A Spectroscopic Study on the Fuel Value of Softwoods in Relation to Chemical Composition

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Abstract

The recent focus on bioenergy has led to interest in developing alternative technologies for assessing the fuel value of available biomass resources. In this study, both near- and mid-infrared spectroscopic datawere used to predict fuel value in relation to extractives and lignin contents for longleaf pine wood. Samples were analyzed both before and after extraction.Using both near- and mid-infrared spectroscopy, strong correlations were found between fuel value and extractives content for the unextracted wood samples, with the mid-IR models providing better correlations while using less factors. These findings were further evident in the plots of the regression coefficients for fuel value and extractives content. Although, total lignin content does impact total fuel value, the predictive ability for both mid-infrared and near-infrareddata were similarly poor for the extractive-free wood samples. The use of these techniques provides further spectroscopic support for the relationships mentioned previously.

Keywords: fuel value, extractives content, lignin content, longleaf pine, near-infrared spectroscopy, mid-infrared spectroscopy.

Introduction

Gross calorific value (GCV)is a measure of fuel valueandis synonymous with higher heating value (HHV) and gross heat of combustion (GHC). Several studies have attempted to relate these fuelvalues to specific chemical constituents comprising different types of biomass. For example, White (1987) used linear regression to show that HHV values from several softwoods and hardwoods could be correlated with lignin content alone ($R^2 = 0.70$) or by including a factor for extractives content ($R^2 = 0.76$). Analysis of extractive-free samples gave a higher correlation ($R^2 = 0.97$) with lignin content. Demirbas (2001) was also able to relateHHV to lignin content using a variety of extractive-free biomasssamples that provideda wide range of lignin values (15.01-55.29%); in a subsequent study, HHV was also related to extractives content (Demirbas 2003).

\The application of near-infrared (NIR) spectroscopy, coupled with multivariate analysis, allows for predictions of values for fuel value.For example, Lestander and Rhen (2005) used this technique to determine the calorific content of Norway spruce samples. However, for determinations of calorific value for poplar samples, the accuracies of the calibration models were limited (Maranan and Laborie 2007). Gillon et al. (1997) found this technique to be half as accurate as the direct determinations. Recently, NIR-based models were successfully used to predict GCV in longleaf pine wood samples(So and Eberhardt 2010). Unlike prior studies, here the GCV models were driven by the extractives, and not the lignin content.Alternatively, mid-IR spectroscopic data can be used to build models. The added benefit to mid-IR spectroscopy is that it allows clearer spectral investigations to determine those chemical features imparting the greatest effect. Only recently, Zhou et al. (2011), used mid-IR spectroscopic data coupled with multivariate analysis, to predict both the calorific value and lignin content for a single species ofhybrid poplar wood, and concluded that calorific value was unrelated to lignin content. In the current study, the impact of both extractives and lignin content on GCV for longleaf pine wood was investigated using both NIR and mid-IR spectroscopic techniques. Building upon prior work (So and Eberhardt 2010), the multivariate analyses were carried using the same sampling populations allowing direct comparisons between the two techniques.

Materials And Methods

Materials. Forty longleaf pine (*Pinuspalustris*) wood sampleswere obtained following a harvest from the Kisatchie National Forest, Louisiana, USA. A strip of wood, from each of 40 tree section disks collected, was reduced in size to allow grinding in a large Wiley mill equipped with a 2 mm mesh sieve plate.

Extractives, lignin and GCV determinations. Milled wood samples were extracted with acetone using a Soxhlet apparatus. Extracts were dried *in vacuo*and weighed. Extractive-free milled wood samples were further ground in a small Wiley mill equipped with a 40-mesh screen. Lignin content was determined using the acetyl bromide method (Morrison 1972) using an absorptivity value of 23.30 g^{-1} L cm^{-1} (Johnson et al. 1961). Moisture contents, determined bydrying samples in an oven (102 ± 3 ℃), were used to adjust values for extractives and lignin

contents to a dry-weight basis.Values for GCV were determined in triplicate using a Parr oxygen bomb calorimeter 6100 per the manufacturer's operating instructions(Parr Instruments 2006).

Mid-IR and NIR spectroscopy. Mid-IR spectra were collected using a ThermonicoletNexus Model 670 FTIR spectrometer equipped with a Golden Gate MKII Single Reflection ATR accessory. Samples were applied directly to the diamond window. Spectra were collected at wavenumbers between 650-4000 cm^{-1}.NIR spectra were collected using an ASD Field Spec spectrometer with a fiber optic probe oriented perpendicular to the sample surface. The samples were illuminated with a DC lamp oriented at 30° above the sample surface, and rotated at 45 rpm to minimize specular interference and surface heterogeneity. Spectra were collected at wavelengths between 350-2500 nm. For both spectroscopic techniques, three spectra were collected from each sample.

Multivariate analysis. Data analyses were performed using the Unscrambler (version 8.0) software. The spectroscopic data were first averaged to one spectrum per sample. The full range was utilized for the mid-IR spectra, while the NIR region was narrowed down to 1100-2400 nm for analysis. Principal component analysis (PCA) was performed on the spectral data to observe any clustering between the samples. Partial least squares (PLS) regression was used to predict GCV, extractives content, and lignin content for the samples. Calibration and test sets were randomly created for the analyses with 30 and 10 samples, respectively. The models were assessed using several common measures of calibration performance, including the correlation coefficient (R^2), the standard error of cross validation (SECV) and the standard error of prediction (SEP), and the ratio of performance to deviation (RPD).

Results And Discussion

Extractives, lignin, and GCV. The extractives content for the 40 longleaf pine wood samples varied between 0.0 to 20.6%, which is smaller than that reported by Via et al. (2007) with values as high as 33%. The mean GCV for the samples, prior to extraction, ranged from 20.2 to 23.6 MJkg^{-1}. The relationship between GCV and extractives content was investigated by applying a standard linear regression to the data and a strong correlation ($R^2 = 0.91$; p-value < 0.0001) was found. The lignin content was determined from the extracted samples and the values ranged between 26.6 to 31.5% similar to those previously reported (Via et al. 2007). The GCV range was lower and narrower following extraction (19.5-20.6 MJkg^{-1}). The relationship between lignin and GCV (extracted) was much poorer ($R^2 = 0.12$; p-value < 0.0266) than that obtained using extractives content.

Mid-IR and NIR spectra. An averaged mid-IR spectrum of all 40 unextracted longleaf pine wood is shown in Figure 1(a), exhibiting the commonly observed bands about 1000-1150 (C-O stretch), 1700-1750 (C=O stretch), 2800-3000 (C-H stretch), and 3100-3600 (O-H stretch) cm^{-1}. Peaks at 1689, 2865and 2925 cm^{-1}, typical of the pine resin components, were greatly reduced following extraction as shown in the spectrum of the corresponding extracted sample in Figure 1(b). Although this not clearly observed in Figure 1 due to scaling, a difference spectrum (Figure 1 (c)) was calculated from these two averaged spectra showing well resolved peaks at the

aforementioned wavenumbers. This mid-IR difference spectrum is very similar to a difference spectrum between resinous and non-resinous Scots pine heartwood (Nuopponen et al. 2003). This was repeated with the NIR data with Figures 2(a) and (b) displaying the unextracted and extracted spectra, respectively. Differences were not readily observable as seen in Figure 1 with the mid-IR spectra.
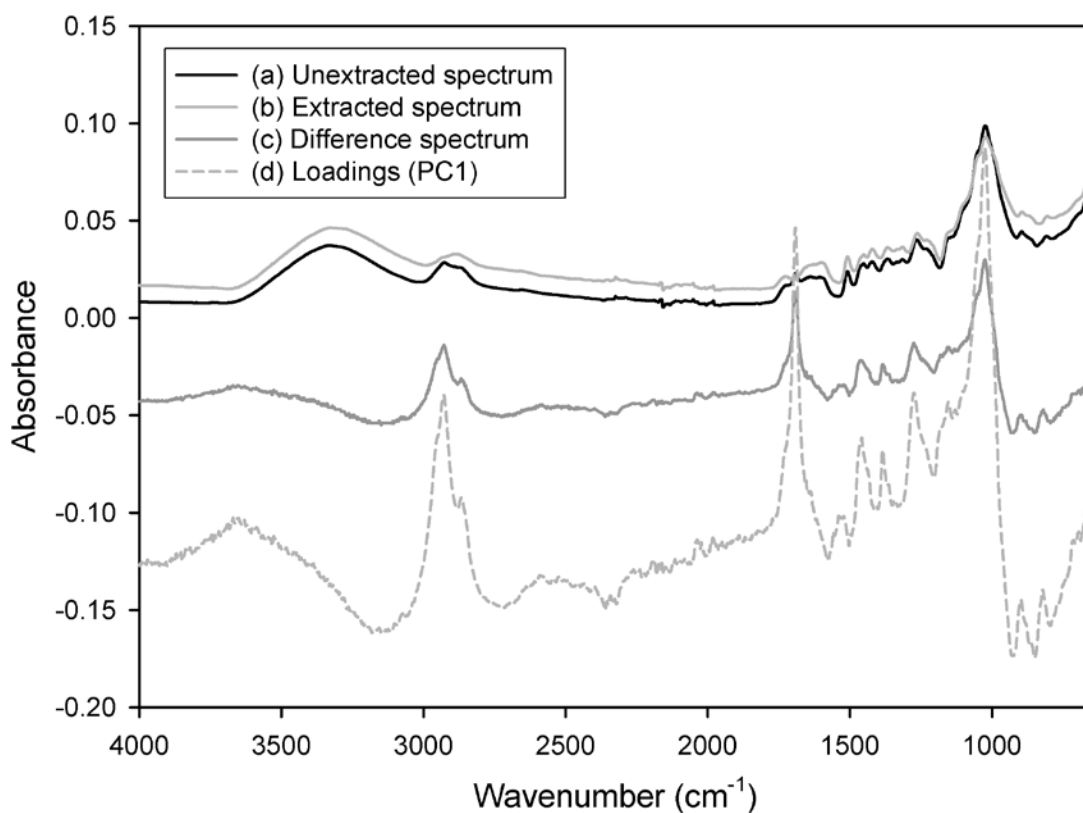

Figure 1.Averaged mid-IR spectra for the (a) unextractedand (b) extracted samples, as well as the resulting (c) difference spectrum, and (d)loadings plot (PC1). The spectra are not to scale.

PCA of unextracted wood samples. PCAwas performed on the mid-IR spectra and the resultant scores plot provided separated clustersof the unextracted and extracted wood samples (plot not shown). Theloadings plot for PC1 (Figure 1(d)), explaining 91% of the variation, exhibited some clearly defined bands at: 1014, 1271, 1389, 1461, 1689, 2865 and 2925 cm^{-1}. These peaks match very closely with the difference spectrum in Figure 1(c). The same analysis with the NIR spectra produced similar results with separation between the extracted and unextracted samples. Figure 2(d) shows the loadings plot for PC1 with broad bands at: 1205, 1455, 1725, 1945 and 2305 nm, matching those observed in the NIR difference spectrum (Figure 2(c)).
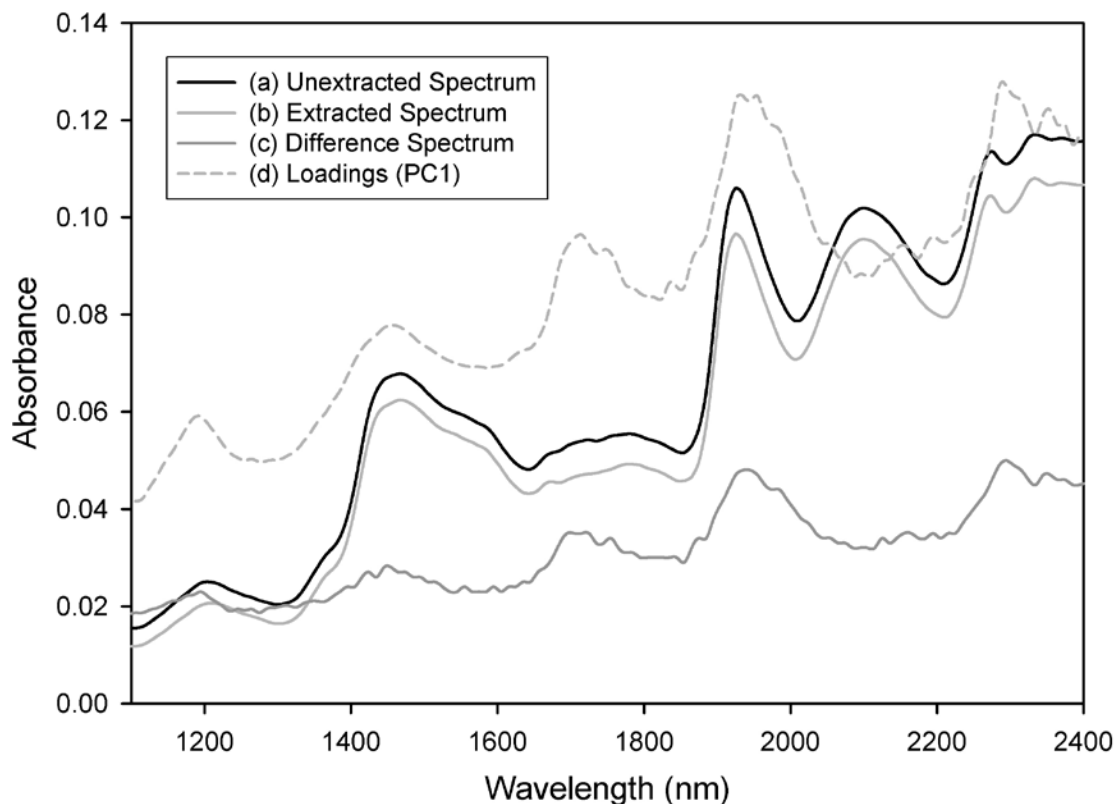
***Figure 2**. Averaged NIR spectra for the (a) unextractedand (b) extracted samples, as well as the resulting (c) difference spectrum, and (d) loadings plot (PC1).The spectra are not to scale.*

PLS of unextracted wood samples. Calibration models for extractives content provided strong calibration statistics (R^2 = 0.94 and 0.93; SECV = 1.46% and 1.78%, RPD = 3.68 and 3.01 for mid-IR and NIR, respectively) with the mid-IR model providing a better RPD while using less factors (Table 1). RPDis a statistical parameter that accounts for the various properties and their ranges. A RPD value of 2.5 is considered satisfactory for screening, while 1.5 may be acceptable for preliminary use (Williams and Sobering 1993).The same trend was noted with the models for GCV. However, these were not as strong as those for extractives content providing lower RPD values (3.09 and 2.39 for mid-IR and NIR, respectively). The predictive ability of the extractives content was very strong for the mid-IR data with a RPD (3.63) very similar to that of the calibration model, but it was notably poorer for the NIR data (1.22) from the same test samples. The predictive ability for GCV was much poorer for both mid-IR and NIR analyses (Table 2) with much lower RPD values (2.14 and 1.31, respectively) than for the calibration models, and also poorer than the predictive ability for extractives.

PLS of extracted wood samples. Models were built for lignin content and GCV using the extracted samples and the results listed in Table 2. The correlations obtained from the mid-IR

data were poor for both lignin ($R^2 = 0.61$; SECV = 0.89%; RPD = 1.01) and GCV ($R^2 = 0.58$; SECV = 0.23 MJkg^{-1}; RPD = 1.06). No improvement was observed when using a reduced wavenumber range (650-1800 cm^{-1}). The use of NIR data led to a slight improvement for the lignin model ($R^2 = 0.65$; SECV = 0.80%; RPD = 1.10) but was poorer for the GCV model ($R^2 = 0.30$; SECV = 0.24 MJkg^{-1}; RPD = 1.03). The predictive ability for both mid-IR and NIR data were similarly poor compared to that obtained from the calibration models (Table 2). It was clearly observed that the models obtained with the extracted samples were much poorer than those from the unextracted samples in Table 1. However, in previous studies, strong correlations for GCV have been obtained from extractive-free hybrid poplar samples (Zhou et al. 2011). R^2 values ranged from 0.86-0.90 in the mid-IR range using a variety of preprocessing methods. Nevertheless, these models did require between 10-12 factors.

Table 1. *PLS model statistics obtained fromunextracted samples.*

Method	Sample	Property	SD	No. of Factors	R^2	SECV/P	RPD
Mid-IR	Calib	GCV	0.85	2	0.91	0.28	3.09
		Extractives	5.36	2	0.94	1.46	3.68
	Test	GCV	0.59	2	0.78	0.28	2.14
		Extractives	4.07	2	0.94	1.12	3.63
NIR	Calib	GCV	0.85	2	0.86	0.36	2.39
		Extractives	5.36	3	0.93	1.78	3.01
	Test	GCV	0.59	2	0.54	0.45	1.31
		Extractives	4.07	3	0.45	3.33	1.22

The units for SECV/P are expressed in GCV (MJkg^{-1}) and extractives (%), respectively.

Table 2. *PLS model statistics obtained from extracted samples.*

Method	Sample	Property	SD	No. of Factors	R^2	SECV/P	RPD
Mid-IR	Calib	GCV	0.24	3	0.58	0.23	1.06
		Lignin	0.90	4	0.61	0.89	1.01
	Test	GCV	0.30	3	0.33	0.25	1.18
		Lignin	1.43	4	0.54	1.03	1.38
NIR	Calib	GCV	0.24	2	0.30	0.24	1.03
		Lignin	0.90	4	0.65	0.80	1.10
	Test	GCV	0.30	2	0.31	0.25	1.17
		Lignin	1.43	4	0.68	0.80	1.79

The units for SECV/P are expressed in GCV (MJkg^{-1}) and lignin (%), respectively.

Regression coefficients. The regression coefficients provide information about the models built in the PLS analyses and are plotted in Figure 3 for the extractives content and GCV models based on the mid-IR data. The plots appear to be very similar, indicating that the strong calibration models for extractives content and GCV were based on the same chemical features. Furthermore, these plots exhibit the same peaks as observed in the loadings plot and the difference spectrum (Figure 1), with particularly strong peaks at 1689, 2865 and 2925 cm^{-1}, in

addition to peaks at1271, 1389 and 1461 cm^{-1}. The models were negatively correlated with 1014 cm^{-1}(C-O stretch) peak.
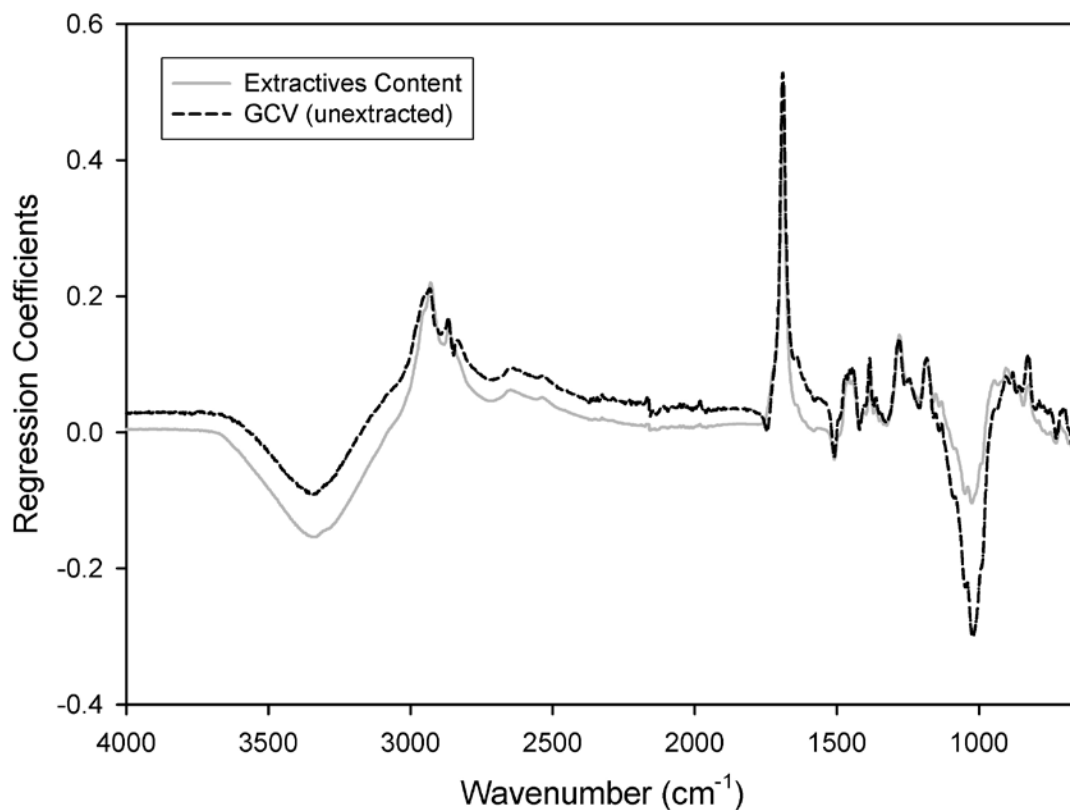

Figure 3*.Regression coefficients for the extractives content and GCV models based on the mid-IR data from the unextracted samples.*

The analyses using the models based on NIR data are plotted in Figure 4. The plots of regression coefficients for extractives content and GCV were again similar with several bands of interest at: 1205, 1725 and 2305 nm. Thepeaks centered near 1705 nm correspond to the 1st overtone of aliphatic and aromatic CH stretching in CH_2 groups present in both lignin and extractives. The other major peak at 2295 nm is due to OH and C-O stretching (Michell and Schimleck, 1996). Similar high regression coefficients for the prediction of GCV, from hybrid poplars, were reported at 1725 and 2270 nm (Maranan and Laborie, 2007). However, unlike the mid-IR results, high regression coefficients are not clearly attributable to the extracts and not lignin.
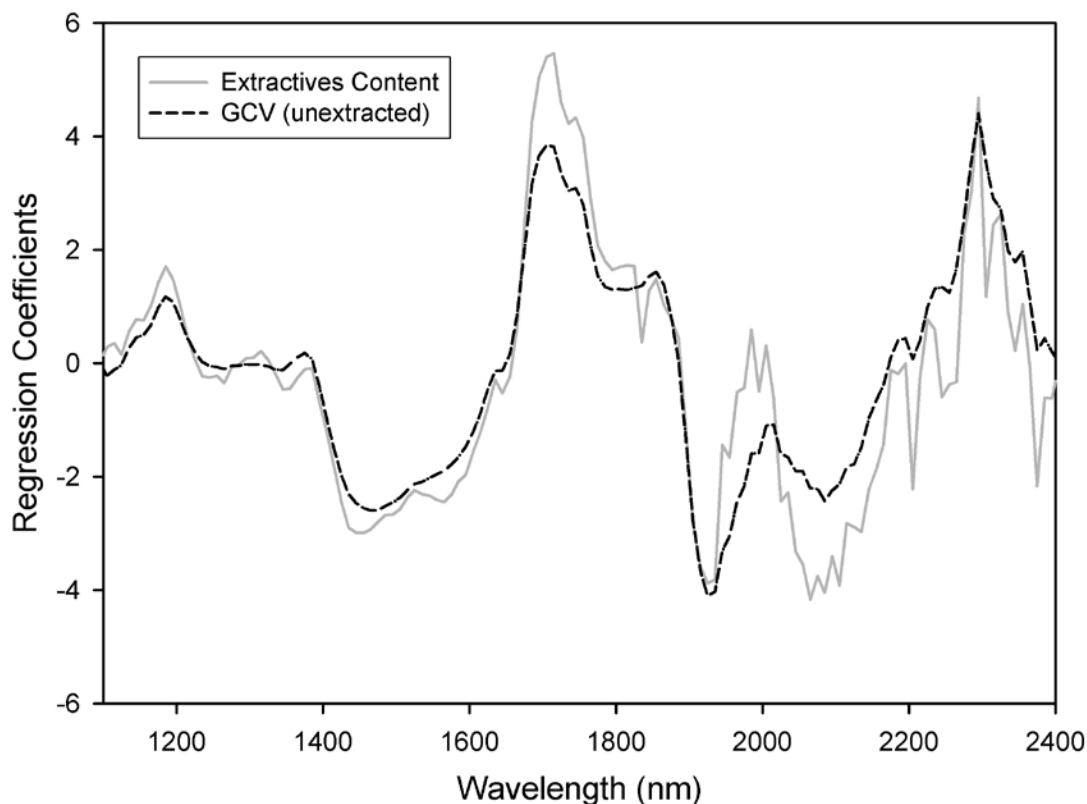
Figure 4*.Regression coefficients for the extractives content and GCV models based on the NIR data from the unextracted samples.*

Conclusions

Strong relationships were apparent between the variation in GCV and variation in extractives content using both mid-IR and NIR spectroscopic data. Plotting the regression coefficients for GCV and extractives content showed that the same bands were responsible for these strong models. Although, total lignin content does impact total GCV, no correlation was found between the variation in GCV with lignin content for the extractive-free wood samples.

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