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# Chemical and calorific characterisation of longleaf pine using near infrared spectroscopy

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Gross calorific value (GCV) has been predicted by building models based on near infrared (NIR) spectroscopy and multivariate analysis; however, to date, the impact of feedstock chemical composition on the models has not been directly assessed. In the present study, 20 longleaf pine trees were sampled at two positions (breast and mid-height) for calorimetric and spectroscopic analyses. The GCVs, which ranged from  $20\text{ MJ kg}^{-1}$  to  $24\text{ MJ kg}^{-1}$ , showed a strong correlation with the wide-ranging values of acetone-soluble extractives content. After extraction of the samples with acetone, the range for the GCV was both lower and slightly narrower [ $19\text{--}21\text{ MJ kg}^{-1}$ ] and was poorly correlated to lignin content with its narrow range of values. Near infrared (NIR) spectroscopy coupled with multivariate analysis was applied to the samples and provided a strong coefficient of determination ( $R^2$ ) between the values predicted by NIR and those determined by calorimetry for the unextracted, but not the extracted, samples. Plotting the regression coefficients validated the results by showing very similar plots for GCV and extractives content, thereby indicating that the same molecular features are driving the models. NIR spectroscopy coupled with multivariate analysis can predict GCV for bioenergy feedstocks and also provide insight into chemical features with the greatest impact on fuel value.

**Keywords:** near infrared spectroscopy, calorimetry, gross calorific value, extractives, lignin, longleaf pine

## Introduction

The properties and chemistry of wood are increasingly being measured by coupling near infrared (NIR) spectroscopy with multivariate analysis to build predictive models based on analytical data for specifically targeted properties and/or chemical compositions. Advantages of the technique are that it is non-destructive, relatively inexpensive and can be rapidly applied after models have been developed. Common physical (for example, density, microfibril angle) and mechanical (for example, stiffness) properties have been predicted for both hardwoods and softwoods. Chemical composition of wood cell wall polymers (cellulose, hemicellulose, lignin) and extractives have also been predicted by using models with high correlations.<sup>1</sup> Spectroscopic analyses have been carried out by

diffuse reflectance<sup>2–5</sup> and transmittance,<sup>6,7</sup> the latter technique requiring much less material for analysis. Physical properties and chemical composition play an integral role in the performance of wood in service, so models have been developed to predict mass losses and/or changes in composition as a result of thermal treatment<sup>8</sup> or exposure to wood decay fungi.<sup>9–11</sup> Recently, increasing interest in biofuels raises questions about the utility of NIR spectroscopy for rapidly assessing feedstock qualities, in particular, fuel value.

The higher heating value (HHV) or gross calorific value (GCV) of a fuel is defined as the amount of heat released by a specified quantity (initially at  $25^\circ\text{C}$ ) once it is combusted and the products have returned to a temperature of  $25^\circ\text{C}$ , which takes

into account the latent heat of vaporisation of water in the combustion products. Although the term HHV may have been used in the studies cited here, the term GCV is used from this point forward to avoid confusion by alternating between the two terms. The GCV of wood has been related to its ultimate and proximate analytical data<sup>12</sup> as well as the amount of fixed carbon.<sup>13</sup> Alternatively, equations for estimating GCV have been based on the amounts of extractives, lignin, and/or holocellulose.<sup>14–16</sup> The GCVs for lignin and extractives are higher than those for cellulose or hemicelluloses, thus the extractive-free wood of *Gmelina arborea* had a lower GCV than unextracted wood.<sup>17</sup> White<sup>16</sup> also studied the effect of chemical composition on GCVs and found that linear regression with lignin content from both hardwoods and softwoods together provided a reasonable correlation, which was further improved by the inclusion of extractives content into the equation. Analysis of the extractive-free samples resulted in lower GCVs and an improved correlation with lignin content.

Given the relationship between chemical composition and GCV, and the ability to predict chemical composition from the statistical analysis of NIR spectral data, studies have shown that values for GCV can also be predicted.<sup>18–20</sup> In addition to GCV, Lestander and Rhen<sup>18</sup> developed models to predict other useful information for biofuels, specifically moisture and ash content. Assessments to date show promise for rapid analyses that would be useful for applications such as the screening of clones from plantations<sup>19</sup> or from a wide variety of potential feedstock sources that may include hardwoods, softwoods, shrubs and grasses;<sup>20</sup> however, it should be noted that accuracy of the predicted GCVs was less than that for the standard laboratory measurement.<sup>19,20</sup>

Based on the above discussion, it is apparent that GCV can be predicted by statistical manipulation of NIR spectra and that the signals on which the correlations are derived are likely based on the relative proportions of lignin and/or extractives to the cell wall carbohydrates (cellulose, hemicelluloses). However, one confounding factor for the correlations with lignin and extractives with GCV is that the studies were based on several different species as opposed to one species with samples having different lignin and extractives contents. As for the NIR studies, these did not relate the variability in chemical composition to variability in GCV. To explore this further, we developed NIR predictive models from a single species, with specific attention given to parallel determinations of lignin and extractive content. Given that the variability of extractives content is much greater than the lignin content for the softwood selected in the present study (longleaf pine), we predicted that the extractives content, and not the lignin content, would be the primary determinant for variability in GCV.

## Experimental Materials

Twenty 70-year-old longleaf pine (*Pinus palustris*) trees, assigned a tree identification number of 1 through 20, were

harvested from a spacing, thinning and pruning study on the Kisatchie National Forest, Louisiana, USA. Discs (5 cm thick) were cut at breast height (135 cm from ground level) as a common sampling point and mid-height along thebole to provide a sample with more intermediate composition. The discs were dried under ambient conditions before further sectioning into 1 cm thick wood slices from pith to bark. The bark was removed and the radial wood slices were cut into strips that were sufficiently thin to be ground in a large Wiley mill equipped with a 2 mm screen plate. Wood meals were stored under ambient conditions until needed.

### Extractives and lignin content

Aliquots of wood meals were exhaustively extracted with acetone using a Soxhlet apparatus. Extracts were concentrated by rotary evaporation, transferred to small vials, evaporated under a stream of nitrogen to afford heavy yellow oils that were dried further *in vacuo* and weighed. Extractive-free wood meals were further ground in a small Wiley mill equipped with a 40-mesh screen and then analysed for lignin content using the acetyl bromide method.<sup>21</sup> A separate sample of extractive-free loblolly pine wood was used with each set of reactions as a control. The acetyl bromide solution was freshly prepared prior to each determination. An absorptivity value of 23.30 g<sup>-1</sup> Lcm<sup>-1</sup>, determined for softwood lignin,<sup>22</sup> was used to calculate the lignin content. Appropriate samples were dried in an oven (102 ± 3°C) to determine the moisture content necessary to adjust the values for extractives and lignin content to a dry-weight basis.

### Calorimetry

Calorimetry was conducted using a Parr oxygen bomb calorimeter 6100 (Parr Instrument Co., Moline, IL, USA). GCV was determined in triplicate following the instructions in the manufacturer's operating manual.<sup>23</sup>

### Near infrared spectroscopy and multivariate analysis

NIR spectra were collected with an ASD Field Spec (Analytical Spectral Devices, Boulder, CO, USA) spectrometer at wavelengths between 350 nm and 2500 nm. A fibre-optic probe oriented perpendicular to the sample surface was used to collect the spectra. The samples were illuminated with a DC lamp oriented at 30° above the sample surface and rotated at 45 rpm to minimise specular interference and surface heterogeneity. Three spectra were collected for each sample.

Multivariate analysis of the data was performed using the Unscrambler (version 8.0) software (CAMO Software, Woodbridge, NJ, USA). The NIR data were first averaged to one spectrum per sample. Multiplicative scatter correction (MSC) was applied to the spectra to reduce the scatter by removing the additive and multiplicative effects.<sup>24</sup> Partial least squares (PLS) regression was used to determine the calorific value, extractives and lignin content in the samples. Two thirds of the samples were used for a calibration set, while the remaining one third was employed as the test set. Models

were generated and fitted using full cross validation and up to five factors. The models were assessed using several common measures of calibration performance: the correlation coefficient,  $R^2$ , is a measure of the strength of the fit to the data; and the standard error of calibration or prediction ( $SEC$  or  $SEP$ ) is a measure of the calibration or prediction error in the fit.

## Results and discussion

### Calorimetry

The GCVs were determined in triplicate and averaged. A summary of the results is provided in Table 1 for all 40 samples together (all), and separately for the 20 samples taken at breast height (BH), the 20 samples taken at mid height (MH), the 27 calibration samples and the 13 test set samples. The mean values from the unextracted breast-height samples are plotted in Figure 1, providing significant variation ranging between  $20\text{ MJ kg}^{-1}$  and  $24\text{ MJ kg}^{-1}$ . The samples were also extracted and all the extracted samples exhibited lower GCVs, between  $19\text{ MJ kg}^{-1}$  and  $21\text{ MJ kg}^{-1}$  (Figure 1). In a previous study, White<sup>16</sup> reported that the GCV of southern pine wood with an extractives content of 5.4% was lowered by  $0.65\text{ MJ kg}^{-1}$  following extraction. In this current study, the change in GCV following extraction was noticeably variable between the samples, ranging between  $0\text{ MJ kg}^{-1}$  and  $4\text{ MJ kg}^{-1}$ .

Thus, determinations of the extractives content were also made and these varied greatly (between 0 and 21%); the non-volatile extractives in pines are a complex mixture of resin and fatty acids accompanied by small amounts of neutral compounds including diterpene alcohols and methyl esters. Figure 1 shows that the variation in GCV for the unextracted breast-height samples closely followed that for the extractives content. This relationship was further analysed and confirmed using a standard linear regression. It can be seen in Figure 2 that there is a strong correlation ( $R^2=0.94$  and a standard error of estimation ( $SEE$ ) of  $0.23\text{ MJ kg}^{-1}$ , providing the linear equation:  $\text{GCV}=20.12+0.17\text{EC}$ , in which, GCV is as defined ( $\text{MJ kg}^{-1}$ ) and EC is the extractives content (%). A similar relationship has been reported by Demirbas,<sup>25</sup> producing a linear equation (correlation coefficient not reported) relating extractives content to GCV. Fuwape reported a statistically significant ( $\alpha=0.05$ ) correlation coefficient of determination ( $R^2=0.52$ ) for the sapwood of *Gmelina arborea*, but not for the heartwood ( $R^2=0.17$ ).<sup>17</sup> Similar results were obtained with the samples at mid-height; although a weaker coefficient of determination was obtained ( $R^2=0.88$ ;  $SEE=0.22\text{ MJ kg}^{-1}$ ) from the narrower range of values for GCV and extractives content.

The acetone extracted samples also exhibited variation in GCV, albeit less than their unextracted counterparts. Thus, it was of particular interest to determine if that variation (Figure 1) could be attributed to the variation in lignin content

**Table 1. Statistics for gross calorific value (GCV), extractives and lignin content.**

Property	Sample	Range	Mean	Standard deviation
GCV* (unextracted)	All	20.2–23.6	21.2	0.80
	BH	20.2–23.6	21.4	0.92
	MH	20.4–22.9	21.0	0.61
	Calibration	20.4–23.6	21.2	0.83
	Test	20.2–22.4	21.2	0.78
Extractives*	All	0.0–20.6	5.9	5.03
	BH	1.1–20.6	7.8	5.37
	MH	0.0–17.2	4.0	3.90
	Calibration	0.0–20.6	5.8	5.07
	Test	0.9–14.8	6.1	5.15
GCV* (extracted)	All	19.5–20.6	20.1	0.25
	BH	19.5–20.6	20.1	0.29
	MH	19.7–20.6	20.1	0.22
	Calibration	19.6–20.6	20.1	0.26
	Test	19.5–20.4	20.2	0.24
Lignin* (extracted)	All	26.6–31.5	28.2	1.06
	BH	26.6–29.1	27.8	0.70
	MH	26.6–31.5	28.6	1.20
	Calibration	26.6–31.5	28.3	1.18
	Test	26.9–29.4	27.9	0.72

\*GCV [ $\text{MJ kg}^{-1}$ ], extractives and lignin content (%).

BH, breast height; MH, mid-height.

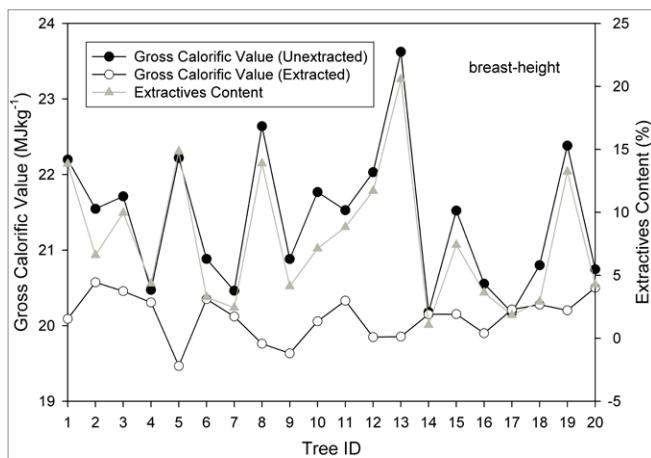


Figure 1. Variation of gross calorific value (both extracted and unextracted samples) and extractives content for the 20 longleaf pine trees sampled at breast height.

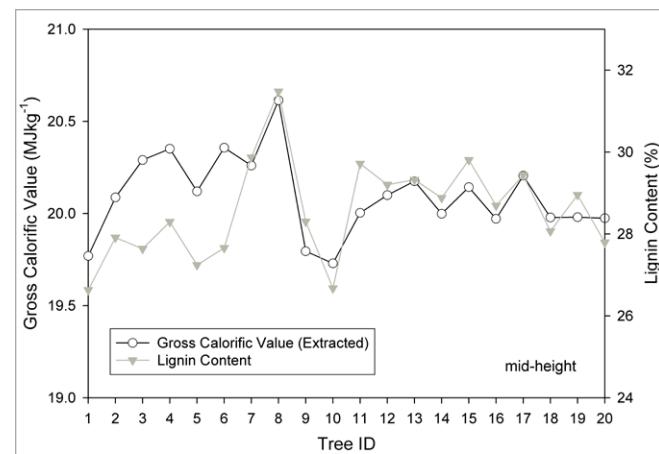


Figure 3. Variation of gross calorific value (extracted samples) and lignin content for the 20 longleaf pine trees sampled at mid-height.

for the extracted samples. Plotting GCV and lignin content appeared to show overlapping patterns for the mid-height samples (Figure 3); however, a standard linear regression of the data from the mid-height samples indicated a poor correlation ( $R^2 = 0.32$ ;  $SEE = 0.18 \text{ MJ kg}^{-1}$ ). It should be noted that relationships of GCV to lignin content reported in the literature were based on analyses of an extremely diverse set of samples (for example, corncob, wood, straw and bark)<sup>14</sup> or different hardwood (yellow-poplar, red oak, maple, basswood) and softwood species (Engelmann spruce, western redcedar, southern pine, redwood).<sup>16</sup> The amounts of protein, extractives and ash, aside from the cell wall polymers (cellulose, hemicelluloses and lignin), undoubtedly covered a wide range of values for these samples. Removal of the extractives dramatically improved the linear relationship between GCV with lignin content.<sup>14,16</sup> It may be argued that there could be

confounding factors, given the differences in the lignin structure between softwoods, hardwoods and grasses. Therefore, these studies did not address the question of whether the lignin content alone, for a single tree species, has a significant effect on GCV. For the longleaf pine samples used in the present study, it is clear that differences in GCV are primarily dictated by differences in extractives content and not lignin content.

### Near infrared spectroscopy and multivariate analysis

Initial analyses using PLS regression showed no large regression coefficients below 1100 nm and that there was slight improvement in prediction power when the wavelength range was reduced to 1100–2500 nm, similar to the results observed by Gillon *et al.*<sup>20</sup> The resulting calibration

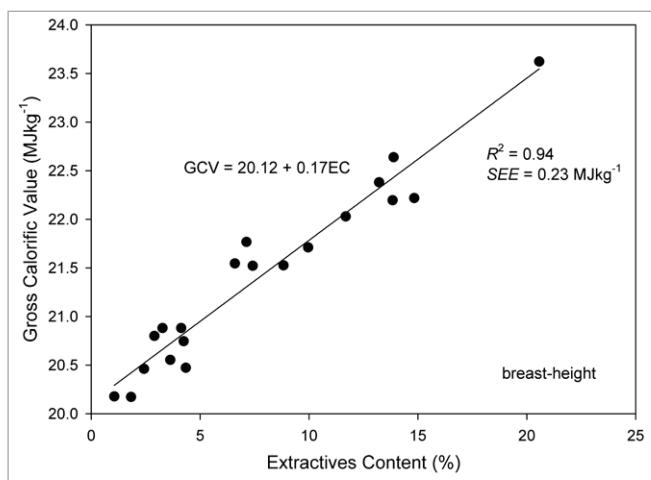


Figure 2. Gross calorific value (unextracted samples) as a function of extractives content for the 20 longleaf pine trees sampled at breast height.

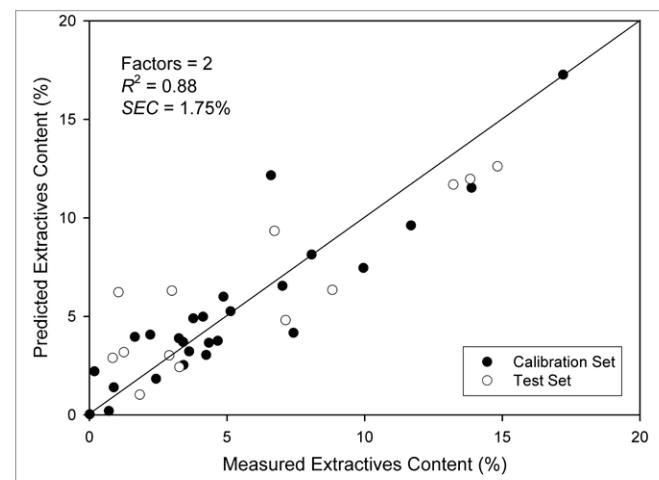


Figure 4. NIR predicted vs measured extractives content for unextracted samples.

**Table 2.** Calibration statistics for gross calorific value (GCV), extractives and lignin content.

Property	Sample	No. of factors	$R^2$	SEC/SEP
GCV (unextracted)	Calibration	2	0.85	0.32
	Test	2	0.72	0.41
Extractives	Calibration	2	0.88	1.75
	Test	2	0.78	2.51
GCV (extracted)	Calibration	2	0.37	0.21
	Test	2	0.05	0.24
Lignin (extracted)	Calibration	3 (5)	0.71 (0.92)	0.64 (0.34)
	Test	3 (5)	0.33 (0.71)	0.72 (0.83)

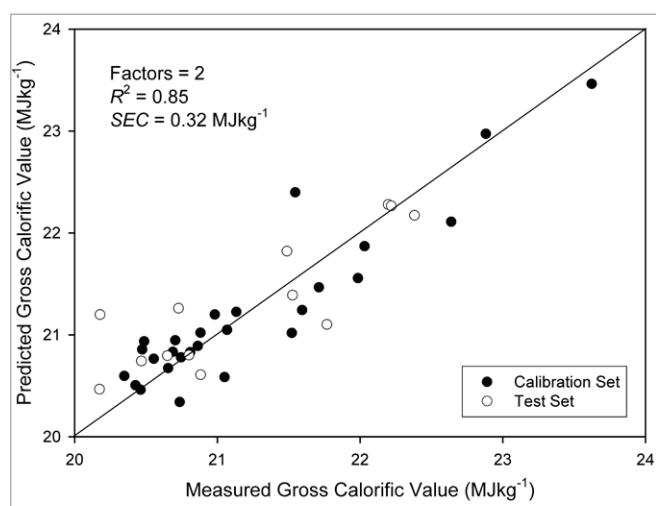
SEC/SEP for GCV ( $\text{MJ kg}^{-1}$ ), extractives and lignin content (%).

for extractives content is shown in Figure 4, providing strong calibration statistics ( $R^2=0.88$ ;  $\text{SEC}=1.75\%$ ) while employing only two factors (Table 2). This was obtained using a set of samples with a large range of extractives values (0.0–20.6%). The test set performed reasonably well with a  $R^2=0.78$  and  $\text{SEP}=2.51\%$  (Table 2). Similarly good calibration statistics were reported by Kelley *et al.*<sup>1</sup> for extractives content from ground samples of loblolly pine ( $R^2=0.86$ ;  $\text{RMSEC}=2.3\%$ ; four factors), using a larger extractives range (2.8–26.9%). These extractive ranges are not uncommon for pine stem wood, when including both heartwood and sapwood. In a study by Esteves and Pereira,<sup>8</sup> pine extractives content was determined by successive Soxhlet extractions using dichloromethane followed by ethanol and, lastly, water. The calibration models gave increasing  $R^2$  values with increasing extractive ranges from successive extractions. The total extractives content provided the greatest range and highest  $R^2$  of 0.84 (with an  $\text{RMSEC}$  of 5.48%). Acetone used for the present study is an efficient solvent with the capacity to remove the predominantly resinous extractives in pine wood. The wide range of values for extractives content we determined resulted in a high value for  $R^2$  that compared well with the corresponding values ( $R^2$ , wide range of values for extractives content) based on total extractive content obtained cumulatively by sequential extraction with solvents having low to high polarities.<sup>8</sup>

GCV has also been studied with NIR spectroscopy and provided strong correlations. The same was expected in this study, especially given the higher GCV for extractives (relative to the cell wall polysaccharides) and the wide range of extractives content. The unextracted samples provided a good calibration model for GCV (Figure 5) with strong calibration statistics as listed in Table 2 ( $R^2=0.85$ ;  $\text{SEC}=0.32 \text{ MJ kg}^{-1}$ ; two factors). Gillon *et al.*<sup>20</sup> previously applied this to a range of forest fuels that included leaves, needles, twigs, bark, leaf and needle litter. A strong calibration model was obtained ( $R=0.95$ ;  $\text{SEC}=0.42 \text{ MJ kg}^{-1}$ ), in which these samples provided a very large range of calorific values ( $17.05$ – $24.59 \text{ MJ kg}^{-1}$ ) and standard deviation ( $1.44 \text{ MJ kg}^{-1}$ ). This is widely known to result in improved correlations. However, Maranan and Laborie<sup>19</sup>

obtained excellent results ( $R=0.97$ ;  $\text{RMSEC}=0.05 \text{ kJ g}^{-1}$ ; four factors) despite the very limited range of GCV encountered ( $18.71$ – $19.68 \text{ kJ g}^{-1}$ ). This was based on second derivative NIR spectra from milled hybrid poplar samples. In our study, the GCV results based upon NIR spectroscopy were less accurate than those obtained using the standard laboratory method, similar to that observed in previous studies.<sup>19,20</sup> In this present study, the GCV model for the extracted samples provided a poor  $R^2$  of 0.37 but with a  $\text{SEC}=0.21 \text{ MJ kg}^{-1}$  (Table 2), with the possibility of fitting up to five factors. It can be seen in Table 1 that the range of values and standard deviation for the extracted samples were much smaller than those for the unextracted samples.

The lignin data from the extracted samples provided a reasonable calibration with three factors ( $R^2=0.71$ ;  $\text{SEC}=0.64\%$ ). This was further improved when using five factors producing a  $R^2=0.92$  and  $\text{SEC}=0.34\%$  (Table 2). Jones *et al.*<sup>2</sup> obtained similar calibration statistics ( $R^2=0.85$ ;  $\text{SEC}=0.48\%$ ; four factors) in a study using radial strips of loblolly pine. Their test set produced poorer results ( $r^2=0.51$ ;  $\text{SEP}=1.21\%$ ), which

**Figure 5.** NIR predicted vs measured gross calorific value for unextracted samples.

was attributed to the diverse origins of their test set. In this present study, the test set also provided poor results ( $R^2=0.33$ ;  $SEP=0.72\%$ ), which may have been partly due to actual differences in lignin content between the extracted calibration and test sets. It can be seen in Table 1 that the test set has a smaller range and standard deviation than the calibration set. Furthermore, these results show the lignin model to be poorer than the extractives model when using the same low number of factors. This was also observed by Kelley *et al.*<sup>1</sup> in which the results from the lignin model ( $R^2=0.66$ ;  $RMSEC=1.1\%$ ) were poorer than that for the extractives ( $R^2=0.86$ ;  $RMSEC=2.3\%$ ). They noted that the majority of the lignin values were clustered close to the mean. However, in a NIR study of transgenic aspen trees, excellent lignin models were obtained for wood meal pellets (for example,  $R^2=0.98$ ;  $SEC=0.57\%$ ; three factors),<sup>7</sup> although these were obtained from samples providing a much larger lignin range (10.7–24.6%) and higher standard deviation of 4.2%. Using different types of forest biomass, such as twigs and needles, can provide much property variability as compared with using stem wood from one species. Nevertheless, in some cases, stem wood can also provide high levels of variability within a single species.

The plot of the regression coefficients (Figure 6) provides a spectroscopic insight into the relationships between GCV with both extractives and lignin content. Gillon *et al.*<sup>20</sup> noted that the high correlation values they obtained in several absorption bands show that the NIR spectrum is strongly correlated with GCV. The plots listed are for the GCV and extractives content from the unextracted samples and the GCV and lignin content from the extracted samples. The same close relationship between the GCV (unextracted) and extractives content shown in Figures 1 and 2 is observed in Figure 6, with very similar plots, indicating that the same molecular features were responsible for the good calibration models. This provides further support, based on spectroscopy, for the relationship between GCV and extractives content. Two of the largest regression coefficients for these two plots were at bands centred around 1705 nm corresponding to the first overtone of aliphatic and aromatic CH stretching in  $\text{CH}_2$  groups present in both lignin and extractives and also at 2295 nm, which is due to OH and C-O stretching.<sup>26</sup> Similar high regression coefficients for the prediction of GCV from hybrid poplars were reported at 1725 nm and 2270 nm.<sup>19</sup> The GCV plot for the extracted samples is very different from the unextracted plot (Figure 6), with very few of the same clearly defined bands. The plot for lignin content is complex with many peaks, some of which are found in the extracted GCV plot but to a much lesser magnitude. One of the high regression coefficients for the plot of lignin content was for the band found around 1675 nm<sup>27</sup> and is assigned to CH in the aromatic skeletal structure lignin.<sup>26</sup> Another band around 2255 nm, due to  $\text{CH}_3$ , has previously been found to be the strongest loading vector for lignin in a study of *Eucalyptus camaldulensis*.<sup>27</sup> These bands, amongst others, are also present in the extracted GCV plot.

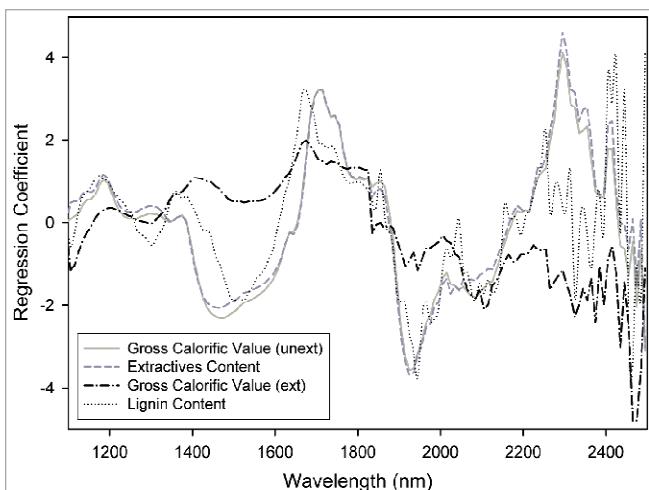


Figure 6. Regression coefficients for gross calorific value (extracted and unextracted samples), extractives and lignin content.

## Conclusions

A strong relationship between the GCV (unextracted) and extractives content has been demonstrated in this study of longleaf pine stem wood and an apparently weaker relationship between the GCV (extracted) and lignin content. The strength of these relationships strongly correlated with the amount of property variability in the samples. It has also been demonstrated that NIR spectroscopy can be used to rapidly determine GCV and chemical composition, with this technique also providing spectroscopic support to the strong relationship between GCV and extractives content. Model improvement is still necessary if this technique is to be used as a replacement for the standard bomb calorimetry method, but may be used when a rapid throughput of samples is necessitated. Thus, with further improvements, it may be possible to apply this to solid wood, greatly reducing the sample preparation and analysis time.

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