Rubber wood properties testing for biomass energy by using visible–near infrared spectroscopy

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ABSTRACT

When the rubber tree (*Hevea brasiliensis*) is 20–25 years old, the latex yield is not economically worthwhile. The rubber tree will be cut down. The rubber wood cut down is processed into dried rubber wood and will be used in downstream industries. The remaining are roots of trees and wood or branches that are not utilized, including rubber waste from wood processing plants and wood production plants, including wood slabs, sawdust, wood (flawed) and shavings. These parts of rubber trees can be used as biomass fuel. The study of timber that provides quality wood for biomass fuel is therefore necessary. Traditional rubber wood quality analysis (conventional method) is complicated, takes time and high cost. Therefore, this research aimed to develop a quality analysis of the biomass rubber with visible–near infrared (Vis-NIR) technique in order to create new alternative testing. In this study, Vis-NIR spectroscopy was employed to determine hemicellulose, cellulose, nitrogen (N), carbon (C), hydrogen (H) and moisture contents in rubber wood as biomass for energy utilization. The 120 rubber samples from 10 varieties were selected from three parts of trunk, limb and root with each aged twenty years. All samples were ground and measured using the reflectance mode in the Vis-NIR region of 680–2,500 nm. Partial least squares regression (PLSR) models for the quantitative determination of hemicellulose, cellulose, N, C, H and moisture contents in rubber wood samples were built. PLSR models were developed from the region of Vis-NIR spectra and the analyzed contents were determined by the reference method. The calibration models yielded acceptable statistical results for quantitative analysis of N with the coefficients of determination (R^2) of 0.847, moisture with R^2 of 0.839, hemicellulose with R^2 of 0.835, H with R^2 of 0.747, C with R^2 of 0.664 and cellulose with R^2 of 0.596. The results showed that the entire wavelength region of 680–2,500 nm provides more reliable PLS models (N, C, cellulose, and moisture) than those of models using a shorter wavelength region of 680–1,246 nm (hemicellulose and H). For rapid biomass testing, the PLS models created by the suitable data obtained from a flexible wavelength range selection of Vis-NIR spectrometer illustrated high feasibility for screening rubber wood properties.

Keywords: Rubber wood, visible–near infrared spectroscopy, wood properties, biomass, energy

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INTRODUCTION

At present, there are a lot of demands for biomass fuel in biomass power plants. The 1 MW power plant will use about 10,000 tons of biomass/year. Based on the assessment of the availability of raw materials, the number of rubber trees in the southern region of Thailand is large enough for the 1,000 MW biomass power plant to be distributed almost throughout the year. Rubber wood is a type of economic wood that is important to Thailand. There are 25–30% of the remaining rubber wood that has not been utilized, which can be processed into biomass energy. The production and quality of rubber wood are important in determining and selecting rubber species for the purpose of biomass energy. Fuel wood properties can be described in terms of proximate and ultimate analysis, density, heating value, composition and tree species. The conversion of waste rubber wood to energy is influenced by its physical characteristics and chemical composition. Therefore, the chemical analysis of waste rubber woods is necessary because these analysts including moisture, hemicellulose, cellulose, carbon, hydrogen and nitrogen are the factor in the heating value generation. Those biomass materials with high carbon and hydrogen contents will have a high heat value as well (Lewandowski and Kicherer, 1997; Hytönen *et al*., 2019). Because the chemical methods for analyzing biomass materials are complex and time–consuming (Stanislav *et al*., 2010), but their results are very essential for improving biofuel conversion processes and for biomass trading (Nurmi, 1992). Therefore, alternative tests must focus on a fast and easy-to-use method. The visible–near infrared (Vis-NIR) spectroscopy has these benefits and has been examined to determine the potential for predicting quantitative and qualitative properties in biomass analysis. Matt *et al*. (1996) employed the near infrared (NIR) technique to analyze components in biomass raw materials by creating various predictive equations including ethanol extractives, ash, lignin, uronic acids, arabinose, xylose, mannose, galactose, glucose, carbon, hydrogen, nitrogen and oxygen from wood biomass feedstock. Xu *et al*. (2012) reported by comparison of NIR technique and chemical methods for the determination of lignocellulosic biomass properties. Nicole *et al*. (2008) applied the NIR method to classify biomass substances, including red oak, yellow poplar, walnut family tree, switch grass, corn cob and bagasse. Tsuchikawa and Kobori (2015) reviewed the application of NIR spectroscopy to wood science including bioenergy technology.

Therefore, the opportunity to bring an alternative analysis method by mean of Vis-NIR for chemical analysis of rubber wood as biomass energy is likely to have a lot of potentials. It will dramatically decrease the time required for and the cost of routine compositional analyses. The objective of this study was to investigate the potential of using Vis-NIR spectroscopy in conjunction with the partial least squares regression to predict the hemicellulose, cellulose, nitrogen, carbon, hydrogen and moisture contents in waste rubber wood as biomass for energy utilization. Afterthat, the recommendation of a spectrometer type by means of setting a suitable wavelength range will be reported.

MATERIALS AND METHODS

Sample

The rubber wood samples were selected from clone trial aged twenty years at Rubber Research Center, Buriram province, Thailand. The experimental design was randomized complete block (RCB) from ten varieties of rubber tree, namely BPM24, PB235, PB260, PB310, PR255, RRIC110, PR305, RRIT226, GT1 and RRIM 600. Four trees of each rubber tree variety were randomly selected. Then, they were cut at a height of 10 cm from the ground. The branches and compartments were separated from the cut rubber tree. Stumps and roots were collected by digging and removing all the attached soil. Subsequently, fresh wood from all 3 parts, namely the branches, the trunk and the stump, were weighted and dried in a hot air oven (UF110, Memmert GmbH + Co. KG, Germany) at 80°C for 5–day before grinding by a cutting mill (SM100, Retsch, Germany) and sieving to a particle size of 60–mesh. A total of 120 ground rubber wood samples were used in the experiment.

Spectra Measurement

NIR spectrometer (SpectraStar™ 2500, Unity Scientific, USA) was used to acquire reflectance spectra (log 1/R) of the rubber wood samples. Samples were filled and scanned in a standard cup for powder sample (Figure 1). All scans were completed in air condition room at 26°C. The reference spectrum of a gold material was automatically scanned inside the NIR spectrometer every 30–minute. The spectral acquisition and instrument were controlled using the Info star software version 3.10.0 (Unity Scientific, USA). Vis-NIR spectra were recorded in a wavelength range of 680–2,500 nm. Each sample was scanned in triplicate and the averaged spectrum with an average resolution every 2 nm, was computed before further model calculations.

Standard Methods to Determine Chemical Composition of Rubber Wood Samples

Moisture content analysis for powder rubber wood samples with a size of 60–mesh was done in a hot air oven at 105°C until a constant weight according to the reference method of National Renewable Energy Laboratory (Sluiter *et al*., 2008). An organic elemental analyzer (Truspec Micro, LECO Instruments (Thailand) Ltd.) was employed to investigate carbon (C), nitrogen (N) and hydrogen (H) contents (LECO, 2003). As for hemicellulose and cellulose analysis, all powder samples with 60–mesh size were prepared by sieving to get the 40–mesh size of the sample and then they were extracted to remove insoluble substance in ethano-benzene (Ethanol-benzene solubility) according to TAPPI T 264 om–02 (TAPPI, 2002). The extractives free-rubber wood powder samples were then employed to hemicellulose and cellulose

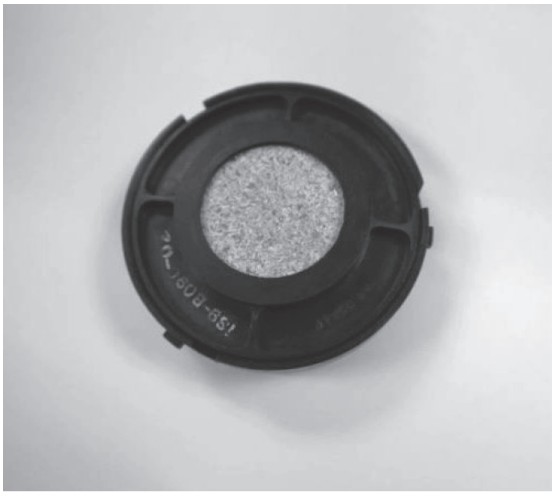

Figure 1 A sample cup uses in the Vis-NIR measurement

Data Analysis

The data analysis was performed by Unscrambler (Ver. 9.8, CAMO AS, Trondheim, Norway). A calibration model was calculated by partial least squares regression (PLSR) method, and validated by the full cross-validation method in visible and a shorter-NIR wavelength range (680–1,246 nm) or visible and a whole NIR wavelength range (680–2,500 nm). The calibration models were developed and compared between the original and three pretreated spectral data using second derivative (2D), multiplicative scatter correction (MSC) and standard normal variate (SNV) algorithms. The optimum number of factor (F) was selected by considering the number at which the lowest root mean squares error of cross–validation (RMSECV) was obtained. We have compared the PLS results obtained using those two regions (680–1,246 nm and 680–2,500 nm) and those pretreatment spectral methods. To avoid the overfitting model, the model giving an optimum low number of F with the high values of regression of determination (R^2) and the RMSECV are indicative of an accurate PLS model.

RESULTS AND DISCUSSION

The statistical contents of each chemical component were depicted in Table 1. Hemicellulose, cellulose, carbon and moisture values showed the standard deviation higher than one. Because the rubber samples were collected from different varieties that reflected the influence of genetics to their chemical properties. The quality of wood for bioenergy production depends on the chemical and mechanical properties. Cellulose and hemicellulose were generally found in the cell walls of rubber wood. The capability of the biomass process depends on its contents in rubber wood. Therefore, high cellulose and hemicellulose values affect the great amount of bioenergy production (McKendry, 2002). Carbon and hydrogen are wood minerals. Their amounts are directly related to the heating value of biomass (Lewandowski and Kicherer, 1997). Rubber wood samples with high carbon and hydrogen values will also have a high heat value. In this study, the carbon content was in the range of 43.3 to 49.7% (Table 1). It was close to the carbon content in rubber tree found by Wauters *et al*. (2008; 47.8–49.5%) and was slightly lower carbon content than that reported by Hytönen *et al*. (2019; 49.8–50.2%). The different carbon content in the rubber wood samples may occur from differences in the selection of tree parts for study. Adler *et al*. (2006) reported that the amount of nitrogen must not be too large in biomass. Nitrogen can be interacted to oxygen as nitrous oxide that is a kind of greenhouse gas affecting global warming. Therefore, nitrogen content in biomass should not exceed 0.60% (Obernberger *et al*., 2006). Table 1 shows that the rubber wood samples contained nitrogen in the range of 0.16 to 0.75% with the average value of 0.30% that falls within the suggested value. The moisture content of dried rubber wood samples is very important for changing energy by burning process. This process requires that the value of moisture content in biomass must not exceed 30–50%. If the biomass has higher humidity, the heat value will decrease and also affect combustion efficiency. Biomass should be in a dry condition or with minimal moisture. Our dried rubber wood samples remained less of moisture value in the range of 1.97–6.90% (Table 1).

Table 1 The statistical summary of chemical contents in rubber wood samples

Component (%)	Range	Mean	Standard deviation
Hemicellulose	12.34–24.14	17.81	3.07
Cellulose	31.22–62.14	46.36	4.58
Nitrogen	0.16–0.75	0.30	0.10
Carbon	43.30–49.70	45.39	1.24
Hydrogen	6.04–7.21	6.65	0.24
Moisture	1.97–6.90	4.10	1.11

The original and pretreated Vis-NIR spectra of rubber wood samples are shown in Figure 2. The summary of statistic result comparisons between the best PLS models developed from Vis-NIR spectral data at 680–1,246 nm and 680–2,500 nm for predicting the content of hemicellulose, cellulose, nitrogen, carbon, hydrogen and moisture in rubber wood samples is shown in Table 2. From the results, the calibration model using the second derivative (2D) pretreated Vis-NIR spectra in the region of 680–1,246 nm yielded a suitable model for prediction hemicellulose content. This PLS model provided the small error of validation (root mean square error of cross-validation, RMSECV) of 1.86% with a reasonable factor number of 8 giving R^2 of 0.835. By the obtained statistic values, the calibration model of hemicellulose can be clarified as a good predictive performance. The band at 1,194 nm related with the second overtone of C-H stretching. The band at 1,372 nm related with C-H vibration of methyl group. The bands at 2,274 and 2,336 nm corresponded to O-H/C–O in glucose molecule and C-H stretching/CH_2 deformation combination in polysaccharide structure, respectively (Workman and Weyer, 2007). They were assigned and shared by cellulose and hemicellulose information, which demonstrated that parts of the structures were similar among them. We found that the PLS calibration for hemicellulose employed the visible-short NIR region of 680–1,246 nm that covered the most information of methyl group. As for PLS model for cellulose prediction, the best model used of second derivative Vis-NIR spectra in the region of 680–2,500 nm. However, the obtained statistic result (R^2 = 0.596) was acceptable for rough screening (Williams, 2007).

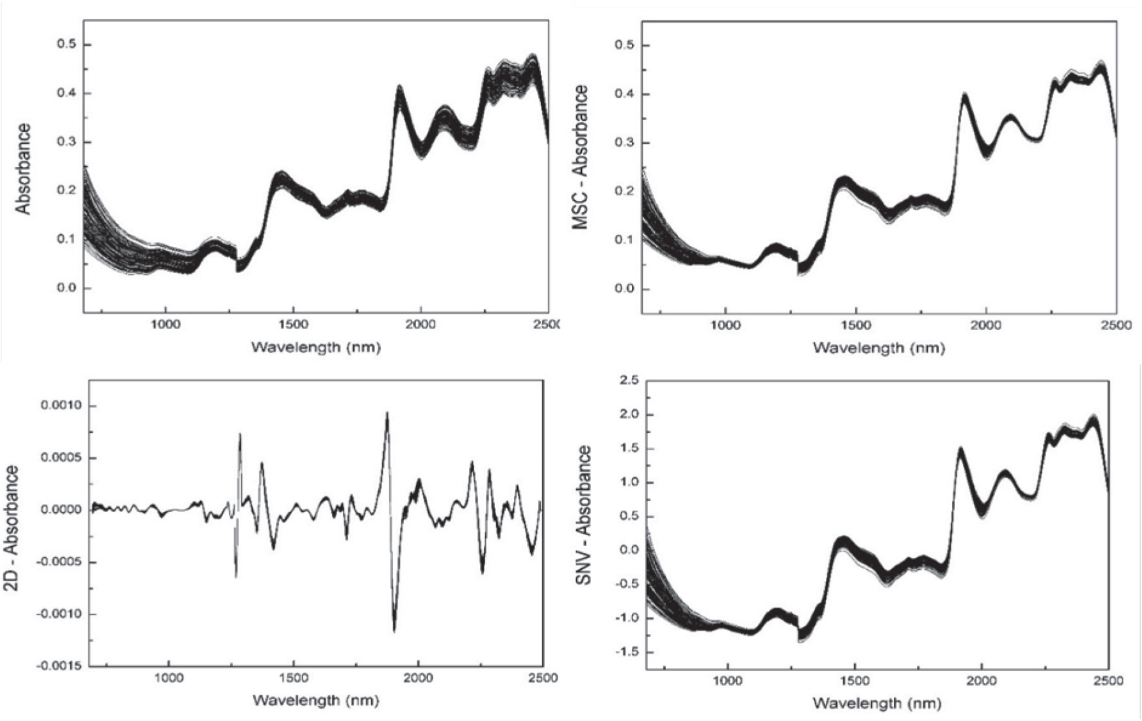

Figure 2 Original and pretreated NIR spectra of rubber wood samples in the whole wavelength region of 680–2,500 nm

Nitrogen, carbon and hydrogen, they all shared NIR information with the cellulose and hemicellulose that are composed of these elements. The calibration model for prediction of nitrogen value built by SNV pre-treated Vis-NIR spectra in the longer region of 680–2,500 nm including the band of N-H first overtone at 1,472 nm. The model predictive performance was good with the statistic results of R^2 of 0.847 at 9 factor number, in which it yielded the less RMSECV of 0.046%. The calibration models for determining carbon and hydrogen contents were developed by using original Vis-NIR spectra in the range of 680–2,500 nm and MSC pretreated Vis-NIR spectra in the range of 680–1,246 nm, respectively. They showed the same predictive performance that was acceptable for approximate calibrations ($0.66 \leq R^2 \leq 0.81$; Williams *et al*., 2019).

Table 2 The comparison of statistical results between the best PLS models developed from Vis-NIR spectral data at 680–1,246 nm and 680–2,500 nm for predicting the amount of hemicellulose, cellulose, nitrogen, carbon, hydrogen and moisture in rubber wood

PLS model	Range (nm)	Pretreatment spectra	F	Calibration		Full cross–validation	
				R^2	RMSEC (%)	R^2	RMSECV (%)
Hemicellulose	680–1,246*	2D	8	0.835	1.231	0.630	1.860
	680–2,500	SNV	15	0.821	1.289	0.507	2.158
Cellulose	680–1,246	None	9	0.612	2.701	0.466	3.198
	680–2,500*	2D	4	0.596	2.573	0.503	2.878
Nitrogen	680–1,246	2D	5	0.582	0.058	0.394	0.070
	680–2,500*	SNV	9	0.847	0.038	0.785	0.046
Carbon	680–1,246	MSC	9	0.652	0.692	0.517	0.822
	680–2,500*	None	8	0.664	0.680	0.583	0.764
Hydrogen	680–1,246*	MSC	5	0.747	0.116	0.705	0.126
	680–2,500	SNV	5	0.706	0.125	0.658	0.136
Moisture	680–1,246	2D	4	0.826	0.462	0.788	0.515
	680–2,500*	2D	4	0.839	0.445	0.806	0.488

Note: F = the number of factors, R^2 = the coefficient of determination, RMSEC = root mean square error of calibration, RMSECV = root mean square error of cross–validation, 2D = second derivative, MSC = multiplicative scattering correction, SNV = standard normal variate, * the selected PLS calibration model

The O-H stretching bands due to water bands clearly showed at 1,426 and 1,920 nm (Figure 2). So, the calibration model for determination of moisture content was calculated by the second derivative pretreated Vis-NIR spectra covering the water bands (680–2,500 nm). The statistic results were R^2 for calibration of 0.839, RMSEC of 0.445% and the lowest RMSECV of 0.488% at an optimal factor number of 4. Note that the level of predictive performance for the PLS calibration model was justified according to the value of coefficient of determination (Williams, 2007). The distributions of the NIR predicted value versus measured value by those reference methods for hemicellulose (a), cellulose (b), nitrogen (c), carbon (d), hydrogen (e), and moisture (f) are shown in Figure 3. The accurate predictive performance of the PLS calibration model can be seen from the distributions that the high accuracy will present the highest slope of the regression line close to one ($R^2 = 1$), and the dots representing predicted values placed at the closest to the regression line.

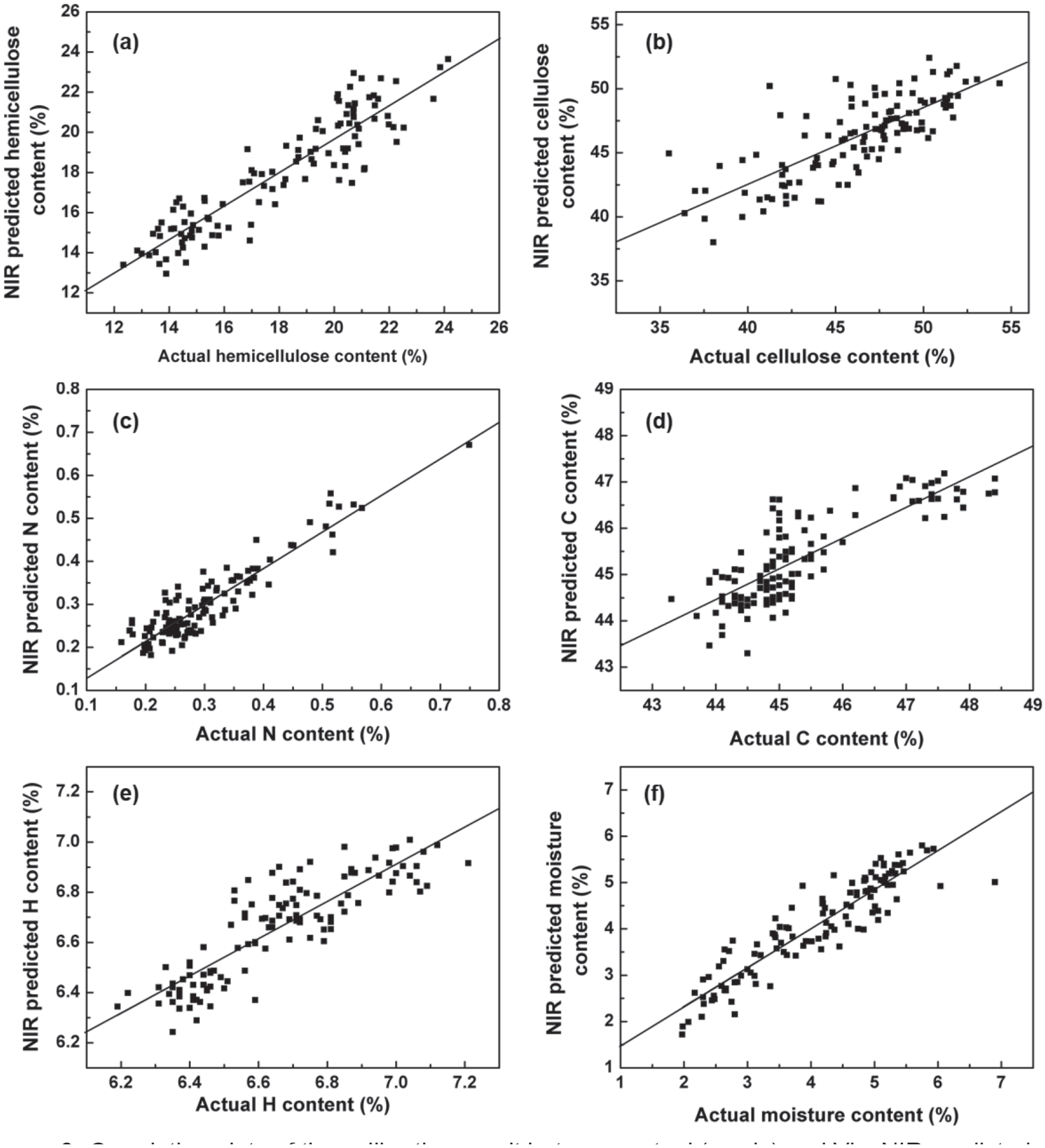

Figure 3 Correlation plots of the calibration result between actual (x axis) and Vis-NIR predicted (y axis) contents of hemicellulose (a), cellulose (b), nitrogen (c), carbon (d), hydrogen (e) and moisture (f) in rubber wood

CONCLUSION

From all the results, we found that the calibration models provided acceptable statistical results while using the calibrations generated by the shorter Vis-NIR wavelength region of 680–1,246 nm for hemicellulose and hydrogen content predictions, and the longer Vis-NIR wavelength region of 680–2,500 nm for nitrogen, carbon, cellulose and moisture content predictions. Therefore, the Vis-NIR method for testing the properties of biomass rubber wood is recommended employing a spectrometer that covers the total wavelength range of 680–2,500 nm. This type of device is flexible to set for the use of both ranges applied in this study. The NIR spectra significantly showed bands of important chemical structure, which is the fundamental information of biomass material. These calibration models may be possible for estimating the contents of chemical components in rubber wood samples for the bioenergy production process. Further study regarding the expansion of sample variations, i.e., age and area of plantation, must be done for model development in the future.

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