USING NIR ANALYSIS FOR DETERMINATION OF
HARDWOOD KRAFT PULP PROPERTIES

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ABSTRACT

Multivariate data analysis and near-infrared region (NIR) spectroscopy was used to determine the physical and mechanical properties of unbleached and bleached hardwood kraft pulps with different chemical compositions and beaten to different levels. The differences between NIR spectra unbleached and bleached hardwood kraft pulps as well as between unbeaten and beaten pulps are very small. The calibration models developed for determination of pulp properties using NIR spectra analysis and conventional method had excellent predictive ability for tensile index (R=0.977-0.989), tear index (R=0.912-0.975) and stiffness (R=0.894-0.986). However, porosity does not show such good correlation (R=0.835-0.875) between measured and NIR predicted value. The correlation coefficients of calibration models made for combined unbleached and bleached pulps and separately for unbleached and bleached pulps were very similar. Average deviation between measured and NIR predicted properties of unknown hardwood kraft pulps confirmed the ability NIR analysis to determine hardwood kraft pulp properties.

KEYWORDS: NIR spectroscopy, multivariate calibration, validation, hardwood kraft pulp, bleaching, tensile index, tear index, stiffness, porosity.

INTRODUCTION

Wood, pulp and final paper products are all materials of profound complexity and variability in both chemical composition and overall structure. The process of paper manufacture out of wood chips is a complex series of steps that include mechanical, physical and chemical alteration of the material. All of these procedures influence quality of the pulp and final paper product and often require complex and costly process control. However, measurements and evaluation of either pulp or paper requires not only an extensive financial spending for many specific instruments but also consumes substantial amount of time as many physical, chemical and optical analyses by means of conventional methods that may take up to several hours to complete. Application of infrared spectroscopy as an alternative approach allows for fast and reliable analysis by non-destructive means. Also, infrared spectroscopy requires much smaller samples than those

necessary for analysis by conventional methods. An advantage to the method is also the fact that in most cases no sample preparation prior to analysis is needed.

Due to robustness and speed of the method, infrared spectroscopy can be applied for on-line or at-line analysis (Fardim et al. 2005, Callis et al. 1987, McLennan 1995), either continuously monitoring pulp processing or paper production, or analysing and evaluating a process at any given time desired. Of course, proper sampling devices and suitable sensors are still under development and bring new challenges to technical solutions.

Infrared spectroscopy (Workman and Weyer 2007) is a powerful analytical method. It is a method that studies electromagnetic spectrum roughly between 700 nm and 3000 um, corresponding to energy levels between 1.24 eV to 0.41 meV. However, in this article we use data obtained from near-infrared region (NIR) of the spectrum, having a range of 1000-2500 nm. NIR has an ability to analyse complex materials such as wood, pulp or paper that are composed of various molecules of complex structures. Infrared spectra result from the periodic motions (or vibration modes) of atomic nuclei within their respective molecules. These nuclei move back and forth along a straight-line vector and result in rotation, vibration, wagging and bending relative to their centres of gravity. The resultant spectra from these vibrational measurement are highly structured and complex. It must be stressed that analysing complex materials such as pulp leads to infrared spectra that depict the entire chemical composition and structure. All individual components in a complex mixture or structure combine and produce a spectrum together. No spectrum of a single chemical compound can be produced from a mixture unless separation is carried out before analysis. Although certain characteristic features of infrared spectra (in our case NIR) are specific for concrete functional groups or bonds, in case of complex structures such as pulp, specific peaks have a tendency to overlap. Water, hydrogen bonds, -CH, -OH groups, double bonds or presence of aromatics are among many functional groups that can be identified directly within a NIR spectrum (Workman and Weyer 2007). Of course, if the sample structure is complex or is composed of many different components, identification and characterization even of specific functional groups with specific overtones may become more difficult due to extensive peak overlap. In such cases it is easier to interpret and analyse the entire spectrum and differentiate between spectra resulting from various samples. Combining NIR spectroscopy with chemometric methods such as partial least squares (PLS) allows extracting valuable information in both a qualitative and quantitative aspect.

Multivariate calibration methods using classical partial least squares (PLS) are suitable for many different applications (Aldrige et al. 1993, Kowalski et al. 1982). NIR combined with multivariate calibration for predictions of the chemical composition of wood and pulp have been extensively studied in numerous applications (Schimleck et al. 1997, Yeh et al. 2004, Olsson et al. 1995, Fadim et al. 2002, Anti et al. 2000). PCA analysis of hardwood NIR spectra was used for estimation of hardwood species content in mixture (Russ et al. 2009). The prediction of pulp mechanical properties by NIR reflectance measurement is also possible because mechanical properties are related to the intra- and intermolecular interactions in the pulp (Walbäcks et al. 1991, Marklund et al. 1999).

Cross-validation is often used as a means of determining whether there is a trend within calibration and whether the calibration model is accurate (Kohavi 1995, Devijver and Kittler 1982, Picard and Cook 1984, Efron and Tibshirani 1997). In cross-validation, there are at least two data sets (or subsets) being used. One subset is called the training set and the other validation or testing set. One-round cross-validation partitions a sample of data into both subsets and the overall aim is to check on accuracy of the calibration model without the need of using too many samples or standards. Cross-validation is an important tool for guarding against the so-called

"type III errors" in situation where availability or use of further samples is restricted due to various reasons, such as hazardous nature of these samples, costs or impossibility of collecting additional samples for any reason. When an independent sample of validation data is taken from the same set of samples as the training data, generally the model does not fit the validation data as well as it fits the training data. This phenomenon is called over fitting and may arise especially due to two reasons. Either the size of training data set is small or the number of parameters the model is large, thus the relationship between the measured property and the analytical signal is not strong enough.

The goal of this article was to investigate the ability of NIR spectroscopy to predict physical and mechanical properties of unbleached and bleached hardwood kraft pulps based on calibration models of dependencies by NIR predicted and classical method measured pulp properties. We have compared the three calibration models, for combined unbleached and bleached kraft pulps, unbleached kraft pulps and bleached kraft pulps.

MATERIAL AND METHODS

Material

Pulps used for study were from SCP Mondi, Ružomberok, Slovakia. The unbleached pulp was produced by CBC kraft cooking process from mixture of hardwoods consisting mainly of beech, oak, hornbeam, turkey oak and black locust. The kappa number of unbleached was 16 and intrinsic viscosity around 860 $dm^3.kg^{-1}$. The oxygen delignified pulp was bleached by the sequence Z(EO)D(PO) to a brightness around 88 % ISO. The intrinsic viscosity of bleached pulp was around 720 $dm^3.kg^{-1}$.

Methods

The unbleached and bleached mixed hardwood kraft pulps were beaten in a Jokro mill to 20, 30, 40 and 50°SR, according to ISO 5264-3. The beating degree was determined according to ISO 5267-1. The laboratory test sheets (80 $g.m^{-2}$) were prepared according to ISO 1924-2. Tensile index and tear index was determined according to ISO 1924-2 and ISO 1974 standard respectively. Stiffness was determined as bending resistance by a two-point method at a 15° bending angle, 10 mm distance of clamp and blade distance according to ISO 2493. Porosity was measured as air permeation resistance according to ISO 5636-5 (Gurley method).

NIR spectra of unbleached and bleached hardwood kraft pulp laboratory sheets were measured in the range 1000-2500 nm. NIR spectra of each laboratory sheet were measured three times on each side, resulting in 6 measurements for every sheet. NIR spectra were determined with Infrared spectrometer iS 10 by Nicolet with methodology of diffused DRIFT. Diffusion-reflectance component of the reflection during sample analysis carries information about absorption properties of the studied sample. For NIR spectroscopic measurements, Integrat IR extension by Pike Technologies was used.

The NIR spectral data were collected using Omnic version 8.0 software by Thermo Scientific. The experiment setup was the following: Number of scans: 128, resolution: 4, data spacing 0.482. cm^{-1}, range of wave numbers 4200-5940. cm^{-1}, final format: absorbance (Log (1/R)). The collected spectra were analyzed and evaluated using TQ Analyst version 8.0 software by Thermo Scientific. The PLS and multivariate method for calibrations, cross-validations and determination of unknown samples was incorporated in the TQ Analyst software.

RESULTS AND DISCUSSION

NIR spectra

The primary goal of this article was to investigate the ability of NIR spectroscopy to predict physical and mechanical properties of pulp. Secondary aim was to investigate how composition of pulp sample set used for calibration models influences the accuracy of these predictions based on calibration models and applied cross-validation.

There were three calibration models used: model 1 includes unbleached and bleached hardwood kraft pulps, model 2 unbleached kraft pulps and model 3 bleached kraft pulps.

Our interest was to distinguish between unbleached and bleached pulp but the distinction was rather small to negligible as calibration models were not significantly influenced by the bleaching process of pulp (Fig. 1).
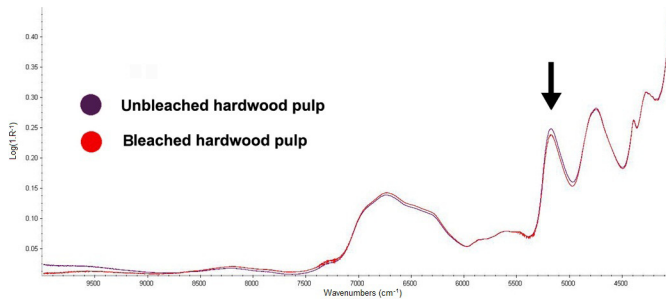

Fig. 1: Average spectra (each from 10 individual spectra) for unbleached and bleached hardwood pulps.

The peak at $5200.cm^{-1}$ is correlated with hydrogen bonds (Fig. 1). Although the average spectra for both bleached and unbleached hardwood pulp almost match, there is a slight elevation of the signal for unbleached hardwood pulp. The decrease of the peak height for bleached hardwood pulp corresponds to decrease of interfibre hydrogen bonds because hemicelluloses are removed during the process of bleaching.

On Fig. 2 presents NIR spectra of unbeaten (15°SR) and beaten (20, 30, 40 and 50°SR) bleached hardwood kraft pulp. The diferences between NIR spectra of unbeaten and beaten bleached hardwood kraft pulp were small. The peak height at $5200.cm^{-1}$ was slightly higher for beaten pulp because during beating shortening and fibrilation of pulp fibres occurs. More interfibre hydrogen bonds in pulp handsheet are a consequence of this creation.
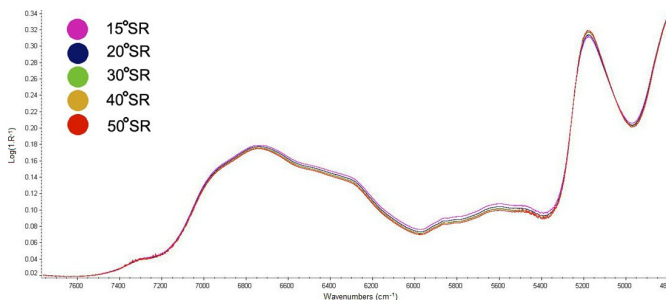

Fig. 2: NIR Spectra of unbeaten and beaten bleached hardwood kraft pulps.

Calibration models

We used three calibration models in this study which were made from combined bleached and unbleached hardwood kraft pulps that were both beaten and unbeaten. In each calibration model, the following hardwood kraft pulps properties were evaluated: tensile index, tear index, stiffness and porosity.

The calibration models were picked up from two data sets, totalling in 100 spectra. These included 50 spectra for unbleached pulp and 50 spectra for bleached pulp. Combining both calibration data sets lead to model 1, with calibration depicted in Figs. 3-6 as example.
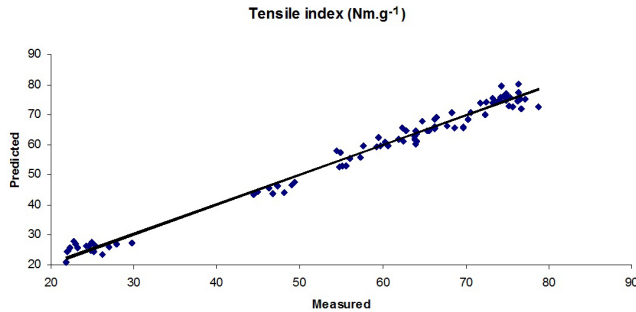

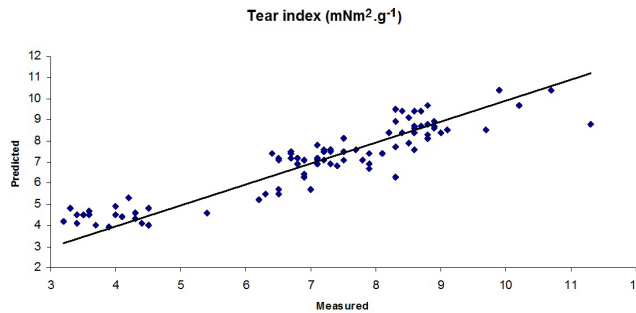*Fig. 3: Calibration model for tensile index of unbleached and bleached hardwood kraft pulps (R=0.989).*

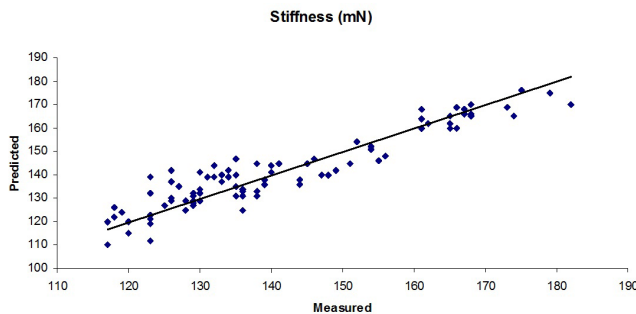*Fig. 4: Calibration model for tear index of unbleached and bleached hardwood kraft pulps (R=0.912).*

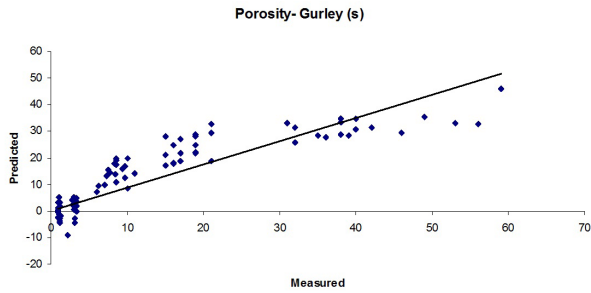*Fig. 5: Calibration model for stiffness of unbleached and bleached hardwood kraft pulps (R=0.926).*

Fig. 6: Calibration model for porosity-Gurley of unbleached and bleached hardwood kraft pulps (R=0.875).

The calibration models determined how precisely was it possible to determine the physical and mechanical properties indirectly by NIR spectroscopy. However, in order to determine accuracy of calibration models, it is necessary to cross-validate data obtained from calibration. Tab. 1 depicts the correlation coefficients (R) of calibration, cross-validation and errors in validation RMSECV for each of the four studied properties of hardwood kraft pulps and three calibration models.

Tab. 1: Overview of correlation coefficients from calibration, errors for RMSEC calibration, correlation coefficients from cross-validation and errors for RMSECV cross-validation for separate properties and calibration models of unbleached and bleached hardwood kraft pulps.

Calibration model		Tensile index	Tear index	Stiffness	Porosity-Gurley
Unbleached and bleached pulp (model 1)	Correlation coefficient	0.989	0.912	0.926	0.875
	RMSEC	2.73	0.8	6.5	7.2
	Cross-validation correlation coefficient	0.979	0.889	0.878	0.804
	RMSECV	3.76	0.9	8.3	9.0
Unbleached pulp (model 2)	Correlation coefficient	0.980	0.961	0.986	0.847
	RMSEC	3.77	0.6	3.1	7.5
	Cross-validation correlation coefficient	0.976	0.924	0.960	0.743
	RMSECV	4.16	0.8	5.1	9.5
Bleached pulp (model 3)	Correlation coefficient	0.977	0.975	0.894	0.835
	RMSEC	3.54	0.3	5.1	7.4
	Cross-validation correlation coefficient	0.971	0.905	0.753	0.776
	RMSECV	3.99	0.5	7.7	8.7

The above obtained correlation coefficients (Tab. 1) for the calibration models made for unbleached and bleached hardwood kraft pulps unbeaten and beaten to 20, 30, 40 a 50°SR, or just for unbleached and bleached hardwood kraft pulps sets either unbeaten or beaten to 20, 30, 40 a 50°SR exhibited rather similar correlation coefficients.

Cross-validation coefficients for all three models related to four physical and mechanical properties of hardwood kraft pulps are slightly lower than correlation coefficients. Cross-validation suggests how accurate the calibration for the prediction model is. Slightly lower cross-validation correlation coefficients are an ideal condition because of validation. Validation cannot lead to more accurate results since the model is not being calibrated but only verified. However, if cross-validation correlation coefficients are much lower than correlation coefficients, validation suggests inaccuracy of calibration. Therefore we can conclude that due to cross-validation correlation values the calibration models have been meaningful and sufficiently accurate.

Determination of pulp properties

Confirmation of the ability of calibration models developed using NIR spectroscopy and multivariate data analysis to determine tensile index, tear index and stiffness based on NIR spectroscopy is presented in Tab. 2, which presents the average deviation between measured and NIR-predicted values. These results were obtained from NIR analysis unknown unbleached and bleached hardwood kraft pulp samples and using three calibration models made for combined unbleached and bleached pulps and separately for unbleached and bleached pulps for determination of tensile index, tear index, stiffness and porosity. The results were very similar to those obtained by conventional methods. However, the NIR method was much faster.

Tab. 2: Average deviation between measured and predicted hardwood kraft pulp properties for unknown samples and measuring range.

Property	Tensile index (Nm.g⁻¹)		Tear index (mNm².g⁻¹)		Stiffness (mN)		Porosity-Gurley (s)	
	Deviation	Range	Deviation	Range	Deviation	Range	Deviation	Range
Model 1	3.70	21.8-78.7	0.77	3.2-11.3	8.97	117-182	5.20	0.9-59.0
Model 2	3.67	24.3-78.7	0.64	3.2-11.3	6.13	123-182	3.77	0.9-59.0
Model 3	3.73	21.8-70.3	0.49	3.9-7.7	5.80	117-156	6.63	1.1-46.0

The pulp properties were validated by means of constructing relationships between values from NIR analyses and values measured by conventional methods. Correlation coefficients of hardwood kraft pulp properties in calibrations models and validations of uknown pulp samples are presented in Tab. 3. The four depicted properties of hardwood kraft pulps show specific correlations. Correlation coefficients from calibrations models and validations of unknown pulp samples were the highest for tensile index (R=0.977-0.989, respectively R= 0.962-0.992). Therefore tensile index can be determined with the highest accuracy among all four studied hardwood kraft pulp properties. However, tear index and stiffness show correlations as well although not as profound as correlation obtained for tensile index.

Tab. 3: Correlation coefficients of hardwood kraft pulp properties in calibration models and validations with unknown hardwood kraft pulp samples.

	Property	Tensile index	Tear index	Stiffness	Porosity-Gurley
Model 1	Calibration	0.989	0.912	0.926	0.875
	Validation	0.992	0.953	0.858	0.699
Model 2	Calibration	0.980	0.961	0.986	0.847
	Validation	0.962	0.921	0.834	0.866
Model 3	Calibration	0.977	0.975	0.894	0.835
	Validation	0.981	0.931	0.827	0.721

The correlation coefficients between NIR predicted and measured values for porosity were the lowest for both calibration models (R = 0.835-0.875) and validations of unknown pulp samples (R = 0.699-0.866). The trends can be explained in the following way. NIR spectroscopy is influenced by chemical structure within the studied samples. NIR spectra are a direct result of samples' chemical composition and thus can be correlated with many physical and mechanical properties that are related with chemical composition of the studied samples.

Tensile index, tear index and stiffness are all mechanical properties that are much related to the number of interfibre hydrogen bonds (or bonding strength) and distribution of these bonds which should be reflected on NIR spectra. Porosity is physical property, which suggests how much air can pass through a pulp. However, large pores do not relate to the chemical structure but to geometrical distribution of individual fibres. Pores within pulp sheet may influence overall strength properties and microscopic pores may be related to cellulose structure. However macroscopic composition of pulp sheet (larger pores) is independent of its chemical structure and composition. Therefore distribution of large pores across the pulp sheet should not be linked to NIR spectra and therefore poorer correlation should be identified in this case.

CONCLUSIONS

In the pulp and paper industry, there is a need to replace some of the time-consuming expensive pulp analyses used at present. These methods could be replaced by rapid, non-destructive NIR spectroscopy analysis. In order to find well-advised calibration model for prediction of physical and mechanical properties for unbleached and bleached hardwood kraft pulps, three models, for unbleached and bleached pulps and separately from unbleached and bleached pulps were tested.

The calibration models developed for determination of tensile index, tear index, stiffness and porosity using NIR spectra analysis and conventional method had excellent predictive ability for tensile index and slightly lower for tear index and stiffness. However, porosity shows lower correlation between measured and NIR predicted values. Testing of unknown pulp samples confirmed that NIR analysis is suitable for determination of unbleached and bleached hardwood kraft pulps properties.

Further developments of proper sensors and sampling devices will make the NIR methods applicable for on-line conditions. On the present, with very low investment, NIR spectroscopy can be an attractive substitute for the routine control laboratories in pulp and paper mills and improves process monitoring and product quality.

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