Methyl-α-D-glucuronic Acid Quantification

4-*O*-Methyl-α-D-glucuronic acid (MeGlcA) content in hemicellulose was quantified in the acid hydrolisates of milled wood by using the colorimetric method proposed by Blumenkrantz and Asboe-Hansen.[29] In a test tube immersed in an ice-water bath, 1 mL of acid hydrolysate and 6 mL of 12.5 mM sodium tetraborate in concentrated sulfuric acid were added. The tube was shaken in a vortex and placed in a water bath at 100°C for 15 min. The solution was cooled in an ice-water bath and 200 μL of m-hydroxydiphenyl solution (0.15% in 0.5% NaOH) was added to the tube. The reactive (m-hydroxydiphenyl) is a sensitive and selective reagent for 5-formyl-2-furoic acid (5FF), which is the main product of MeGlcA degradation during acid hydrolysis. After 5 min of reaction, the absorbance of the solution was read at 520 nm (Molar absorptivity = 1.33 L mol^{-1} cm^{-1}). For the blank solution, the m-hydroxydiphenyl was replaced by 200 μL of 0.5% NaOH. A calibration curve was prepared by using D-galacturonic acid (GalA) as standard with concentrations between 4 and 24 mg L^{-1}. GalA was a convenient standard suitable for MeGlcA quantification because both compounds had the same molar absorptivity.[30] All samples were analyzed in triplicate. The analytical error for the determination was lower than 5%.

FT-NIR Analysis and Multivariate Calibration

Kraft pulps were initially dried at 50°C for 24 h, and then conditioned in the spectrophotometer room at 50% relative air humidity and 23°C. Spectra were recorded in diffuse reflectance mode at 2 nm intervals from 1000 and 2500 nm using 32 scans, by using a Perkin Elmer Identicheck FT-NIR equipment (Perkin Elmer, Inc., Waltham, MA, USA). Two spectra were recorded from each pulp sample. Both spectra were averaged using the software facilities. Raw reflectance data were converted to Kubelka-Munk units (K-M) and the spectra baselines were corrected to the regions near 1320 nm, 1870 nm, 2220 nm, and 2410 nm. Calibration models were developed based on the spectra with baseline correction and also with the same spectra converted to the second derivative. The spectral data were analyzed and converted with the software package available with the equipment: Spectrum v. 5.0.1 and QUANT+ (Perkin Elmer, Inc., Waltham, MA, USA).

PLS models were based on the PLS-1 algorithm relating spectral data to the pulp properties. PCR models were based on principal component analysis (PCA) performed on spectral information followed by multiple linear regressions between each pulp property and selected principal components. PCR and PLS models were made using Unscrambler software v. 9.7 (CAMO Software Inc., Woodbridge, NJ, USA). All models were internally and externally validated. The internal validation was based on full cross-validation (CV). The optimum number of factors used was the software recommended value unless otherwise indicated. The models were developed based on PCR or PLS algorithms using whole data of the spectra with baseline correction and second derivative NIR spectra (Figure 1). Multivariate analyses were used to relate the values of the wavelengths in the spectrum to values given by the chemical analysis for each of the components evaluated in this work. The number of factors or principal components was chosen by the software in order to optimize the models' performance to predict a given property rather than to maximize the correlation coefficient. A group of 135 kraft pulps was analyzed by FT-NIR spectroscopy in order to establish prediction models for glucan, xylan, MeGlAc, and pulp yield. One hundred samples were used to construct the calibration models and 35 samples were selected from the entire group in order to cover the whole range of values and were used for external validation (prediction set). The accuracy of the calibrations was expressed by the root mean square error of calibration (RMSEC, Eq. [1]) (determined from the residuals of the final calibration), the root mean square error of cross-validation (RMSECV, Eq. [2]) (determined from the residuals of the each cross-validation phase) and the coefficient of determination (r_c^2, Eq. [3]) (defined as the proportion of variation in the calibration set that was explained by the model).

$$\mathrm{RMSEC} = \sqrt{\sum_{i=1}^{N} (\hat{y}_i - y_i)^2/(N - a - 1)} \tag{1}$$

$$\mathrm{RMSECV} = \sqrt{\sum_{i=1}^{N} (\hat{y}_{cv,i} - y_i)^2/N} \tag{2}$$

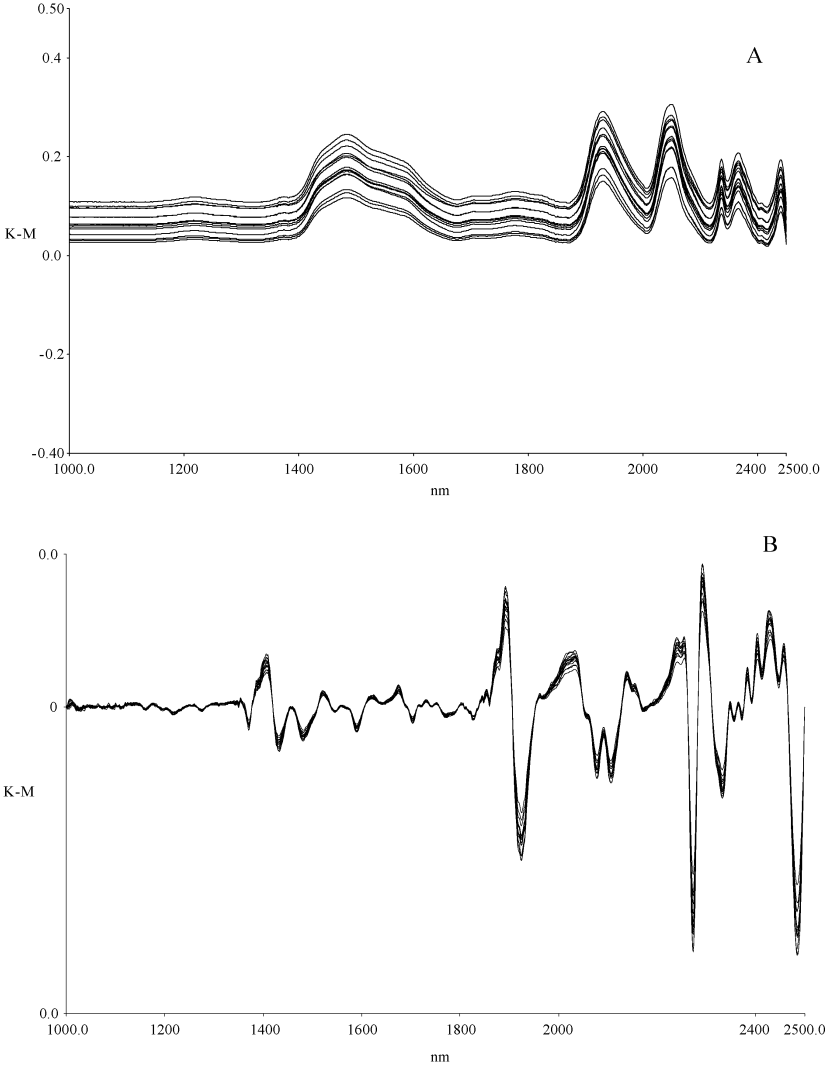

Figure 1. Normal and second derivative FT-NIR spectra for samples of *Eucalyptus globulus* kraft pulps.

$$r_c^2 = 1 - \sum (y_i - \hat{y}_i)^2 \Big/ \sum (y_i - \bar{y}_i)^2 \qquad (3)$$

where $\hat{y}_i$ and $\hat{y}_{cv,i}$ are the property content for calibration and validation of a sample *i* estimated, respectively; y_i is the known property content of a sample *i*; $\overline{y}_i$ is the average property content of a sample *i*; *N* is the number of samples used to develop the calibration, and *a* is the number of factors used to develop the calibration.[31]

For the external validation, the standard error prediction (SEP, Eq. [4]) (determined from the residuals of the predictions), the Bias (average difference between y and y in the prediction set, Eq. [5]) and the root mean square error of prediction (RMSEP, Eq. [6]) were calculated. These parameters give a measure of how well calibrated the predicted properties of interest are in a set of samples. The predictive ability of the calibration models developed was also assessed by calculating the coefficient of determination (r_p^2, Eq. [7]) (defined as the proportion of variation in the independent prediction set that was explained by the calibration).

$$\mathrm{SEP} = \sqrt{\sum_{i=1}^{N_p} (\hat{y}_i - y_i - \mathrm{BIAS})^2/(N_p - 1)} \tag{4}$$

$$\mathrm{BIAS} = \sum_{i=1}^{N_p} (\hat{y}_i - y_i)/N_p \tag{5}$$

$$\mathrm{RMSEP} = \sqrt{\sum_{i=1}^{N_p} (\hat{y}_i - y_i)^2/N_p} \tag{6}$$

$$\mathrm{r_p}^2 = 1 - \sum (y_i - \hat{y}_i)^2 \Big/ \sum (y_i - \bar{y}_i)^2 \tag{7}$$

where $\hat{y}_i$ is the property content for a sample *i* predicted by the calibration model; y_i is the known property content of a external sample *i*; $\hat{y}_i$ is the average property content of a external sample, and *Np* is the number of samples used in the prediction set.[31]

RESULTS AND DISCUSSION

The chemical composition of *E. globulus* wood chips used in this work was 49.6% glucan, 16.1% xylan, 26.3% lignin, 255 mmol kg^{-1} MeGlcA, and 1.2% ethanol/toluene-soluble extractives.[32] *E. globulus* kraft pulps were obtained in different pulping conditions covering a wide range of concentrations for glucan, xylan, MeGlcA, and pulp yield. Glucan content varied from 64 to 77%, xylan content was from 12 to 18%, MeGlcA content varied from 204 to 363 mmol/kg pulp and pulp yield was in the range of 46 to 70%. Other carbohydrates such as arabinans and galactans, and acetic acid from acetyl groups of xylans were present in low amounts or were not detected in the acid hydrolizates of the kraft pulps. The data set obtained can be considered representative for the chemical composition of kraft pulps produced at different delignification degrees (kappa number between 8.5 and 62.4).[32]

All pulps obtained were analyzed by FT-NIR spectroscopy. Table 1 shows the sample number used for developing each model as well as the range of values for each property measured. The validation set was selected from the entire group in a way to cover the entire range of values for the properties and were not used in calibration models development.

Only spectral information that was related to some property variation was used to develop algorithms. Outliers were not detected for the properties measured using leverage and X residuals plots. Table 2 summarizes the details of the calibration models obtained. The variance explained by the models varied from poor to high (r_c^2 between 0.47 and 0.92). In both, PCR and PLS models, the number of factors was lower for the model developed with the second derivative spectra than with the NIR spectra without derivatization. This occurrence can be attributed to the fact that overlapping peaks are better resolved in second derivate,[33] therefore giving a better correlation with low number of factors. Too many factors can result in overfitting of the model and do not substantially improve model quality, while too few factors can result in a less accurate model.[22,34]

The best models (determined by the low number of factors, low RMSECV, and high r_c^2) were obtained by using PLS performed on the second derivative of the spectral data in which r_c^2 for calibration was between 0.71–0.92 (Table 2). The models obtained for glucan, xylan, and MeGlcA content presented RMSECV of 1.6%, 0.5%, and 19.0 mmol kg^{-1} pulp, respectively. Many studies have demonstrated the potential to use NIR to predict the chemical components in pulps from different wood species, although the estimation of MeGlcA content in kraft pulps by NIR and multivariate analysis had been less studied with only two studies published.[25,35] Fardim et al.[25] evaluated PLS models for calibration of glucan, xylan, and MeGlcA content in kraft pulps of *E.grandis* and reported RMSECV of 1.7%, 0.7%, and 12.0 mmol kg $pulp^{-1}$, respectively. Olsson et al.[35] developed models for carbohydrate components of kraft pulps from birch wood with 15 factors and informed RMSECV of 0.50% and 0.47%, for glucan and xylan, respectively. They also evaluated MeGlcA content, obtaining RMSECV of 7 mmol kg $pulp^{-1}$ with 14 factors in the calibration. Our calibration models developed for pulp yield using a PLS model with 4 factors resulted in $r_c^2 = 0.92$ and RMSECV = 2.03, while Schimleck et al.[3] reported pulp yield using several *Eucalyptus* species and hybrids for NIR-PLS calibration models values of $r_c^2 = 0.42$, RMSECV = 1.51 and 4 factors. Olsson et al.[35] NIR models for pulp yield gave values of $r_c^2 = 0.42$, RMSECV = 1.1, and 12 factors. Very good and even better calibration models were obtained in the present study to predict glucan, xylan, MeGlcA, and pulp yield for the *E. globulus* kraft pulps as compared with the aforementioned works.

For all calibrations, the RMSECV, which is considered to be a better measure of calibration error than the RMSEC, was slightly greater that RMSEC. Jones et al.[36] showed that a high RMSECV indicated that the sample excluded

Table 1. Calibration and prediction set (samples number and range of properties values) for *E. globulus* kraft pulps

	Calibration set				Prediction set			
Trait	Sample number	Minimal content	Maximal content	Average std (SD)	Sample number	Minimal content	Maximal content	Average std (SD)
Glucan (%)	103	64	77	0.7	25	66.2	75	0.6
Xylan (%)	103	12	18	0.3	25	13.2	16.9	0.3
MeGlcA (mmol kg^{-1})	110	204	363	10.3	25	220	341	9.4
Pulp yield (%)	110	46	70	1.0	25	48.7	66	1.0

Table 2. Summary of calibration for developed FT-NIR models with corresponding statistical values

Model no.	Algorithm	Spectral data*	Samples	Spectral range	Factors	r_c^2	SEC	SECV
Glucan								
1	PCR	Normal	100	all	14	0.47	1.61	1.92
2	PLS1	Normal	100	all	16	0.84	0.88	1.70
3	PCR	2nd der	100	all	11	0.54	1.51	1.74
4	PLS1	2nd der	100	all	7	0.71	1.20	1.60
Xylan								
5	PCR	Normal	100	all	11	0.61	0.54	0.62
6	PLS1	Normal	100	all	14	0.87	0.31	0.55
7	PCR	2nd der	100	all	7	0.70	0.47	0.51
8	PLS1	2nd der	100	all	5	0.78	0.40	0.47
Methylglucuronic acid								
9	PCR	Normal	100	all	12	0.76	15.52	17.85
10	PLS1	Normal	100	all	9	0.76	15.46	18.05
11	PCR	2nd der	100	all	5	0.68	17.88	19.10
12	PLS1	2nd der	100	all	4	0.74	16.35	18.76
Pulp yield								
13	PCR	Normal	100	all	10	0.91	1.81	2.03
14	PLS1	Normal	100	all	8	0.91	1.77	2.03
15	PCR	2nd der	100	all	5	0.89	2.00	2.12
16	PLS1	2nd der	100	all	4	0.92	1.75	2.03

*Normal: spectra with baseline correction; 2nd der: spectra with baseline correction and second derivative.

in each cross-validation step was not well predicted by the corresponding calibration and that the RMSEC is overly optimistic. Also, a large difference between the RMSEC and RMSECV may be due to the small number of samples. The use of a large calibration set to build our models resulted in similar or only slightly different values for RMSEC and RMSECV. The PLS models for all the FT-NIR spectral information provided a good estimate for all major pulp components of *E.globulus* kraft pulps.

The best models (selected from those with the best statistics) were used to predict pulp titers of 35 independent samples in an external validation set. Validation models provided an idea of how well a regression model would perform if it were used to predict new and unknown samples. The results of the prediction assays are summarized in Table 3. The PCR models performed on normal NIR data were used as a reference for each pulp titer. The correlation between the observed and predicted values is presented in Figure 2. In general, the SEP of the validation data set was lower than the RMSECV obtained from the calibration model. For all components, the SEP and RMSEP were relatively

Table 3. Summary of predictions (external validation) for carbohydrates, MeGlcA, and pulp yield with PCR and PLS models

Pulp titer and NIR model	Factors	r_p^2	SEP	Bias	RMSEP
Glucan					
PCR—model 1	14	0.78	1.07	–0.10	1.05
PLS—model 4	7	0.84	0.93	–0.10	0.91
Xylan					
PCR—model 5	11	0.69	0.52	–0.11	0.52
PLS—model 8	5	0.75	0.47	–0.07	0.46
Methylglucuronic acid					
PCR—model 9	12	0.70	16.17	–0.79	16.00
PLS—model 12	4	0.74	15.20	–0.40	15.21
Yield					
PCR—model 13	10	0.92	1.47	–0.66	1.60
PLS—model 16	4	0.92	1.40	–0.86	1.63

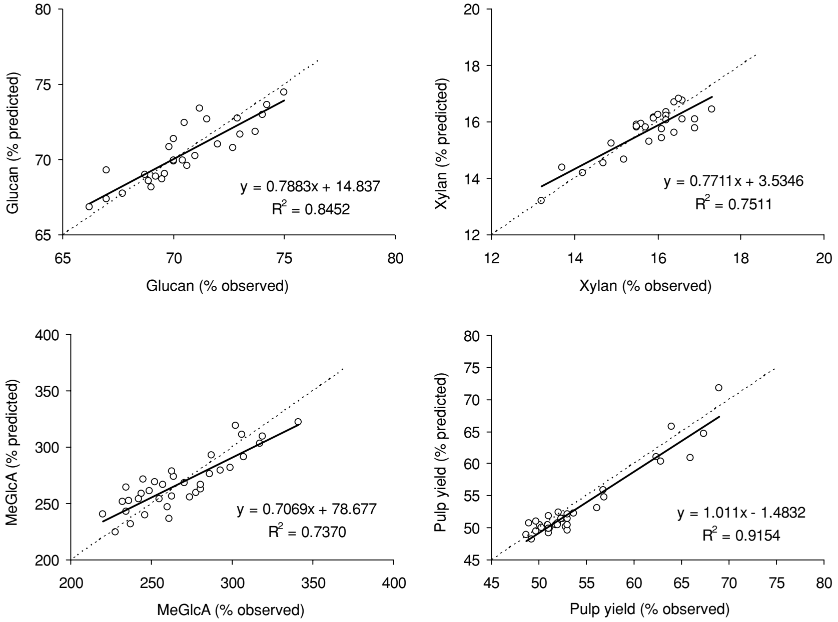

Figure 2. Correlations between observed and PLS-predicted concentrations for 35 samples evaluated as a validation data set. Solid lines represent the lineal regression and broken lines represent the line of equivalence.

lower or of the same magnitude than the standard deviation values obtained from wet chemistry, indicating that the models are appropriate to estimate these pulp titers in routine cooking experiments where these properties are key properties for evaluating kraft process efficiency. Regression equations for all properties had multipliers on the X factor of 0.71–1.0, indicating the predictions were quite accurate, particularly for pulp yield. Table 3 also included the calculated bias for the prediction sets, where this value is a measure of the difference between the predicted and the observed value for the property. Therefore, this parameter can give a certainty of the prediction accuracy or show if SEP is giving an over-optimistic impression of the prediction ability. RMSEP included the bias, while SEP excludes it. Thus, the RMSEP is a combined measure of accuracy and precision; while the SEP is a measure of precision only.[31] PLS models performed on the second derivative of the spectral data explained a large amount of variance and had lower bias than PCR on normal spectra.

CONCLUSION

NIR spectroscopy can be an attractive alternative to replace the time-consuming conventional methods and diminish the cost of chemicals used to process a large number samples. The method is multianalytical, which facilities the estimation of a number of properties from a single spectrum. In this work, we demonstrated that glucan, xylan, MeGlcA composition, and pulp yield can be accurately estimated in kraft pulps of *E. globulus* by using FT-NIR and multivariate analysis.

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