The Prediction of Gross Calorific Value Using Infrared (IR) Spectroscopy and Multivariate Analysis

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Background and Objectives

The gross calorific value (GCV) of a fuel, also known as the higher heating value (HHV) or gross heat of combustion, is the amount of heat released by a specified quantity (initially at 25°C) once it is combusted and the products returned to that temperature. Fuwape (1989) noted that extractive-free wood from *Gmelina arborea* (Roxb), a hardwood, had a lower gross heat of combustion than the unextracted wood. In a later study, finding that extractive-free plant parts resulted in lower HHVs than the unextracted parts, Demirbas (2003) produced an equation relating the differential HHV to extractives content.

The application of near-infrared (NIR) spectroscopy, coupled with multivariate analysis, has been used as a rapid means to determine a range of woody biomass properties. Recently, it has been applied to biofuel properties. For example, Lestander and Rhen (2005) used this technique to determine the calorific content in Norway spruce, and suggested its applicability to process monitoring in biofuel plants. Maranan and Laborie (2007) applied this technique to the determination of calorific value of *Populus* spp. Calibration models proved useful for the rapid determination of calorific value, however, it was less accurate than the standard method. This is not surprising given that Gillon et al. (1997) had previously determined this technique to be considerably less accurate than results obtained directly by calorimetry, based on various fuel samples (e.g., wood, leaves, and bark). Nevertheless, it was stated that this method could be a useful tool when a large number of measurements are required.

The first objective of the current study is to determine if there is a significant (i.e., measurable) impact of extractives content on GCV when using a single softwood species. The other objective being the rapid determination of the GCV of milled samples of longleaf pine (*Pinus palustris*) using infrared (IR) spectroscopy coupled with multivariate analysis. The application of IR spectroscopy (as opposed to NIR spectroscopy) also allows the spectral investigation of the samples to determine the chemical features that are important in the GCV and extractive predictions.

Experimental Procedure

Materials

Twenty 70-year-old longleaf pine (*Pinus palustris*) trees were harvested from a spacing, thinning, and pruning study on the Kisatchie National Forest, LA. Trees were collected and 5 cm disks were cut at a height of 1.4 m (i.e., breast height). A 1.2-cm-thick wood slice was sectioned along the north-south direction, through the center of each disk, encompassing the pith. The wood slices were then broken down and ground in a Wiley mill equipped with a 30-mesh screen.

Calorimetry

Calorimetry was conducted using a Parr oxygen bomb calorimeter 6100 (Parr Instruments, Moine, IL). Gross calorific value was determined in triplicate following the instructions in the manufacturer's operating manual.

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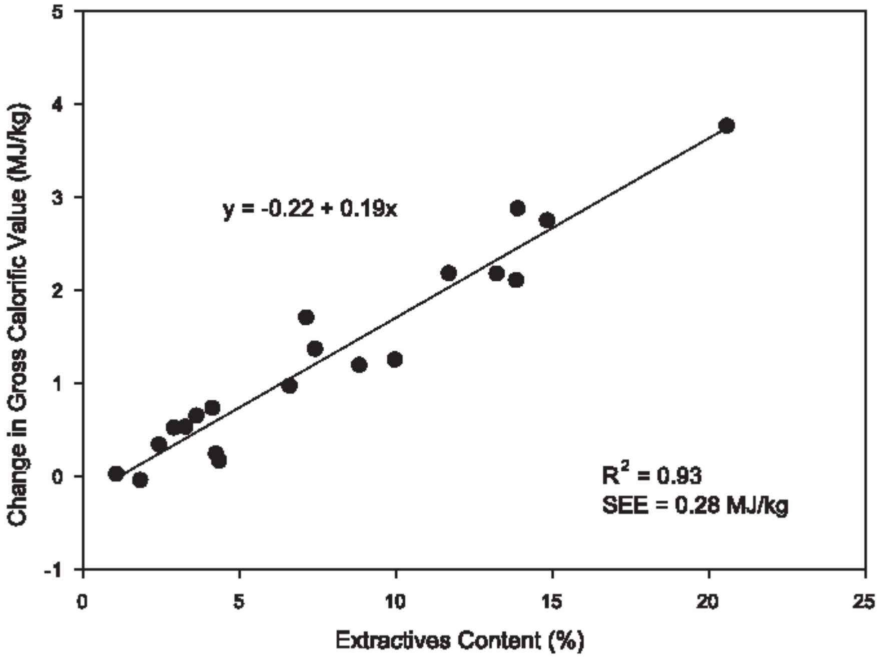


Figure 1: Variation of GCV as a function of extractives content.

Infrared Spectroscopy and Multivariate Analysis

IR spectra of the samples were collected using a Nexus model 670 Fourier Transform IR spectrometer (Thermo Nicolet Instruments, Madison, WI), equipped with a Golden Gate MKII Single Reflection ATR accessory. Milled wood and extract samples were applied directly to the diamond window, with three spectra collected for each sample.

Multivariate analysis of the data was performed using the Unscrambler (version 8.0) software (CAMO, Corvallis, OR). The IR data were first averaged to one spectrum per sample followed by applying multiplicative scatter correction. Partial least squares (PLS) regression was used to predict the gross calorific value and extractives content of the samples.

Results and Conclusions

Calorimetry

The mean GCVs for the unextracted samples from each of the 20 trees ranged from 20.17 to 23.62 MJ/kg with extractives contents ranging from 1.1 to 20.6%. After extraction, the GCVs were all lower with a much narrower range of values. The effect of extractives content on GCV was investigated, and determined, quantitatively, for the unextracted samples. The change in GCV between the extracted and unextracted samples was plotted as a function of extractives content (Figure 1). It can be seen that there is a strong correlation with a R^2 = 0.93, producing the equation: GCV = 0.19 (EC) - 0.22, in which GCV is gross calorific value (MJ/kg) and EC is extractives content (%). This roughly equates to an increase of 0.19 MJ/kg per 1% increase in extractives content. Previously, Demirbas (2003) reported a similar type of correlation, observing a linear relationship between differential HHVs and extractives content; however, this was obtained using different plant parts from several tree species.

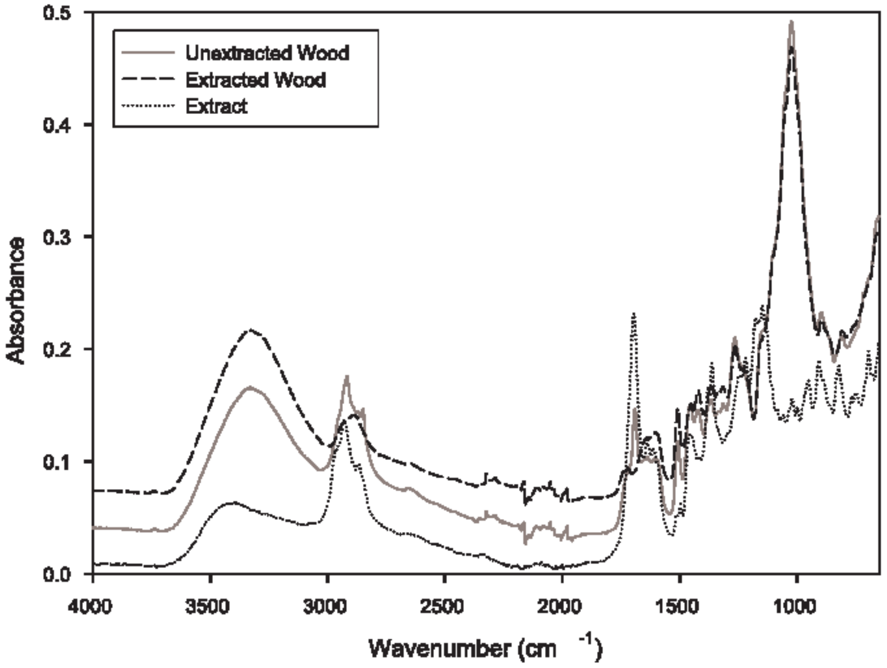
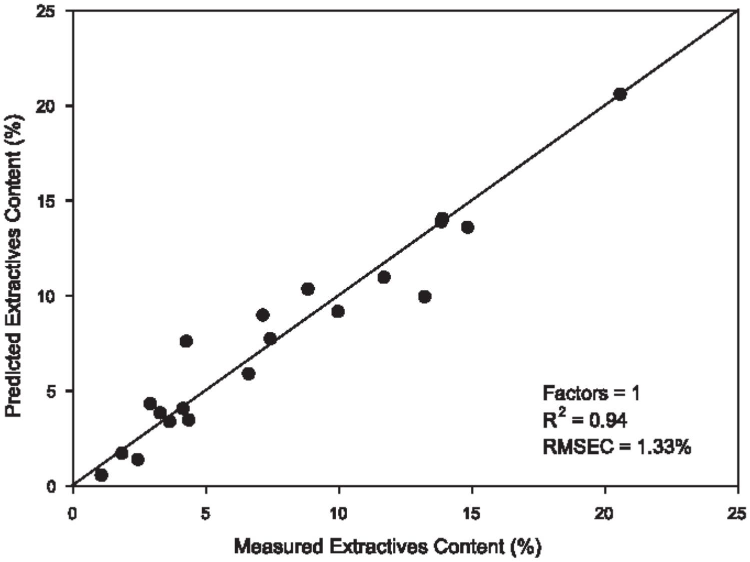
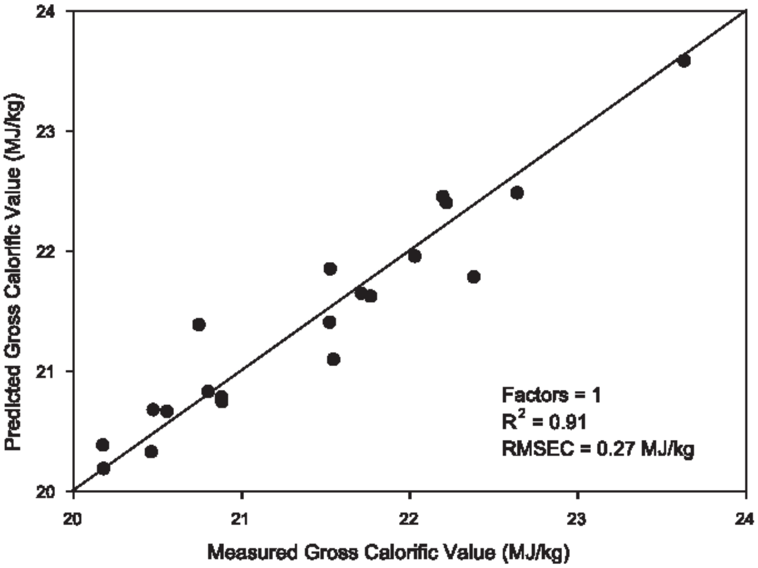
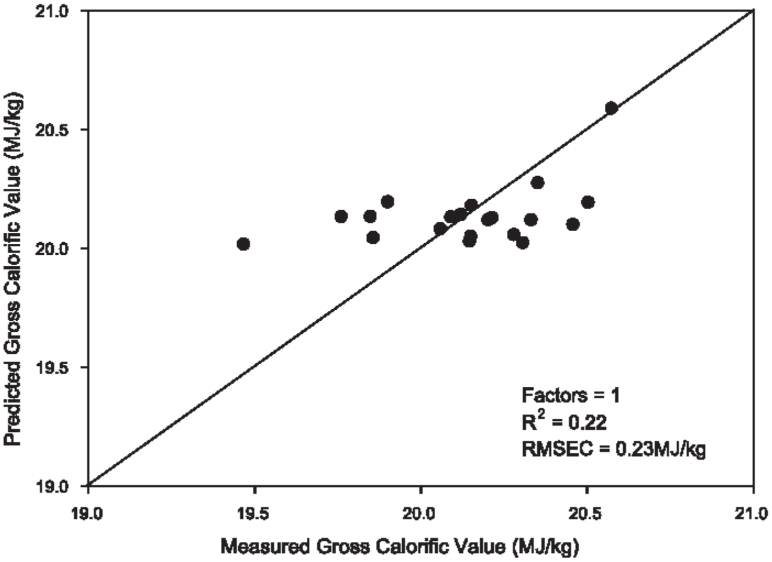


Figure 2: IR spectra of unextracted and extracted wood samples (including extract).

(From top to bottom)
Figure 3a: Calibrations for extractives content.
Figure 3b: Calibrations for GCV (unextracted).
Figure 3c: Calibrations for GCV (extracted).







Infrared Spectroscopy and Multivariate Analysis

Representative spectra from the extracted and unextracted samples are plotted in Figure 2. A spectrum obtained from a representative extract is also displayed. It can be seen that the spectrum for the unextracted wood is rather typical with bands between: 1000-1150 (C-O stretch), 1700-1750 (C=O stretch), 2800-3000 (C-H stretch), and 3100-3600 (O-H stretch) cm^{-1}. The spectrum of the extract, comprising mostly of resin and fatty acids, shows strong bands also between 1700 -1750 (C=O stretch) and 2800-3000 (C-H stretch) cm^{-1}. As one would expect, these bands are substantially reduced for the spectrum of the extracted sample.

Partial least squares (PLS) regression was undertaken to determine both extractives content and GCV. In Figures 3 (a), (b), and (c) the predicted values represent the calorific values determined from the IR data. Figure 3(a) shows the calibration for extractives content, and its strong calibration statistics (R^2 = 0.94; RMSEC = 1.33%) with the wide range of extractives contents. Kelley et al. (2004) also reported good calibration statistics for extractives content but using NIR spectroscopy. Milled samples of loblolly pine were analyzed, with similar extractives contents ranging from 2.8-26.9%, resulting in a R^2 of 0.86 (R = 0.93) with a RMSEC of 2.3%. The result for the regression with GCV was similar to the extractives content with a strong correlation (R^2 = 0.91; RMSEC = 0.27 MJ/kg), as shown in Figure 3(b). Maranan and Laborie (2007) obtained a R^2 of 0.84 (R = 0.97) when analyzing milled wood cores of hybrid poplar, while Gillon et al. (1997) obtained R^2 values between 0.76-0.79 from milled samples of twigs and leaves from two shrub species. The same GCV regression was performed with the extracted samples; however, this provided a poor R^2 =

0.22 with a RMSEC = 0.23 MJ/kg (Figure 3(c)). The absence of resin and fatty acids, as observed in the spectra of the extracted samples, appear to have played an important role in the lack of such a correlation.

Conclusions

GCVs determined from a set of longleaf pine trees were found to directly correlate with the extractives content. There was minimal variation of GCV for the extracted samples. IR spectroscopy coupled with multivariate analysis was applied to the samples, providing good predictions for calorific value and extractives content for the unextracted samples. The use of these techniques provided an indication of which chemical features played a significant role in such relationships. This method also provides a rapid means for determining fuel value, along with the well-established determinations (e.g., chemical properties).

Acknowledgments

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