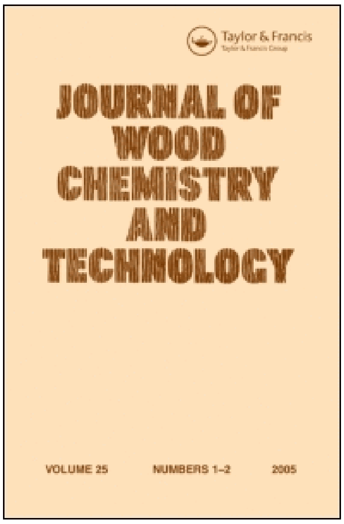

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

Near-Infrared Spectroscopy and Chemometric Analysis for Determining Oxygen Delignification Yield

Yunqiao Pu[a]; Arthur J. Ragauskas[b]; Lucian A. Lucia[c]; Ved Naithani[c]; Hasan Jameel[c]
[a] Institute of Paper Science and Technology, Georgia Institute of Technology, Atlanta, Georgia, USA [b] School of Chemistry and Biochemistry, Georgia, Institute of Technology, Atlanta, Georgia, USA [c] Department of Wood and Paper Science, North Carolina State University, Raleigh, North Carolina, USA

To cite this Article Pu, Yunqiao , Ragauskas, Arthur J. , Lucia, Lucian A. , Naithani, Ved and Jameel, Hasan(2008) 'Near-Infrared Spectroscopy and Chemometric Analysis for Determining Oxygen Delignification Yield', Journal of Wood Chemistry and Technology, 28: 2, 122 — 136

To link to this Article: DOI: 10.1080/02773810802125008

URL: http://dx.doi.org/10.1080/02773810802125008

Journal of Wood Chemistry and Technology, 28: 122–136, 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 0277-3813 print / 1532-2319 online
DOI: 10.1080/02773810802125008

Taylor & Francis
Taylor & Francis Group

Near-Infrared Spectroscopy and Chemometric Analysis for Determining Oxygen Delignification Yield

Yunqiao Pu,[1] Arthur J. Ragauskas,[2] Lucian A. Lucia,[3]
Ved Naithani,[3] and Hasan Jameel[3]
[1]Institute of Paper Science and Technology, Georgia Institute of Technology, Atlanta, Georgia, USA
[2]School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia, USA
[3]Department of Wood and Paper Science, North Carolina State University, Raleigh, North Carolina, USA

Abstract: Oxygen delignification studies were carried out using a softwood kraft pulp under varying reaction temperatures (80–140°C) and alkaline charges (1–12%). Near-infrared (NIR) spectroscopy combined with chemometric methods was employed to analyze oxygen delignification pulp yields, which were compared to gravimetric analysis. Principal component analysis (PCA) of the NIR spectra data was performed and a partial least-square (PLS) regression model was developed to predict the pulp yield of oxygen delignified pulps based on the NIR spectra data. PCA analysis indicated that 99.1% of total variances of NIR spectra data in the range of 1100–2266 nm could be expressed by three principle components. A PLS1 model based on the NIR spectra data had good predictive ability and appeared to be an effective tool for pulp yield prediction for the oxygen delignification process.

Keywords: Kraft softwood pulp, near-infrared, oxygen delignification, partial least-square regression, principal component analysis, yield

The authors sincerely recognize Professor Hou-min Chang's life-long contribution to the wood chemistry community and its science and engineering. We also thank the U.S. Department of Energy (DOE) and the member companies of the Institute of Paper Science and Technology for their support of this research. This manuscript was prepared, in part, with the support of DOE Cooperative Agreement No. DE-FC07-00ID13870. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the author(s) and do not necessarily reflect the views of the DOE.

Address correspondence to Arthur J. Ragauskas, School of Chemistry and Biochemistry, Georgia Institute of Technology, 500 Tenth Street, Atlanta, GA 30332, USA. E-mail: arthur.ragauskas@chemistry.gatech.edu

INTRODUCTION

Advances in near-infrared (NIR) spectroscopy and chemometric analysis have combined to provide a powerful practical technology for a host of process chemistry applications. An examination of the literature demonstrates the application of NIR spectrometry for several industries, including chemicals,[1] food,[2,3] pharmaceutical,[4] polymer,[5,6] and pulp and paper.[7] These applications are being developed in light of several practical advantages of NIR for on-line/at-line process analysis. For example, NIR spectroscopy readily facilitates low-cost nondestructive in-situ testing with a non-contact probe and optical fiber. The ability of NIR spectroscopy to characterize liquid and solid samples with little or no pretreatment, to provide quick spectral data and to predict physical and chemical parameters from the spectral data ensures its continuing application as an analytical tool for process chemistry.

The burgeoning field of biomass processing either for conventional pulp and paper applications or for biofuels/biochemicals processes can clearly benefit from NIR spectroscopy analysis. The chemical characterization of fibrous biomass with its multi-component chemical constituents provides a challenge that few other analytical methods can adequately characterize in an on-line manner. Sanderson et al.[8] demonstrated that NIR could be employed for lignocellulose analysis of a broad range of biomass feedstocks and with proper models yielded a technique that could be useful for rapid analysis of biomass. Studies by Kelley et al.[9] illustrated that this technique coupled with multivariate analysis techniques could be used to predict chemical compositions of disparate agricultural biomass samples.

The benefits of characterizing biomass have drawn the attention of several researchers in the forest products sector. The application of NIR has been used to characterize the chemical constituents,[10,11] physical[12,13] and mechanical[14] properties of wood. Fardim et al. and others have employed NIR spectroscopy and multivariate data analysis to develop a predictive models for the chemical composition and physicochemical characteristics of unbleached and bleached kraft pulps.[15–20] This analytical procedure has facilitated rapid spectroscopic determination of pulp viscosity, kappa number, brightness, and contents of glucan, xylan, uronic acids, and lignin in pulp. Although most of these studies have been directed at laboratory studies, research activities at characterizing mill-pulping liquors have demonstrated the application of these technologies for novel mill process sensors.[21]

A key parameter in the conversion of wood into paper is pulp yield, especially for kraft pulping and the initial stages of a modern bleach sequence. Indeed, over the past decade increased research efforts have been directed at improving the selectivity of oxygen (O) delignification of kraft pulps.[22] Oxygen-stage chemistry relies on elevated temperatures, sodium hydroxide, and oxygen pressure to oxidatively remove lignin in an environmentally benign manner. The oxidative degradation of lignin is initiated by single electron reactions involving phenolate anions of lignin and the ground state oxygen. Typically, 30–50% of the residual lignin in kraft pulp is removed during oxygen delignification. Although additional lignin removal is possible, the chemical selectivity between lignin and pulp polysaccharides begins to decrease, resulting in decreased pulp yield and diminished physical strength properties. Recently, studies by Pu et al. and others have reported several strategies to maximize lignin removal and pulp yield from an O and double oxygen (OO)-stages.[22–25] A key challenge for the effective utilization of these technologies is the need to efficiently monitor pulp yields in a practical industrial setting.[26,27]

In this study, changes in oxygen delignification pulp yield for a softwood kraft pulp were evaluated gravimetrically and by NIR spectroscopy under varying reaction temperatures and sodium hydroxide charges. Two multivariate analysis methods, principle component analysis (PCA) and partial least-squares (PLS) regression, were employed to correlate NIR spectroscopic data with pulp yield results. The results of these studies provide a rapid, facile methodology to predict pulp yield for oxygen delignification.

EXPERIMENTAL

Chemicals and Materials

All chemical reagents were commercially purchased and used as received. A softwood (SW) kraft pulp (kappa number 29.4) was acquired from a commercial kraft pulp mill operating in the southeastern USA. The pulp was washed with distilled water until the effluents were pH neutral and colorless. This pulp was air-dried and stored at 2°C prior to usage.

Oxygen Delignification

Oxygen delignification of a softwood kraft pulp was accomplished using a Parr reactor.[24,25] The pulp was well mixed with the desired amount of chemicals and charged into the reactor pre-warmed to 70°C. The reactor was sealed, rapidly heated up to a desired temperature while mixing and pressurized with oxygen. Upon completion, heating was halted, oxygen pressure was released and the pulp was discharged, water-washed, and air-dried. Table 1 summarizes the oxygen delignification conditions employed. Reaction temperatures and alkali charges were varied to obtain oxygen delignified pulps with a yield range of 86–99%. The statistical summary for oxygen delignification samples prepared with different parameters is shown in Table 2.

Pulp Analysis and Handsheet Preparation

Oxygen delignification pulp yield was gravimetrically determined based on the oven-dried weight of pre- and post-oxygen delignified kraft pulps. Kappa

Table 1. Oxygen delignification conditions

Temperature, °C	80.0–140.0
NaOH charge, %	1.0–12.0
$MgSO_4$, %	0.05
O_2 pressure, N/m^2	6.2×10^5
Consistency, %	10.0
Time, min	60.0

number of the oxygen delignified pulps was measured following standard Tappi test method T 236 om-99. Kappa number measurement had a standard deviation of 0.25 kappa units with three replicates. Handsheets for NIR analysis were prepared according to Tappi method T 272 sp-02.

NIR Measurements

NIR spectra of the handsheet samples were measured in the diffuse reflectance mode using a Lambda 900 UV/VIS/NIR Spectrometer (PerkinElmer Inc., USA). Spectra absorbance data are collected at 1.0 nm wavelength intervals over the range of 1100–2500 nm. Eight scans were taken for each handsheet and 32 scans were accumulated for each sample. Absorbance (A) values were converted from reflectance (R) values using the formula $A = \log(1/R)$. The NIR spectra results were averaged for each sample and the averaged data was used for multivariate analysis.

Multivariate Analysis

Principal component analysis (PCA) is a mathematical method for multivariate analysis dealing with large multi-dimensional data sets, yielding fewer principal components (PCs), which account for as much as possible of the variability of the data.[28,29] PCA enables one to perform data description and interpretation with significantly fewer variables than originally present. The PCs are uncorrelated to each other, with the first principal component (PC_1) carrying the greatest amount of variation and the second principal component (PC_2) carrying the maximum share of the residual information, and so on. PCA

Table 2. Statistical summary for the oxygen delignified pulp samples

	Min.	Max.	Avg.	Std. dev.
Yield, %	86.7	9.3	94.4	3.7
Delignification, %	25.7	84.1	57.7	17.1

computes each principal component as linear summation of the original data multiplied by a coefficient. The original data matrix (X) can be decomposed into score matrix (S) and loading matrix (L) after PCA decomposition. The S matrix contains score vectors that describe the sample patterns and generally show sample difference or similarities, whereas the L matrix contains loading vectors that describe the variable relationships.

Partial least-squares (PLS) regression is a predictive technique that decomposes both independent and response variables matrices simultaneously.[28,29] PLS maximizes the correlation between independent and response variables matrices and the latent variables in a independent matrix is modeled to predict response variables the best. In PLS modeling, there are generally two PLS algorithms: PLS1 and PLS2. PLS1 deals with only one response variable at a time, whereas PLS2 calculates several response variables simultaneously. Explained variances in a PLS model are used to indicate how much of the information the model can describe in the original data matrices. Root-mean-square error of calibration (RMSEC) is calculated from average difference between predicted and measured response values for calibration samples (see Eq. 1)).[28,29] Root-mean-square error of prediction (RMSEP) is square root of the average of squared differences between predicted and measured response values of validation samples, as shown in Eq. (2).

$$\mathrm{RMSEC} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(y_c^* - y_c)i} \tag{1}$$

$$\mathrm{RMSEP} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(y_v^* - y_v)i} \tag{2}$$

where n is number of samples; y_c^* and y_c are predicted and measured response value for calibration samples, respectively; y_v^* and y_v are predicted and measured response value for validation samples, respectively. RMSEC is usually used to show an average modeling error. RMSEP measures the average prediction error in a model and tells an expected deviation in a future prediction.

The multivariate analysis was carried out by using the Unscrambler software (Unscrambler 9.2, CAMO Software Inc., USA). The NIR spectra data of oxygen delignified pulps was transformed into data matrices and subjected to principle component analysis and partial least-square regression. Since there is only one response variable, that is, yield, PLS1 was employed to develop the yield prediction model for the oxygen delignified pulps. The PLS1 regression model was built with full cross validation procedure during calibration step. Full cross validation is considered an efficient way of model building for rather small amounts of samples in which all the samples are used for both model calibration and validation.[29,30] In full cross validation, one sample is kept out of the calibration data set at a time and the model is calibrated on the remaining samples. The left-out sample is then used for prediction with the built model and a predicted residual is computed. This process is repeated until all samples have been kept out once.

RESULTS AND DISCUSSION

Oxygen Delignification

A series of oxygen delignification experiments were carried out to produce pulps with a wide range of yields. Table 3 summarized the yield and delignification results under varying reaction temperatures and alkaline charges. Two-way analysis of variance (ANOVA) was carried out to investigate the effects of temperature and alkali charge on O-delignification yield. The ANOVA results were presented in Table 4. Both temperature and alkali charge had a larger F-ratio value than the critical value of $F_{0.05}$, indicating that both temperature and alkali charge had a significant effect on the O-delignification yield. The F-ratio value for temperature was further observed to be larger than the critical

Table 3. Oxygen delignification of a softwood kraft pulp

Sample #	Temperature, °C	Alkaline Charge, wt%	Yield, Wt%	Delignification,* %
80-1	80	1.0	99.3	25.7
80-3	80	3.0	97.9	40.4
80-6	80	6.0	97.0	45.9
80-9	80	9.0	98.0	40.7
80-12	80	12.0	97.0	40.9
100-1	100	1.0	97.8	44.4
100-6	100	6.0	95.8	61.9
100-12	100	12.0	95.3	62.4
110-1	110	1.0	98.5	36.0
110-3	110	3.0	96.1	60.8
110-6	110	6.0	92.8	64.0
110-9	110	9.0	92.0	71.5
110-12	110	12.0	91.6	66.4
140-1	140	1.0	94.6	60.4
140-3	140	3.0	91.1	76.5
140-6	140	6.0	90.0	75.2
140-9	140	9.0	88.5	81.0
140-12	140	12.0	86.7	84.1

*Calculated from kappa number.

Table 4. ANOVA results of temperature and alkali charge for oxygen delignification yield*

Source of variance	Sum of square	Degree of freedom	Variance	F-ratio	$F_{0.05}$	$F_{0.01}$
Temperature	146.81	2	73.40	39.83	4.46	8.65
Alkali charge	59.84	4	14.6	8.12	3.84	7.01
Error	14.74	8	1.84			

*With the assumption that yields are normally distributed and variances are homogenous, and interaction between temperature and alkali charge is not taken into account.

value of $F_{0.01}$, suggesting that the effect of temperature on O-delignification yield was very significant.

Figure 1 shows the relationship of pulp yield versus temperature and alkali charge for oxygen delignification. High temperature and high alkaline charge were observed to result in a decreased yield for the oxygen delignified pulp. Oxygen-delignification under the most drastic conditions (i.e., 140°C and 12% alkaline charge) had a low yield of 86.7%. Figure 2 summarized the relationship between pulp yield versus delignification ratio for the post-oxygen delignified pulps. The extent of pulp yield decrease was enhanced once approximately 60% delignification was accomplished. When 84.1% of residual lignin in the original pulp was removed under aggressive reaction conditions, the pulp yield decreased to 86.7%.

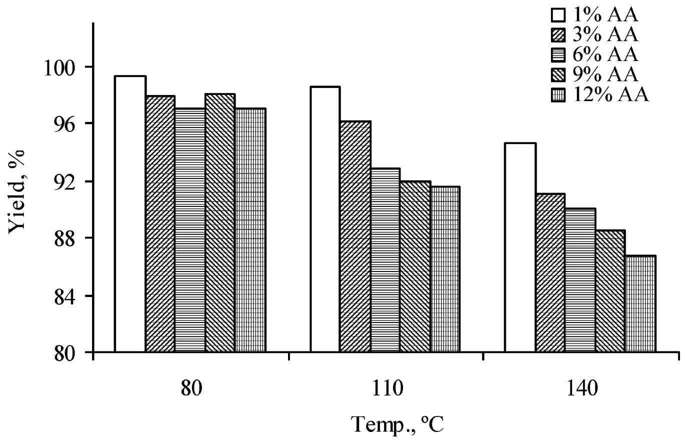

Figure 1. Pulp yield versus temperature and alkali charge (AA) for oxygen delignification.

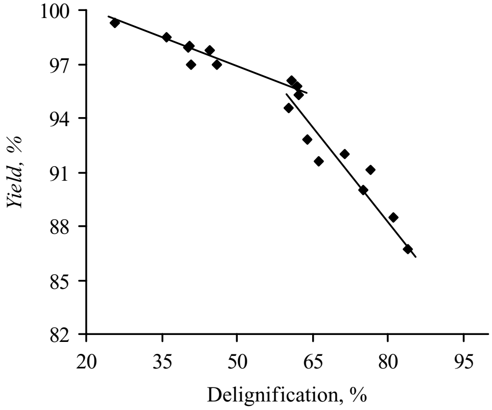

Figure 2. Pulp yield versus delignification ratio for a series of oxygen delignification.

NIR Spectroscopy

A typical near-infrared spectrum from 1100 to 2500 nm is presented in Figure 3 and this data is consistent with NIR data presented by Michell et al. for wood samples.[31] Three prominent bands were observed in the regions from 1328–1671, 1868–1999, and 2013–2220 nm. The band in the region from 1328–1671 nm corresponds primarily to the first overtone of C—H and O-H stretching vibrations, whereas the band in the region from 1868–1999 nm was assigned to the combinations of O-H stretching and bending vibrations as well as second overtone of C=O stretching vibrations.[32] The peaks near 2102 nm were assigned to combinations of O—H, C—H stretching vibrations

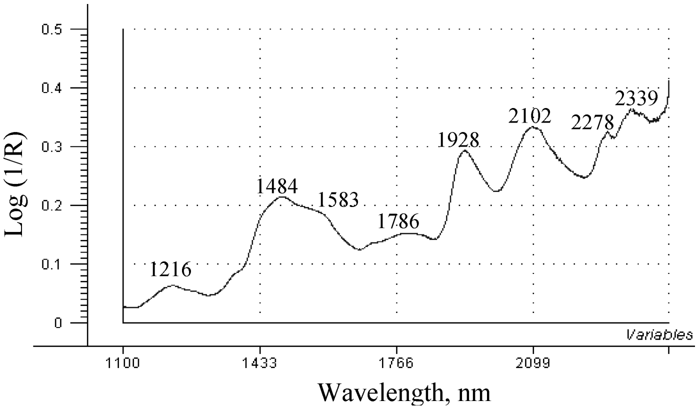

Figure 3. Typical NIR spectrum of oxygen-delignified pulp.

in the cellulose and xylan molecules.[31] A weak second overtone of C—H stretching vibrations appeared near 1216 nm. Two strong bands appeared near 1484 nm and 1928 nm, which have been assigned to vibrations from hydrated cellulose.[32] Aromatic functionalities from lignin were reported to appear at 1143 nm (second overtone of C—H stretching), 1445 and 1678 nm (first overtone of C—H stretching), and 2136 nm (C—H, C=C combinations).[30,31,33] All the oxygen-delignified pulps showed similar patterns in their NIR spectra. As discussed earlier, the NIR spectroscopic data contains broad vibration bands derived from C—H, O—H and aromatic functional groups from major chemical constituents of kraft pulps (i.e., cellulose, hemicellulose and lignin). Hence, it was anticipated that the NIR spectral data from a series of closely related pulps could be used to develop a predictive pulp yield model with the assistance of chemometric analysis.

Principal Component Analysis

PCA analysis was carried out in the range of 1100–2266 nm in the NIR spectra of pulps where most features attributed to the molecular bond vibrations in various pulp components were observed. The NIR spectra were considered a data matrix in the range of 1100–2266 nm and principal components were determined by the use of cross validation. As a result, 99.1% of total variances of the original data set was expressed by three principle components with PC_1 taking into account of 95.0% of total variance, PC_2 3.2% and PC_3 0.9%, respectively. This indicated that three principle components were able to describe the majority of variance in the NIR spectra, which was promising for partial least square regression model development.

Figure 4 showed a loading plot for the first principal component (PC_1). The highest loadings along the PC_1 appeared at the bands at 1915 and 1938 nm and a relatively low loading emerged at the bands peaked at 1418 nm. The bands near 1915 and 1938 nm were reported primarily from combinations of O-H vibrations in water and wood components.[31] Bassett et al. has observed strong absorbance signals near 1915 and 1938 nm derived from combinations of O-H in the cellulose.[32] The sugar and lignin analysis results showed that the oxygen-delignified pulps contained 78.0–85.0% cellulose, 7.0–8.5% xylan, 5.0–7.5% mannan, and 0.8–3.5% lignin.[34] With the cellulose content being around 80% in the pulp samples, the high loading signals near 1915 and 1938 nm along the PC_1 might suggest that PC_1 had a positive relationship with cellulose. The two peaks at 1915 and 1938 nm with high loadings along the PC_1 were observed to be highly positively correlated. Interestingly, all the bands along the PC_1 positively correlated with a positive loading. Figure 5 illustrates a score plot of PC_1 versus PC_2. The samples were spread along the PC_1 in accordance with the differences in temperature employed for the oxygen delignification. Samples with high temperatures (140°C) were located in the

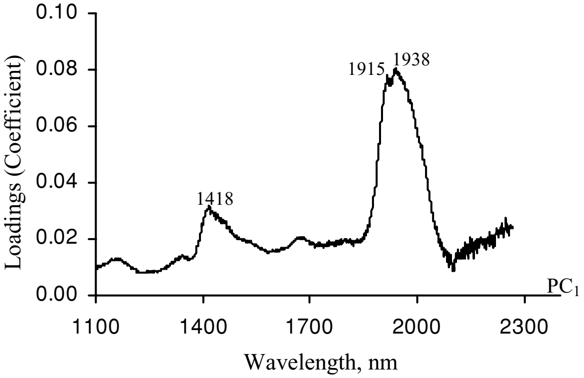

Figure 4. Loading plot for the first principal component from principal component analysis of NIR spectra.

left side of PC_1, whereas samples with intermediate temperatures (110 and 100°C) and low temperatures (80°C) were positioned in the middle and right side of PC_1, respectively. No noticeable sample grouping was observed along the PC_2. The temperature parameter appeared to play the most critical role in the pulp yield for oxygen delignification, with high temperature resulting in a decreased pulp yield. This was in accordance with the foregoing ANOVA results that temperature had a very significant effect on oxygen delignification yield.

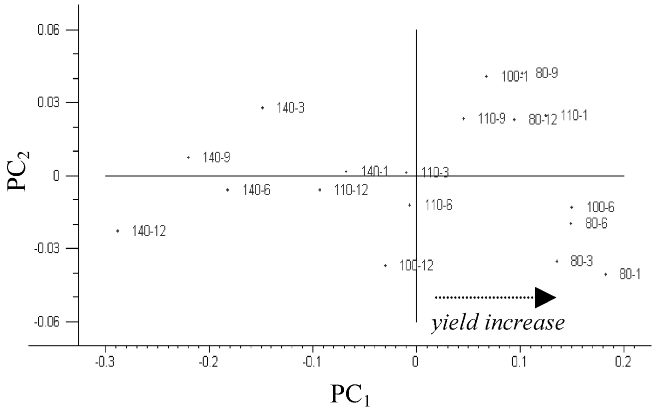

Figure 5. Score plot (PC_1 versus PC_2) from principal component analysis of NIR spectra.

Table 5. Quality parameters for the PLS1 regression model at different principal components built based on NIR spectra

PCs	X-expl[a] %	Y-expl[b] %	RMSEC[c] wt%	RMSEP[d] wt%
1	95.9	94.7	0.88	1.05
2	98.5	96.3	0.75	0.93
3	99.3	97.6	0.60	0.87
4	99.5	99.9	0.08	0.12

[a] Explained variance in X matrix (NIR spectra).
[b] explained variance in Y matrix (yield).
[c] Root-mean-square error of calibration.
[d] Root-mean-square error of prediction.

Partial Least-Square Modeling

PLS1 algorithm was used for modeling the pulp yield and NIR spectra data for oxygen delignification. NIR spectra data in the range of 1100–2266 nm were used as the independent variables matrix X and pulp yield was employed as the response variable matrix Y. The number of principal components that optimally predict the pulp yield were determined by cross validation and monitored with RMSEC and RMSEP. Table 5 listed some of the quality parameters of the built models at differing numbers of principal components. As an additional PC was introduced, the RMSEC decreased because the PCs were generated in such a way that the residuals calculated from calibration samples were minimized. However, improved model fit with a minimized RMSEC could be over-fitted and would not lead to a model with enhanced predictive ability. If the introduced PC primarily carries noise or spectral regions not related to the pulp yield, the model would fail to predict pulp yield without optimal accuracy, indicated by an increased RMSEP value. The optimal number of principal components was selected from the point where RMSEP had a minimum or leveled off.[30] In this study, the RMSEP value of PLS1 model continued to decrease until the regression model consisted of four PCs with a leveled-off value of RMSEP of 0.12. The PLS1 model with four PCs captured the majority of the systemic variation in the data matrices with 99.5% of variance in X variables (NIR spectra data) and 99.9% of variance in Y variables (pulp yield) described.

Figure 6 showed the correlation of predicted versus gravimetrically measured pulp yield for the PLS1 model with four PCs using NIR spectra data. A high correlation coefficient of 0.99 was observed. To further validate this model, a set of five oxygen delignified pulp yields were predicted using the PLS1 model based on their NIR spectra data. Figure 7 summarized predicted yield results based on NIR data versus experimentally measured yield values

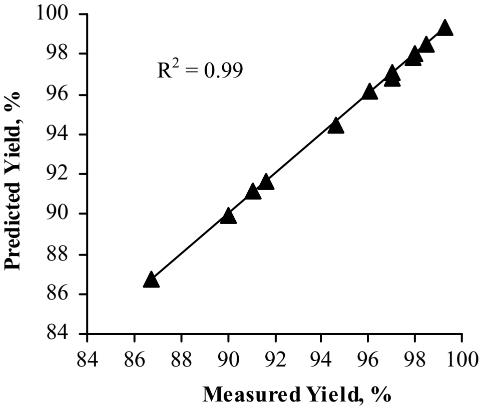

Figure 6. Correlation of measured pulp yield to predicted yield from PLS model with 4 principal components for calibration samples. R^2: correlation coefficient.

based on oven dried pulp measurements. The predicted values were in good agreement with the measured values with a correlation coefficient of 0.94 and a SEP of 0.97. This indicated that the PLS1 model built based on the NIR spectra data had good predictive ability and could be used for pulp yield prediction in oxygen delignification.

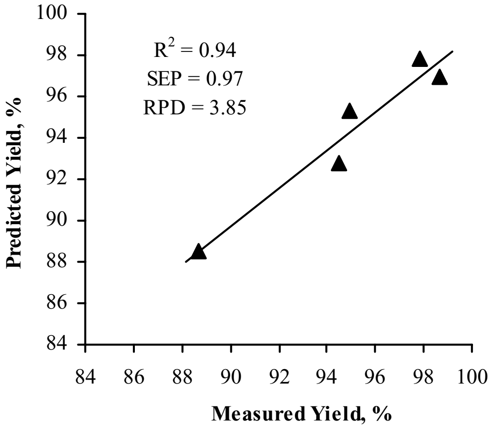

Figure 7. Plot of correlation between measured and predicted oxygen delignification pulp yield with PLS model using NIR spectra data. SEP: Standard error of prediction; RPD: Ratio of performance to deviation.

CONCLUSIONS

Near-infrared spectroscopy combined with chemometric analysis provided an effective tool for predicting oxygen delignification pulp yields. Principal component analysis demonstrated that 99.1% of total variances of NIR spectra data of oxygen delignified pulp samples in the range of 1100–2266 nm could be expressed by three principal components. PLS1 model developed with NIR spectra data had good predictive ability with a correlation coefficient of 0.94 between prediction and measured pulp yield. A PLS1 model built with pulp NIR spectra appeared to be an effective methodology for pulp yield prediction after oxygen delignification.

REFERENCES

1. Workman, J., Jr. A brief review of near infrared in petroleum product analysis. J. Near Infrared Spectrosc. **1996**, *4* (1–4), 69–74.
2. Lafargue, M.; Jaillais, B. Near-IR spectroscopy in food science. Principles and instrumentation, data processing, and applications. Spectra Anal. **2002**, *31* (228), 15–22.
3. Siemens, B.J.; Daun, J.K. Determination of the fatty acid composition of canola, flax, and solin by near-infrared spectroscopy. J. Am. Oil Chem. Soc. **2005**, *82* (3), 153–157.
4. Lunney, P.D.; Venham, L.D. Pharmaceutical process control by NIR spectroscopy. Am. Pharm. Rev. **2001**, *4* (3), 99–103.
5. Barnes, S.E.; Brown, E.C.; Sibley, M.G.; Edwards, H.G.M.; Scowen, I.J.; Coates, P.D. Vibrational spectroscopic and ultrasound analysis for in-process characterization of high-density polyethylene/polypropylene blends during melt extrusion. Appl. Spectrosc. **2005**, *59* (5), 611–619.
6. Okretic, S.; Volkl, N.; Siesler, H.W. Mid- and near-infrared spectroscopy of polymers: Time-resolved studies and remote-sensing applications. Crit. Rev. Opt. Sci. Technol., CR69 (Materials Characterization and Optical Probes Techniques), **1997**, 3–22.
7. Tsuchikawa, S. A review of recent near infrared research for wood and paper. Appl. Spectrosc. Rev. **2007**, *42* (1), 43–71.
8. Sanderson, M.A.; Agblevor, F.; Collins, M.; Johnson, D.K. Compositional analysis of biomass feedstocks by near infrared reflectance spectroscopy. Biomass Bioenergy **1996**, *11* (5), 365–370.
9. Kelley, S.S.; Rowell, R.M.; Davis, M.; Jurich, C.K.; Ibach, R. Rapid analysis of the chemical composition of agricultural fibers using near infrared spectroscopy and pyrolysis molecular beam mass spectrometry. Biomass Bioenergy **2004**, *27* (1), 77–88.
10. Kelley, S.S.; Rials, T.G.; Snell, R.; Groom, L.H.; Sluiter, A. Use of near infrared spectroscopy to measure the chemical and mechanical properties of solid wood. Wood Sci. Technol. **2004**, *38* (4), 257–276.

11. Yeh, T.-F.; Yamada, T.; Capanema, E.; Chang, H.-M.; Chiang, V.; Kadla, J.F. Rapid screening of wood chemical component variations using transmittance near-infrared spectroscopy. J. Agric. Food Chem. **2005**, *53* (9), 3328–3332.
12. Cogdill, R.P.; Schimleck, L.R.; Jones, P.D.; Peter, G.F.; Daniels, R.F.; Clark, A., III. Estimation of the physical wood properties of Pinus taeda L. Radial strips using least squares support vector machines. J. Near Infrared Spectrosc. **2004**, *12* (4), 263–269.
13. Schimleck, L.R.; Stuerzenbecher, R.; Mora, C.; Jones, P.D.; Daniels, R.F. Comparison of Pinus taeda L. wood property calibrations based on NIR spectra from the radial-longitudinal and radial-transverse faces of wooden strips. Holzforschung. **2005**, *59* (2), 214–218.
14. Tsuchikawa, S.; Hirashima, Y.; Sasaki, Y.; Ando, K. Near-infrared spectroscopic study of the physical and mechanical properties of wood with meso- and micro-scale anatomical observation. Appl. Spectrosc. **2005**, *59* (1), 86–93.
15. Fardim, P.; Ferreira, M.M.C.; Duran, N. Multivariate calibration for quantitative analysis of eucalypt kraft pulp by NIR spectrometry. J. Wood Chem. Technol. **2002**, *22* (1), 67–81.
16. Antti, H.; Alexandersson, D.; Sjostrom, M.; Wallbacks, L. Detection of kappa number distributions in kraft pulps using NIR spectroscopy and multivariate calibration. Tappi J. **2000**, *83* (3), 102–108.
17. Wallbaecks, L.; Edlund, U.; Norden, B.; Berglund, I. Multivariate characterization of pulp using solid-state carbon-13 NMR, FTIR, and NIR. Tappi J. **1991**, *74* (10), 201–206.
18. Marklund, A.; Hauksson, J.B.; Edlund, U.; Sjostrom, M. Multivariate data analysis based on orthogonal signal correction and near infrared spectroscopy. Nord. Pulp Pap. Res. J. **1999**, *14* (2), 140–148.
19. Ferraz, A.; Mendonca, R.; Guerra, A.; Ruiz, J.; Rodriguez, J.; Baeza, J.; Freer, J. Near-infrared spectra and chemical characteristics of *Pinus taeda* (loblolly pine) wood chips biotreated by the white-rot fungus *Ceriporiopsis subvermispora*. J. Wood Chem. Technol. **2004**, *24* (2), 99–113.
20. Schimleck, L.R.; Kube, P.D.; Raymond, C.A.; Michell, A. J.; French, J. Extending near infrared reflectance (NIR) pulp yield calibrations to new sites and species. J. Wood Chem. Technol. **2006**, *26* (4), 299–311.
21. Patrick, K.L. New sensor technology holds promise for better control of chemical fiberline. Pulp Pap. **1998**, *72* (3), 39–42, 47.
22. Pu, Y.; Yang, R.; Lucia, L.; Ragauskas, A. J.; Jameel, H. *Finding the Sweet Spot for Oxygen Delignification*. Proceedings of 2002 International Pulp Bleaching Conference, Portland, OR, **2002**, pp. 105–120.
23. Antonsson, S.; Lindstroem, Mikael E.; Ragnar, M. A comparative study of the impact of the cooking process on oxygen delignification. Nord. Pulp Pap. Res. J. **2003**, *18* (4), 388–394.
24. Zhang, D.; Pu, Y.; Chai, X.-S.; Naithani, V.; Jameel, H.; Ragauskas, A.J. Elucidating carboxylic acid profiles for extended oxygen delignification of high-kappa softwood kraft pulps. Holzforschung. **2006**, *60* (2), 123–129.
25. Zhang, D.; Chai, X.-S.; Pu, Y.; Ragauskas, A.J. Lignocellulosic fiber charge enhancement by catalytic oxidation during oxygen delignification. J. Colloid Interf. Sci. **2007**, *306* (2), 248–254.

26. Ala-Kaila, K.; Salmela, M.; Alen, R. Estimation of selectivity in industrial oxygen-alkali delignification of softwood kraft pulp. Nord. Pulp Pap. Res. J. **2002**, *17* (4), 405–409.
27. Ala-Kaila, K.; Salmela, M.; Alen, R. Estimation of pulp yield in industrial oxygen-alkali delignification of softwood kraft pulp. Nord. Pulp Pap. Res. J. **2002**, *17* (4), 401–404.
28. Martens, H.; Naes, T. Multivariate calibration. New York: John Wiley & Sons; 1989.
29. Esbensen, K.H. Multivariate data analysis—in practice. Oslo, Norway: CAMO Process AS; 2004.
30. Hannisdal, A.; Hemmingsen, P.V.; Sjoeblom, J. Group-type analysis of heavy crude oils using vibrational spectroscopy in combination with multivariate analysis. Ind. Eng. Chem. Res. **2005**, *44* (5), 1349–1357.
31. Michell, A.J.; Schimleck, L.R. NIR spectroscopy of woods from Eucalyptus globulus. Appita J. **1996**, *49* (1), 23–26.
32. Bassett, K.H.; Liang, C.Y.; Marchessault, R.H. Infrared spectrum of crystalline polysaccharides. IX. Near infrared spectrum of cellulose. J. Polym. Sci. A. **1963**, *1*, 1687–1692.
33. Barton, F.E. II; Himmelsbach, D.S.; Duckworth, J.H.; Smith, M.J. Two-dimensional vibration spectroscopy: Correlation of mid- and near-infrared regions. Appl. Spectrosc. **1992**, *46* (3), 420–429.
34. Yang, R.; Pu,Y.; Lucia, L.; Ragauskas, A.J.; Jameel, H. Developing predictive relationships between oxygen delignification and physical pulp properties. Proceedings of 12th International Symposium on Wood and Pulping Chemistry, Madison, Wisconsin, **2003**, *3*, 79–81.