Carbohydrate Polymers 81 (2010) 937–941

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Fast compositional analysis of ramie using near-infrared spectroscopy

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ARTICLE INFO

Article history:
Received 4 December 2009
Received in revised form 4 February 2010
Accepted 7 April 2010
Available online 14 April 2010

Keywords:
Ramie
Near-infrared
Chemical composition
Fast analysis

ABSTRACT

Rapid and accurate determination of chemical compositions of ramie is crucial to its application. In this paper, calibration models were established using near-infrared (NIR) spectroscopy to predict the main chemical compositions of ramie. A wet chemical analysis method which was improved on the basis of Chinese national standard for getting calibration data was used in this paper. NIR data of 59 ramie samples were collected using Fourier transform near-infrared spectrometer. The calibration models of chemical compositions of ramie were derived by partial least square (PLS) regression. Prediction of chemical composition of independent ramie samples showed that these models were rapid and accurate in the chemical composition analysis, giving residual predictive deviation (RPD) value higher than 2.5. Such NIR calibration models can be utilized by ramie fiber manufacturers and breeding workers, in order to better manage the degumming process and evaluate the quality of ramie varieties.

1. Introduction

Ramie is widely used in textile industry due to its good properties (Zheng, Du, & Zhang, 2001); it is also a good raw material for reinforced composites (Angelini, Lazzeri, Levita, Fontanelli, & Bozzi, 2000; Kishi & Fujita, 2008). As a kind of bast-fibre material, ramie needs degumming process before it can be used for textile industry. Many degumming methods were investigated for the application of ramie (Brühlmann, Leupin, Erismann, & Fiechter, 2000; Zheng et al., 2001; Basu & Saha, 2009; Saikia, Boruah, & Samanta, 2009). It is noteworthy to point out that the contents of hemicellulose, cellulose and gum in ramie play an important role in selecting the technological parameters for the degumming process in industry and laboratory. And they can provide important information for breeding work. Moreover, hemicellulose has a great value for papermaking (Bhaduri, Ghosh, & Deb Sarkar, 1995). Therefore, it is important to analyze hemicellulose, cellulose and gum in ramie quantitatively before it can be used in industry and other areas.

China is the provenance of ramie, and has the most varieties and productions of ramie in the world. A national standard which is named "method of quantitative analysis of ramie chemical components" (ramie criterion in short) (Jiang & Shao, 1986) has been promulgated as wet chemical analysis method for the determination of ramie chemical compositions. In most cases, the ramie criterion is the only method to quantitatively analyze the chemical compositions in ramie and other plant fibrous materials in textile industry in China. However, to the best of our knowledge, the wet chemical analysis has its drawbacks such as time consuming, complicated steps, potential dangers to tester and pollution to environment (Kelley, Rowell, Davis, Jurich, & Ibach, 2004; Zheng et al., 2001). Therefore, simple and fast analysis of the chemical compositions of ramie is essential in textile industry and other fields.

As a spectral analysis technique, NIR technique can achieve the requirement of the fast and multiple composition analysis (Cornish, Myers, & Kelley, 2004; Jin & Chen, 2007). What is more, the sample does not need pretreatment (Jin & Chen, 2007), so the test can be free of chemical substances. In recent years, a lot of research works have shown the value of fast analyzing chemical composition of plant materials using NIR technique. Ye et al. (2008) demonstrated the potential of Fourier transform near-infrared (FT-NIR) techniques in quantitatively analyzing chemical composition of cornstover. NIR models were also found to be suitable for fast and accurate analysis of the chemical composition in maize silage (Cozzolino, Fassio, Fernández, Restaino, & Manna, 2006), rice straw (Jin & Chen, 2007), and tobacco (Zhang, Cong, Xie, Yang, & Zhao, 2008). Kelley et al. (2004) got the high-quality calibration model for most of biomass components in various agricultural samples. However, very limited research work that applied NIR spectroscopy to analyze chemical compositions of ramie was found.

In this study, Fourier transform near-infrared spectroscopy has been used to establish the calibration models of the contents of hemicellulose, cellulose and gum in ramie. The models derived

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doi:10.1016/j.carbpol.2010.04.009

from this work can be used to fast analyze the chemical compositions of ramie.

2. Methods

2.1. Sample preparation

A total of 59 samples were collected from the research center of bast-fibre plant in Hunan Province, People's Republic of China. The weight of each sample was more than 200 g. After the storage of all the samples (all the samples were tiled <1 cm thick) under the ambient condition (20–30 °C and <50% humidity) for more than one week, around 100 g of each sample was cut into pieces of 3 cm × 0.5 cm × 0.5 cm, well mixed, then milled to powder which was allowed to pass #60 mesh screen (~250 μm), and oven-dried at 105 °C for at least 6 h until a constant weight is obtained, finally cooled to 20 °C in desiccator. 20 g of the powder was placed into plastic automatic sealing bag for NIR data acquisition, and wet chemical analysis was carried out using another 20 g of powder.

2.2. FT-NIR data acquisition

About 20 g of each sample was put in a non-NIR absorbing specimen cup, the sample spectra were collected in diffuse reflectance mode. MPA Fourier transform near-infrared spectrometer (BRUKER OPTICS, Germany) equipped with a 10 cm integrating sphere was used in this experiment. The spectrum covers a range of 12,000–4000 cm^{-1} with a spectral resolution of 8 cm^{-1}. Each spectrum is the average of 64 co-additions of scans.

2.3. Wet chemical analysis

Reliable calibration data is one of the key factors to determine a successful application of NIR techniques for the fast chemical characterization (Ye et al., 2008). As indicated in Section 1, ramie criterion is the only wet chemical analysis method, which is shown in Fig. 1. Firstly, the samples are dried at 105 °C for at least 6 h, then 3 dried samples are prepared separately, each sample is about 5 g. The procedure of sample 1: Benzene/Ethanol for extraction of wax →water boil for extraction of water soluble matter →dilute Ammonium oxalate for extraction of pectin →Soda boil for extraction hemicellulose. Sample 2 is treated using klason method to analyze lignin, and sample 3 is treated using soda boil to analyze gum. But we found that some flaws make the ramie criterion inaccurate for some chemical composition analysis. The content of hemicellulose was considered to be the weight loss after the soda boil using ramie criterion. However, the lignin can be partially dissolved during soda boil because of the nucleophilic reaction (Tan, 2002; Yang, 2001), and then the content of hemicellulose was a little higher than the true value because some of lignin (lignin A) was mistaken for hemicellulose. The content of cellulose was calculated by 100% deducting other chemical composition contents using ramie criterion, therefore, it was inaccurate, either.

So we carried out a thorough investigation of the principle for the ramie criterion, and optimized the traditional criterion. A new

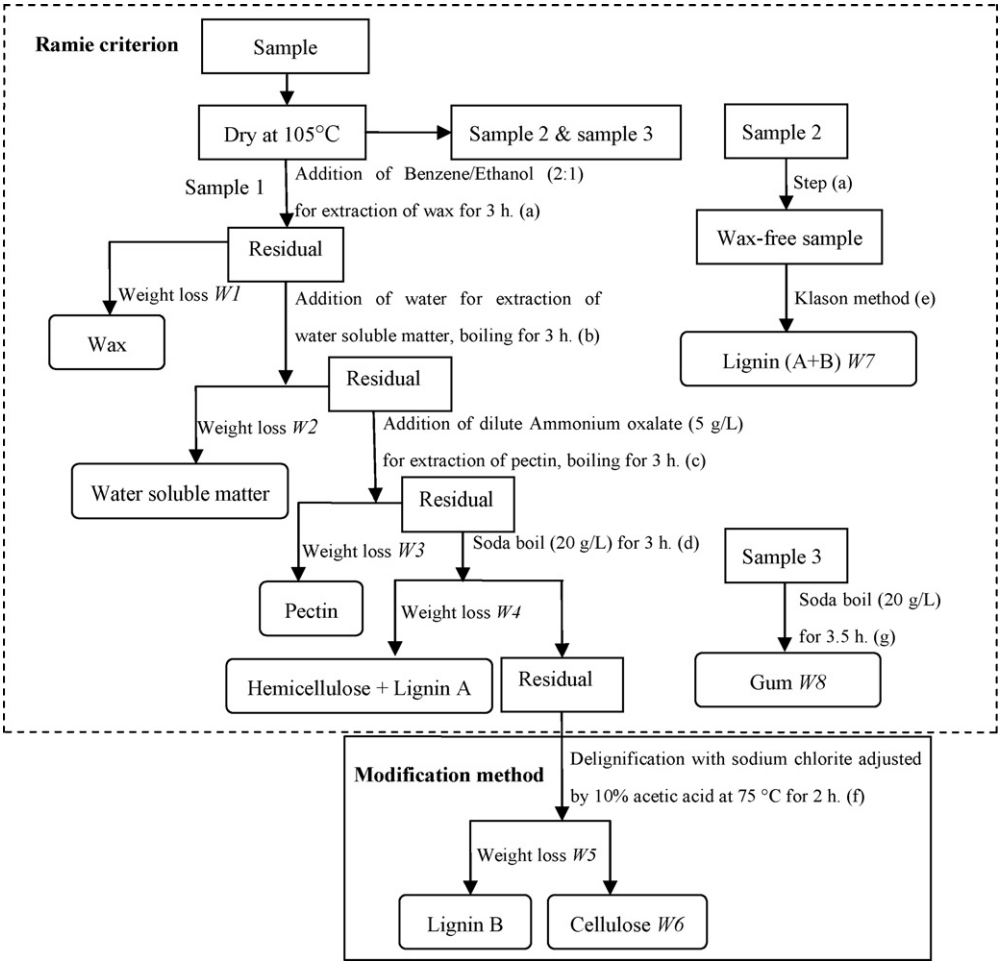

Fig. 1. Schematic diagram for the wet chemical analysis process.

Table 1
Computational method for chemical compositions.

	Hemicellulose	Gum	Cellulose
Ramie criterion	*W*4	*W*8	100–*W*1–*W*2–*W*3–*W*4–*W*7
Modification method	*W*4–(*W*7–*W*5)	*W*8	*W*6

All the data (%, w/w) are on a moisture-free basis. *W*1–*W*8 represent the weight percentage of wax, water soluble matter, pectin, hemicellulose + lignin A, lignin B, cellulose, lignin (A + B) and gum, respectively.

method (modification method, Fig. 1, Table 1) was proposed. From Fig. 1 we can see that one more chemical treatment step (delignification) was added in the modification method after the soda boil which was the last step in ramie criterion. Delignification, treating the samples with acetic acid and sodium chlorite, was widely used in many research works (Chen & Zhu, 1996; Sun, Fang, Goodwin, Lawther, & Bolton, 1998; Sun & Hughes, 1998). Therefore, as shown in Fig. 1, the lignin which was not dissolved in the soda boil (lignin B) can be obtained using this method, and the content of hemicellulose can be achieved from calculation (Table 1), then the error caused by lignin A can be avoided using this method. The residual after the delignification was almost the pure cellulose. It is more accurate to determine the content of hemicellulose and cellulose using the modification method than the ramie criterion.

Chemical contents measured by wet chemistry were carried out using the modification method, and all analyses were performed in duplicate.

2.4. Chemometric analysis

All the multivariate analysis of FT-NIR spectra for quantitative chemical composition prediction were conducted using OPUS software (BRUKER OPTICS, Germany), and partial least square regression was used to construct models. About 80% of samples were used to construct calibration models and other 20% to construct validation models. Samples were selected separately and differently in each model to meet the same range and mean value between calibration and validation data of each chemical composition. The predictive performance of models in this paper was evaluated by several standards, such as coefficient of determination (r^2), root mean square error of prediction (RMSEP), residual predictive deviation (RPD), and average relative error (ARE).

$$\mathrm{RPD} = \frac{\mathrm{SD}}{\mathrm{RMSEP}};\ \mathrm{SD} = \sqrt{\frac{\sum_{i=1}^{n}(C_i - \overline{C}_i)^2}{n-1}} \quad (1)$$

where C_i is the wet chemical analysis measured values in the validation; $\overline{C_i}$ the mean of the wet chemical analysis measured values in the validation; n is the number of samples in the validation.

$$\mathrm{ARE} = \sum_{i=1}^{n} \frac{|C_i' - C_i|}{n\overline{C_i}} \quad (2)$$

where C_i' the NIR modeled values.

A good model should have high r^2, RPD, and low RMSEP values.

3. Results and discussion

3.1. Wet chemical analysis

Before the wet chemical analysis, one sample was chosen to validate the modification method by analyzing the lignin content using sulphuric acid treatment (Klason method). The total lignin content of the sample was 1.01% while it became 0.43% after soda boil, which confirmed that lignin can be partially dissolved during the soda boil, and the analysis mentioned above (Section 2.3) is correct, so the modification method is more accurate than the ramie criterion.

A lot of statistics of ramie chemical compositions can be found (Wei, 2004). Data obtained by wet chemical analysis for calibration set (shown in Table 2) presented content of hemicellulose, cellulose, gum ranged from 13.14 to 20.67%, from 58.2 to 73.17%, and from 21.61 to 41.8%, respectively, which covered the statistical data. The broader the calibration set data, the wider the application range of the calibration model. Therefore, the calibration set in Table 2 can establish a good calibration model for the prediction of ramie chemical composition.

3.2. Calibration models for chemical compositions in ramie

After the NIR data acquisition, several data pretreatment methods were tested on the spectral dataset, including constant offset elimination (COE), straight line subtraction (SLS), min–max normalization (MMN), multiplication scattering correction (MSC), first derivative (FD) and second derivative (SD) (Xiao et al., 2009). Also different spectrum ranges were compared to confirm the characteristic wavelength of each chemical composition separately. In our work, the best pretreatment and the spectrum range were determined using OPUS software. MSC pretreatment for cellulose and SLS pretreatment for hemicellulose and gum were determined in this study. The number of PLS components of the calibration models were 8, 11 and 12, respectively; and spectrum ranges of hemicellulose, cellulose and gum were 7502–4546 cm^{-1}, 7502–4597 cm^{-1} and 6102–5446 cm^{-1}, respectively, which are approximately the same as spectrum ranges of hemicellulose and cellulose of rice straw (Jin & Chen, 2007).

Calibration models for the content of hemicelluloses, cellulose and gum were constructed using PLS separately. The statistics of the calibration models for chemical compositions in ramie are presented in Table 3. Results show that the coefficient of determination for the calibration model (R^2) of cellulose and gum are 0.8325 and 0.9703 (which means their correlation coefficient for the calibration model (R) are 0.91 and 0.99) respectively, are very high. The R^2 and R values of the hemicellulose are 0.7218 and 0.85 which are acceptable for calibration (Kelley et al., 2004; Lovett, Deaville, Mould, Givens, & Owen, 2004).

3.3. Model validation

The robustness of the models was checked by using the calibration models to predict the chemical composition contents of several ramie samples which were not used to develop the NIR calibration models, and the chemical compositions predicted by NIR techniques vs. measured by wet chemistry were shown in Fig. 2.

For cellulose and gum, the r^2 are both more than 0.9 and RMSEP is relatively small, demonstrating the good predicting capability of the model for these two constitutes. The prediction of hemicellulose is not so accurate as cellulose and gum. To evaluate the accuracy of models, the coefficient of determination (r^2) and residual predictive deviation (RPD) statistics were used. Predicted result was evaluated as excellent when $r^2 > 0.90$ and RPD > 3; considered as good when $0.81 < r^2 < 0.90$ and $2.5 < \mathrm{RPD} < 3$; regarded as an approximate prediction if $0.66 < r^2 < 0.80$ and $2.0 < \mathrm{RPD} < 2.5$; considered as poor prediction when $r^2 < 0.66$ and RPD < 2 (Nicolaï et al., 2007; Zornoza et al., 2008). Therefore, the model performance for both cellulose and gum satisfies the criteria for excellent prediction. The predictive performance of hemicellulose content, as established in Table 3, were $r^2 = 0.7525$, RPD = 2.61. The r^2 was lower than 0.80 but RPD was more than 2.50. Average relative error (ARE) can be more intuitive to show the capability of the model prediction. As shown in Table 3, ARE between the predictive value and the wet chemistry measured value of hemicellulose contents was

Table 2
Chemical composition content (%, w/w) of calibration and validation set.

		Hemicellulose	Cellulose	Gum
Calibration	Samples	44	43	43
	Mean	16.30	68.94	29.75
	Range	13.14–20.67	58.2–73.17	21.61–41.8
	Statistical data	14–16	65–75	
Validation	Samples	15	16	16
	Mean	16.48	67.16	30.85
	Range	13.69–19.29	58.46–73.02	24.65–37.71
	SD	1.49	3.82	3.57

Table 3
Model calibration and validation.

	Calibration			Validation			
	R^2	RMSEC (%, w/w)	T-value	r^2	RMSEP (%, w/w)	ARE (%, w/w)	RPD
Hemicellulose	0.7218	0.87	0.238	0.7525	0.74	3.46	2.61
Cellulose	0.8325	1.26	0.891	0.9512	0.842	1.09	4.54
Gum	0.9703	0.72	0.068	0.9125	1.06	3.14	3.37

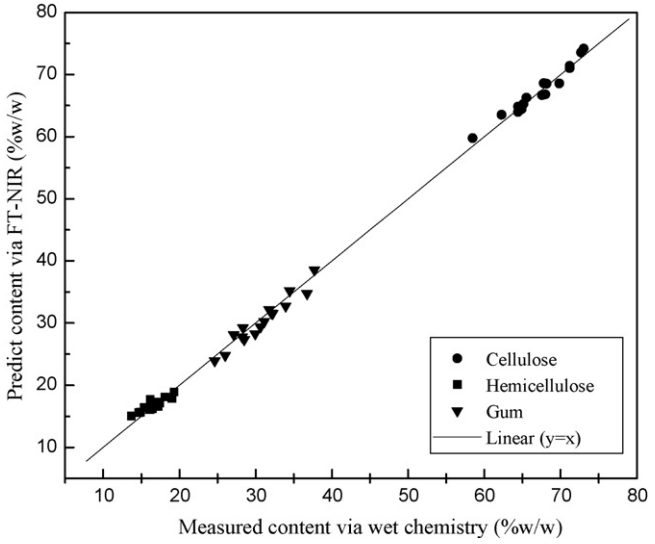

Fig. 2. Chemical content (%, w/w) predicted by FT-NIR techniques vs. measured by wet chemistry.

3.14%, and it is low enough for prediction. Moreover, according to the T-test between the data predicted by the NIR calibration model and the referenced measured values of the chemical compositions, T-value of hemicellulose was $<T_{0.05}$ (1.7613). Take all the factors into account, the calibration model could be considered as good predictions for hemicellulose.

Hemicellulose has a poor chemical durability, which influences the content accuracy obtained by wet chemical analysis (Sun, Fang, Tomkinson, Geng, & Liu, 2001). More accurate analysis method of the hemicellulose content would be helpful for NIR model calibration and prediction.

4. Conclusions

Fourier transform near-infrared spectroscopy, together with multivariate analysis was applied to quantitative prediction of ramie hemicellulose, cellulose and gum contents. The results show that NIR models can be suitable for rapid and accurate prediction of cellulose and gum content in ramie, which will be very helpful for textile industry and agricultural breeding. Moreover, the model is good prediction of hemicellulose content, too. In the future work, more accurate wet chemical analysis method should be studied in detail, and reasonable increase calibration sample size for wider range to balance model robustness is needed.

Acknowledgements

This work was supported in part by the National Basic Research Program of China (973 project, 2009CB626606), National Natural Science Foundation of China (50973048) and the Provincial Key Sci-Tech Special Project of Shandong Province, China (2006GG1103088). We thank the research center of bast-fibre plant for supplying samples, and BRUKER OPTICS for carrying out the NIR spectroscopy of ramie. We also thank Dr. Yiqian Wang at Qingdao University for helpful discussions.

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