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REVIEW ARTICLE

A review of recent application of near infrared spectroscopy to wood science and technology

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Abstract This review article introduces recent scientific and technical reports due to near infrared spectroscopy (NIRS) at wood science and technology, most of which was published between 2006 and 2013. Many researchers reported that NIR technique was useful to detect multi traits of chemical, physical, mechanical and anatomical properties of wood materials although it was widely used in a state where characteristic cellular structure was retained. However, we should be sensitive and careful for application of NIRS, when spectra coupled with chemometrics presents unexpected good results (especially, for mechanical physical and anatomical properties). The real application for on-line or at-line monitoring in wood industry is desired as next step. Basic spectroscopic research for wooden material is also progressed. It should be a powerful and meaningful analytical spectroscopic tool.

Keywords Near infrared spectroscopy · Non-destructive measurement · Chemometrics · On-line measurement · Physico-chemical properties

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Introduction

It is of importance to inspect the physical property and chemical composition of woods correctly, rapidly and simply, when we utilize woods as lumber, timber and so on. Especially, non-destructive measurement is strongly required. Many researchers have proposed and developed various technologies and devices, however, there are many problems concerning with accuracy, precise, measurement time, device size, etc. Construction of new methodology is, therefore, strongly desirable.

Recently, we aimed at near infrared spectroscopy (NIRS) to overcome these problems. NIRS is used as on-line or on-site measurement of various organic materials such as agricultural products, foods, polymers, textiles, pharmaceuticals, petrochemicals, etc. In this article, we explain the outline of NIRS and introduce many reports due to wood science and technology, which might be helpful to consider its applicability.

Spectroscopic background of NIRS

Electromagnetic wave range between 800 and 2500 nm, that is among the visible range (380–780 nm) and the infrared (IR) range (2500–25,000 nm), is defined as near infrared (NIR) range. Spectroscopy based on absorption or emission at NIR range is called as NIRS. Organic compounds consist of various functional groups, whose fundamental vibration (molecular vibration) is observed at IR range. As they are the most intense and the simplest, we could decide the molecular structure of organic materials using IR spectra.

Figure 1 shows IR and NIR spectra of Douglas fir wood. Also in case of NIR region, same phenomena could be observed, however, as this region contains absorption bands corresponding to overtones or combinations of fundamental vibrations, they are overlapped each other. Therefore, absorpity of NIR light in organic materials is very weak compared to that of IR light. This means that we could measure high density and concentration materials directly using NIR light, that is, non-destructive measurement is available. In case of water, molar absorpity at NIR range is 1/1000–1/10,000 compared to that of IR region, so that, NIR range is useful for high moisture content materials such as wood. Then, NIR spectra are normally analyzed with the aid of statistics and computer to observe "useful material information". Chemometrics is a keyword applied to the generic discipline involving computers and mathematics to derive meaningful chemical information from samples of varying complexity. Effective quality evaluation could be achieved by them. Karl Norris, who was agro-industrial researcher at USDA, discovered the usefulness of NIRS at 1960s [1]. It should be unique spectroscopy, which was originated from agricultural technology.

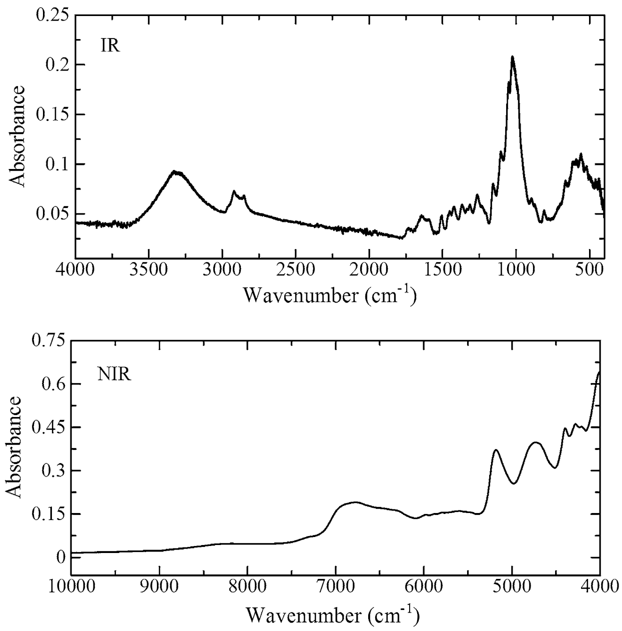

Fig. 1 Infrared (*IR*) and near infrared (*NIR*) spectra of Douglas fir

Trend of NIR research at wood science and technology

In the area of pulp and paper industry, Brikett and Gambino investigated NIRS for evaluation of Kappa number at 25 years ago [2]. Many paper-making companies have already used NIR type on-line moisture content device, which is also available for high moisture sample. In the case of wood science and technology, the publication related to NIRS is dramatically increasing [3]. Figure 2 shows the trend of number of publications including keywords "NIR" and "Wood" since 1995. Table 1 shows number of publications at each country during 1990–2014. USA, Japan, Australia, China are main country to promote aggressive NIR research and development.

Following review article introduces NIR research in the wood science and technology, most of which was

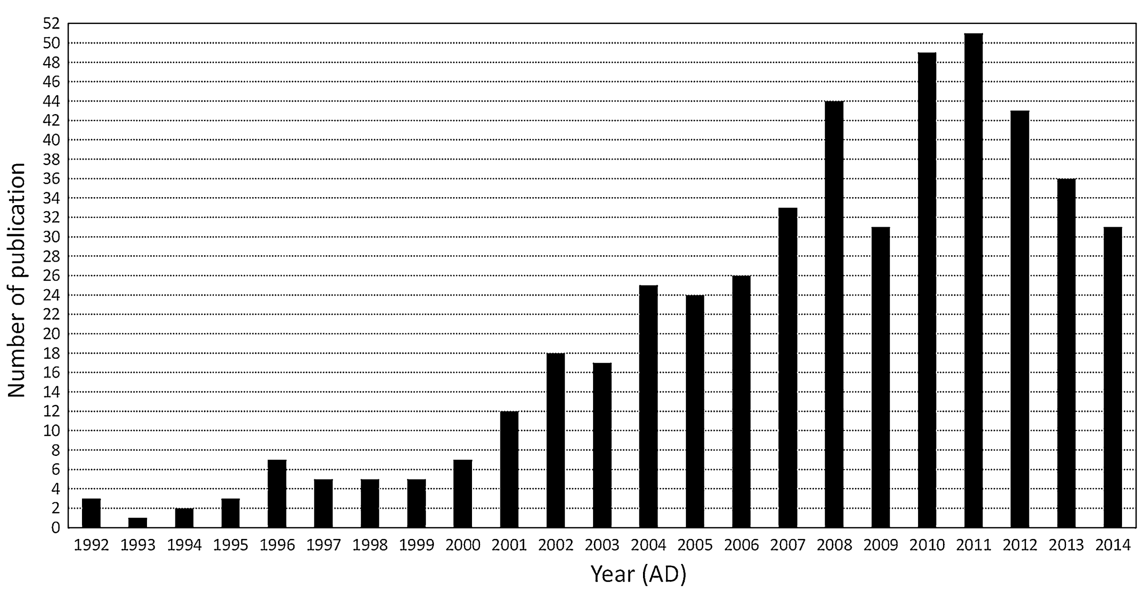

Fig. 2 Number of publications due to "NIR" and "Wood" [3]

Table 1 Major country of publication due to "NIR" and "Wood" [3]

Country	Number of publications
USA	139
Japan	65
Australia	59
Peoples Republic of China	51
Austria	46
Brazil	42
Sweden	32
France	27
Germany	25
Portugal	18
Canada	18

published between 2006 and 2011. We also reviewed many articles published between 1990 and 2011 [4, 5].

Chemical composition

Investigation of chemical component of wood using NIR technique is typical spectroscopic topic, where possibility of estimation of lignin and extractives is mainly discussed. Alves et al. [6] used NIRS for the determination of the S/G ratio of Eucalyptus wood. They reported that rapid screening the S/G ratio of Eucalyptus wood could be qualified. They also estimated the wood extractives content [7]. The developed models are well-suited for screening of the ethanol and total extractives content. Da Silva et al. [8] also assessed the total phenols and extractives of mahogany wood. The results indicated that NIRS can be a useful tool for a rapid evaluation of the extractive contents and total phenolic compounds of mahogany wood. He and Hu investigated the feasibility of using FT-NIR to rapidly determine the lignin and extractive content of various wood species [9]. The selection of relevant wavenumbers combined with the appropriate data pre-processing methods which produced satisfactory prediction models. In the case of Maritime pine, Lepoittevin et al. [10] showed that removal of extractives prior to NIR spectra acquisition is highly recommended for achieving high accuracy in partial least squares regression (PLSR) prediction for wood chemistry traits. Schwanninger et al. [11, 12] built a predictive model for lignin content in Norway spruce wood. The most appropriate model was found with the underlying assumption that it will cover a wide range of the natural variability of spruce wood. Uner et al. [13] determined the lignin and extractive content of Turkish pine trees. Overall, standard error of calibration (SEC) and standard error of prediction (SEP) ranged between 0.35 (w/w) and 2.40 % (w/w).

Moisture content

As NIR range includes rich information due to moisture, many researchers have tried to apply NIRS to wood science and technology. Eom et al. [14] measured surface moisture content of yellow poplar wood by NIRS technique, non-destructively and continuously, during unsteady-state desorption conditions. Such conversion method indicated that the boundary layer theory was useful in evaluating the degree of external moisture resistance while the wood dried. Watanabe et al. [15] established a rapid, non-destructive, in-line method suitable for sorting green hem-fir timbers based on moisture content by NIRS. The accuracy of NIR sorting was compared with a commercial capacitance-type moisture meter. They pointed out that NIRS has a potential to estimate average moisture of green timber indirectly, although it inherently gives only surface moisture content values, as it is limited by scan depth.

Density

Density is not chemical composition, however, it could be estimated from the relationship between density and main three chemical wood components (i.e., cellulose, hemicellulose and lignin) with the aid of chemometrics. Alves et al. [16] calculated PLSR models for wood density based on X-ray microdensity data for each species Maritime pine and Hybrid larch. The best PLSR models were the first ones that fulfill the requirements according to the guidelines for NIR model development and maintenance provided by the American association of cereal chemists (AACC Method 39-00). Fujimoto et al. [17] reported that wood density could be estimated independently of moisture content. The loadings from PLSR analysis indicated that the absorption bands in the vicinity of 7320, 7160 and 7000 cm^{-1} played an important role in predicting wood density. Santos et al. [18] also estimated wood basic density of Australian Blackwood using NIRS. It was also concluded that at least 45 samples for calibration and a further 16 samples for validation are necessary to obtain acceptable models for screening.

Wooden anatomical features

Wooden anatomical features also could be estimated using NIRS, where characteristic relationship between chemical components and them should be argued. Gheradi and Paulo [19] have developed NIR models for some anatomical features of Eucalyptus wood. The calibration for the micro fibril angle (MFA) provided NIR predicted values suitable; however, the statistics for shrinkage indicated that the models were not satisfactory. Inagaki et al. [20] demonstrated that the fiber length of Eucalyptus solid wood could be predicted with high accuracy and precision and that the ratios of performance to deviation (RPD) obtained are the first that fully fulfill the requirements of AACC Method 39-00 (AACC 1999) for screening in breeding programs. Isik et al. [21] have built the NIR predictive model for cell wall thickness and coarseness as well as air-dry density, MFA, modulus of elasticity (MOE) of Loblolly pine. The high heritabilities suggest that acoustic and NIR-based methods can efficiently be used for screening loblolly pine progeny tests for surrogate wood traits. Pfautsch et al. [22] assessed sapwood depth and wood properties in Eucalyptus and Corymbia using visual methods and NIRS. Models developed for differentiation between sapwood and heartwood using NIRS were very robust for four species, but sapwood depth could only be predicted well for one of the four species. Sun et al. [23] estimated the MFA and fiber length of bamboo by NIRS. The results showed that the PLS models of MFA and fiber length, based on noise combined with orthogonal signal selection spectra, gave the strongest correlations.

Mechanical properties

Also in case of mechanical property, it could be predicted using NIRS with aid of chemometrics, where cellulosic feature is key point from viewpoint of chemical absorption band. Horvath et al. [24] used transmittance NIRS to predict the green mechanical properties of 1- and 2-year-old transgenic and wild-type aspen. Green MOE and green ultimate compression strength (UCS) were predicted from the NIR spectra of dry wood meal pellets. Green UCS had strong correlation ($R^2 = 0.91$) and green MOE had good correlation ($R^2 = 0.78$) with the spectra. Kothyyal et al. [25] investigated the estimation of mechanical properties and specific gravity for 5-year-old Eucalyptus having broad moisture content range by NIRS. Calibrations had good relationships between values measured in laboratory and NIR predicted values obtained from small clear samples. Scimleck et al. [26] examined the estimation of density, MOE and modulus of rupture (MOR) using NIR spectra collected from the transverse surface of Pernambuco blocks. The success of calibrations suggests that NIR assessment of Pernambuco wood properties in the field may be possible. Watanabe et al. [27] used NIRS for rapidly predicting the longitudinal growth strain (LGS). NIR spectra and LGS were measured from peripheral locations of three Sugi green logs. The predicted peripheral LGS distribution moderately fitted with the measured one. Calibration and prediction models for balsam and black spruce wood disk average properties were developed using NIR spectral data by Xu et al. [28]. Results showed that using NIR spectra from three spots per wood strip was sufficient for the modeling and prediction for density and MOE.

Engineering wood

As engineering wood is composed of some kinds of wooden materials and adhesives, NIRS is useful to inspect their chemical contents. Belini et al. [29] estimated sugarcane bagasse content in medium density fiberboard (MDF) using NIR technique with the aid of chemometrics. The NIR-based models can be useful to quickly estimate sugarcane bagasse vs. Eucalyptus wood content ratio in unknown MDF samples and to verify the quality of these engineered wood products in an online process. Gosselin et al. [30] examined the ability of multivariate image analysis (MIA) and gray level co-occurrence matrix analysis (GLCM) to extract meaningful information from visible and NIR spectral images of extruded wood/plastic composite materials for predicting spatio-temporal variations in their properties. A Bootstrap-PLS regression technique was first used for selecting the spectral bands. The imaging sensor was able to simultaneously monitor 7 properties in both steady-state operation and during transitions. Hein et al. [31] estimated the physical and mechanical properties of particleboards by NIR spectra. The NIR models for internal bonding strength, water absorption and thickness swelling after 24 h presented satisfactory coefficient of determination. Kohan et al. [32] predicted the mechanical properties of strand feedstock by NIRS. Wood strands either prepared in the laboratory or from a manufacturing plant were assessed and then NIRS was utilized for prediction. This study demonstrates the potential to monitor the ultimate tensile strength, tensile MOE, bending strength, and bending stiffness.

Bioenergy

Recently, some researchers investigated the applicability of NIRS to inspect some traits of bioenergy. However, it should be strongly considered to clarify the spectroscopic background due to the prediction of such traits. Andrade et al. estimated the charcoal properties by NIRS. PLSR were established for estimating fixed-carbon, volatile matter content and gravimetric yield of charcoal [33]. They pointed out that these models can be useful for monitoring charcoal quality in steel industries. Castillo et al. [34] tried to predict Eucalyptus ethanol yield by NIRS. Mid-infrared (mid-IR)/NIR PLS models to quantify ethanol concentration were also compared with a mathematical approach to predict ethanol yield estimated from the chemical composition of the pulps determined by wet chemical methods. Results show the high ability of the infrared spectra in both regions, mid-IR and NIR, to calibrate and predict the ethanol yield and the chemical components of pulps. Horikawa et al. [35] reported the combination of a spectroscopic method with multivariate analysis to develop a calibration model of the saccharification ratio of chemically pretreated Erianthus. The information of CH and aromatic framework vibrations contributed most effectively to the alkaline dataset. They pointed out that NIRS can be a rapid screening method for the saccharification ratio. Lestander et al. [36] used NIRS for the quality control of industrial scale biofuel pallet production. On-line instruments were used to acquire reflectance spectra from the stream of raw and dried particles. The response variables examined were pellet bulk density, mechanical durability, moisture content and ash content. It was useful for the direct and indirect control of critical pellet quality variables.

Wood modification and degradation

Wood modification and degradation are high topic of NIR-Wood research because of convenient detection of chemical changes as spectral variation. Schwanninger et al. [37] assessed acetylated wood. The weight percentage gain and the acetyl group content of wood due to acetylation with acetic anhydride have been analyzed using FT-IR spectroscopy. It was possible to follow chemical changes in wood due to acetylation. Green et al. [38] used NIRS for predicting the advancement of wood decay in pine sapwood wafers. They pointed out that the early stages of wood decay could be predicted with high accuracy. They also predicted the levels of white-rot degradation (exposure period, mass loss and compression strength) in cottonwood [39]. The weak statistical data can be interpreted only in a way that the data are not robust and thus an early prediction of fungal attack by NIRS is not yet reliable. Jones et al. [40] applied NIRS for the prediction of natural durability of the heartwood of coast redwood. PLS regression models of mass loss with fungal decay testing, based on spectra collected with the FT-NIR spectrometer, had better predictive performance than the NIR line camera. Sandak et al. [41] used FT-NIR spectroscopy for waste paper with the addition of cereal bran biodegraded by Ascomycetes fungi. FT-NIR analysis revealed that spectra displayed the most significant difference in the wavenumber bands 4280, 4404 and 4620–4890 cm^{-1}, which correspond to CH, CH_2 and OH functional groups of cellulose. Differences in FT-NIR spectra were in good agreement with the reference methods.

Pulp and paper

Application of NIRS to pulp and paper research is traditional and typical topic. Downs et al. [42] investigated the radial variation in Kraft pulp yield and cellulose content in Eucalyptus wood using NIRS. Gigac and Fiserova [43] also used NIRS for monitoring of raw materials and paper properties. Data of NIR spectra of semichemical fluting correlate with the filler content, Kappa number as well as directly with strength properties. NIRS calibrations were developed to allow prediction of pulp yield from analysis of wood by Mcdonough et al. [44]. The yield of pulp from 13-year-old trees can be predicted from the amounts of xylan and lignin present in the wood. Meder et al. [45] performed non-destructive prediction of Kraft pulp yield from increment cores using NIRS with sufficient prediction accuracy. Tyson et al. [46] investigated the potential of NIRS to create calibrations for eucalyptus pulp properties of mill-line origin. Seven mechanical properties coefficients of determination for all mechanical and physical properties were poor. The poor performance of the calibrations is likely due to the low variability of dataset, which is generally inherent in samples of mill-line origin. White et al. [47] investigated the effects of wood properties on the strength of bleachable and linerboard grade Kraft pulps from 13-year-old Loblolly pine trees. NIR spectra collected in 10 mm sections from the surface radial strips correlated very well with air-dry density, MFA, MOE, and tracheid wall thickness and were used to develop whole tree predictions.

Classification

Near infrared spectroscopy with aid of chemometrics is useful not only for quantification but also for qualification. Some researchers investigated utility of NIR spectra for classification of wood materials. Batista et al. [48] explored the probability of classification of several wood species using a fiber optic NIR scan of solid wood surfaces. The discriminant models showed small errors for each species, indicating that reliable identifications can be made with NIRS of solid wood surfaces in these species. Cooper et al. [49] also used NIRS for the separation of wood species. They pointed out that the broad applicability and response of NIRS to a number of factors may be its greatest weakness, since measurements for a specific response, such as MC or species differentiation, may be confounded by the effects of other variables, such as surface roughness and localized density differences. The results reported by Espinoza et al. [50] indicate that NIRS can be used as an effective tool to distinguish between pure pine species and suggest that it will also distinguish hybrids from their parents. Prades et al. [51] assessed the potential of visible-NIR spectroscopy for identifying the geographical origin of cork. They found good classification results. Russ and Fiserova [52] estimated the hardwood species in mixture by NIRS. Principal component analysis (PCA) of hardwood NIR spectra showed high separation capabilities between ten various hardwood species. Yang et al. [53] investigated the feasibility of NIRS for the classification of eight rosewood species. The eight rosewood samples can be distinctly divided into eight categories by PCA. They also tried to identify softwood and hardwood by NIRS coupled with partial least squares discriminant analysis (PLS-DA) [54]. It was suggested that NIR can be used to rapidly and accurately identify softwood and hardwood samples.

Imaging

One of active topic due to NIRS is application of imaging. Also in case of Wood-NIR research, many researchers try to introduce NIR-imaging technique. Fernandes et al. [55] measured intra-ring wood density by means of visible-NIR hyperspectral imaging. The measurements were performed with a spatial resolution of 79 μm. The coefficient of determination value between the present method and X-ray microdensitometry is 0.810 with a root mean squared error of 6.54×10.2 g cm^{-3}. Lestander et al. [56] applied NIR hyperspectral images to explore various fractions of pine and spruce wood. The average image PLS models could be used to make prediction of images showing the location of the regions with high extractive content in knotwood. Meder et al. used hyperspectral images for compression wood. NIRS has been used to predict the severity of compression wood in samples of Radiata pine using a subjective microscopic assessment of compression wood as the reference method [57]. The calibration statistics are only moderate which may be due to the subjectivity of the traditional method. Mora et al. [58] also used NIR hyperspectral imaging for the estimation of basic density (BD) and moisture content (MC) of Loblolly pine disks. The predictive ability of the calibrations was acceptable, with RMSEP of 23.6 kg m^{-3} for BD and 2.1 % for MC. Kobori et al. [59] monitored the surface moisture content of wood using hyperspectral imaging during natural drying. Visible-NIR hyperspectral imaging was tested for its suitability for monitoring MC of wood samples. Hyperspectral imaging has a high potential for monitoring the water distribution of wood.

Others

Some interesting reports have been published due to data analysis or methodology. De Sousa et al. [60] applied the Kennard-Stone algorithm to select *Eucalyptus* spp. wood samples for development of NIRS calibration models to minimize number of samples but maintaining the model precisions. Analysis of the models statistics parameters demonstrated the possibility of substantial savings in time and costs for wood analysis. Kurata et al. [61] investigated the optical characteristics of wood by Time-of-Flight NIRS. They introduced a new optical measurement system, the main components of which are a diode-pumped solid state laser and avalanche photodiodes. The optical model based on the diffusion approximation to the radiative transfer equation proved to be useful for thick samples, which can be optically regarded as an ideal diffuser, although wood is a structural material with non-homogeneous cellular structure.

Conclusion

As shown above, activity of NIR-Wood research is increasing year by year. The real application for on-line or at-line monitoring in wood industry is desired as next step. Basic spectroscopic research for wooden material should be also proceeded. However, we should be sensitive and careful for application of NIRS, when spectra coupled with chemometrics present unexpected good results (especially, for mechanical physical and anatomical properties). In any case, it is very important to clarify spectroscopic background and know the limitation of NIRS. Then, it should be a powerful and meaningful tool.

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