

## RAPID PREDICTIVE MODELS FOR MINIMALLY DESTRUCTIVE KAPPA NUMBER AND PULP YIELD OF ACACIA SPP. WITH NEAR INFRARED REFLECTANCE (NIR) SPECTROSCOPY

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Kraft pulp and wood powder from *Acacia* spp. were selected for the development of rapid, minimally-destructive, and environmentally friendly predictions of kappa number and pulp yield, by means of near infrared reflectance (NIR) spectra. The models, based on Partial Least Squares Regression (PLS-R), were established with fifty-four calibration samples selected by Principle Component Analysis (PCA), while the validation models resulted from nineteen samples that were not included in the calibration set. The accuracy and stability of calibration models were evaluated by coefficient of determination for calibration ( $R^2_{cal}$ ) and root mean square error of cross-validation (RMSECV). The coefficient of determination for validation ( $R^2_{val}$ ) and root mean square error of prediction (RMSEP) were used for validation models. The main results showed that: (1) the predictive models from pulp were more credible in terms of the  $R^2_{cal}$  and  $R^2_{val}$  values than those from wood powder by 25 to 70%; and (2) a validation model for kappa number from pulp showed a better stability than the corresponding calibration model, since RMSEP was 23.5% less than RMSECV, while calibration models for pulp yield were more steady than validation models. This study provided reliable models for predicting kappa number and pulp yield rapidly and with a minimal need for physical sampling.

*Keywords:* NIR; Predictive model; Kappa number; Pulp yield; *Acacia* spp.

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### INTRODUCTION

The traditional methods for predicting kappa number and pulp yield for a given sample of wood are time-consuming and require the destruction of samples, which can have negative implications when there is a need to evaluate large numbers of living trees. A new method for improving the situation is needed. Predictive models from NIR spectra have been used to improve predictions of kappa number and pulp yield quickly and in an environmentally friendly manner.

Predictive NIR spectroscopic techniques have been studied for the purpose of determining wood components (Elg-Christofferson et al. 1999; Hauksson et al. 2001; Kelley et al. 2004; Sykes et al. 2005; Alves et al. 2007), and the chemical and mechanical properties of wood have been researched by means of NIR spectra (Hoffmeyer and Pedersen 1995; Gab et al. 2006). Wood stiffness of increment cores was estimated by NIR (Schimleck and Evans 2002). The tools from NIR spectra have become sufficiently

advanced for the quick and non-destructive evaluation of wood (Xie et al. 2008; Isik et al. 2011).

The residual lignin in pulp can be approximately expressed as kappa number, which is regarded as an important indication of delignification (Iribarne and Schroeder 1997). Likewise, pulp yield is a quality index that is very useful for the selection of raw material for pulping. The distribution of kappa number was studied by NIR several years ago (Antti et al. 2000). VIS and NIR spectral data were used as a rapid method for determining the kappa number of pulp (Malkavaara and Alen 1998; Fardim et al. 2002; Hodge and Woodbridge 2004). The determination of pulp yield by NIR has been studied (Sefara et al. 2000; Terdwongworakul et al. 2005), and the samples for prediction of pulp yield were obtained from the chips used for chemical pulping (Downes et al. 2009).

In the present study, kraft pulp and wood powder from *Acacia* spp. were used as raw materials for establishing the predictive models with NIR spectra. Then the predictive models from pulp and wood powder were compared with each other in order to determine the optimal wood samples in terms of kappa number and pulp yield. The ability to predict kappa number and pulp yield for a large sampling of living trees was improved greatly by the rapid predictive models from NIR. The minimally-destructive nature of the approach employed is due to the fact that predictions can be derived from relatively small samples, e.g. from branches or increment cores, such that a living tree experiences minimal harm.

## EXPERIMENTAL

### Materials

Sixteen *Acacia* spp. plantation trees (five to eight years-old) were felled for removing wood samples. The forest, with a steady site index, was located within Nanning, Guangxi, China. Four to six wood disks were cut above the base of each tree at a regular interval up each stem at 1.5 m, 3.0 m, 4.5 m, and 6.0 m. Seventy-three samples in total were collected for this study. Fifty-four samples were selected by PCA for calibration set and the other nineteen samples for validation set. All the disks were divided into two parts. Half of the disks were shaved into chips with a specification of 25 mm × 20 mm × 3 mm after artificial peeling and then sealed in plastic bags for water balance. The other part was ground into wood powder (mesh 40 to 60), and the equilibrium moisture content of wood powder was 8.0%. All chemicals were of analytical grade and used as received without further purification.

### Methods

#### *Cooking conditions*

The conditions of pulping were as follows: Oven-dried chips of *Acacia* spp. were separated into four parts, of which each part weighed 150 g. The four parts were placed in a 15 L stainless steel cooking pot within four stainless steel tubes of volume 1.0 L. A 4:1 liquor-to-wood ratio was used in the experiment with 15% (w/w) NaOH and 25% (w/w) sulfidity. The time to reach the maximum temperature of 170 °C was 90 min, and the duration at 170 °C was 90 min.

### *Methods for kappa number and pulp yield*

The pulp was oxidized with potassium permanganate, and the oxidization was stopped with potassium iodide. The free iodine was titrated with a standard solution of sodium thiosulfate to determine the amount of potassium permanganate consumed. The way to analyze the kappa number was determined using Chinese National Standard GB/T 1546-1989. The pulp yield of crude pulp was calculated as follows:

$$X = \frac{m_2}{m_1} \times 100\% \quad (1)$$

(Where  $m_1$  is the mass of dry raw material and  $m_2$  is the mass of pulp after cooking)

### *Estimation of the predictive models*

Diffuse reflectance spectra were obtained by NIR from BRUKER, Germany. The range of wavenumber was from  $12000 \text{ cm}^{-1}$  to  $4000 \text{ cm}^{-1}$  (833.3 to 2500 nm). All the spectral data were collected with  $8 \text{ cm}^{-1}$  spectral resolution. Sixty-four scans were collected and averaged into a single average spectrum to ensure an adequate signal-to-noise ratio.

Fifty-four calibration samples selected by PCA for the NIR spectra were used to establish the calibration models. The NIR spectra with appropriate pre-processes were associated with the kappa number and pulp yield. Constant offset elimination (COE), straight line subtraction (SLS), vector normalization (VN), min-max normalization (MMN), and multiplicative scattering correction (MSC) were included in the pre-process method of NIR spectra. Calibration models based on PLS were developed by OPUS/QUANT 6.5 of BRUKER, and the predictive accuracy of calibration models was estimated by validation models established using nineteen validation samples. Kappa numbers and pulp yields forecasted by calibration and validation models were compared with the values from chemical analysis, and the accuracy and stability of the calibration and validation models were assessed by  $R^2$ , RMSECV, and RMSEP.

The quantity  $R^2$  is defined as the coefficient of determination of the predictive models. Two closely related terms were defined:  $R^2_{\text{cal}}$  is the coefficient of determination for calibration models, and  $R^2_{\text{val}}$  is the same for validation models. Predictive stability of the calibration models from samples that were not used to generate the calibration equation were recorded as RMSECV. The RMSECV was regarded as the indication of the accuracy of calibration models when there were insufficient external validation samples. RMSEP was used to estimate the predictive stability of validation models with unknown samples that were not included in the calibration set.

The optimal wavenumber range, pre-treatment method, and rank of predictive models were determined by the index of  $R^2$ , RMSECV, and RMSEP.

## RESULTS AND DISCUSSION

### **Near Infrared Spectroscopy**

The kappa number and pulp yield of the samples and their distribution are given in Table 1.

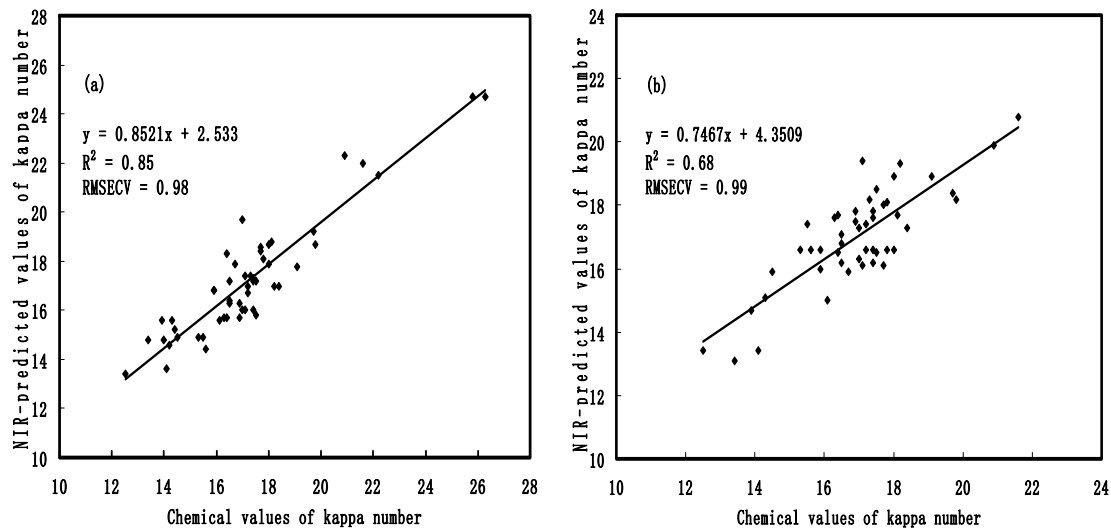
**Table 1.** Distribution of the Kappa Number and Pulp Yield from Calibration and Validation Samples

	Kappa number				Pulp yield (%)			
	Min.	Max.	Avg.	Stdv.	Min.	Max.	Avg.	Stdv.
Calibration (54 samples)	12.5	26.3	17.2	2.59	50.3	55.8	53.0	1.17
Validation (19 samples)	13.7	21.0	17.0	1.68	50.7	56.6	53.5	1.50

Stdv. = standard deviation of the reference method values

### Calibration and Validation Models for Kappa Number

With the experimental conditions optimized by PLS regression, fifty-four samples were chosen to compose the calibration set. The deviations between NIR-predicted kappa numbers and chemical values of kappa number for the calibration set are shown in Fig. 1. The characteristic wavenumber ranges of the calibration model from pulp (shown in Fig. 1a) were selected between 6101.9 and 5446.2  $\text{cm}^{-1}$  (1638.8 to 1836.1 nm) and 4601.5 and 4246.1  $\text{cm}^{-1}$  (2173.2 to 2355.1 nm).  $R^2_{\text{cal}}$  values indicated that the accuracy of prediction was 0.85, and RMSECV indicated the stability of calibration model as 0.98. A calibration model for kappa number from wood powder (40 to 60 mesh) was established with the characteristic wavenumber ranges between 6102.0 and 5446.3  $\text{cm}^{-1}$  (1638.8 to 1836.1 nm) and 4601.6 to 4246.7  $\text{cm}^{-1}$  (2173.2 to 2354.8 nm), and the accuracy of the model from wood powder was significantly lower compared with the model from pulp. RMSECV from wood powder was steady compared with that from pulp (shown in Fig. 1b).



**Fig. 1.** Scatter of kappa number using calibration model and chemical analysis: (a) pulp; (b) wood powder

Kappa number validation models obtained from nineteen validation samples were established for testing the accuracy and stability of calibration models with external samples. Deviations between calibration models and validation models are indicated in Table 2.

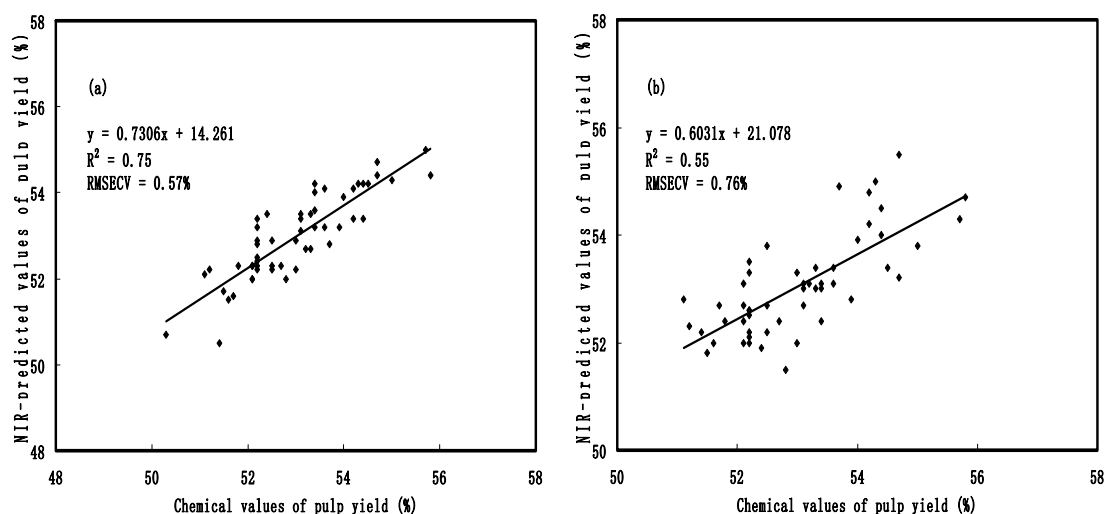
**Table 2.** Comparison of Calibration and Validation Models for Kappa Number

	Properties	Predictive model from pulp	Predictive model from wood powder
Calibration	$R^2_{cal}$	0.85	0.68
	RMSECV	0.98	0.99
Validation	$R^2_{val}$	0.80	0.48
	RMSEP	0.75	0.96

$R^2_{val}$ , which stands for the accuracy of the validation model from pulp, was 5.9% less than  $R^2_{cal}$  from pulp, while the  $R^2_{cal}$  from wood powder decreased from 0.68 to 0.48 of the corresponding  $R^2_{val}$ . Stability of the validation model from pulp was worse than that of the calibration model, representing a 23.5% decline from RMSECV to RMSEP. There was little difference between RMSECV and RMSEP of predictive models from wood powder.

### Calibration Models and Validation Models for Pulp Yield

The characteristic wavenumber ranges of the calibration model for pulp yield from pulp were selected between 11995.6 and 7498.2  $\text{cm}^{-1}$  (833.6 to 1333.7 nm) and 5450.1 and 4246.7  $\text{cm}^{-1}$  (1834.9 to 2354.8 nm). In addition, the accuracy and errors between NIR-predicted values and chemical values of pulp yield are shown in Fig. 2a. The  $R^2_{cal}$  value was 0.75, which demonstrated the reliability of the model from pulp, and RMSECV was 0.57%. The calibration model for pulp yield from 40 to 60 mesh wood powder is indicated in Fig. 2b. The characteristic wavenumber ranges of the model were between 7502.1 and 5446.3  $\text{cm}^{-1}$  (1333.0 to 1836.1 nm) and 4601.6 to 4246.7  $\text{cm}^{-1}$  (2173.2 to 2354.8 nm). The  $R^2_{cal}$  value of the model from wood powder was 0.55, and RMSECV was 33.3% more than that of the model from pulp, which impacted the predictive accuracy and stability of model for pulp yield from wood powder.



**Fig. 2.** Scatter of pulp yield using calibration model and chemical analysis: (a) pulp; (b) wood powder

The validation models for pulp yield from pulp and wood powder were obtained with nineteen external samples, and the validation models for pulp yield were compared with calibration models (shown in Table 3).

**Table 3.** Comparison of Calibration and Validation Models for Pulp Yield

	Properties	Predictive model from pulp	Predictive model from wood powder
Calibration	$R^2_{cal}$	0.75	0.55
	RMSECV	0.57%	0.76%
Validation	$R^2_{val}$	0.71	0.54
	RMSEP	0.95%	1.12%

$R^2_{cal}$  from pulp was 5.6% more than corresponding  $R^2_{val}$  and this phenomenon indicated a better accuracy of the calibration model from pulp. The accuracy of calibration model from wood powder was almost the same to that of validation model from wood powder. 40.0% decline from RMSEP to RMSECV of models from pulp and 32.1% decline from RMSEP to RMSECV of models from wood powder showed an excellent predictive stability of calibration models for pulp yield.

## CONCLUSIONS

1. The predictive accuracy of NIR calibration models from pulp was more credible than that from wood powder. The  $R^2_{cal}$  values for kappa number and pulp yield from pulp were more than those from wood powder by 25.0% and 36.4%. The predictive stability of external samples was estimated by validation models.  $R^2_{val}$  values from pulp for kappa number and pulp yield were more than those of the models from wood powder by 66.7% and 31.5%.
2. A validation model for kappa number from pulp showed worse stability than the corresponding calibration model because the RMSEP was 23.5% less than the RMSECV. Differences of the stability between calibration and validation models for kappa number from wood powder were not significant. The RMSECV of calibration models for pulp yield from pulp and wood powder were less than corresponding RMSEP by 40.0% and 32.1%, respectively. Predictive stability of calibration models for pulp yield was better than that of validation models.
3. The predictive models from wood powder for kappa number and pulp yield without pulping were valuable.  $R^2_{cal}$  and  $R^2_{val}$  indicated the predictive accuracy for kappa number and pulp yield from wood powder were as much as 60 to 80% of those from pulp. The RMSECV and RMSEP showed the steady reliability of predictive models from wood powder.

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