

Selected properties of alternative lignocellulose materials characterized with FT-NIR

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Abstract: *Selected properties of alternative lignocellulose materials characterized with FT-NIR.* Lignocellulose materials (other than trees) have been recently recognized as a very valuable bio-resource. The goal of this research was to explore the potential of near infrared spectroscopy to evaluate the chemical composition of selected lignocellulose materials (grass (*Carex riparia* L.), coconut shell (*Cocos nucifera* L.) and tamarind seeds (*Tamarindus indica*). It was shown that near infrared (NIR) spectroscopy can be an alternative to standard analytical methods, a technique supporting research and development of production technologies for lignocellulose materials. Partial Least Squares (PLS) regression models for quantitative prediction of wood components were developed. Selected chemometric techniques (PCA and CA) allowed discrimination of samples. Moreover, spectral analysis provided information regarding differentiation among investigated lignocellulose materials.

Keywords: lignocellulose materials, FT-NIR, chemometrics

INTRODUCTION

Widespread interest in the utilization of bio-resources for bio-energy, bio-fuels, bio-polymers and other bio-material production is observed all over the world. The use of lignocellulose materials is nowadays an essential issue due to the uncertain supply of non-renewable resources (such as oil/coal) and an increased recognition of environmental problems related to global warming and pollution. According to current calculations, renewable feedstock can replace today up to 30% of current petroleum consumption. This number can be extended even more if additional natural resources and agricultural/forest areas were cultivated with suitable plants and lignocellulose material were properly managed (BISYPLAN web-based handbook, 2012). Alternative lignocellulose materials are presently widely used as energy crops. The production of pellet fuels is mainly based on sawdust from wood industry and sawmills. However, availability of this material is limited, as the above mentioned industries utilize wood residue for their own purposes. In consequence the price of raw materials has increased (between 60 to 150% depending on countries) in the last few years. Therefore, pellet producers are interested in other raw materials such as sunflower shells, coffee and oat seeds, buckwheat dust and much more post-production waste (Stolarski and Kwiatkowski 2009). The utilisation of alternative lignocellulose materials is also increasingly common to produce active carbons for electrochemical hydrogen adsorption. The materials may include stones or seed shells (Wesełucha–Birczyńska et al. 2012)

It is well known, that physico-chemical, structural and compositional factors complicate lignocellulose materials conversion processes of lignocellulose materials. Lignocellulose materials generally have high water and ash contents, low heating value, are heterogeneous and difficult to transport. Conversion technologies, such as combustion, gasification and pyrolysis, are well-suited for lignocellulose material feedstock material with a relatively low moisture content. For very wet lignocellulose materials biochemical conversion is an alternative for conversion into suitable energy carriers. However, applications for lignocellulose materials are dependent on their specific characteristics.

Therefore it is extremely important to properly convert lignocellulose materials, to know at the early stage the full characteristics including chemical, physical or energetic properties. We may observe a trend towards application of non-destructive and rapid techniques as support tools in the characterization of lignocellulose materials. The goal of this research was to verify if near infrared spectroscopy (FT-NIR) is suitable for characterization of lignocellulose materials and especially for its utilization in rapid estimation of lignocellulose material chemical composition.

MATERIALS AND METHODS

The analyses were performed on lignocellulose materials (grass (*Carex riparia* L.), coconut shells (*Cocos nucifera* L.) and tamarind seeds (*Tamaryndus indica*)). The material was milled in the laboratory on the Pulverisette 15 (Fritsch GmbH) cutting mill into particles of less than 0.4 mm in size. The fraction of 0.1 mm to 0.4 mm was used for chemical analyses according to the standard PN-75/50025 procedure. The samples were subsequently measured using a VECTOR 22-N FT-NIR spectrometer by Bruker Optics GmbH. The spectra were measured within the range of 4000cm^{-1} - 12000cm^{-1} with the resolution of 8cm^{-1} . Each spectrum was computed as an average of 32 internal scans to increase the signal-to-noise ratio. Five measurements were performed on each sample. All measurements were conducted in a climatic chamber (25°C and 65% RH) to minimize the influence of the environment (temperature and relative humidity). OPUS 7.0 software was used for signal processing and data analysis. Spectra interpretation was performed according to Schwanninger et al. (2011) summarizing the body of knowledge developed for wood. Band assignment is presented in Table 1. Derivatives were calculated according to the Savitzky-Golay algorithm. For the mathematical management of the spectra and then for the evaluation of the results, Principal Component Analysis (PCA), cluster analysis (CA) and Partial Least Squares (PLS) were applied.

Tab. 1 Band assignment of FT-NIR spectra

code	wavenumber (cm^{-1})	band assignment
1	4198	CH deformation in holocellulose
2	4280	CH stretching + CH deformation in semi- and crystalline region in cellulose
3	4404	CH_2 stretching + CH_2 deformation of cellulose
4	4620	OH stretching + CH deformation of cellulose
5	4890	OH stretching + CH deformation of cellulose
6	5219	OH stretching + OH deformation of water
7	5464	OH stretching + CH stretching semi- or crystalline regions of cellulose
8	5587	CH stretching semi- or crystalline regions of cellulose
9	5800	CH stretching in furanose/pyranose due to hemicelluloses
10	5883	CH stretching in aliphatic chains
11	5935	CH stretching of aromatic skeletal in lignin
12	5980	CH stretching of aromatic skeletal in lignin
13	6287	OH stretching in crystalline region in cellulose
14	6450	OH stretching in crystalline region in cellulose
15	6722	OH stretching in semi-crystalline region in cellulose
16	6785	OH stretching in semi-crystalline region of cellulose
17	7008	OH stretching in amorphous region in cellulose
18	7309	CH stretching in aliphatic chains
19	7418	CH stretching in aliphatic chains

RESULTS

Results of the wet chemical analysis of investigated lignocellulose materials presented previously by Babeł et al. (2012) are summarized in Table 2. Concentration of extractive substances varies within a wide range from 1.8 to 21.7%. The highest value was obtained in the case of tamarind seeds and the lowest in the case of grass. A very low amount of holocellulose was recorded in tamarind seeds (19.8%). In the case of grass and coconut shells

the content of carbohydrates was significantly higher (56 and 60.5%, respectively). Amounts of cellulose, the component responsible for mechanical properties of lignocellulose materials, varied from 14.6 to 46.2 and the lower value was obtained again in the case of tamarind seeds. The highest percentage of lignin, above 40%, was determined in coconut shells and the lowest once more in the case of tamarind seeds.

Tab. 2 Chemical composition of investigated lignocellulose materials

Type of lignocellulose material	Extractive substances	Holocellulose	Cellulose	Lignin
grass (<i>Carex riparia</i> L.),	8.1	56.0	46.2	28.1
coconut shells (<i>Cocos nucifera</i> L.)	1.8	60.5	28.9	43.5
tamarind seeds (<i>Tamaryndus indica</i>)	21.7	19.8	14.6	11.6

Variations in spectra were observed for all chemical components and in nearly all NIR bands of interest. The most significant deviations are however related to the first overtone and combination bands of fundamental vibrations. Major changes were observed in bands related to carbohydrates (1, 2, 3, 4 and 5). Band 17 (7008 cm^{-1}) related to OH stretching in the amorphous region in cellulose seems to be more varied than bands characteristic of semi-crystalline (15, 16) or crystalline cellulose (13, 14). However, the most significant changes to the spectra were observed for the aromatic skeleton of lignin (11 and 12) and those related to hemicelluloses (band 9). Variation of peak intensity related to the water band (6) can suggest that also the investigated lignocellulose materials also vary in terms of their hygroscopic properties.

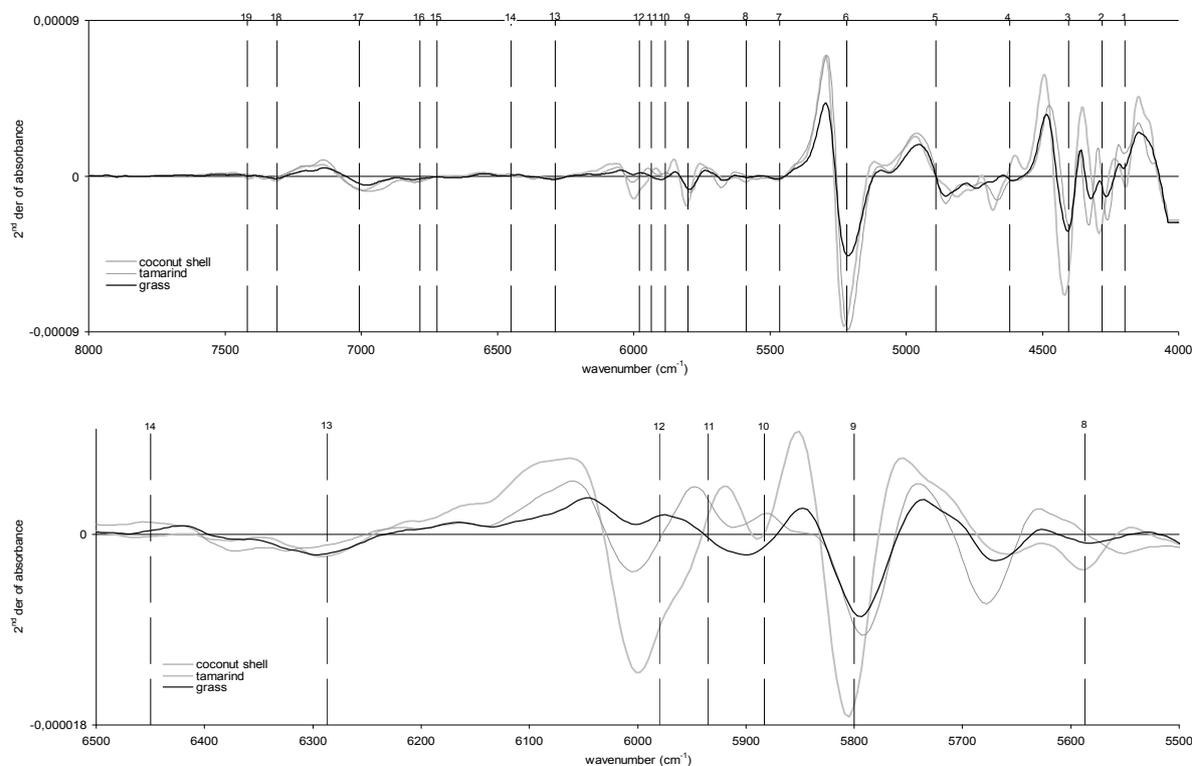


Fig. 1. The second derivative of spectra of investigated lignocellulose materials.

Significant variations in spectra were confirmed by selected chemometric techniques. Cluster analysis presented in Figure 2a shows good separation among investigated lignocellulose materials. Principal Component Analysis was additionally performed on the spectra in order to investigate if the differences in chemical composition might be used for fast lignocellulose material discrimination. The results presented in Figure 2b confirm the applicability of the NIR technique. Points on the chart, representing different lignocellulose materials, are grouped and separated from each other. The selectivity index in all cases is $\gg 1$, which confirmed clear groups separation. One of the prospective uses of the NIR would be to provide an automatic classification of unknown samples with the reference samples belonging to the previously developed data base. The apparent separation of samples indicates also a potential for quantitative analysis.

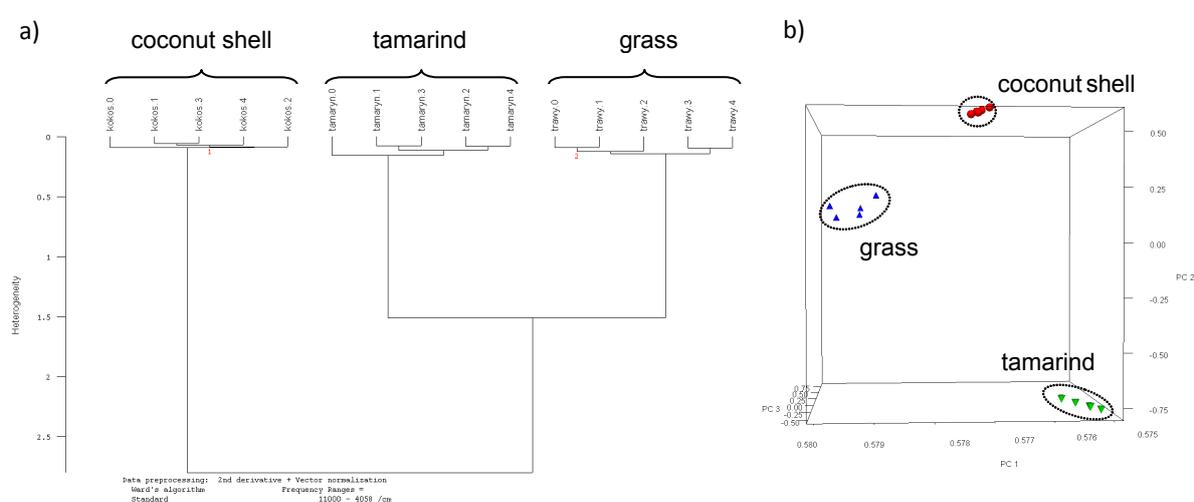


Fig. 2 Cluster analysis (a) and Principal Component Analysis (b) of investigated lignocellulose materials

Partial Least Squares (PLS) regression algorithms are frequently applied for computation of regression models linking near infrared spectra and reference values. Values from Table 2 were entered into the Quant2 software (PLS regression algorithm, a part of OPUS 6.5 package) as they-variable. Additionally, the chemical composition of softwood and hardwood was also included in order to enrich the model with reference data concentrations of investigated chemical components. The optimization procedure was applied in order to obtain the best performing models. The cross-validation used in this research was the “one leave out” approach. Finally each model was characterized by several indicators including the coefficient of determination (r^2), root mean square error of cross-validation (*RMSECV*), residual prediction deviation (*RPD*) and rank (the number of principal components used). Values estimated by the PLS models were regressed against reference values and are presented in Table 3. As it can be seen, the *RPD* values indicate that high quality models were obtained. The relatively small number of reference samples is however a limitation for the robustness of the models presented.

Tab. 3 Validating parameters for PLS regression prediction models developed for investigated lignocellulose materials. Note: MSC - multiplicative scattering correction, VN - vector normalization

component	pre-processing method	spectral range, cm ⁻¹	rank	cross validation		
				<i>r</i> ²	<i>RMSECV</i>	<i>RPD</i>
cellulose	Second derivative	6233-5453	4	0.99	0.59	21
holocellulose	First derivative + MSC	6233-5453	3	0.96	3.67	5
lignin	Second derivative	6233-5453	4	0.99	0.39	25
extractives	First derivative + VN	6233-5453	3	0.95	1.57	4.7

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Strzeszczenie: *Charakteryzacja wybranych właściwości materiałów ligno-celulozowych za pomocą FT-NIR.* Badania zmierzały do oznaczenia wybranych właściwości alternatywnych materiałów lignocelulozowych za pomocą techniki spektroskopowej FT-NIR. Badaniom poddano alternatywne materiały lignocelulozowe (trawę, (*Carex riparia* L.), łupiny kokosa (*Cocos nucifera* L.) oraz ziarna tamaryndowca (*Tamaryndus indica*)), które w wybranych gałęziach przemysłu mogą być stosowane jako surowce zastępujące trociny pochodzące z przemysłu drzewnego i tartaków. Na podstawie wyników analizy FT-NIR stwierdzono znaczne różnice w strukturze związków węglowodanowych w trzech porównywanych surowcach. Jednak największe różnice wykazano w przypadku struktury aromatycznego składnika drewna - ligniny. Wyniki te korespondują z rezultatami analizy chemicznej prowadzonej zgodnie z PN-75/50025. Zastosowane techniki chemometryczne (PCA, CA) potwierdziły znaczące różnice, w składzie chemicznym analizowanych materiałów, natomiast algorytm PLS posłużył do stworzenia modeli kalibracyjnych o wysokiej precyzji.

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