Characterization of Pre-treatments on Wood Chips Prior to Delignification by Near Infrared Spectroscopy

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A near infrared (NIR) spectroscopy-based method for predicting yields and lignin contents of differently pre-treated silver/white birch (*Betula pendula/B. pubescens*) and Scots pine (*Pinus sylvestris*) chips was developed. The approach was to create multivariate calibration models from the NIR data by the partial least squares (PLS) method. Both parameters are important factors when adjusting adequate conditions for pre-treatments either with hot-water (HW) as such and slightly acidified HW (collectively referred to as autohydrolysis) or dilute alkaline aqueous solutions prior to alkaline pulping. Pre-treatment conditions were varied with respect to temperature (130 °C and 150 °C) and treatment time (from 30 min to 120 min). In the case of alkaline pre-treatments, the NaOH charge was 1% to 8% NaOH on wood dry solids (DS). The yields varied in the range 81.2% to 99.3% (in autohydrolyses) and 83.5% to 97.9% (in alkaline pre-treatments). High correlation coefficients and low prediction errors in relation to conventional yield and lignin content data clearly indicated the suitability of NIR spectroscopy combined with the multivariate modeling as an effective and fast tool for this purpose. This technique also showed promising possibilities for developing practical process control methods to follow such pre-treatments.

Keywords: Alkaline; Near infrared; Partial least squares; Pre-treatment; Scots pine; Silver/white birch; Spectroscopy

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INTRODUCTION

Integrated forest biorefineries (IFBRs) have great potential for economic production of biofuels, chemicals, and biomaterials in addition to paper, board, and wood products (Bajpai 2012). The favorable techno-economics results from capital and operational cost savings due to readily available operations for wood harvesting, transport, and processing together with appropriate facilities, chemical circulations, water treatment and boiler systems, permits, and labor (van Heiningen *et al.* 2011). An IFBR has been defined as the "full integration of the incoming biomass and other raw materials, including energy, for simultaneous production of fibers for paper products, chemicals, and energy" (Chambost and Stuart 2007; Bajpai 2012). By applying IFBR activities at an existing plant, pulp and paper mills have the opportunity to produce significant amounts of bioenergy and bioproducts, and thus increase their revenues while continuing to produce conventional products. Manufacturing new value-added byproducts (*e.g.*, biofuels, bulk and specialty chemicals, and pharmaceuticals) from biomass represents for forestry companies an unprecedented opportunity for revenue diversification.

Lignocellulosic biomass is mainly composed of cellulose, hemicellulose, and lignin (Sjöström and Westermark 1999; Alén 2000). Both the cellulose and hemicellulose fractions are composed of polymeric sugars; therefore, they can be considered as potential sources for production of fermentable sugars (Alén 2011). Hemicelluloses especially can be readily hydrolyzed under mild acidic or alkaline conditions, yielding carbohydrate-rich hydrolysates and effluents that can be further processed, for example, *via* fermentation into value-added chemicals and fuels. The cellulose fraction is more resistant and thus requires more rigorous treatment.

Removal of hemicelluloses from wood as a pre-treatment step is presently being practiced commercially in the production of dissolving pulps (Bajpai 2012; Lehto 2015). Extraction of hemicelluloses prior to pulping can provide an additional feedstock for biofuel/bioethanol production, thus increasing the total revenue stream for the pulp and paper industry (Ragauskas *et al.* 2006; van Heiningen 2006). It is, therefore, desirable to develop a pre-treatment process that can solubilize hemicellulose sugars with minimal formation of fermentation inhibitors, while preserving fiber quality. This creates a need for rapid analytical techniques by which the effects of various pre-treatments on wood material can be determined.

Due to the need for rapid feedstock characterization, reliable and fast methods for measuring the chemical components left in the wood materials after pre-treatments are highly appreciated. Several spectroscopic analysis methods, such as Fourier transform infrared (FTIR) (Nuopponen *et al.* 2004; Fan *et al*. 2012; Esteves *et al*. 2013), near infrared (NIR) (Mehrotra *et al.* 2010; Schwanninger *et al.* 2011), and attenuated total reflectance (ATR) (Chen *et al.* 2015; Pizzo *et al.* 2015; Lehto *et al.* 2017) infrared spectroscopy, have been proposed and utilized for providing a solution to many problems linked to conventional wet chemical analyses, which are accurate but simultaneously have many limitations, especially with regard to the amount of material required to confirm the analysis and to the overall time-consuming processes. In general, spectroscopic methods are fast and non-destructive, requiring only simple low-cost instrumentation and very little sample preparation (Xu *et al.* 2013). In our earlier work, the influences of pre-treatments on wood were studied by FTIR-ATR spectroscopy. In that study, chemical changes in hemicelluloses and lignin during pre-treatments were clearly detected by infrared spectroscopy (Lehto *et al*. 2017).

In this study, hot-water (HW)-extracted, slightly acidic-extracted, and alkali-extracted silver/white birch (*Betula pendula/B. pubescens*) and Scots pine (*Pinus sylvestris*) wood materials were investigated by NIR spectroscopy with a view towards their potential utilization in biorefineries. The data acquired by this straightforward analysis method were subjected to statistical analysis by which the aim was to create multivariate calibration models from the NIR data by the partial least squares (PLS) method.

The main goal was to clarify whether the essential effects of varying pre-treatments conditions on the original wood materials could be easily detected by this method. Hence, special emphasis on clarifying the feasibility of this detection method through analytical and statistical analysis was geared towards creating a model for total wood yield and total content of residual lignin in wood residues, as these parameters can be considered to have the most effect in the subsequent pulping process.

EXPERIMENTAL

Feedstock Materials and Pre-Treatment Experiments

Industrial silver/white birch (*Betula pendula/B. pubescens*) and Scots pine (*Pinus sylvestris*) chips were used in the laboratory-scale pre-treatment (autohydrolysis and alkaline) experiments. Laboratory-scale pre-treatment experiments of screened (SCAN-CM 40:94) chips were conducted in 1.25-L rotating stainless steel autoclaves heated in an oil bath (CRS Autoclave System 420, Stenkullen, Sweden). The maximum thickness of the used chips was 7 mm, maximum width 13 mm, and minimum width 7 mm. Chips with bark, knots, and other visible impurities were manually removed. Chips were treated at two treatment temperatures (130 °C and 150 °C) and with four treatment times (30, 60, 90, and 120 min), thus corresponding to the P-factor range from 10 to 238. In each case, a 30-min heating period was added to the treatment times. The liquid-to-wood (L:W) ratio was 5 L/kg. The chosen cooking liquors were ultra-high quality (UHQ) water (internal resistance $\geq$ 18.2 MΩcm at 25 °C) obtained from a Milli-Q Plus water system (Millipore, Bedford, MA, USA), UHQ water with the pH adjusted to 3, and aqueous NaOH solutions having chemical additions adjusted to 1%, 2%, 3%, 4%, 6%, and 8% of NaOH on oven-dried wood. Pre-treated wood chips were separated from the hydrolysates by using filtration bags. Chips were washed with tap water, and the yield was calculated based on the dry solids (DS) content of untreated and pre-treated chips.

Analytical Determinations: Feedstock Materials

The extractives content was determined by extracting a ground (by means of a Retsch SM100 cutting laboratory mill equipped with a bottom sieve with trapezoid holes having perforation size of <1.0 mm) sample with acetone for 4 h in a Soxhlet apparatus according to TAPPI Test Method T280 pm-99 (1999). The extract obtained was first concentrated by vacuum evaporation with a rotary evaporator (Heidolph VV2000, Gemini BV Laboratory, Apeldoorn, Netherlands) apparatus, and drying was finally accomplished before weighing via a gentle nitrogen gas stream.

The lignin content of the extractives-free samples (each about 200 mg) was determined as the sum of "acid-insoluble Klason lignin" by using TAPPI Test Methods T222 om-98 (1998) and T249 cm-00 (2000) and "acid-soluble lignin." The content of acid-soluble lignin was determined using a Beckman DU 640 UV/Vis-spectrophotometer (Beckman Instruments Inc., Fullerton, CA, USA) at 205 nm after quantitative dilution of the sample with aqueous 0.5% H_2SO_4 until the absorbance (A) was in the 0.3 to 0.8 range. The concentration of dissolved lignin (c, g/L) was calculated according to Eq. 1,

$$c = A/(a*b) \tag{1}$$

where a is absorptivity [120 L/(gcm) for pine and 110 L/(gcm) for birch (Swan 1965)] and b is the light path (cm). The content of wood carbohydrates was determined from Klason hydrolysates according to TAPPI test method T249 cm-00 (2000).

NIR Characterization and Data Analysis

NIR measurements were performed with pellets prepared from ground and homogenized chips. A Fritsch Pulverisette analytical grinder (Fritsch GmbH, Idar-Oberstein, Germany) equipped with 0.5 mm sieve was used for grinding. The analyses were carried out with a Thermo Antaris II NIR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) equipped with an integrating sphere module in the wavenumber range from 4,000 cm^{-1} to 10,000 cm^{-1}. In each measurement, 64 scans were accumulated at a resolution of 8 cm^{-1}.

The samples from alkaline pre-treatments (48 samples, for both chip types) were divided by the chemometric software TQ Analyst 9 (Thermo Fisher Scientific, Waltham, MA, USA) into the calibration and validation sets, whereas all samples from autohydrolysis pre-treatments (16 samples, for both chip types) were used for calibration due to the limited amount of different samples. In addition, leave-one-out cross-validation method was applied to the model evaluations. A range of spectral processing methods, such as multiplicative signal correction and mean centering, was used before the multivariate regressions. The quality of the calibration models was evaluated according to the values obtained for the correlation coefficients and the root mean square error of calibration (RMSEC), root mean square error of prediction (RMSEP), and root mean square error of cross validation (RMSECV).

RESULTS AND DISCUSSION

Feedstock Materials and Pre-treatments

The chemical composition of the feedstock materials used in the HW and alkaline pre-treatment experiments is presented in Table 1.

Table 1. Chemical Composition of the Feedstock Materials, Percent of Dry Wood

	Autohydrolysis Pre-treatments		Alkaline Pre-treatments	
Component	Birch	Pine	Birch	Pine
Monosaccharides*	61.9	58.8	64.1	60.4
Arabinose	0.6	1.9	0.4	1.4
Galactose	0.7	2.9	1.3	1.8
Glucose	38.2	37.7	39.7	39.3
Mannose	1.5	10.7	1.6	13.8
Xylose	20.9	5.6	21.1	4.1
Lignin	24.2	31.6	22.1	27.7
Acid-soluble	5.8	0.4	4.8	0.5
Klason	18.4	31.2	17.3	27.2
Extractives	2.7	3.3	3.7	3.1
Unidentified	11.2	6.3	8.2	10.7

* Monosaccharide moieties are presented as anhydrosugars

The yield data after autohydrolysis and alkaline pre-treatments are presented in Fig. 1. For birch, the yield after autohydrolysis pre-treatments ranged from 81.2% to 99.3% and for pine the corresponding yield ranged from 85.4% to 97.8%. In alkaline pre-treatments, corresponding yields ranged from 83.5% to 97.9% and from 86.8% to 97.8% for birch and pine, respectively. The main part of the materials dissolved (described earlier by Lehto 2015) during the pretreatments consisted of various mainly hemicellulose-derived carbohydrates and carbohydrate-derived degradation products, such as furanoic compounds [*i.e.*, 2-furfural and 5-(hydroxymethyl)furfural (HMF)] and aliphatic organic acids (*i.e.*, volatile acids and non-volatile hydroxy acids), with only a minor part of this fraction consisting of dissolved lignin.

On the other hand, lignin and cellulosic fibers were clearly more resistant towards mild pre-treatment conditions presented in this study; thus, their relative contents in the residual wood samples were clearly increased. The lignin content for birch after autohydrolysis pre-treatments ranged from 21.3% to 24.3%, and for pine the corresponding yield ranged from 28.4% to 32.6%. In alkaline pre-treatments, corresponding lignin content ranged from 24.1% to 33.4% and from 27.6% to 31.0% for birch and pine, respectively.

NIR Measurements

Reliable and repeatable collection of NIR spectra is essential for making valid calibrations. There are many equipment-dependent factors that influence the NIR spectra collection, including measurement type (*e.g.*, integrating sphere, fiber optics probe, and transmission), number of scans, spectral resolution, and wavenumber range. However, factors such as the particle size, size distribution, and other physical aspects can be influenced to a great extent by the user.

The effect of the particle size of wood on the various calibration models has been considered (Hein *et al.* 2010; Jiang *et al.* 2013; Jiang *et al.* 2014). By grinding the samples prior to measurement, the calibration can be improved compared to that of solid wood, but the particle size of the ground wood is not a critical factor. In this study, the physical appearance of the chips after pre-treatment varied according to the severity of the treatment. This variation resulted in differences in size distribution of the ground samples. Therefore, to standardize the influence of these differences of sample powders during NIR measurements, the pellets were pressed before measurements.

Multivariate Models

Due to numerous broad and overlapping bands consisting of combination and overtone (OT) modes in the NIR spectra of wood, their visual interpretation is difficult (Fig. 2). Thus, multivariate statistical methods are required to create calibration models for the chemical composition and/or physical properties of wood (Schwanninger *et al.* 2011)

Some studies utilizing NIR spectral data to create multivariate models for predicting yield (or mass loss) or different chemical components of wood have employed specific wavenumber ranges or bands (Esteves and Pereira 2008; Jiang *et al.* 2014; McLean *et al.* 2014; Pulkka *et al.* 2016; Santos *et al.* 2016). In such cases, for example, for modeling the lignin content, the wavenumber range from 5,400 cm^{-1} to 6,900 cm^{-1} or parts of it have been selected. This range includes several bands based on vibrations of C-H stretching (1st OT) of aromatic, CH_2 and CH_3 bonds, phenolic O-H (1st OT), and non-specified band at 5,522 cm^{-1} of lignin structures (Schwanninger *et al.* 2011). Alternatively, the whole range of NIR spectroscopy (from 3,800-4,000 cm^{-1} to 10,000-12,000 cm^{-1}) has been used to create multivariate prediction models (Kelley *et al.* 2002; Monrroy *et al.* 2015) for similar purposes in wood chemistry studies.

Herein, the whole range from 4,000 cm^{-1} to 10,000 cm^{-1} was used for making multivariate calibration models for predicting yields and lignin contents of chips. Considering the yield prediction, our earlier studies showed that chemical changes occur in a wide range of ATR spectra; and considering that the NIR spectrum consists of combination and OT (1st and 2nd) bands of the same vibrations, it was assumed and also observed that this approach gave the best results

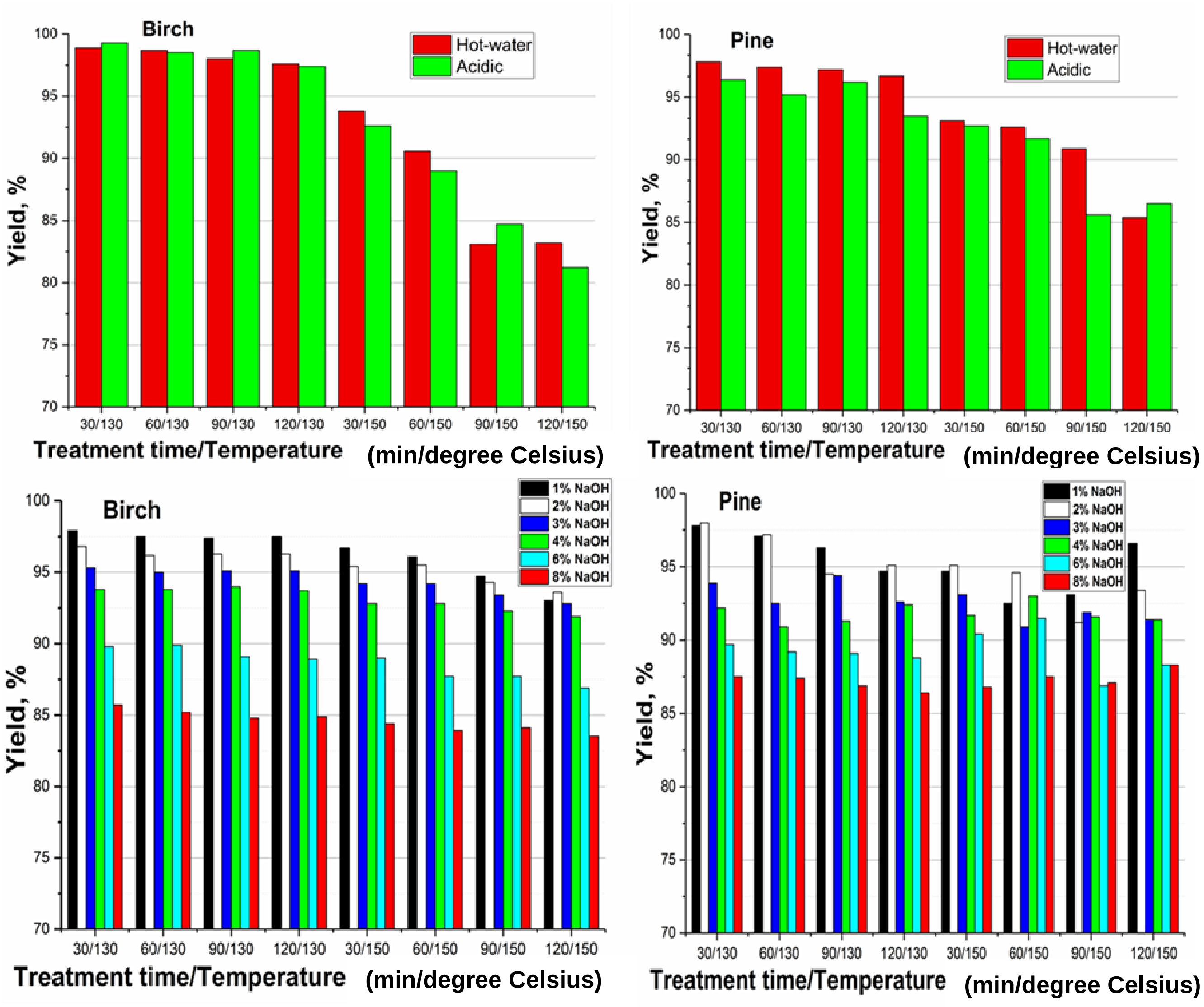

Fig. 1. Yield (% of original dry wood) data on autohydrolysis (top) and alkaline (bottom) pre-treatments

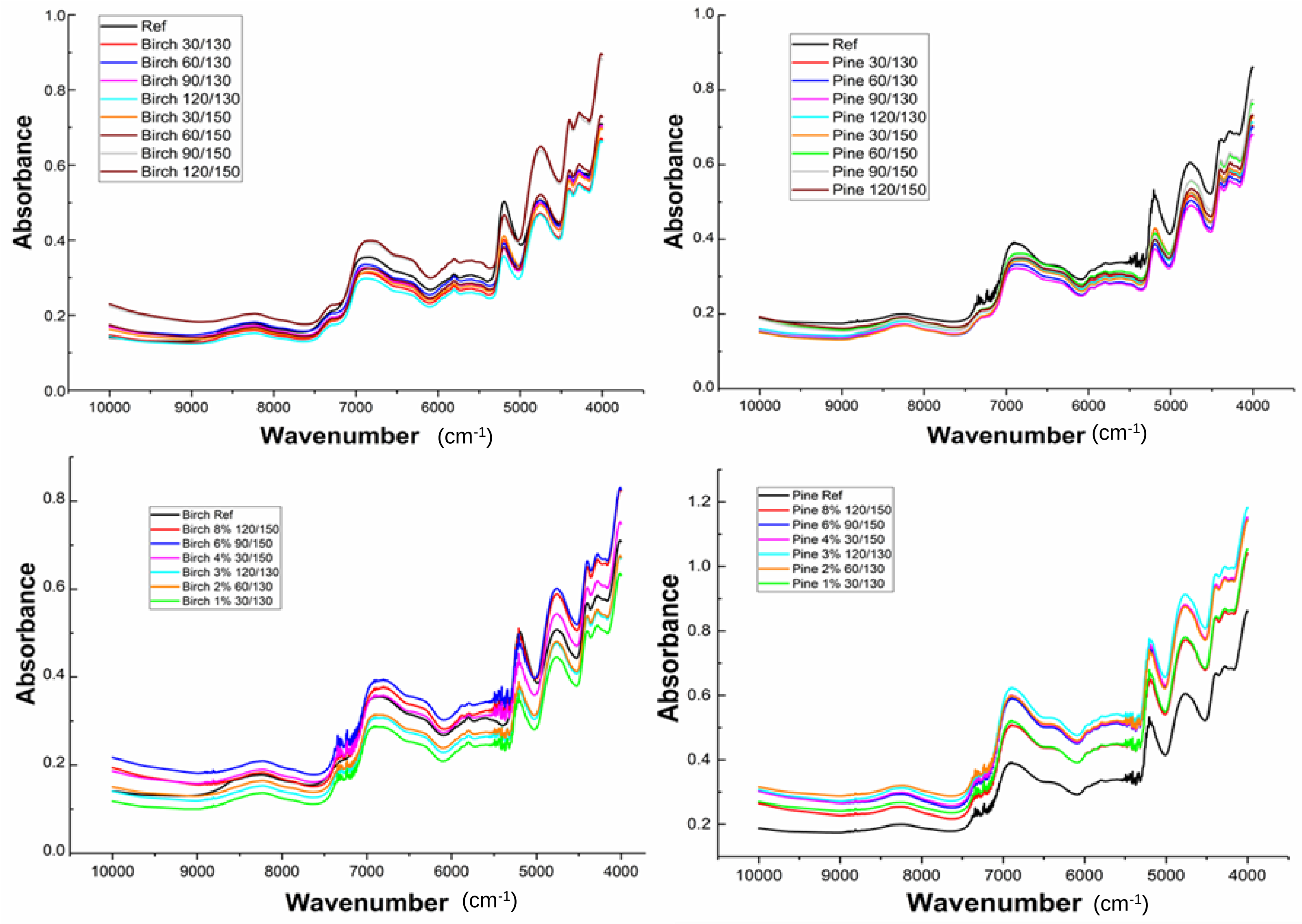

Fig. 2. Selected NIR spectral data for HW (top) and alkaline (bottom) pre-treatments

In the case of lignin content, the specific wavenumber range and several different bands characteristic for lignin were separately tested. However, using the whole NIR range gave similar or better results in calibrations compared to the results using limited range(s). Thus, the results in Table 2 are based on the 4,000 cm^{-1} to 10,000 cm^{-1} wavenumber range. In general, in including only characteristic wavenumbers for making multivariate calibration models (*i.e.*, excluding the unnecessary spectrum range), the prediction could be more accurate in many cases. In this study, the model can benefit from using a larger wavenumber range, since the changes in other wood constituents (mainly carbohydrates) also follow the progress of the pre-treatment.

In almost all calibration models, the first derivative of the normalized spectra was used to get the best models. The only exceptions to this method were the calibration models for the yield prediction of autohydrolysis treatments of both birch and pine chips, in which the normalized spectra were used without derivatization.

In this study, good calibration models were obtained to predict the yield and lignin content of hardwood and softwood during different pre-treatments (Figs. 3 and 4). In our earlier studies (Lehto *et al.* 2017), the influence of the different pre-treatments on the ATR spectra of the hardwood and softwood chips was investigated. These studies showed clear changes in the characteristic lignin and carbohydrate bands in the fingerprint region of the mid-infrared spectra. Utilizing those systematic changes, NIR spectroscopic methods for predicting yield and lignin content in wood residues were successfully created. These kinds of methods could be used to monitor and adjust the severity of the pre-treatments, and thus, optimize the subsequent pulping process.

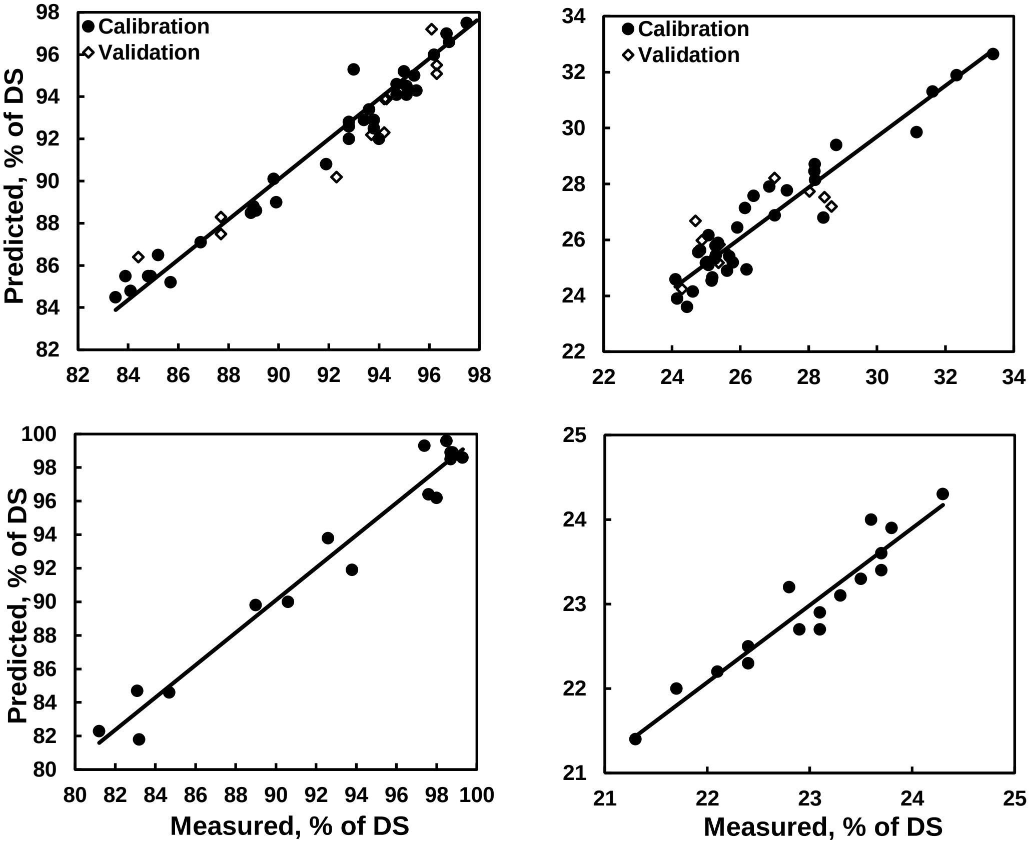

Fig. 3. Predicted *vs.* measured yield (left) and lignin content (right) of the alkaline (upper) and autohydrolysis (lower) pre-treated birch chips

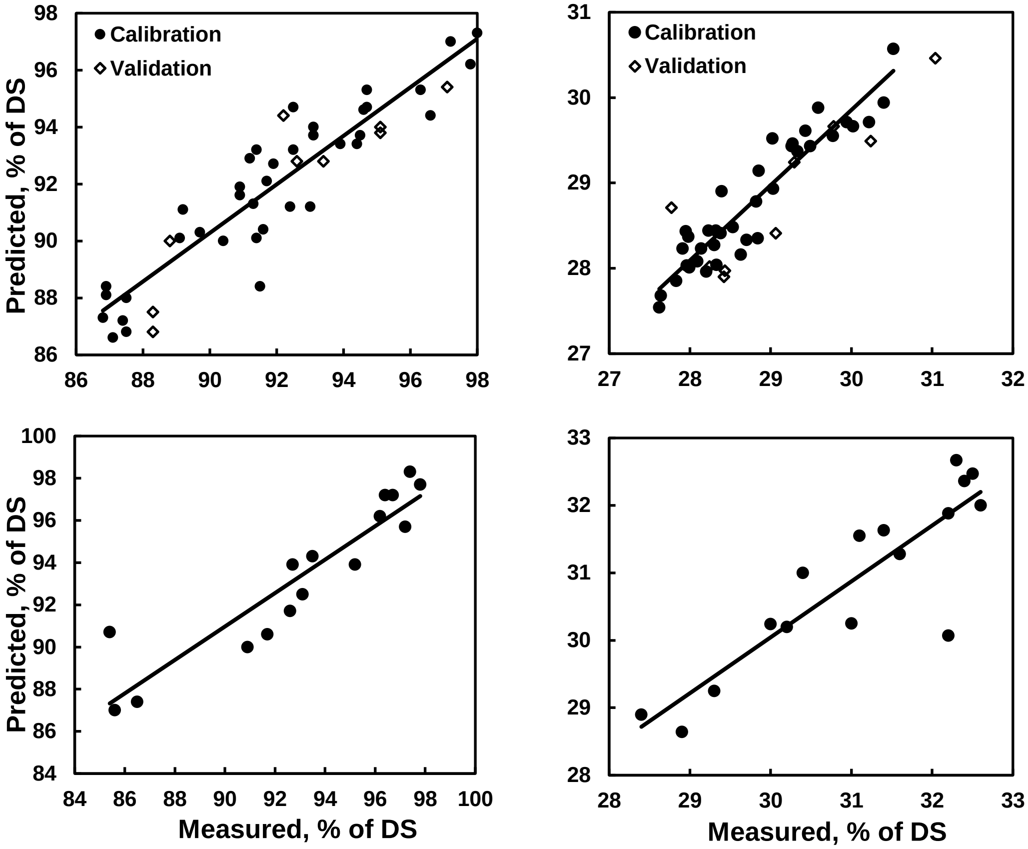

Fig. 4. Predicted *vs.* measured yield (left) and lignin content (right) of the alkaline (upper) and autohydrolysis (lower) pre-treated pine chips

Table 2. Results of the Calibration and Prediction of Yields and Lignin Contents of Alkaline and (HW) Pre-treated Wood Chips

Wood species - yield		Factors	Correlation coefficient	RMSEC	RMSEP	RMSECV
	Pine	2	0.943	1.1	1.5	1.5
	Birch	4	0.977	0.9	1.3	1.6
	Pine	4	0.965	1.0		1.6
	Birch	2	0.983	1.2		1.6
Wood species – lignin						
	Pine	3	0.938	0.3	0.5	0.5
	Birch	4	0.947	0.7	1.0	2.1
	Pine	3	0.956	0.4		0.9
	Birch	3	0.957	0.2		0.8

RMSEP values of the alkaline pre-treated birch and pine showed that the NIR could be used to predict the yield of an unknown sample with an accuracy of 1.3% to 1.6% and 1.7% to 1.8%, whereas for predicting the lignin content of the unknown sample, the accuracy was 4.1% to 4.7% and 1.5% to 2.1%, respectively. It could be assumed that the accuracy of the prediction would improve to some extent by increasing the number of calibration samples. However, it should be pointed out that the accuracy of the prediction cannot be better than that of the method used to obtain the reference data. In this case, the accuracy of the yield determination was estimated to be from 0.5% to 1.0%, and that of lignin around 1%. Accurate determination of lignin content from wood and other lignocellulosic materials is known to be challenging task (Hatfield and Fukushima 2005). NIR could offer a rapid and reproducible method for lignin determination when an adequate number of samples are included in the calibration. The Klason method is probably the most suitable reference method for lignin determination.

CONCLUSIONS

1. High correlation coefficients and low prediction errors of yields and lignin contents of pre-treated hardwood and softwood clearly indicated the suitability of NIR spectroscopy, combined with the multivariate modeling, as an effective and fast tool for this purpose.
2. The accuracy of the prediction models for yields and lignin contents was very good, considering the challenges on the accuracy of the reference methods used for making models, especially in the case of lignin content.
3. This NIR technique showed promising possibilities for developing practical process control methods to follow the progress of these pre-treatments, when calibration and validation of the models are carefully made for the wood species processed and the number of samples tested is large enough.

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