NEAR-INFRARED SPECTROSCOPY FOR THE ESTIMATION OF YIELD IN SEMI-CHEMICAL PULPING

Project 3534-43

Final Report

to

Members of the

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EXPLORATORY PROJECT FINAL REPORT

PROJECT TITLE: NEAR-INFRARED SPECTROSCOPY FOR THE ESTIMATION OF YIELD IN SEMI-CHEMICAL PULPING

PROJECT NO.: 3534-43

OBJECTIVE:
The objective of this exploratory project was to generate basic information regarding the applicability of near-infrared spectroscopy (NIRS) to the analysis of high-yield pulps. The results described here lay the groundwork for a more in-depth investigation of the potential usefulness of this method as an estimator of yield in semi-chemical pulping. The ultimate objective of this, and subsequent related work, is to identify the best nongravimetric method of estimating yield and to develop empirical correlations between yield and specific end-use properties.

INTRODUCTION:
In near-infrared spectroscopy, a sample is sequentially irradiated with bands of light energy having an extremely narrow wavelength range. During exposure to each individual band, the absorption of radiation is measured indirectly by detecting the amount of incident energy that has interacted with and reflected from the sample. Exposing a sample to a continuum of such bands results in absorption measurements that cover a wide spectral region (1100 to 2500 nm). A plot of absorption as a function of wavelength for a particular sample is called its absorption spectrum.
Near-infrared absorption spectra consist primarily of overlapping bands that result in broad spectral features from which it is difficult to derive structural information. The spectra, however, have been found to be very useful for quantitative analysis, and the technique is widely employed as an analytical tool in a variety of industries. The appeal of NIRS lies in its fast analysis time with minimal sample preparation, its relatively compact and rugged design, and its recently emerged compatibility with fiber optic technologies. These attributes have rendered NIRS an ideal candidate for several on-line applications in the pulp and paper industry.

One current need in our industry is an improved control strategy for semi-chemical pulping. A major advance in this area could be achieved by developing the ability to rapidly and accurately measure pulp yield in the mill. Such an accomplishment might enable the real-time prediction of product properties, an extremely desirable control capability.

Earlier studies have already demonstrated the potential usefulness of NIRS in pulping applications. Easty has reported correlations between intensities observed in second derivative transformations of NIR absorption spectra and the kappa number of unbleached loblolly pine kraft pulp and cotton linter mixtures (1). The same report also indicates a correlation between similar NIR intensities and the lignin content of larch kraft pulp handsheets. Birkett and Gambino have reported a correlation between untransformed NIR absorption intensities and the kappa number of kraft pulps prepared from a variety of species.
(2). Wright et. al. have reported the ability to predict yield from the NIR absorption intensities measured from raw wood (3). Except for this most recent work by Wright, these studies were all limited to laboratory pulps that were cooked to typical kraft yield levels of approximately 50%. The effort summarized in this report is the first ever to use NIRS for the analysis of high-yield pulps.

EXPERIMENTAL APPROACH:
Chestnut oak chips were cooked under neutral sulfite semi-chemical (NSSC) conditions in a multi-unit digester to eight different yield levels that varied over the range of 74.7% to 82.7%. Samples at the two extremes of the range were extensively washed, fiberized, fluffed, and analyzed using near-infrared spectrometry. The samples were presented in three different conditions: 1) dried handsheet form; 2) dried fluff form; and 3) moist fluff form. Two reloads of each sample were scanned from 1100 to 2500 nm using a NIRSystems Model 6250 spectrophotometer in the reflectance mode with a ceramic standard as reference.

RESULTS AND DISCUSSION:
Figure 1 shows NIR spectra acquired from two different high-yield pulp samples. One sample was a pulp that was cooked to a yield of 82.7% and the other was a pulp cooked to a 74.7% yield. The spectra in Figure 1 were recorded from samples that were presented in air-dried handsheet form. Two sheets were made from each sample and one spectrum was recorded from each sheet.
Differences appear to be significant between spectra acquired from two different handsheets made from the same sample. Possible contributing factors include instrument variability, handsheet variability (such as formation differences), and inherent sample inhomogeneity. Future efforts should aim to identify, or at least quantify, the effects that these, or other factors, have on data variability associated with a single sample. Despite the interfering single-sample variability described above, a spectral difference between the two samples is readily apparent in Figure 1 and in Figure 2 where the paired spectra from each sample were averaged to give a single representative spectrum. The observed difference is primarily a baseline shift, greater in magnitude, but yet, similar to the difference that is attributed to single-sample variability.

Because baseline shift can also be caused, at least in part, by a variety of sampling-related factors, the feature is virtually useless as a predictor of a specific sample characteristic. It therefore becomes desirable to compensate for baseline differences so that differences in other spectral features may be enhanced. A convenient way of accomplishing this is to mathematically transform raw spectral data into second derivative spectra. The second derivative inverts absorption maxima to minima and increases the apparent resolution in a spectrum.

Second derivative spectra obtained from the raw spectral data shown in Figure 1 are depicted in Figure 3. Single-sample variability appears significantly reduced in the transformed spectra while narrow-band differences between the two samples are enhanced.
Selecting spectral regions that are known to be devoid of water absorption bands (1500-1800 nm and 2000-2400 nm), we can expand along the wavelength-axis and further magnify sample differences, as seen in Figures 4 and 5. Both regions exhibit spectral differences between samples that are potentially indicative of sample yield. The most notable differences involve features centered at approximately 1527, 1635, 1717, 1748, 2015, and 2226 nm.

When the same pulp samples were mechanically fluffed and presented for NIRS analysis, the spectra shown in Figure 6 were obtained. With fluffed pulp, differences between samples were considerably less pronounced than what was observed in the case of the handsheets. In fact, it is difficult to distinguish sample differences from single-sample variations. The significance of these differences remains questionable even though they are made more apparent when the paired spectra in Figure 6 (spectra acquired from two reloads of each sample) are averaged (Figure 7). Further enhancement by second derivative transformation is shown in Figures 8 and 9. The overall shape of the transformed fluff spectra is very similar to that observed in the transformed handsheet spectra. Some sample-to-sample differences are also consistent: the intensities at 1635, 1748 and 2226 increase with yield; the intensity of the shoulder at 1670 decreases with yield; and the minimum at 1717 exhibits a shift to lower wavelength as yield decreases.

Near-infrared spectra were also recorded on portions of the same two samples that were fluffed but not allowed to completely air dry (Figure 10). The moisture content of these samples, estimated at approximately 60-70%, significantly alters gross spectral features. As
in the case of the dry fluff, sample-to-sample differences are largely obscured by single-sample variations.

Some potentially significant differences stand out, however, in the averaged spectra shown in Figure 11. The transformed and expanded spectral regions shown in Figures 12 and 13 reveal sample-to-sample differences consistent with those observed in the corresponding spectra obtained from the handsheet and dry fluff sample forms. This observed consistency suggests that the presence of moisture does not interfere with the most prominent sample-to-sample spectral differences. If this finding is upheld in future experiments, sample drying may not be required prior to NIR analysis.

CONCLUSIONS:

Significant differences are evident in the transformed near-infrared absorption spectra recorded from laboratory pulps that have been cooked under semi-chemical conditions to different yields. This represents the first direct evidence that NIRS is potentially useful for yield estimation in high-yield pulps.

Spectral differences between samples are most pronounced when the samples are presented for analysis in air-dried handsheet form. If the samples are presented in a fluffed form that still contains an appreciable amount of moisture, spectral differences are reduced. The differences remain significant, however, and may justify the elimination of a drying step in the sample preparation procedure, thereby simplifying the NIRS analysis.
These conclusions should be regarded as somewhat tentative because the data base at this time is minimal in size. Future work should focus on the analysis of samples that have yields intermediate to that of the samples reported on here. The plan will be to verify the observed effects of yield, sample form, moisture content, and loading.

EXPERIMENTAL:

Sample Preparation:
Chestnut oak chips were kindly supplied by the Willamette Industries pulp mill located at Hawesville, Kentucky. Prior to use, the chips were hand sorted to isolate approximately 900 grams of chips (oven-dried basis) that were roughly uniform in size. After overnight moisture equilibration, nine samples, with a combined weight of over 200 grams (oven-dried basis), were removed for consistency determination (TAPPI Test Method: T258 om-89). These samples were placed in drying tins and dried in a 105°C oven for at least 24 hours. The resulting consistency measurements gave an average of 0.619 with the standard deviation (S_w) equal to ± 0.003.

A chip charge of 96.93 grams at 61.9% consistency (equivalent to 60 grams on an oven-dried basis) was placed in each of two 500 ml stainless steel digesters. Cooking conditions were as follows:
Liquor-to-wood ratio: 4:1

$\text{Na}_2\text{SO}_3$: 10%  
(as $\text{Na}_2\text{SO}_3$ on o.d. wood)

$\text{Na}_2\text{CO}_3$: 3%  
(as $\text{Na}_2\text{CO}_3$ on o.d. wood)

Temperature: 170°C

The digesters were placed in a circulating oil bath and were heated from room temperature up to the reaction temperature over a period of 75 minutes. At a point 66 minutes into the heat-up, the first digester was removed and the reaction quenched by rapid cooling. The other sample used in this study came from a digester that was removed approximately 45 minutes later. The contents of both were separately washed in a 4-liter sintered glass funnel, each with approximately 20 liters of deionized water. After refrigerated storage overnight, the samples were again washed, this time with about 10 liters of deionized water each.

Following this extensive washing, the samples were fiberized in a Waring blender for a period of 15 minutes and then washed again, using approximately another 8 liters of deionized water. After breaking up the final washed pad by hand, the pulp was allowed to equilibrate overnight in cold storage. Consistency was then determined in duplicate for each pulp sample using Tappi Method T240 om-88. The method involves forming a weighed
amount of pulp into a pad on a sheet of filter paper, followed by thorough drying and subsequent reweighing. The pooled standard deviation of the pulp consistency measurements was less than ± 0.001.

Pulp yield was calculated as follows:

\[
\text{% Yield} = \frac{\text{weight of pulp} \times \text{pulp consistency}}{\text{weight of wood} \times \text{wood consistency}} \times 100
\]

\[
= \frac{W_p \ C_p}{W_w \ C_w} \times 100
\]

The approximate error associated with a given pulp yield value is ± 0.7. It was estimated as

\[
\frac{W_p (C_p + S_p)}{W_w (C_w - S_w)} \quad \text{and} \quad \frac{W_p (C_p - S_p)}{W_w (C_w + S_w)}
\]

After consistency determination, the samples were formed into thick pads and pressed for 1 minute at 10 psi followed by another minute at 15 psi to give a consistency of about 25%. The pulps were then fluffed using a narrow diameter dual-impeller benchtop device. After a few hours of exposure to forced air currents, a portion of each sample was presented for analysis as moist fluff. The remainder of the fluff from each sample was left exposed to air overnight and then analyzed as dry fluff. The sample pads that were formed on filter paper to determine consistency served as the air-dried pads that were analyzed.
Visual inspection of the dried consistency pads revealed that pulp fiberization was extensive but also that shive content was high. Uneven formation had resulted in poor uniformity across the sample pads, especially in the higher yield sample. It was possible, however, to avoid those areas of the pad that exhibited the poorest quality because only a 4 cm X 5 cm piece was used for the analysis.

It should be noted that the consistency pad pieces were analyzed while still attached to the filter paper upon which they were formed. It is not known to what extent this filter paper backing contributed to the reflectance measurements. It is possible, however, that this effect would be the same for each sample and would not contribute to the differences observed between samples. At any rate, this added source of uncertainty will be eliminated in future experiments by separating the pads from their filter paper backing immediately after formation.

**Equipment:**

The instrument used for NIRS was a NIRSystems Model 6250 spectrophotometer controlled by an IBM PS/2 personal computer. It is a fully scanning instrument that utilizes an oscillating concave holographic grating as a dispersing element. In this study, the instrument was used exclusively in the reflectance mode. The diffusely reflected radiation from a sample is detected by an array of lead sulfide detectors that are positioned to exclude specular radiation.
All spectra reported here were acquired from samples mounted in a quartz-windowed stationary sample cell. With this sampling arrangement, the area of sample exposed to incident radiation was approximately 2 cm X 4 cm. To compensate for variations in light source energy output and detector response over the wavelength range covered, sample data were corrected by subtracting data acquired from an internal ceramic reference.

**FUTURE WORK:**

In future work, the original experimental approach will be expanded in scope to accommodate more detailed analyses of a greater number of pulp samples. Two separate sample sets will be prepared and analyzed. One set (which includes the two samples discussed here) is known as the calibration set and will be used to establish a quantitative correlation between NIRS data and laboratory yield determinations. A second, independent sample set, the validation set, will then be used to test how accurately the instrument can estimate yield. Each sample set will consist of eight samples cooked to different yield levels. The targeted yield range will be from approximately 70 to 85% with yield differences between samples achieved by varying individual retention times.

Laboratory determinations of yield will be conducted gravimetrically, keeping in mind that the non-homogeneous nature of the wood and pulp necessitates extensive sampling if a high degree of accuracy is desired. Since the gravimetric yield determinations are to be conducted in only one laboratory, it is not possible to quantify the accuracy of the laboratory method. An estimate of laboratory precision is possible, however, and will allow a comparison.
between the laboratory and instrumental precision.

Aside from yield, other sample-related variables will be examined in terms of their effect on spectroscopic features. These will include sample presentation form, the moisture content of the sample, and sample loading. The goal here, from the standpoint of simplifying eventual on-line implementation, is to identify the analysis procedure that involves the least sample preparation, yet gives an adequate correlation between yield and spectroscopic data. For example, the ability to obtain meaningful results from pulp that is wet and compacted would render the method ideally suited to the analysis of pulp as it exits a washer.

The different analysis procedures can be evaluated by monitoring the degree of correlation in the calibration set between NIRS yield estimations and laboratory yield measurements. The degree of correlation can be assessed via the standard statistical techniques described below.

In evaluating the effect of sample presentation form, three different forms will be used: sheet, fluffed, and unfluffed. The results obtained from these sample forms will provide an indication of the importance of surface homogeneity in the analysis of reflectance. The unfluffed pulp is to be prepared by hand-disintegrating the final washed pulp pad. It contains many, relatively large fiber clumps, or knots. The prevalence of the clumps is significantly decreased by applying the fluffing treatment, and almost completely eliminated in a good quality handsheet. It should be relatively straightforward to quantify surface homogeneity by applying image analysis routines to low magnification optical or electron micrographs of the
samples as packed for analysis.

Over the yield range being investigated, unscreened pulps are expected to exhibit an increase in average particle size as yield levels increase. If significant spectral differences are observed between samples, and if near-infrared reflectance is found to be influenced by particle size, then it may become difficult to separate the effects of yield and particle size. To avoid this complication, it might be necessary to include some type of grinding procedure prior to NIRS analysis so that all samples have a similar particle size distribution.

When analyzing pulps in handsheet form, the effect of sample thickness on spectral data will also need to be evaluated. Knowledge of this effect will allow the determination of adequate sample thickness, thus ensuring that all reflected radiation detected during a NIRS analysis emanates exclusively from the sample and does not include radiation reflected from sample backing materials.

Different sample thicknesses will be achieved by varying the number of handsheet pieces that are layered together in the sample cell. Variability associated with inhomogeneity across an individual handsheet will be explored by acquiring several spectra from the layered pieces, each time shifting one piece from the bottom to the top of the layered stack. In addition, more than one handsheet will be prepared from some samples so that it will be possible to assess variability between different handsheets from the same pulp.
The influence of pulp moisture levels on acquired spectral data will be assessed by analyzing all forms of all samples at two widely different moisture contents. Specifically, samples will be analyzed in an air-dried state and in a condition in which they contain 60-70% water. It will also be necessary to characterize the effect of more subtle variations in moisture content since it is not feasible to hold moisture levels constant within the wet sample set.

Variability attributed to sample loading can be quantified by applying statistical analysis to data acquired from several reloads of each sample. There is also a quantifiable variability associated with the rotational orientation of a sample when the circular, cup-shaped cell is used. The effect of sample cell type will also be explored by using a large rectangular cell that slowly moves past the incident radiation during spectral acquisition, thus greatly increasing the sample area analyzed.

Raw absorption data are rarely used to develop a calibration equation because the results can be much improved if the raw data are enhanced by mathematical transformation. For this reason, several math options are available in the NIRSystems software including a variety of smoothing algorithms; first, second, third, and fourth derivatives; and a Kubelka-Munk transformation. Although a second derivative transformation is recommended for inhomogeneous samples with broad particle size distribution, the other transformations should be explored. If it turns out that one of the derivative transformations is most useful, the transform algorithm may be further optimized by adjusting specific derivation parameters (i.e., gap size and segment size).
Once the spectral data acquired from the calibration samples are mathematically transformed, a calibration equation will be generated by a stepwise linear regression program that is also resident in the instrument software. The program searches a specified wavelength range for the single wavelength that gives the best correlation between absorption and laboratory determined yield. Additional software capabilities allow the user to assess the reliability of the selected wavelength and its associated calibration equation. Options exist to modify the selected wavelength (e.g., dividing the data at the selected wavelength by the data at another wavelength), to replace the selected wavelength by another wavelength, or to add additional wavelength terms to the equation. The determination of reliability is aided by inspecting plots of the correlation coefficient and K1 magnitude as a function of wavelength (the variable K1 being a designator for the coefficient of the first term in the calibration equation). The reliability of the selected wavelength is compromised if the K1 value is unreasonably large or if the shape of the correlation curve is sharp or jagged at that particular wavelength.

Other statistical indicators that will be used to evaluate how well a given regression equation fits the calibration data include: the standard deviation of the residuals (standard error of calibration), the value of the squared correlation coefficient ($R^2$), a plot of residuals vs. calculated values, a plot of laboratory values vs. calculated values, and a plot of the average residual and the range of residuals for each data set (control chart).
With the exception of $R^2$, all of the above statistical indicators will also be used to evaluate the performance of a given calibration equation as it is used to predict yield in an independent data set (the validation set).

REFERENCES:


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AIR-DRIED PADS

- YIELD = 82.7%
- YIELD = 74.4%
AIR-DRIED PADS

- YIELD = 82.7%
- YIELD = 74.7%

FIGURE 2
AIR-DRIED PADS

- YIELD = 82.7%
- YIELD = 74.7%

FIGURE 3
AIR-DRIED PADS

YIELD = 82.7%
YIELD = 74.7%

SECOND DERIVATIVE (LOG 1/R)

WAVELENGTH (NANOMETERS)

FIGURE 4
AIR-DRIED FLUFF

- YIELD = 82.7%
- YIELD = 74.7%

FIGURE 7
AIR-DRIED FLUFF

- YIELD = 82.7%
- YIELD = 74.7%

FIGURE 9
Figure 10

MOIST FLUFF

- YIELD = 82.7%
- YIELD = 74.7%
MOIST FLUFF

- YIELD = 82.7%
- YIELD = 74.7%

FIGURE 11
SECOND DERIVATIVE (LOG 1/R)

MOIST FLUFF

YIELD = 82.7%
YIELD = 74.7%

WAVELENGTH (NANOMETERS)

FIGURE 12
MOIST FLUFF

SECOND DERIVATIVE (LOG 1/R)

- YIELD = 82.7%
- YIELD = 74.7%

WAVELENGTH (NANOMETERS)

FIGURE 13
Excitation Spectra

Em $\lambda = 490$ nm

82.7%

74.7%

FIGURE 14
Excitation Spectra

74.7% Yield
Em\(_\lambda\) = 490 nm

FIGURE 15