Peer reviewed

Application of Photoacoustic Rapid Scan FTIR for the Determination of Kappa Number of Pulp

VINH Q. DANG*, NISHI K. BHARDWAJ*, KIEN L. NGUYEN†

*Graduate students, †Senior Lecturer
Australian Pulp and Paper Institute, Monash University, Wellington Rd, VIC 3800, Australia
E-mail: loi.nguyen@eng.monash.edu.au

ABSTRACT

High-yield *Pinus radiata* kraft pulps with various Kappa number were produced from flow-through laboratory pulping. The samples were prepared and scanned using a rapid scan photoacoustic Fourier transform infrared (PAS-FTIR) spectrometer. A partial-least-squares (PLS) model was established based on the spectral data collected at different mirror velocities. The model was used to predict the Kappa number of the pulps and its robustness was statistically evaluated. The outcomes indicate that the PLS model can be used to predict the Kappa number of *Pinus radiata* kraft pulps with a high degree of accuracy provided that the moving mirror velocity is ≤ 0.5 cm/s.

INTRODUCTION

Photoacoustic (PA) spectroscopy has been increasingly used for the qualitative analysis of samples because it does not require that the sample be transmitting, has low sensitivity to surface condition, and can probe over a range of selectable sampling depths from several micrometers to more than 100 μm. The PA signal contains information on the sample's absorption spectrum and on the depth below the sample's surface from which the signal evolves, allowing materials with layered or gradient compositions to be studied. The PA signal is generated when infrared radiation absorbed by the sample converts into heat within the sample. This heat (thermal waves) diffuses to the sample surface and into an adjacent gas atmosphere. As the thermal waves propagate from the region where absorption occurred to the sample's light-irradiated surface they decay rapidly. This decay process limits the depth beneath the sample surface from which signal generation occurs. This thermal diffusive depth, μ_t, is given by Equation 1 below.

$$\mu_t = \sqrt{\frac{D}{\pi V \nu}} \qquad (1)$$

where
μ_t is the thermal diffusive length (cm);
D is sample thermal diffusivity (cm^2/s);
V is the moving mirror velocity (cm/s);
ν is the wavenumber (cm^{-1}).

In wood, pulp, and paper analysis, PAS-FTIR technology has been used in a number of instances. Ohkoshi (2002) used PAS-FTIR to study the effect of light-induced changes to surface properties of acetylated or polyethylene glycol-impregnated wood. The important bands in the spectra are C-O-C stretching in polysaccharides at 1161 cm^{-1}, C=O stretching at 1732 cm^{-1} (carbonyl group), and benzene ring in lignin at 1508 cm^{-1}. A qualitative analysis was presented based on PAS-FTIR spectra of different surface-treated wood species.

PAS-FTIR technique was also used by Yamauchi et al. (2004) to conduct depth profiling of puspa and kapur wood species exposed to various weathering environments. The study presented spectral information at various moving mirror velocities in the 1900-900 cm^{-1} region. The variation of moving mirror velocities leads to changes in spectral intensities; however, the thermal diffusive length was not conclusively determined inside the samples.

Halttunen et al. (1999) investigated the applicability of PAS-FTIR depth profiling for the study of coated papers. The chemical compositions of coating applied on to papers with depth ranging from 20 to 60 μm were examined. Analyses of magnitude and phase spectra were conducted. The report presented a modified method for calculation of thickness from spectral information. This method was used to eliminate the influence of the signals when bands of substrate and overlying material are overlapping without the need to measure the overlying material separately. The modulation frequency was within the range of 100 to 1200 Hz. The PAS spectra were recorded from a step-scan FTIR spectrometer. The penetration depth is given by Equation 2.

$$\mu_t = \Delta\theta \sqrt{\frac{D}{\pi f}} \qquad (2)$$

where
$\Delta\theta = \theta v_b - \theta v_a$ is the phase difference between the bands at different wavenumbers of the surface and substrate;
D is sample thermal diffusivity (cm^2/s);
f is the modulation frequency (Hz).

Multivariate calibration, such as partial-least-squares (PLS) are often used in conjunction with FTIR for the quantitative analysis. PLS analysis can be used to correlate the predictors, such as FTIR spectral data, to the response parameters, i.e., data obtained by chemical analysis with the aim of being able to predict the latter from the former. To enhance the predictive power of multivariate calibration models, spectral data are often pre-processed prior to analysis, in attempt to minimize variation in these data that are unrelated to the response parameters of interest. Meder et al. (1999) used the PLS calibration method together with diffuse reflectance FTIR spectroscopy for the predictions of extractives, lignin, carbohydrates and density in *Pinus radiata* samples. The PLS analysis can also be used in conjunction with UV resonance Raman spectroscopy for the determination of lignin and hexenuronic acid contents directly from unbleached and fully bleached chemical pulps (Saariaho et al., 2003).

One important parameter in pulping and bleaching is the Kappa number, which represents the amount of potassium permanganate consumption during the treatment of pulps under standardized conditions. The Kappa number can be determined as per the standard TAPPI test method T236 om-99. Kappa number value can be used as the amount of oxidants required for pulp bleaching. The aim of this study is to evaluate the use of PAS-FTIR technique to quantitatively determine the Kappa number of chemical pulps. Two sets of spectral data, which included the characteristic bands of lignin, were collected. The first set was integrated with a multivariate analysis to formulate a model for correlating the selected spectral information with the Kappa number of kraft pulps. The second set was used to validate the model.

EXPERIMENTAL METHODS

Pulp samples

Kraft pulps were produced from cooking thin *Pinus radiata* wood chips (mean dimension 25x25x3 mm) in 2-litre flow-through reactors at 0.5-1.0 M effective alkali as Na_2O and 25% sulfidity. The chips were first impregnated with the cooking liquor for 30 minutes at 108°C before being cooked at 143-152°C. Different cooking times were used to produce pulps of different Kappa number. The pulps were thoroughly washed and sieved through a screen with 0.15 mm slots prior to the measurements of the Kappa number.

Kappa number measurement

Kappa number was determined using the standard TAPPI test method T236 om-99. For various pulps, the Kappa number of the pulps is within the range 20.8-128.

PAS-FTIR measurements

All PAS spectra were obtained by using a Perkin Elmer FTIR (GX model) spectrometer equipped with MTEC300 PA cell using macro-sampling head. Prior to PAS measurement, it was necessary to purge moisture in the sample chamber. Successful purge increases the signal level by approximately a factor of 2 to 3. Purging was attained by using clean, pure and dry helium gas at a flow rate of 10-20 cc/s for approximately 20 minutes prior to the first measurement and at least 10 seconds for subsequent measurements.

The reference spectrum was acquired by using the carbon black reference. The appropriate sizes of the pulp samples from 120 g/m^2 handsheets were prepared using a hand punch for use in the macro-sampling head of PA cell. Each sample was scanned 8, 16, 32, 50 and 100 times using the moving mirror velocity of 0.05, 0.1, 0.2, 0.5 and 1 cm/s, respectively. The wavenumber range used is 4000-750 cm^{-1} with a resolution of 8 cm^{-1} and interval of 1 cm^{-1}.

RESULTS AND DISCUSSION

PAS-FTIR spectra

The characteristic bands of lignin such as aromatic skeletal vibrations have been previously found at 1605-1593, 1515-1505 and 1430-1422 cm^{-1} (Faix, 1992). The PAS spectra of three pulp samples (Kappa numbers 20.8, 89.4 and 128) at V=0.05 cm/s are presented in Figure 1. The characteristic bands representing the vibration of aromatic groups in lignin compounds are noticed at 1507 cm^{-1} and two shoulders at 1598 and 1428 cm^{-1}. It is anticipated that these peaks are associated with the lignin content in the pulp. It is also noticed that the spectra show the characteristic bands of lignin with higher absorption intensity for pulps with higher Kappa number.

Multivariate analysis

The PLS regression method was used to develop a correlation between the PAS spectra and the Kappa number of the pulp samples. A general form of the PLS model is expressed as:

$$X = TP^T + E \quad (3)$$

$$Y = UQ^T + F \quad (4)$$

where
X is the variable predictor matrix (PAS spectral data);
Y is the variable response matrix (Kappa number);
T and U are the X-score and Y-score matrices;
P and Q are the X-loading and Y-loading matrices;
E and F are the X residual and Y-residual matrices.

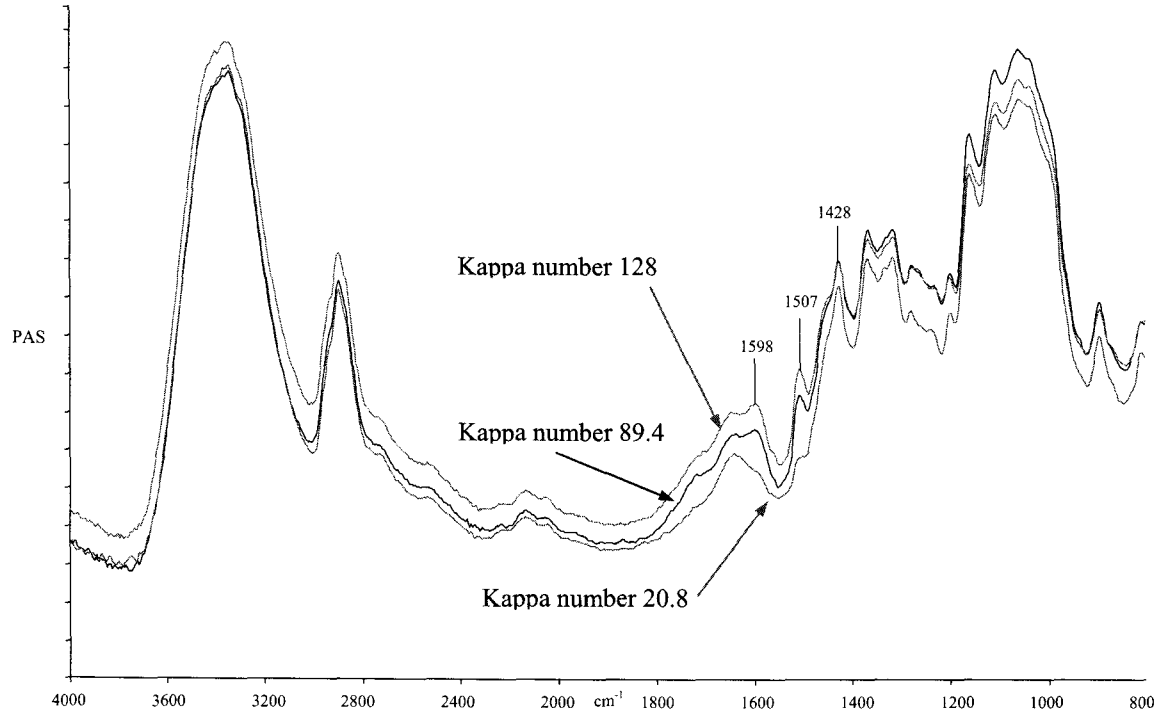

Fig.1: PAS-FTIR spectra (V=0.05 cm/s) of different *Pinus radiata* pulp samples (Kappa numbers 20.8, 89.4, and 128).

In the PLS analysis, the matrices X and Y are initially column centered and normalized. PLS algorithm chooses successive orthogonal factors that maximize the covariance between each X-score and the corresponding Y-score. In order to specify T and U, two sets of weights w (X-weights) and c (Y-weights) are computed to create a linear combination t=Xw and u=Yc with the constraints that $w^Tw=1$ and $t^Tt=1$ and the regression weight $b=t^Tu$ be maximal. The columns of T are also called the latent vectors. When the first latent vector is found, it is subtracted from both X and Y and the procedure is re-iterated until X becomes a null matrix. Once the correlation is established, Y of the new sample is estimated as $Y=TBC^T$ where B is a diagonal matrix with b as diagonal elements. The detailed PLS algorithm is well described by Geladi and Kowalski (1986). In this study, the Spectrum Quant+^{TM} software is used to perform the PLS analysis. Half of the samples was used for the calibration and the other half was used to verify the established model.

Prior to the PLS analysis, all spectra were automatically baseline corrected and then normalized at the cellulose peak at 1317 cm^{-1}. The PLS analysis was first performed using spectral data at the moving velocity of 0.05 cm/s within the wavenumber region 1650-1200 cm^{-1}. It is anticipated that all the characteristic bands of lignin are inclusive in this wavenumber region. Thirteen samples were used for the calibration. In choosing the calibration samples, it was important to include the extremes of the data (i.e., Kappa numbers 20.8-128). The PLS decomposition of the X and Y matrices resulted in three Principle Components (PCs) that can explain for 94% of the variance in the Kappa number. The relationship between the first set of spectral data and the Kappa number was established by the PLS analysis. The calibration chart extracted from Spectrum Quant+^{TM} for V=0.05 cm/s is presented in Figure 2a. The model was then validated by comparing the predicted values of Kappa number from the resultant model using the spectral data of the second set against the actual values of Kappa number. The regression coefficient R^2 value was 0.94 for V=0.05 cm/s (Figure 2b).

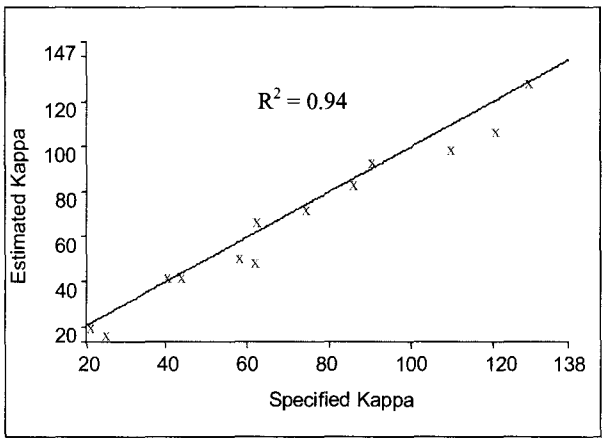

Fig.2a. Calibration model for Kappa number at V=0.05 cm/s.

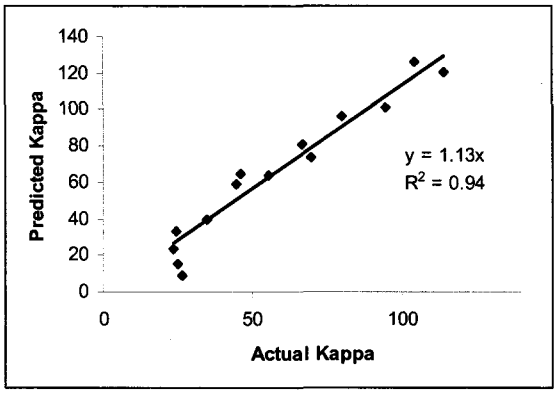

Fig.2b. PLS Prediction (V=0.05 cm/s) for Kappa number, Predicted vs. Actual values.

Effect of moving mirror velocity

The effect of mirror velocity on the obtained spectra was also investigated. In Figure 3, the spectra of the pulp sample (Kappa number 26.4) using moving mirror velocity values of 0.05, 0.1, 0.2 and 0.5 cm/s are presented. It was found that at increasing mirror velocity, the spectra were shifted downward. It is anticipated that at increasing moving mirror velocity, the thermal diffusive depth will decrease in accordance with Equation 1, hence yielding lower-intensity signals.

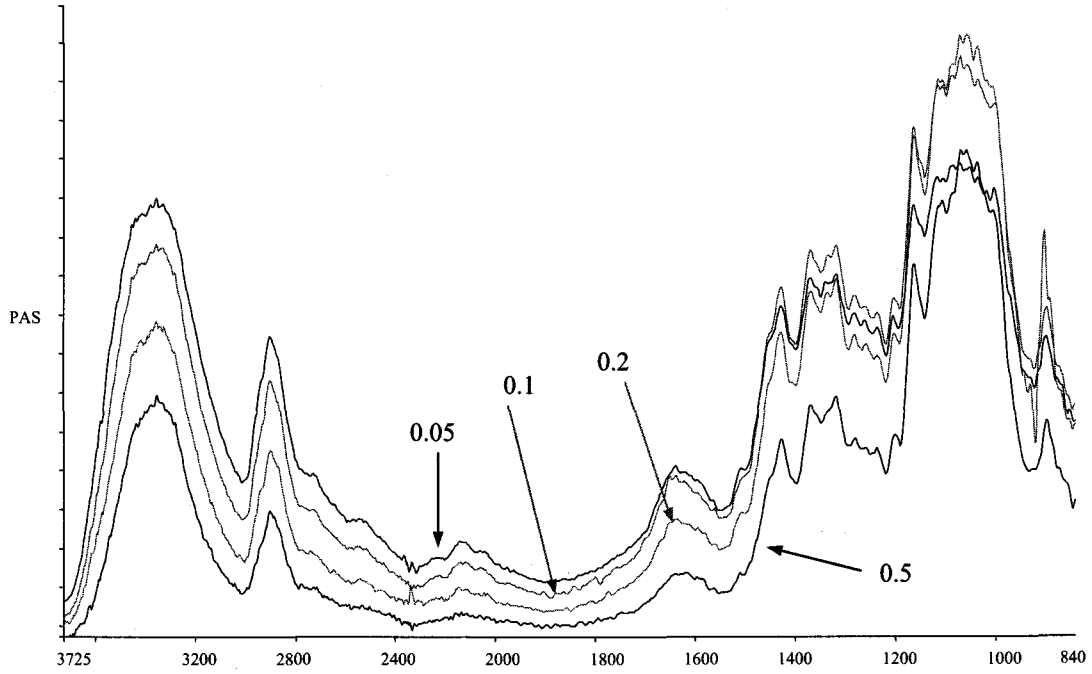

Fig.3. Effect of mirror velocity (V=0.05, 0.1, 0.2, 0.5 cm/s) on the spectra of pulp sample (Kappa number 26.4).

It was found that the PLS analysis can be used to calibrate and predict Kappa number with a high degree of accuracy at different moving mirror velocities. Table 1 presents the calibration and prediction regression coefficients for the Kappa number models at different moving mirror velocities. It was noted that at a higher moving mirror velocity (1.0 cm/s), the regression coefficient became lower. This is probably due to the fact that the scanned depth was not adequate to represent the average Kappa number in the samples and/or due to a lower signal-to-noise ratio. Figure 4 represents the prediction of Kappa number at different moving mirror velocities. It is evident that the PLS model can accurately predict the total Kappa number in pulp samples provided that the scanned depth and moving mirror velocity are chosen appropriately.

V (cm/s)	Calibration R^2 (PC used)	Prediction trendline equation	Prediction R^2
0.05	0.94 (3)	y=1.13x	0.94
0.10	0.95 (3)	y=1.13x	0.95
0.20	0.97 (3)	y=1.12x	0.92
0.50	0.95 (3)	y=1.03x	0.94
1.00	0.97 (3)	y=1.08x	0.68

Table 1: Regression coefficients derived from PLS analyses applied to spectra obtained at different moving mirror velocities.

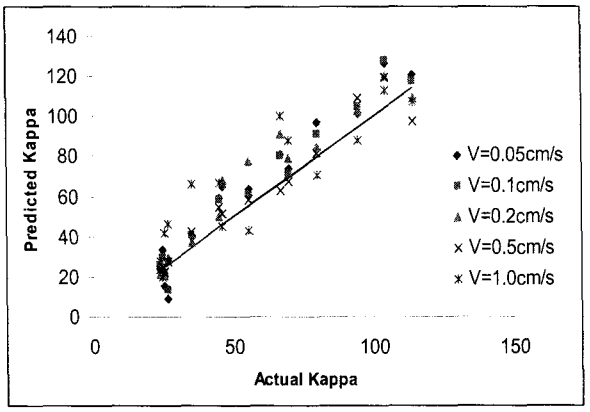

Fig.4. Kappa number prediction at different moving mirror velocities.

Thermal diffusive length

The PA probing depth should be determined from the shorter of the thermal diffusive length μ_S and the optical wave decay length μ_β. The thermal diffusive length can be controlled by the moving mirror velocity as described in Equation 1. In a previous study by Lima et al. (2000), the thermal diffusivity of kraft pulps was correlated with pulp brightness. In our study, we used these correlations to estimate the thermal diffusivity of pulps. Using an estimated thermal diffusivity value of 4.78×10^{-3} cm^2/s for the pulp sample (Kappa number 23.7), the penetration depth could be determined using Equation 1, and shown in Figure 5. Assuming each penetrated layer could be used to approximate the Kappa number of the pulp, the established PLS models were used to predict the Kappa numbers in these layers and plotted against the average estimated layer depth (Figure 6). The results confirm that the variation of lignin content at different depths in this pulp sheet sample is insignificant when the estimated depth is greater than 12 μm, suggesting that the method is acceptably accurate only when the mirror speed is ≤ 0.5 cm/s.

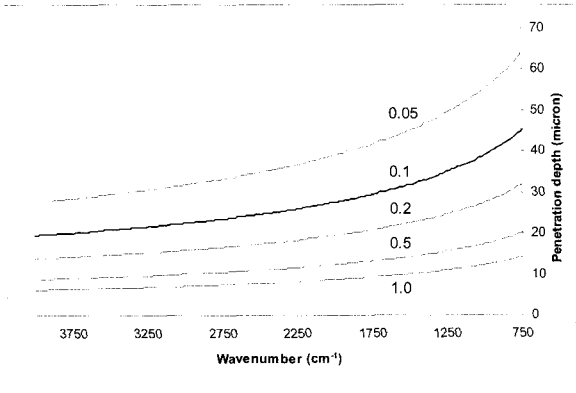

Fig.5. Estimated thermal penetration depth as a function of wavenumber at different velocities (V = 0.05, 0.1, 0.2, 0.5 and 1 cm/s).

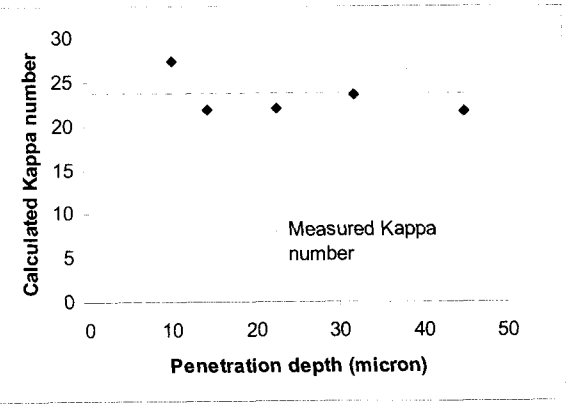

Fig.6. Kappa number profile from the surface of pulp sample (Kappa number 23.7).

CONCLUSION

This study describes how PAS-FTIR can be used to measure the Kappa number of *Pinus radiata* kraft pulps. The spectral data in 1650–1200 cm^{-1} region are found to have strong correlations with the Kappa number in kraft pulps, provided that the scan depth is adequate.

REFERENCES

Faix, O., In Lin S.Y. and Dence C.W. (Eds.), Methods in lignin chemistry (chapter 4):p.93. New York: Springer (1992).

Geladi, P. and Kowalski, B.R., Partial least squares regression: A tutorial, Analytica Chimica Acta, 185:1-17 (1986).

Halttunen, M., Tenhunen, J., Saarinen, T. and Stenius, P., Applicability of PAS-FTIR depth profiling for the study of coated papers, Vibrational Spectroscopy 19:261-269 (1999).

Lima, C.A.S., Lima, M.B.S., Miranda, L.C.M., Baeza, J., Freer, J., Reyes, N., Ruiz, J. and Silva, M.D., Photoacoustic characterization of bleached wood pulp and finished papers, Measurement Science and Technology, 11:504-508 (2000).

Meder, R., Gallagher, S., Mackie, K.L., Bohler, H., Meglen, R., Rapid determination of the chemical composition and density of *Pinus radiata* by PLS modeling of transmission and diffuse reflectance FTIR spectra, Holzforschung, 53(3):261-266 (1999).

Ohkoshi, M., PAS-FTIR study of light-induced changes in the surface of acetylated or polyethylene glycol-impregnated wood. Journal of Wood Science, 48:394-401 (2002).

Saariaho, A.-M., Hortling, B., Jaaskelainen, A.S., Tamminen, T., Vourinen, T., Simultaneous

quantification of residual lignin and hexenuronic acid from chemical pulps with UV resonance Raman spectroscopy and multivariate calibration, Journal of Pulp and Paper Science, 29(11):363-370 (2003).

Yamauchi, S., Sudiyani, Y., Imamura, Y. and Doi, S., Depth profiling of weathered tropical wood using Fourier transform infrared photoacoustic spectroscopy, Journal of Wood Science, 50:433-438 (2004).