Near-Infrared Analysis of Ground Barley for Use as a Feedstock for Fuel Ethanol Production

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The objective of this study was to explore the potential of near-infrared spectroscopy for determining the compositional quality properties of barley as a feedstock for fuel ethanol production and to compare the prediction accuracy between calibration models obtained using a Fourier transform near-infrared system (FT-NIR) and a dispersive near-infrared system. The total sample set contained 206 samples of three types of barley, hull-less, malt, and hulled varieties, which were grown at various locations in the eastern U.S. from 2002 to 2005 years. A new hull-less barley variety, Doyce, which was specially bred for potential use in ethanol production, was included in the sample set. One hundred and thirty-eight barley samples were used for calibration and sixty-eight were used for validation. Ground barley samples were scanned on both a FT-NIR spectrometer (10000 to 4000 cm⁻¹ at 4 cm⁻¹ resolution) and a dispersive NIR spectrometer (400 to 2498 nm at 10 nm resolution), respectively. Six grain components, moisture, starch, b-glucan, protein, oil, and ash content, were analyzed as parameters of barley quality. Principal component analysis showed that barley samples could be classified by their types: hull-less, malt, and hulled. Partial least squares regression indicated that both FT-NIR and dispersive NIR spectroscopy have the potential to determine quality properties of barley with an acceptable accuracy, except for b-glucan content. There was no predictive advantage in using a high-resolution FT-NIR instrument over a dispersive system for most components of barley.

Index Headings: Near-infrared spectroscopy; NIRS; Dispersive spectroscopy; Fourier transform near-infrared spectroscopy; FT-NIR spectroscopy; Barley; Fuel ethanol; Partial least squares; PLS regression.

INTRODUCTION

Higher energy costs have become a reality for everyone worldwide and development of renewable fuels has been emphasized. Farm-based cash crops such as corn, wheat, and sorghum, other plant materials such as switchgrass, and agricultural waste such as citrus peel have been considered as sources for fuel ethanol production. Corn is the main feedstock for ethanol in the U.S.; over 90% of the ethanol made today is made by fermentation of corn grain. In 2004 and 2005, approximately 10% and 14% of the total corn crop was used for the purpose of ethanol production and it resulted in about 3.4 and 3.9 billion gallons of ethanol, respectively.¹ In 2006, about 4.8 billion gallons of ethanol were produced.¹ The amount of fuel ethanol produced from corn alone will not be enough to cover the U.S. transportation fuel needs (about 140 billion gallons per year). Obviously, other feedstocks for ethanol production are needed.

Barley has been mainly used as an animal feed or in the malting and brewing industries.² Recently, there has been growing interest in using barley as a feedstock for fuel ethanol in the U.S. Barley grows well outside the corn belt, where there is demand for ethanol in the upper Midwest, in the Northwest and on the East Coast. On the East Coast and other similar climatic regions in the U.S., “winter” barley can be seeded in the fall and harvested early enough in the spring to follow with a full crop of soybeans in the same season. Following the next year with corn and then repeating the rotation allows for sustainable production of three crops in two years. Barley has been successfully used as a feedstock for fuel ethanol production in Europe where corn is less common, whereas it has not been considered a viable feedstock in the U.S. The primary reason for this is higher production cost and less ethanol yield compared to corn. Barley’s physical and chemical properties—an abrasive hull, low starch content, high fiber content, and high viscosity of barley fermentations—impede production efficiency.³ Com has about 72% starch content, whereas typical feed barley has about 50–55% starch content.

Recently, a new hull-less variety of barley (Doyce) has been developed and released by breeders at Virginia Polytechnic Institute and State University. The new variety has a loosely attached hull, which results in removal of the hull easily during harvest and during grain cleaning. Due to loss of the hull and superior genetics, Doyce has higher levels of starch (62–66%) and protein (9.5–11.4%) and lower levels of ash and crude fiber than hulled varieties.² The high starch and protein content of Doyce makes it a potentially useful variety for fuel ethanol production. Also, research on converting b-glucan in barley to glucose by new enzymes is ongoing, so that additional fermentable glucose will lead to a detectable increase in ethanol yield. Initial studies suggest that the new variety of barley is a promising feedstock for fuel ethanol production.

Determination of the components in barley is important to estimate ethanol yield or to evaluate co-product quality. Starch and b-glucan are the most important constituents. Starch is the main material that is broken down to glucose by enzymes and then fermentated to produce ethanol. High starch leads to high ethanol yield. b-glucan is related to the viscosity. Low b-glucan means lower viscosity and less need for expensive enzymes to break it down for suitable processing and fermentation. Alternatively, if enzymes are used to break b-glucan down to glucose, to increase ethanol yield, higher levels of b-glucan will be advantageous for ethanol production as long as starch levels are still high. Therefore, knowledge of the amount of b-glucan is also important in order to determine the dose of enzymes required. After barley grain is fermented, ethanol is distilled off. Everything left is evaporated and dried down to yield distillers dried grains with solubles (DDGS). The DDGS contains everything that was in the kernel except for the starch and b-glucan that was converted to ethanol. The DDGS

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TABLE I. Source of barley samples used in this study.

<table>
<thead>
<tr>
<th>Subset</th>
<th>Crop year</th>
<th>Barley type</th>
<th>Number of varieties</th>
<th>Growing location</th>
<th>Number of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>2002–2003</td>
<td>Hull-less, malt, hulled</td>
<td>59</td>
<td>1</td>
<td>59</td>
</tr>
<tr>
<td>II</td>
<td>2003–2004</td>
<td>Hull-less, malt, hulled</td>
<td>60</td>
<td>1</td>
<td>60</td>
</tr>
<tr>
<td>III</td>
<td>2004–2005</td>
<td>Hull-less, hulled</td>
<td>57</td>
<td>1</td>
<td>57</td>
</tr>
<tr>
<td>IV</td>
<td>2002–2003</td>
<td>Hull-less (Doyce)</td>
<td>1</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>V</td>
<td>2003–2004</td>
<td>Hull-less (Doyce)</td>
<td>1</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>VI</td>
<td>2004–2005</td>
<td>Hull-less (Doyce)</td>
<td>1</td>
<td>6</td>
<td>6</td>
</tr>
</tbody>
</table>

is a co-product and usually sold for animal feed. Protein and oil are important components of the DDGS. The greater their content in the DDGS, the more valuable it is. Currently used analytical methods for barley quality are very time consuming and expensive. Therefore, a more rapid, inexpensive, and accurate analytical method is desirable.

Near-infrared (NIR) spectroscopy has been extensively utilized for grain analysis over the past thirty years. The advantages of using NIR spectroscopy are based on its ability to analyze rapidly and to save considerable time by simultaneous multi-compositional analyses. Previous NIR studies for barley were mostly conducted for ingredients of animal feed or malt quality and they reported the prediction of moisture, protein, starch, and β-glucan.4–9 The aim of this study was to investigate the possibility of using NIR spectroscopy to evaluate barley as a feedstock source for ethanol production. More extensive analysis was conducted to predict six components: moisture, starch, β-glucan, protein, oil, and ash contents. We used three types of barleys, hull-less, malt, and hulled, to develop robust calibrations for evaluation of barley quality. In addition, the new hull-less variety of barley, Doyce, that was specifically bred for potential use in ethanol production was added to the sample set to test. Calibration models for barley quality were conducted using two types of NIR instruments, a Fourier transform NIR system and a dispersive NIR system, and the accuracy of the models were compared.

EXPERIMENTAL

Barley Samples. All barley samples were provided by researchers at Virginia Polytechnic Institute and State University and chemical analyses were conducted at the Eastern Regional Research Center (USDA-ARS) in Wyndmoor, Pennsylvania. The barley samples included six subsets described in Table I. A first subset of 59 barley varieties contains three types, hull-less, malt, and hulled barley, that were grown during the 2002–2003 crop season. A second subset contains 60 samples of three barley types grown during the 2003–2004 crop season. A third subset of 57 samples is from the 2004–2005 crop and includes hull-less and hulled barley. Additionally, the new hull-less variety, Doyce, which was specially bred for its potential in ethanol production, is added to the sample set. These are a single variety and grown from 2002 to 2005 at different locations (subsets IV, V, VI). The total sample set (n = 206) contains 164 samples of hull-less barley, 16 samples of malt barley, and 26 samples of hulled barley. All barley samples used for analyses were ground in a cyclone mill (Udy Corp., Fort Collins, CO) fitted with a 0.5 mm screen.

Reference Analysis. Reference analyses were performed for six grain compositional quality parameters: moisture, starch, β-glucan, protein, oil, and ash. A total of 206 samples were used for moisture, starch, β-glucan, protein, and ash analysis, whereas only 142 samples were used for oil analysis. Moisture content was determined by oven drying 2 g samples at 135 °C for 2 h.10 Starch content was determined using a kit from Megazyme (Megazyme International Ireland Ltd., Bray, Ireland) based on the standard enzymatic method.11–13 This method was modified by use of a YSI 2700 Analyzer (YSI Incorporated, Yellow Springs, Ohio) fitted with a YSI 2710 turntable for automated glucose determination of enzymatically hydrolyzed starch. The β-glucan content was determined using another Megazyme test kit (Megazyme International Ireland Ltd., Bray, Ireland)14 and following the instructions for the “streamlined method” provided by the manufacturer. This method conforms with standard methods.15,16 Protein content was determined in accordance with standard methods,17,18 which outline the procedure for use of a combustion instrument and subsequent thermal conductivity detection of nitrogen for the estimation of protein using an appropriate conversion factor. A Flash EA 1112 Elemental Analyzer (CE Elantech Inc., Lakewood, NJ), calibrated with aspartic acid (%N 10.52) was used for the protein determinations. About 50 to 100 mg samples were run, and the conversion factor used to obtain protein values was 6.25.19 Oil content was determined by extracting20 4 g samples with hexane in an Accelerated Solvent Extractor ( Dionex Corporation, Sunnyvale, CA). The instrument was operated at 1000 psi and a temperature of 100 °C for three 10 min cycles, after which the hexane extract obtained was dried under a stream of nitrogen and oil content was determined gravimetrically. The ash content was determined by heating barley flour in a muffle furnace at 550 °C until a light gray ash was obtained (16–20 h).21 All chemical analyses were conducted using ground samples and performed at least in triplicate; average results of all analyses were expressed on a dry weight basis (dwb). Reference values of each component analyzed are presented in Table II.

Near-Infrared Spectroscopy. Two near-infrared spectrometers were utilized in this study: a Fourier transform near-infrared (FT-NIR) interferometer (Vector 22/N, Bruker Optics, Billerica, MA) equipped with a tungsten source, an integrating sphere, and a PbS detector and a dispersive near-infrared (NIR) monochromater (NIRSystems 6500, FOSS NIRSystems, Inc., Laurel, MD) with a tungsten source and a PbS detector. The FT-NIR spectra were collected in the diffuse reflection mode over a range of 10,000–4000 cm⁻¹ using Bruker OPUS software (v. 3.0.19) and each spectrum was obtained by accumulating 128 scans at a resolution of 4 cm⁻¹ (3112 data points). The dispersive NIR spectra were also collected in the diffuse reflection mode over a range of 400–2498 nm at 2 nm intervals with a 10 nm resolution (1050 data points) using WinISI software (ver. 2.01, Infrasoft International Inc., Port Matilda, PA). Samples were packed in a round cup with a quartz window (30 mm diameter), which contained approximately 4 g samples. Triplicate spectra were collected from separately packed cells on each sample and then averaged. Samples were scanned on both instruments in the same cup.

Data Process and Chemometrics. All spectral data collected were imported into Matlab (ver. 7.3, Mathworks, Inc., Natick, MA) and analyzed using PLS_Toolbox software (ver. 4.0, Eigenvector Research, Inc., Manson, WA). The original samples (n = 206) were divided into a calibration set (n
Principal component analysis (PCA) was performed to extract information from the $x$-variables. Partial least squares (PLS) regression was used to build calibration models. The cross-validation was performed by omitting one of the calibration samples at a time from the calibration set and was performed during model development to determine the optimal PLS factors. The preprocessings for the spectral data included multiplicative scatter correction (MSC), Savitzky–Golay derivatives, mean centering (MC), and various combinations of the above preprocessings. For the derivative processing, first derivatives (D1) and second derivatives (D2) with third polynomial and 7-point (or 15-point) convolution intervals were employed. All data were mean centered before analysis.

Performance of each PLS model was reported as a multiple coefficient for determination ($R^2$), root mean squared error of calibration (RMSEC), and root mean squared error of cross-validation (RMSECV). Prediction performance was reported as a root mean squared error of prediction (RMSEP) and a ratio of deviation to performance (RPD), which is the ratio of the standard deviation of the reference data to the RMSEP, which provides a method-independent standardization of the RMSEP. Correlation methods with RPD values of 2.4–3.0 are considered adequate for rough screening purposes, while values of 3.1–4.9 are adequate for standard screening purposes, and values of 5.0–6.4 are adequate for quality control.

RESULTS AND DISCUSSION

Compositional Data and Near-Infrared Spectra of Barley Samples. Table II shows the compositional data of the ground barley samples used in this study. The varieties were grown over a three-year period to cover a broad range of the components but the range of values is still very narrow for β-glucan, oil, and ash. This could increase the relative error of the reference techniques and subsequently contribute to the prediction error from spectroscopic analyses. The β-glucan content was determined using a method based on use of the special enzyme, endo-(1→3)(1→4)-β-D-glucan-4-glucanohydrolase (lichenase), along with a β-glucosidase. Based on previous research with barley with mixed grains and in a review of the available methods, it was concluded that this is the only method that produces reliable estimates of β-glucans and therefore is the best method to use as a reference for correlation to spectroscopic techniques. Table II indicated that, on average, the hull-less variety had higher levels of starch and protein and lower levels of ash than the malt and hulled varieties. For other components, there were no significant differences between the barley types. The hulled and malt varieties averaged 55% and 58% starch, respectively, whereas the hull-less varieties had a mean of 62% starch with the Doyce variety reaching 68%. Hull-less barley has a loosely attached hull that usually falls off during grain harvest and cleaning. Removal of the hull results in loss of only the abrasive, non-starchy portion of the kernel.

Figure 1 shows the spectra of the ground barley samples ($n = 206$) over the spectral range of 10,000–4000 cm$^{-1}$ on the FT-NIR system (top) and over the spectral range of 400–2498 nm on the dispersive NIR system (bottom) after applying multiplicative scatter correction.
variables for the sample clustering are around 5184 cm
very little variation in the spectra. tent NIR spectra can be obtained on barley but also that there is
multiplicative scatter correction. This shows that very consistent NIR spectra can be obtained on barley but also that there is very little variation in the spectra.

Principal Component Analysis. Figure 2 shows the principal component analysis (PCA) results from the FT-NIR data (n = 206) pretreated with MSC followed by MC processing. The PCA score plot (Fig. 2a) shows that the first and second principal components (PCs) explain about 82% and 15% of the x-variables, respectively. The first PC provided a good separation of the barley samples according to their types: hull-less, malt, and hulled, from left to right, respectively. One hull-less sample and two hulled samples were in or close to the malt group, indicating some minor overlap in classifications. The hulled barley variety, Thoroughbred, has some malt barley characteristics, so this is not surprising. The loading plot for PC1 (Fig. 2b) explains that the most highly correlated x-variables for the sample clustering are around 5184 cm\(^{-1}\) (1930 nm), 4760–4780 cm\(^{-1}\) (2100–2092 nm), and 4252 cm\(^{-1}\) (2352 nm), which are mainly assigned to the absorption of starch and protein. The analytical values of the samples in Table II are consistent with these results, and here the starch and protein content caused the ranking into hull-less, malt, and hulled types, respectively.

Partial Least Squares Calibration Model. The PLS regressions for each component were performed using the calibration set (n = 138) with different types of pretreatment.

The FT-NIR data included six pretreatments: none, MSC, D1 (7 points and 15 points), and D2 (7 points and 15 points). The dispersive NIR data included four pretreatments: none, MSC, D1 (7 points) followed by MSC, and D2 (7 points) followed by MSC. The RMSECV and PLS factors were evaluated to determine the best pretreatment for each component (the least RMSECV and the lowest number of factors). Here samples with a high student y-residual over 2 were eliminated from the data set as outliers. The best PLS models were applied to the validation set. Table III summarizes the results of PLS regressions for six components in barley using the FT-NIR and dispersive NIR systems. The result for each component was dependent on specific pretreatment. For the FT-NIR, the derivative preprocessing was useful for most of the components, except that MSC was sufficient for the protein model. For the dispersive NIR spectrometer, using the NIR region (1100–2498 nm) gave slightly better results than using the entire visible–NIR region (400–2498 nm). All components were best predicted using the derivative followed by MSC. The D1 was the best pretreatment for most of the components, except for oil, where D2 was used. The calibration models obtained from the FT-NIR data and the dispersive NIR data were comparable for most of the components on the basis of RMSEP. The dispersive system did better job in prediction of starch. This could be understood from the fact that the band for starch centered around 2100 nm is a broad band and it does not require high resolution for analysis. It appears to benefit from the better signal-to-noise ratio generated at lower resolution. The high-resolution FT system only seems to prove slightly better for the prediction of protein but more factors were required to achieve this result than for the dispersive NIR. Consequently, there was no predictive advantage in using a higher-resolution FT instrument over a lower-resolution dispersive instrument for most of the components in ground barley.

Figure 3 shows the scatter plots of measured versus NIR predicted values of the components in barley by the best fit models shown in Table III. For starch, an RMSEP of 1.31% using six factors was obtained. When it is considered that the minimum laboratory error for the determination of starch by modern enzymic methods is about 0.9%, and this error often exceeds 2.0% in interlaboratory tests,\(^{25}\) the NIR result is better in accuracy than the result obtained from the enzymatic reference method. The protein model was the best among all of the components, showing an \(R^2\) of 0.96 and an RMSEP of 0.2%. For the oil model, samples were divided into two populations, high-oil samples (>2.5%) and low-oil samples (<2.5%). The high-oil samples are from 2003–2004 crop and the low-oil samples are from 2002–2003 crop, indicating a great variation by crop year. Further samples in between 2.3% and 2.5% oil content would be needed to improve the oil model. The estimation of moisture and ash contents in barley by the NIR method resulted in an RMSEP of 0.3% and 0.11%, respectively. An apparently poor result for \(\beta\)-glucan, an \(R^2 = 0.67\) and an RMSEP of 0.41%, could be related to the accuracy of the reference method and the narrow range of values encountered (2.3–5.8%, mean value of 4.3%). This result is slightly better than the result of another study that was obtained from other barley varieties with a similar range of \(\beta\)-glucan content (\(R^2 = 0.59\) and standard error of estimate = 0.58%),\(^{26}\) but it is still unacceptable for analytical use. The previous study showed that barley with a wider range of \(\beta\)-glucan content (2.7–9.5%) from regular and waxy varieties resulted in a better
### TABLE III. PLS models for determining six properties in ground barley developed using FT-NIR and dispersive NIR spectrometers.\(^a\)

<table>
<thead>
<tr>
<th>Instruments</th>
<th>Wavenumber/wavelength</th>
<th>Components</th>
<th>Pretreatments</th>
<th>Calibration</th>
<th>Validation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>N</td>
<td>PLS factors</td>
</tr>
<tr>
<td>FT-NIR</td>
<td>10 000-4000 cm(^{-1})</td>
<td>Moisture</td>
<td>Der(1,3,7)(^b)</td>
<td>138</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Starch</td>
<td>Der(1,3,7)</td>
<td>138</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>β-glucan</td>
<td>Der(2,3,15)(^c)</td>
<td>138</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Protein</td>
<td>MSC</td>
<td>138</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Oil</td>
<td>Der(2,3,7)</td>
<td>95</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ash</td>
<td>Der(1,3,7)</td>
<td>138</td>
<td>3</td>
</tr>
<tr>
<td>Dispersive NIR</td>
<td>1100–2498 nm</td>
<td>Moisture</td>
<td>Der(1,3,7)+MSC</td>
<td>138</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Starch</td>
<td>Der(1,3,7)+MSC</td>
<td>138</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>β-glucan</td>
<td>Der(1,3,7)+MSC</td>
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<td>8</td>
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<tr>
<td></td>
<td></td>
<td>Protein</td>
<td>Der(1,3,7)+MSC</td>
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<td></td>
<td></td>
<td>Oil</td>
<td>Der(2,3,7)+MSC</td>
<td>95</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ash</td>
<td>Der(1,3,7)+MSC</td>
<td>138</td>
<td>7</td>
</tr>
</tbody>
</table>

\(^a\) \(N\) = number of samples, \(R^2\) = multiple coefficients of determination of calibration, RMSECV = root mean squared error of cross-validation, RMSEP = root mean squared error of prediction, and RPD = SD/RMSEP.

\(^b\) Der(1,3,7) = 1st derivative with 3rd polynomial and 7 points.

\(^c\) Der(2,3,15) = 2nd derivative with 3rd polynomial and 15 points.

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**Fig. 3.** Near-infrared predicted versus measured values of moisture, starch, β-glucan, protein, oil, and ash content in barley on the best PLS models from Table III. Black circles are for the calibration set (\(n = 138\)) and white circles are for the validation set (\(n = 68\)).

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correlation coefficient than barley with a narrow range of β-glucan (2.7–5.6%) from regular variety only. In another study, a good RPD value of 3.47 was obtained for total β-glucan, but this was also due to a wide range of β-glucan content (0.09–5.12%) expanded by the use of other grains as well as barley. These studies suggested that the accuracy of the NIR model for determining β-glucan content in barley is affected by the range of the reference data. It is well known that β-glucan content is influenced by variety, growing location, and climate. Additional barley samples, with consideration of the various factors above, would be helpful to expand the reference data and to improve the β-glucan model.

On the basis of these statistics and RPD values, the NIR method is suitable for quality control for protein and suitable for classification or screening for starch, moisture, oil, and ash content of barley. However, the results for β-glucan were of marginal utility.

CONCLUSION

This study reveals that NIR-based analysis for barley quality could provide a useful tool for the rapid estimation of ethanol yield and evaluation of the co-product quality. There is no apparent advantage to using a higher resolution FT-NIR system over a lower resolution dispersive NIR system for prediction of most of the components in ground barley. For starch, the dispersive NIR system resulted in better prediction than the FT-NIR system. PCA classified barley samples according to their types as hull-less, malt, and hulled barley. PLS regression revealed that the NIR method would be suitable for quality control for protein and for classifying or screening purposes for starch, moisture, oil, and ash. However, the β-glucan model was still unacceptable for use. Additional studies will be conducted on the the analysis of the whole kernel barley using various NIR instruments.

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10. AACC Method 44-19.
12. AACC Method 32-32.
15. AOAC Method 995.16.
16. AACC Method 32-23.
17. AOAC Method 990.03.
21. AACC Method 08-01.