JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

ARTICLE

pubs.acs.org/JAFC

Rapid Determination of Carbohydrates, Ash, and Extractives Contents of Straw Using Attenuated Total Reflectance Fourier Transform Mid-Infrared Spectroscopy

Yukihiro Tamaki and Giuseppe Mazza*

Pacific Agri-Food Research Centre, Agriculture and Agri-Food Canada, 4200 Highway 97, Summerland, British Columbia, Canada V0H 1Z0

Supporting Information

ABSTRACT: Analysis of the chemical components of lignocellulosic biomass is essential to understanding its potential for utilization. Mid-infrared spectroscopy and partial least-squares regression were used for rapid measurement of the carbohydrate (total glycans; glucan; xylan; galactan; arabinan; mannan), ash, and extractives content of triticale and wheat straws. Calibration models for total glycans, glucan, and extractives showed good and excellent predictive performance on the basis of slope, r^2, RPD, and R/SEP criteria. The xylan model showed good and acceptable predictive performance. However, the ash model was evaluated as providing only approximate quantification and screening. The models for galactan, arabinan, and mannan indicated poor and insufficient prediction for application. Most models could predict both triticale and wheat straw samples with the same degree of accuracy. Mid-infrared spectroscopic techniques coupled with partial least-squares regression can be used for rapid prediction of total glycans, glucan, xylan, and extractives in triticale and wheat straw samples.

KEYWORDS: carbohydrates, ash, extractives, rapid determination, Fourier transform mid infrared spectroscopy, attenuated total reflection, partial least-squares regression, triticale, × *Triticosecale*, wheat, *Triticum aestivum*, straw, biomass

INTRODUCTION

Lignocellulosic biomass such as straw, corn stover, and switchgrass has attracted interest as a renewable energy source due to fossil fuels depletion and environmental problems. It has both quantitative availability and economic benefits and can be utilized for biofuel and value-added biochemical production in biorefinery.[1−3]

Analysis of the chemical components of lignocellulosic biomass is essential to understand its utilization potential because lignocellulose structure and composition can be variable, depending on factors such as plant species, plant tissues, production location, harvest date, and storage time.[4−6] Chemical compositional data are used for calculating mass balance and process yields and for technoeconomic analysis and the data affect evaluations of process configuration, reactor design, and process performance.[7] Conventional wet chemical analysis is generally based on gravimetric, colorimetric, and chromatographic techniques; unfortunately, these analytical methods have drawbacks such as being time-consuming, labor-intensive, and expensive and, in addition, result in the production of hazardous waste.[5−7] These disadvantages hinder at-line or on-line operation in a commercial setting.[5,6]

Mid- and near-infrared spectroscopic techniques combined with chemometric tools have been studied for the rapid chemical compositional determination of lignocellulosic biomass,[5,6,8−21] as well as in several other fields such as food, soil, pharmaceutical, and biomedical applications.[22−27] Infrared spectroscopy (near, 14000−4000 cm^{-1}; mid, 4000−400 cm^{-1}; far, 400−10 cm^{-1}) is based on the absorption by molecules of specific frequencies that are characteristic of their structure based on the bond or group that vibrates.[28] These infrared techniques have the advantage of providing simple, rapid, and noninvasive measurements that require minimal sample processing prior to analysis and are also relatively inexpensive and environmentally benign.[29] Chemometrics has become an essential tool for linking the methods and their application in chemistry. The combination of infrared spectroscopy and chemometrics provides calibration models for specific complex-matrix analysis and classification/discrimination tools.[30]

We previously reported rapid determination of lignin content of triticale and wheat straws using Fourier transform mid-infrared spectroscopy.[31] The models developed using averaged spectra of triticale, wheat, or both straws showed good or excellent predictive ability based on the criteria of slope, r^2, RPD, and R/SEP. The model using both straws was developed for generating a flexible and broad-based model to predict lignin content of both kinds of straw simultaneously. The model could predict the lignin content of both straws with the same accuracy. The broad-based model developed using mid-infrared spectroscopic techniques showed the feasibility of rapid lignin content prediction of triticale and wheat straw samples.

Carbohydrates, especially glucose, are resources for biofuel and biochemical production. Ash possesses detrimental qualities such as fouling problems in combustion for industrial applications.[6] Extractives, such as wood resin or pitch, affect biomass

Received: January 12, 2011
Revised: May 3, 2011
Accepted: May 5, 2011
Published: May 05, 2011

quality and pulping and papermaking processes.[10,32] Determination of these components of biomass is useful and necessary for biorefinery applications. Various studies have been published on the use of mid-infrared spectroscopy to predict carbohydrates, ash, and extractives from woody samples[17−21] as well as on the use of near-infrared spectroscopy for herbaceous and woody samples, including straw;[5,6,8−15] however, to our knowledge, no study has been published on the prediction of straw components using mid-infrared spectroscopy and chemometric techniques. Here we report the rapid measurement of carbohydrates (total glycans; glucan; xylan; galactan; arabinan; mannan), ash, and extractives in triticale and wheat straws using the same samples and techniques as before:[31] (1) the straw samples were collected over two production seasons, from different cultivars, and from different locations, with or without irrigation; (2) mid-infrared spectroscopy coupled with an attenuated total reflectance (ATR) accessory was used for spectrum acquisition; (3) the chemometric method, partial least-squares (PLS) regression, was used for modeling; and (4) the models were developed using different spectral pretreatments and wavenumber regions for improvement of the accuracy of the predictions. Predictive techniques using infrared spectroscopy have been frequently developed for one species only; however, several calibration model developments have been investigated using different biomass feedstocks to enable broad-based modeling.[6,9,11,13] The broad-based model for lignin content we reported previously showed excellent predictive performance.[31] Therefore, all of the calibration models were developed using both triticale and wheat straw samples for broad-based model development.

MATERIALS AND METHODS

Plant Materials. Straw samples used here were the same as those reported previously.[31] Triticale (× *Triticosecale* Wittm. ex A. Camus. cultivars AC Ultima, Pronghorn, and Tyndal) and wheat (*Triticum aestivum* L. cultivars AC Andrew and Hoffman) straws were collected from various areas across Canada: Lethbridge, Alberta; Spirit River, Alberta; Brandon, Manitoba; Normandin, Quebec; and Charlottetown, Prince Edward Island. The straws were harvested in 2007 (Lethbridge only) and 2008. Part of the straw harvested in Lethbridge came from an irrigated field. One to three straw samples were collected for each variety, irrigation treatment, year, and location, resulting in 67 and 47 samples for triticale and wheat straw, respectively (114 straw samples in total).

Sample Preparation. Raw samples were milled using a Retsch SM 2000 cutting mill (Retsch GmbH, Haan, Germany) with a 2 mm square discharge screen. Milled samples were sieved using a Retsch AS 200 tap sieve shaker (Retsch GmbH) with 20 (850 μm) and 80 (180 μm) mesh sieves. The fraction retained on the 80 mesh sieve (approximately 70% of original sample) was subjected to wet chemical analysis. For mid-infrared spectroscopy measurement, approximately 1 g of sample was ball-milled for 3 min at 30 Hz, using a Mix Mill MM301 equipped with a 50 mL grinding jar and a 25 mm grinding ball (Retsch GmbH) prior to analysis.

Wet Chemical Determination of Carbohydrates, Ash, and Extractives. All samples were analyzed using NREL analytical procedures.[33−35]

Extractives were removed using a conventional Soxhlet apparatus (85 mL extraction tube; 500 mL boiling flask; heating mantle (Glas-Col, Terre Haute, IN)) with water and ethanol for 16 h each. The reflux rate was adjusted to provide 4−5 siphon cycles per hour for water extraction and 6−10 siphon cycles per hour for ethanol extraction. The extractives were evaporated at 40 °C using a rotary evaporator to remove most of the solvent, then freeze-dried for water extractives, and dried using a convection oven at 60 °C for ethanol extractives. The extractives were further dried using a vacuum oven at 40 °C prior to weighing. Extractives content was determined as the amount of water and ethanol extractives.

The extractives-free samples were hydrolyzed with a sequential acid hydrolysis procedure utilizing 72% H_2SO_4 at 30 °C for 1 h and followed by 4% H_2SO_4 at 121 °C for 1 h. The hydrolysate was neutralized by adding $CaCO_3$ and then filtered. Monosaccharides in the neutralized filtrate were quantitatively measured with HPLC using an Agilent 1100 equipped with a refractive index detector (Agilent Technologies Inc., Palo Alto, CA). The HPLC analysis was carried out using a Bio-Rad Aminex HPX-87P column (300 × 7.8 mm, Bio-Rad Laboratories, Hercules, CA) with a H^+/CO_3^- De-Ashing Refill Cartridge guard column (30 × 4.6 mm, Bio-Rad Laboratories, Hercules, CA) operating at 75 °C with a Milli-Q water mobile phase at a flow rate of 0.5 mL/min.

Ash content was determined by complete combustion in a muffle furnace (model F-A1730, Thermolyne Corp., Dubuque, IA) equipped with a temperature controller (Furnatrol II series 413, Thermolyne Corp.) running a temperature ramp program: ramp from room temperature to 105 °C; hold at 105 °C for 12 min; ramp to 250 °C at 10 °C/min; hold at 250 °C for 30 min; ramp to 575 °C at 20 °C/min; hold at 575 °C for 180 min; and drop to and hold at 105 °C until removed. The remaining residue in the crucible was taken as the ash content.

Fourier Transform Mid-infrared Measurement. All of the Fourier transform mid-infrared spectra were measured using a Nicolet 380 spectrometer (Thermo Fisher Scientific Inc., Madison, WI) with SMART iTR diamond attenuated total reflectance (ATR) with a 45° incident angle generating one bounce. The spectrometer was equipped with a deuterated triglycine sulfate (DTGS) detector scanning over the wavenumber range of 4000−650 cm^{-1} at a resolution of 4 cm^{-1}. For each spectrum, a total of 32 repetitive scans was accumulated using OMNIC 8.0 software (Thermo Fisher Scientific Inc.). Approximately 2−3 mg of a ball-milled sample was placed on the head of the ATR crystal (2 mm diameter) and then, to apply the same pressure, pressed using a pressure tower. Spectra were collected in triplicate for each sample and then averaged to one spectrum.

Chemometric Analysis. All multivariate analyses of mid-infrared spectra for carbohydrates, ash, and extractives contents predictions were performed using TQ Analyst 8.0 (Thermo Fisher Scientific Inc.).

Principal component analysis (PCA) was calculated using whole averaged triticale and wheat straw spectra without spectral treatments to see if the spectra between the straws form the same group.

Partial least-squares (PLS) regression was used to generate calibration models. The models were developed for each straw component using both triticale and wheat straw samples. Approximately 75% of samples (n = 87; triticale, n = 51; wheat, n = 36) were used to develop the calibration models, and the other 25% (n = 27; triticale, n = 16; wheat, n = 11) were used for validation (Table 1). The sample selection for calibration and validation was carried out randomly but to reflect the range and mean values of the calibration and validation data determined by the wet chemical analysis.

Spectral pretreatments were used prior to generating the calibration models: raw spectrum, first derivative, or second derivative was used in spectrum format; constant, standard normal variate (SNV), or multiplicative signal correction (MSC) was used in path length. The first- and second-derivative spectra were smoothed using a Norris derivative filter (segment length, 5; gap between segments, 5). The calibration models were generated for three wavenumber regions: 4000−650 cm^{-1}, 1800−700 cm^{-1}, or both 3700−2700 and 1800−700 cm^{-1}. The TQ Analyst software was allowed to determine the optimum number of PLS factors based on the predicted residual error sum of squared (PRESS) value to avoid under- or overfitting of the model.

The predictive performance of the models was evaluated using validation samples to calculate root-mean-square error of prediction (RMSEP), coefficient of regression of predicted values against reference

Table 1. Content (%, w/w, Oven-Dry Basis) of Eight Components of Triticale and Wheat Straws Measured by Wet Chemical Analysis[a]

	calibration (n = 87)				validation (n = 27)				total (n = 114)			
component	mean	SD	min	max	mean	SD	min	max	mean	SD	min	max
total glycans	60.24	2.79	53.88	65.58	60.20	2.92	54.32	64.84	60.23	2.81	53.88	65.58
glucan	35.89	2.17	29.96	40.33	35.45	2.58	30.40	39.43	35.79	2.27	29.96	40.33
xylan	21.11	1.03	18.93	23.78	21.26	1.20	19.24	23.63	21.15	1.07	18.93	23.78
galactan	0.79	0.12	0.59	1.15	0.82	0.13	0.60	1.13	0.80	0.12	0.59	1.15
arabinan	2.20	0.16	1.85	2.74	2.23	0.20	1.89	2.65	2.21	0.17	1.85	2.74
mannan	0.28	0.09	0.12	0.56	0.30	0.10	0.14	0.55	0.29	0.09	0.12	0.56
ash	1.62	0.86	0.49	3.95	1.78	0.94	0.52	3.68	1.66	0.88	0.49	3.95
extractives	15.12	3.00	9.53	22.98	15.44	3.20	10.51	22.19	15.20	3.04	9.53	22.98

[a] SD, standard deviation; min, minimum; max, maximum.

data (i.e., slope), coefficient of determination (r^2), standard error of performance (SEP), residual predictive deviation (RPD), R/SEP, and relative error. The following equations were used:

$$\text{RMSEP} = \sqrt{\frac{\sum_{i=1}^{n} (\hat{y} - y_i)^2}{n}} \quad (1)$$

$$\text{SEP} = \sqrt{\frac{\sum_{i=1}^{n} (\hat{y}_i - y_i - \text{bias})^2}{n-1}} \quad (2)$$

$$\text{RPD} = \frac{\text{SD}}{\text{RMSEP}} \quad (3)$$

$$\frac{\text{R}}{\text{SEP}} = \frac{\text{data range}}{\text{SEP}} \quad (4)$$

$$\text{relative error} = \frac{\text{RMSEP}}{\text{mean}} \times 100 \quad (5)$$

y_i is the actual value by wet chemical analysis for the ith sample; $\hat{y}_i$ is the predicted value by mid-infrared spectrum for the same sample; n is the number of samples used in each set; SD is the standard deviation in each set; and, data range is the difference between maximum and minimum values in each set.

In RMSEP, the values provide the average uncertainty that can be expected for prediction of the samples.[23] In slope, values of <0.8 or >1.2, 0.8−1.2, 0.9−1.1 are assessed as less reliable, reliable, and very reliable, respectively.[27] In r^2, a value between 0.66 and 0.80 indicates approximate quantitative predictions, whereas a value between 0.81 and 0.90 indicates good prediction. Calibration models having a value of >0.90 are considered to be excellent.[36,37] In RPD, values of <2.0 are considered to be insufficient for application, whereas values between 2.0 and 2.5 make approximate quantitative predictions possible. For values between 2.5 and 3.0, the prediction can be classified as a good prediction and values of >3.0 indicate excellent prediction.[23,36,37] In R/SEP, values of ≥4 are qualified for screening calibration, values of ≥10 are acceptable for quality control, and values of ≥15 are very good for research quantification.[6]

Statistical Analysis. Microsoft Excel 2007 was used for the F test. A difference with $p < 0.05$ was considered to be significant.

RESULTS AND DISCUSSION

Wet Chemical Analysis of Carbohydrates, Ash, Extractives. Figure 1 shows the distribution of the contents of total glycans, glucan, xylan, galactan, arabinan, mannan, ash, and extractives of triticale and wheat straws harvested under different conditions as determined by wet chemical analysis. The distributions between triticale and wheat in each component were similar. The mean values of total glycans, glucan, xylan, galactan, arabinan, mannan, ash, and extractives of triticale straw were 60.2, 35.8, 21.1, 0.8, 2.2, 0.3, 1.6, and 15.5%, respectively. The mean values of the wheat straw were 60.3, 35.7, 21.2, 0.8, 2.3, 0.3, 1.7, and 14.8%, as well. The extractives had the largest standard deviations (triticale, 3.0%; wheat, 3.1%) followed by total glycans (2.8%; 2.9%), glucan (2.4%; 2.2%), xylan (0.9%; 1.3%), and ash (0.9%; 0.9%) in each straw.

Mid-Infrared Spectra. After the triplicate mid-infrared spectral measurements, the triplicate spectra for each sample were averaged into one spectrum. All of the averaged mid-infrared spectra of triticale and wheat straws were similar, and there was no distinguishable difference between the two straws in the spectra.

PCA was carried out to justify similarity between the spectra of the triticale samples and those of the wheat straw samples. Figure 2 shows that the triticale and wheat straw samples were similar in the dimensions of principal component (PC) 1 and PC2. The PCA indicated that mid-infrared spectra between both straw samples were not differentiable, representing 92% of total variance. The PCA demonstrates a rationale for the development of a broad-based model using both triticale and wheat straw samples.

Development of the Broad-Based Models. After confirmation of similarities of compositional values and mid-infrared spectra between the triticale and wheat straw samples, we developed the broad-based models using both straws. The calibration models were generated after applying several spectral pretreatments: first or second derivatives in spectrum format; SNV or MSC in path length; and, three different wavenumber regions. The pretreatments were applied to improve the predictive accuracy of the calibration models. All the results of the PLS calibration models developed using different pretreatments for the eight components are shown in Tables S1−S8 (see the Supporting Information).

Model selection was based on the lowest RMSEP value in the models developed using the different pretreatments. Table 2

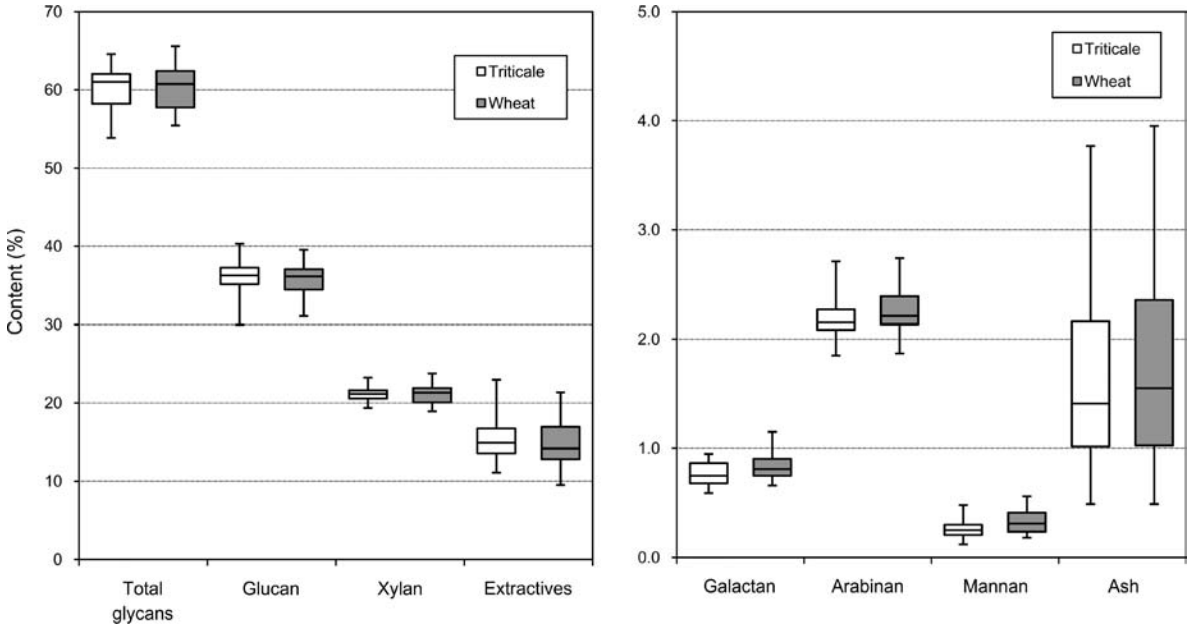

Figure 1. Box plot of eight components of triticale and wheat straws. The bottom and top of the box represent the 25th and 75th percentiles, respectively; the band in the box represents the median; and the ends of whiskers represent the minimum and maximum of all the data.

shows pretreatment conditions, the number of PLS factors, correlation coefficient of calibration (r), RMSEC, RMSECV, and RMSEP of the selected models for each component. Figure 3 shows the plots of predicted versus actual value of each component in the selected models. In spectral pretreatments, the raw spectrum in spectrum format was suitable for modeling in all of the components; however, suitable pretreatments for path length and wavenumber regions in selected models depended on each component. The correlation coefficients of the models indicated more than 0.9 except for the galactan, arabinan and mannan models. Differences between the values of RMSECV and RMSEP and the value of RMSEC were relatively small. The ratios of RMSECV and RMSEP to RMSEC in all of the models were between 1 and 2. These results indicated that the models were well developed for each component.

Evaluation of the Broad-Based Models Using the Criteria. Table 3 shows the performance of the selected models based on the values of slope, coefficient of determination (r^2), SEP, RPD, R/SEP, and relative error for the validation sample.

The models for total glycans, glucan, and extractives had values of 0.9−1.1 for slope, >0.90 for r^2, >3 for RPD, and ≥15 for R/SEP. These three models had the highest rank for all of the criteria and were evaluated as being very reliable and excellent for prediction. The model for xylan showed excellent performance based on r^2 and RPD and reliable and acceptable performance for quality control based on slope and R/SEP, respectively. The model for ash showed reliable and good prediction based on slope and r^2, respectively, but approximate quantitative prediction and screening calibration based on RPD and R/SEP. The models for galactan, arabinan, and mannan were evaluated as less reliable or insufficient for application based on slope and RPD, respectively, although they are qualified for screening calibration based on R/SEP. Relative error values of total glycans, glucan, xylan, and extractives were <5%, indicating that the models are reliable. The other components, especially mannan and ash, had poor relative error values.

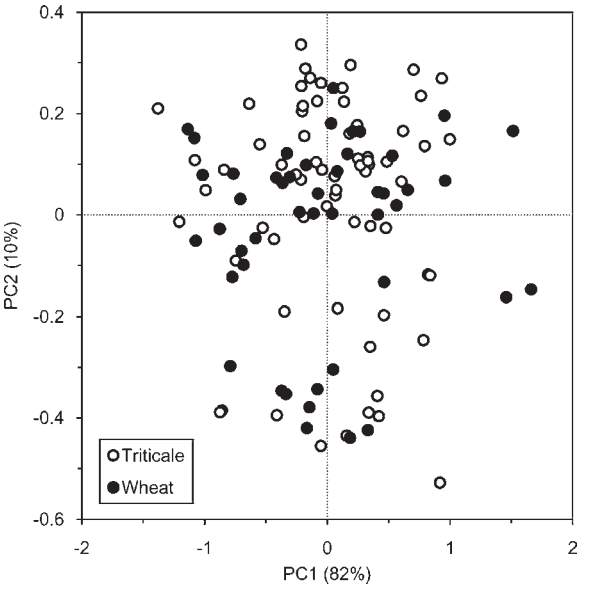

Figure 2. Score plot of PC1 versus PC2 of triticale and wheat straws using FT-MIR spectra.

The models for major components, total glycans, glucan, xylan, and extractives, showed good and excellent prediction performance. The accuracy of our models was comparable to that of those reported previously for wood samples using mid-infrared spectroscopy based on r^2, RMSEP, and relative error values.[17−21] For example, in the study by Rodrigues et al. using *Eucalyptus globulus* wood sample,[19] the r^2 and RMSEP values for glucan were 0.94 and 0.96, respectively. The corresponding values for xylan were 0.93 and 0.54, respectively. In the study by Meder et al. using *Pinus radiata* wood sample,[17] the best RMSEP and relative error values for total glycans were 2.36 and 3.7, respectively. In addition, the accuracy of glucan and xylan models was

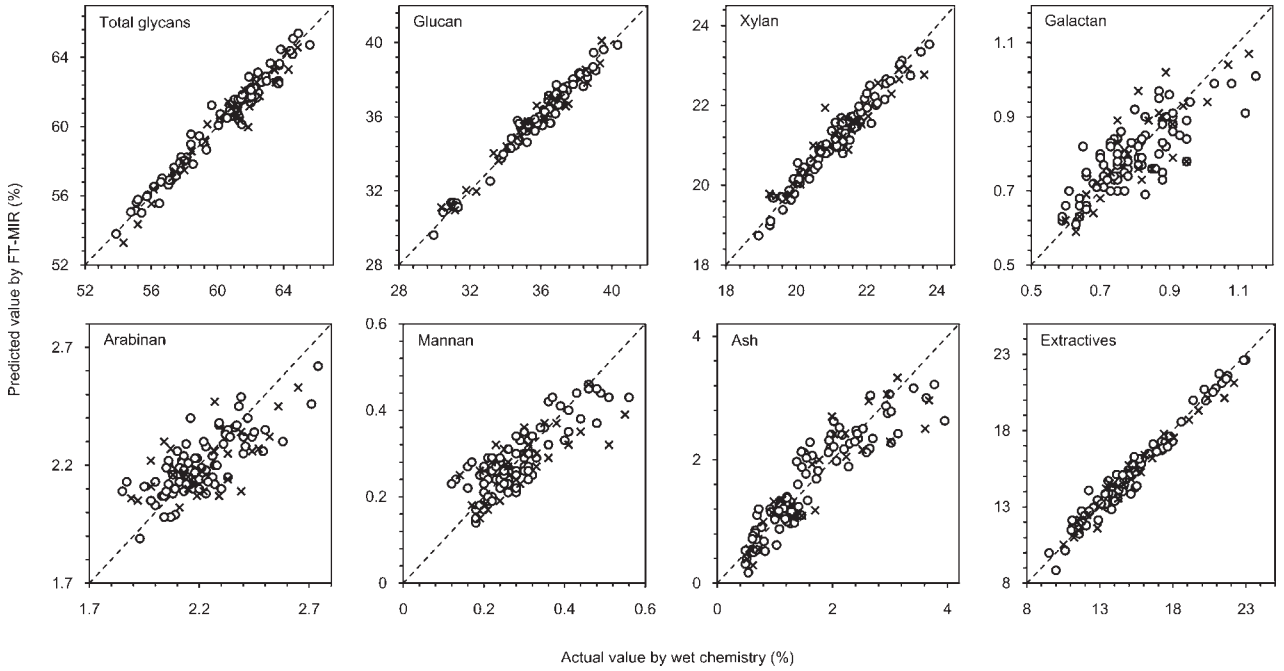

Figure 3. Plots of predicted versus actual value of eight component contents (%) in triticale and wheat straws: ○, calibration sample; ×, validation sample; dashed line, $X = Y$.

Table 2. Selected PLS Calibration Models Developed Using FT-MIR Spectra of Triticale and Wheat Straws

	pretreatment							
component	spectrum format	pathlength	wavenumber (cm^{-1})	no. of PLS factors [a]	r [b]	RMSEC [c]	RMSECV [d]	RMSEP [e]
total glycans	raw spectrum	SNV[f]	1800−700	11	0.983	0.504	0.982	0.666
glucan	raw spectrum	MSC[g]	1800−700, 3700−2700	10	0.985	0.373	0.586	0.477
xylan	raw spectrum	MSC	1800−700	11	0.976	0.224	0.409	0.383
galactan	raw spectrum	SNV	4000−650	7	0.795	0.0697	0.0976	0.0750
arabinan	raw spectrum	SNV	1800−700	6	0.752	0.107	0.138	0.155
mannan	raw spectrum	SNV	4000−650	6	0.842	0.0488	0.0663	0.0714
ash	raw spectrum	SNV	1800−700	7	0.919	0.337	0.418	0.404
extractives	raw spectrum	MSC	1800−700, 3700−2700	10	0.983	0.540	0.812	0.591

[a] Number of PLS factors used. [b] Correlation coefficient of calibration. [c] Root-mean-square error of calibration. [d] Root-mean-square error of cross-validation. [e] Root-mean-square error of prediction. [f] Standard normal variate. [g] Multiplicative signal correction.

comparable to that of the model built for wheat and rice straw samples using near-infrared spectroscopy based on slope, r^2, and RMSEP values.[12,14] In the report by Lomborg et al. using wheat straw,[14] the slope, r^2, and RMSEP values for glucan were 0.89, 0.87, and 0.45, respectively, and the values for xylan were estimated as 0.94, 0.87, and 0.32, respectively. The poor predictive power of the models for minor components, galactan, arabinan, mannan, and ash, could be possibly a function of their low concentration and less accurate measurement using wet chemical analysis relative to the major components.[7] To obtain a more reliable and robust model, further work should consider increasing the sample size in the calibration and a wider range of concentration and perhaps improving spectral pretreatments such as wavenumber region selection optimized for each component to remove spectral variation unrelated to sample component. Also, improvements in the accuracy of the wet chemical analysis, especially for the minor components, are recommended.

Table 3. Performance of Models in Predicting the Component Contents Using Triticale and Wheat Straw Samples

component	slope[a]	r^2 [b]	RMSEP	SEP [c]	RPD [d]	R/SEP [e]	relative error [f]
total glycans	0.987	0.956	0.666	0.618	4.39	17.02	1.11
glucan	0.939	0.966	0.477	0.478	5.41	18.89	1.35
xylan	0.814	0.904	0.383	0.390	3.14	11.25	1.80
galactan	0.824	0.697	0.0750	0.0769	1.79	6.90	9.15
arabinan	0.425	0.386	0.155	0.155	1.27	4.90	6.95
mannan	0.523	0.548	0.0714	0.0704	1.46	5.82	23.80
ash	0.850	0.813	0.404	0.408	2.32	7.75	22.70
extractives	0.907	0.970	0.591	0.591	5.41	19.77	3.83

[a] Coefficient of regression of predicted against actual value in validation. [b] Coefficient of determination of validation. [c] Standard error of performance. [d] Residual predictive deviation. [e] Ratio of data range (R) to SEP. [f] Percentage of RMSEP to mean.

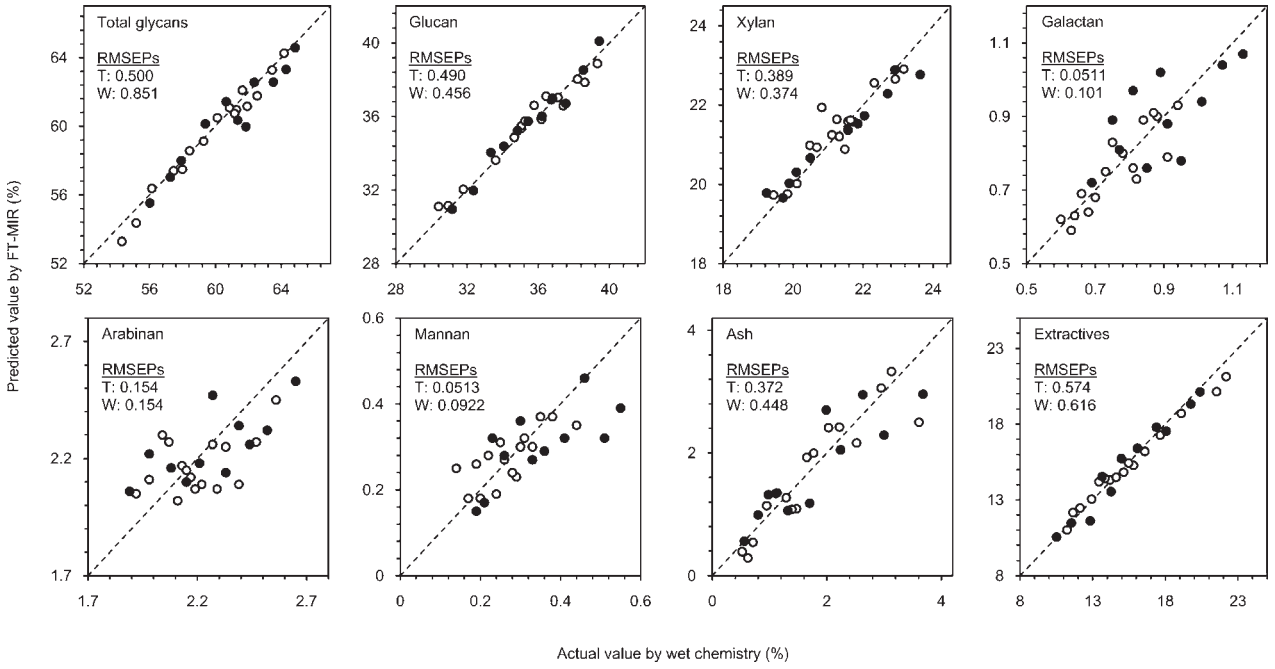

Figure 4. Plots of predicted versus actual value of eight components of triticale and wheat straws in validation set: ○, triticale straw; ●, wheat straw; dashed line, $X = Y$. RMSEPs indicate each RMSE of triticale (T) and wheat (W).

Comparison of the Predictive Performance for Triticale and Wheat Straw Components in the Validation Set. The compositional values and distributions of triticale and wheat straw were similar. In addition, there was no distinguishable difference between the straws in the mid-infrared spectra. Therefore, the broad-based models were developed using both kinds of straw. Figure 4 shows the plots of predicted versus actual value of the components of triticale and wheat straws in the validation set. RMSEP values for each straw were shown in each component as well. The differences of the RMSE values in glucan, xylan, arabinan, and extractives were small. However, the differences in total glycans, galactan, mannan, and ash were relatively large. An F test was carried out to compare the degrees of variability of error (difference of predicted and actual values) between triticale and wheat straw. The p values for all components except for galactan were calculated to be >0.05, indicating that the degree of error was not significantly different between triticale and wheat straw. These results indicated that the broad-based models developed using triticale and wheat straws could be used for prediction for both straws for almost all components.

In conclusion, the models for total glycans, glucan, and extractives showed good and excellent predictive performance on the basis of slope, r^2, RPD, and R/SEP criteria. The xylan model showed good and acceptable predictive performance. However, the ash model was evaluated as approximate for quantification and screening. The models for galactan, arabinan, and mannan indicated poor and insufficient prediction for application. Almost all of the models except for galactan could predict both triticale and wheat straw samples with the same degree of accuracy. Mid-infrared spectroscopic techniques can be used for rapid prediction of total glycans, glucan, xylan, and extractives of triticale and wheat straw samples.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Results of PLS calibration models developed for total glycans, glucan, xylan, galactan, arabinan, mannan, ash, and extractives using the spectral pretreatments. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: (250) 494-6376. Fax: (250) 494-0755. E-mail: Giuseppe.Mazza@agr.gc.ca.

Funding Sources

We are grateful to the ABIP-CTBI Network, ABIP-CBioNet, and ABIP-NAFGEN for financial support.

■ ACKNOWLEDGMENT

We are grateful to Mark Stumborg and his group for providing the straw. We appreciate the technical assistance provided by Lana Fukumono, David Godfrey, Robert Yuen, David Park, and Cody Fowler.

■ REFERENCES

(1) Ohara, H. Biorefinery. *Appl. Microbiol. Biotechnol.* **2003**, *62*, 474–477.

(2) Kamm, B.; Kamm, M. Principles of biorefineries. *Appl. Microbiol. Biotechnol.* **2004**, *64*, 137–145.

(3) Carvalheiro, F.; Duarte, L. C.; Gírio, F. M. Hemicellulose biorefineries: a review on biomass pretreatments. *J. Sci. Ind. Res.* **2008**, *67*, 849–864.

(4) Zhang, Y.-H. P.; Ding, S.-Y.; Mielenz, J. R.; Cui, J.-B.; Elander, R. T.; Laser, M.; Himmel, M. E.; McMillan, J. R.; Lynd, L. R.

Fractionating recalcitrant lignocellulose at modest reaction conditions. *Biotechnol. Bioeng.* **2007**, *97*, 214–223.

(5) Ye, X. P.; Liu, L.; Hayes, D.; Womac, A.; Hong, K.; Sokhansanj, S. Fast classification and compositional analysis of cornstover fractions using Fourier transform near-infrared techniques. *Bioresour. Technol.* **2008**, *99*, 7323–7332.

(6) Liu, L.; Ye, X. P.; Womac, A. R.; Sokhansanj, S. Variability of biomass chemical composition and rapid analysis using FT-NIR techniques. *Carbohydr. Polym.* **2010**, *81*, 820–829.

(7) Pronyk, C.; Mazza, G. Optimization of processing conditions for the fractionation of triticale straw using pressurized low polarity water. *Bioresour. Technol.* **2011**, *102*, 2016–2025.

(8) Jiang, W.; Han, G.; Zhang, Y.; Wang, M. Fast compositional analysis of ramie using near-infrared spectroscopy. *Carbohydr. Polym.* **2010**, *81*, 937–941.

(9) Sanderson, M. A.; Agblevor, F.; Collins, M.; Johnson, D. K. Compositional analysis of biomass feedstocks by near infrared reflectance spectroscopy. *Biomass Bioenergy* **1996**, *11*, 365–370.

(10) Gierlinger, N.; Schwanninger, M.; Hinterstoisser, B.; Wimmer, R. Rapid determination of heartwood extractives in *Larix* sp. by means of Fourier transform near infrared spectroscopy. *J. Near Infrared Spectrosc.* **2002**, *10*, 203–214.

(11) 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*, 77–88.

(12) Jin, S.; Chen, H. Near-infrared analysis of the chemical composition of rice straw. *Ind. Crops Prod.* **2007**, *26*, 207–211.

(13) Wolfrum, E. J.; Sluiter, A. D. Improved multivariate calibration models for corn stover feedstock and dilute-acid pretreated corn stover. *Cellulose* **2009**, *16*, 567–576.

(14) Lomborg, C. J.; Thomsen, M. H.; Jensen, E. S.; Esbensen, K. H. Power plant intake quantification of wheat straw composition for 2nd generation bioethanol optimization – a near infrared spectroscopy (NIRS) feasibility study. *Bioresour. Technol.* **2010**, *101*, 1199–1205.

(15) Nkansah, K.; Dawson-Andoh, B.; Slahor, J. Rapid characterization of biomass using near infrared spectroscopy coupled with multivariate data analysis: part 1 yellow-poplar (*Liriodendron tulipifera* L.). *Bioresour. Technol.* **2010**, *101*, 4570–4576.

(16) Rodrigues, J.; Faix, O.; Pereira, H. Determination of lignin content of *Eucalyptus globulus* wood using FTIR spectroscopy. *Holzforschung* **1998**, *52*, 46–50.

(17) Meder, R.; Gallagher, S.; Mackie, K. L.; Böhler, H.; Meglen, R. R. Rapid determination of the chemical composition and density of *Pinus radiata* by PLS modelling of transmission and diffuse reflectance FTIR spectra. *Holzforschung* **1999**, *53*, 261–266.

(18) Ferraz, A.; Baeza, J.; Rodriguez, J.; Freer, J. Estimating the chemical composition of biodegraded pine and eucalyptus wood by DRIFT spectroscopy and multivariate analysis. *Bioresour. Technol.* **2000**, *74*, 201–212.

(19) Rodrigues, J.; Puls, J.; Faix, O.; Pereira, H. Determination of monosaccharide composition of *Eucalyptus globulus* wood by FTIR spectroscopy. *Holzforschung* **2001**, *55*, 265–269.

(20) Bjarnestad, S.; Dahlman, O. Chemical compositions of hardwood and softwood pulps employing photoacoustic Fourier transform infrared spectroscopy in combination with partial least-squares analysis. *Anal. Chem.* **2002**, *74*, 5851–5858.

(21) Chen, H.; Ferrari, C.; Angiuli, M.; Yao, J.; Raspi, C.; Bramanti, E. Qualitative and quantitative analysis of wood samples by Fourier transform infrared spectroscopy and multivariate analysis. *Carbohydr. Polym.* **2010**, *82*, 772–778.

(22) Roychoudhury, P.; Harvey, L. M.; McNeil, B. The potential of mid infrared spectroscopy (MIRS) for real time bioprocess monitoring. *Anal. Chim. Acta* **2006**, *571*, 159–166.

(23) Nicolaï, B. M.; Beullens, K.; Bobelyn, E.; Peirs, A.; Saeys, W.; Theron, K. I.; Lammertyn, J. Nondestructive measurement of fruit and vegetable quality by means of NIR spectroscopy: a review. *Postharvest Biol. Technol.* **2007**, *46*, 99–118.

(24) Cen, H.; He, Y. Theory and application of near infrared reflectance spectroscopy in determination of food quality. *Trends Food Sci. Technol.* **2007**, *18*, 72–83.

(25) Wang, L.; Mizaikoff, B. Application of multivariate data-analysis techniques to biomedical diagnostics based on mid-infrared spectroscopy. *Anal. Bioanal. Chem.* **2008**, *391*, 1641–1654.

(26) Burns, D. A.; Ciurczak, E. W. *Handbook of Near-Infrared Analysis*; CRC Press: Boca Raton, FL, 2008.

(27) Nduwamungu, C.; Ziadi, N.; Parent, L.-É.; Tremblay, G. F.; Thuriès, L. Opportunities for, and limitations of, near infrared reflectance spectroscopy applications in soil analysis: a review. *Can. J. Soil Sci.* **2009**, *89*, 531–541.

(28) Luykx, D. M. A. M.; van Ruth, S. M. An overview of analytical methods for determining the geographical origin of food products. *Food Chem.* **2008**, *107*, 897–911.

(29) Sinelli, N.; Spinardi, A.; Di Egidio, V.; Mignani, I.; Casiraghi, E. Evaluation of quality and nutraceutical content of blueberries (*Vaccinium corymbosum* L.) by near and mid-infrared spectroscopy. *Postharvest Biol. Technol.* **2008**, *50*, 31–36.

(30) Moros, J.; Garrigues, S.; de la Guardia, M. Vibrational spectroscopy provides a green tool for multi-component analysis. *Trends Anal. Chem.* **2010**, *29*, 578–591.

(31) Tamaki, Y.; Mazza, G. Rapid determination of lignin content of straw using Fourier transform mid-infrared spectroscopy. *J. Agric. Food Chem.* **2011**, *59* (2), 504–512.

(32) Qin, M. H.; Xu, Q. H.; Shao, Z. Y.; Gao, Y.; Fu, Y. J.; Lu, X. M.; Gao, P. J.; Holmbom, B. Effect of bio-treatment on the lipophilic and hydrophilic extractives of wheat straw. *Bioresour. Technol.* **2009**, *100*, 3082–3087.

(33) Sluiter, A.; Ruiz, R.; Scarlata, C.; Sluiter, J.; Templeton, D. *Determination of Extractives in Biomass*; National Renewable Energy Laboratory, Golden, CO, July 17, 2005; http://www.nrel.gov/biomass/pdfs/42619.pdf (accessed Dec 2010).

(34) Sluiter, A.; Hames, B.; Ruiz, R.; Scarlata, C.; Sluiter, J.; Templeton, D.; Crocker, D. *Determination of Structural Carbohydrates and Lignin in Biomass*; National Renewable Energy Laboratory, Golden, CO, April 25, 2008; http://www.nrel.gov/biomass/pdfs/42618.pdf (accessed Dec 2010).

(35) Tamaki, Y.; Mazza, G. Measurement of structural carbohydrates, lignins, and micro-comoponents of straw and shives: effects of extractives, particle size and crop species. *Ind. Crops Prod.* **2010**, *31*, 534–541.

(36) Zornoza, R.; Guerrero, C.; Mataix-Solera, J.; Scow, K. M.; Arcenegui, V.; Mataix-Beneyto, J. Near infrared spectroscopy for determination of various physical, chemical and biochemical properties in Mediterranean soil. *Soil Biol. Biochem.* **2008**, *40*, 1923–1930.

(37) Saeys, W.; Mouazen, A. M.; Ramon, H. Potential for onsite and online analysis of pig manure using visible and near infrared reflectance spectroscopy. *Biosyst. Eng.* **2005**, *91*, 393–402.