RAPID ASSESSMENT OF CHEMICAL COMPOSITION, CALORIFIC VALUE AND SPECIFIC GRAVITY OF HYBRID POPLAR WOOD USING NEAR INFRARED SPECTROSCOPY

By

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A thesis submitted in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE IN MECHANICAL ENGINEERING

WASHINGTON STATE UNIVERSITY
School of Material and Mechanical Engineering

AUGUST 2006

To the Faculty of Washington State University:

The members of the Committee appointed to examine the thesis of Melchor C. Maranan find it satisfactory and recommend that it be accepted.

Chair

ACKNOWLEDGMENT

First, I would like to thank Greenwood Resources Company for their generous donation and support in this research. My research has been funded by Greenwood Resources DOE/SBIR under contract number 11W-3047-4454. I would like also to acknowledge National Renewable Energy Laboratory and Washington State University Extension Program at Puyallup, Washington for their contributions on supplying samples for my experiments.

Secondly, I would like to thank Dr. Laborie for her guidance and support throughout my years at WSU. Thank you for giving me the opportunity to work with you and I have greatly enjoyed it. I am also grateful for the help extended by my committee members.

Finally, to my officemates who supported me through my entire research. I sincerely am thankful for the time, efforts and constructive criticism you gave to me during group meeting.

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Abstract

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August 2006

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With a growing interest in renewable energy, hybrid poplars (HP) could be optimized for bioenergy production via direct combustion or conversion into cellulosic ethanol. This project, in collaboration with Greenwood Resources Inc., aims at developing analytical tools for rapidly assessing and screening traits of HP that are relevant to bioenergy production.

In particular, the ability of near infrared spectroscopy for determining the chemical composition, calorific value and specific gravity of HP was evaluated. The objectives of this study were: (1) to develop NIR calibration models for assessing the chemical composition of HP, (2) to develop NIR calibration models for assessing both calorific value and specific gravity of HP wood and (3) to evaluate whether parentage, age and growing site of HP trees affect the calorific value and specific gravity of the wood.

The chemical composition, energy content and specific gravity of HPs were reviewed and the correlations between wood chemical composition and energy content were established. The effectiveness of near infrared spectroscopy and multivariate analysis to develop calibration models for chemical composition of HPs were established. The study suggests that 1st derivative of the NIR spectral data are best suited for developing predictive models of the chemical composition of HP. Good calibrations were obtained for lignin, galactan and mannan contents with correlation coefficients higher than 0.90 while the model quality for xylan, ash and S/G ratio was slightly lower. On the other hand, the calibration models for extractives, glucan and arabinan contents gave poor results.

Furthermore, NIR calibration models were developed for predicting calorific value and specific gravity of HP. Differences in calorific values and specific gravity between parentages, ages and growing sites were also evaluated. Good correlation coefficients for calorific value and specific gravity, 0.81 and 0.84 respectively, were obtained from calibration models based on the 1st derivative spectra. Parentages, tree ages and growth sites had no significant effect on the HP calorific value. On the other hand, a significant difference in wood specific gravity was found between HP woods of distinct parentage and age. The growing site of the tree did not affect wood specific gravity.

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CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Biomass energy, one of the renewable energy resources, is increasingly considered as an alternative source to fossil fuel. This demand is attributed to diminishing fossil fuels and environmental concerns such as global warming, air and water pollution (Graham, 1995; DiPardo, 2002; Perlack *et al.,* 2005, Wu *et al.,* 2005). Furthermore, the US currently strives to reduce its dependence on foreign oil. With this goal, U.S. Department of Energy (DOE) Biomass Program aims to promote an integrated approach to the simultaneous production of liquid fuels, power, and products. Such a "biorefinery" would produce a suite of bioproducts much in the manner of an oil refinery (Garman, 2004), so as to make production costs more competitive in the overall energy market place.

GreenWood Resources is promoting hybrid poplar (HP) woods to play an important role in the future renewable energy industry. It is hoped that through hybridization techniques, HP clones can be developed as energy crops - such clones should have high efficiency biomass energy conversion either by direct combustion or by ethanol production. To do this, a better understanding on selective hybridization of poplars is required. In particular, traits such as energy content and specific gravity must be enhanced. In addition, high sugar content, that are favorable for ethanol production must also be targeted in HP energy crop. Fundamental information such as chemical composition, energy content and specific gravity are therefore important aspects that must be considered to assist the selective hybridization of poplars as an energy crop. Furthermore, several studies show that there is a significant effect on calorific value and specific gravity of hybrid poplar wood in terms of clones, tree age and growing sites (Blankenhorn *et al.,* 1985; Klasnja *et al.,* 2002; Movessessian, 2003; Thakaran *et al.,* 2003). Therefore, a better understanding of their clones, tree age and growing sites should also be considered.

Wood chemical composition is standardly determined using conventional wet chemical analysis (Browning, 1967). Wood energy content is determined by bomb calorimetry (ASTM E870-82), whereas, the wood specific gravity can be measured using water displacement and ovendrying method (ASTM D 2395-02). These methods often require extensive laboratory work, thus preventing their common use as assessment techniques for optimizing HP as an energy crop. As a result, analytical tools (fast, inexpensive, and reliable) to determine these three properties – chemical composition, calorific value and specific gravity- are needed.

Near-infrared (NIR) spectroscopy together with multivariate analysis have recently emerged as a powerful analytical technique to quickly estimate a wood property of interest (So *et al.,* 2004). Several studies have showed that NIR could be used to predict the chemical composition of wood (Bailleres *et al.,* 2002; Ferraz *et al.,* 2000; Kelley *et.al.,* 2004a, 2004b; Schimleck *et al.,* 1997). Gillon *et al.,* (1996) has also demonstrated the potential of NIR spectroscopy for determining the energy content of forest fuels. More so, different studies have shown that NIR analysis could be used to predict wood densities (Hauksson *et al.,* 2001; Hoffmeyer and Pedersen, 1995; Schimleck *et al.,* 2003a, 2003b).

NIR spectroscopy method allows measuring the absorbance of the wood sample with the use of near infrared light. The translation from measured absorbance values to wood property of interest is done through multivariate analysis techniques. This allows the development of a calibration model for the desired properties of wood (e.g. chemical content). Such a calibration model can be used to predict values of wood properties for unknown samples.

This research has 3 objectives 1) to develop calibration model that would help to find a rapid screening tool for assessment of chemical composition of HP, 2) to develop calibration models for both calorific value and specific gravity of HP wood and 3) to evaluate if there is variability of calorific value and specific gravity in terms of their parentages, ages and growing sites. This thesis comprises three parts; 1st part: review of literature, 2nd part: the use of NIR spectroscopy for predicting chemical composition of HP wood and the 3rd part: predicting the calorific value and specific gravity of HP wood using NIR spectroscopy.

1.2 Significance of the Study

This study is in collaboration with GreenWood Resources project to optimize hybrid poplar clones for the production of energy both in direct combustion and ethanol production. The use of NIR spectroscopy coupled with multivariate analysis will allow an easy, fast and reliable determination of chemical composition, calorific value and specific gravity of hybrid poplars. As a result, NIR spectroscopy will assist in a strategic and cost effective hybridization of HP.

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CHAPTER 2

REVIEW OF LITERATURE

2.1 Introduction

The review first presents the characterization of hybrid poplar (HP) wood. It focuses on the chemical composition, energy content and specific gravity of HP. Correlations between wood chemical composition and energy content have been established in the literature; they are reported next. These correlations will help define the constituents that dictate the energy traits of HP and guide for optimization. Finally, combination of NIRS and multivariate analysis as a chemometric tool for wood properties is reported.

2.2 Chemical Composition of Hybrid-Poplars

The genus *Populus* includes trees that are commonly called "poplar'. Poplar woods belong to hardwood species. Wood is made up of three main polymers, lignin, cellulose and hemicellulose. It also contains extractives and ash. The wood chemical composition is reviewed in detail below. Understanding on their chemical constituents should be considered in selective tree hybridization for optimizing HP as energy crop.

2.2.1 Holocellulose

Holocellulose is a term used to denote the polysaccharides present in wood (Farmer, 1967), cellulose and hemicellulose. Cellulose, the principal constituent, constitutes approximately 40 to 45 percent of dry wood by mass (Sjöström, 1981). It consists of as a linear-high molecular weight polymer built up exclusively of β-D glucose units (Fengel and Wegner, 1984) that is linked by β-1.4 linkages (Fig. 2.1). Cellulose chains are linked laterally by hydrogen bonds into linear bundles, therefore forming crystalline structures (Goldstein, 1977).

The simplest formula of purified cellulose is $C_6H_{10}O_5$; that has the composition of carbon 44.4%, hydrogen 6.2% oxygen 49.4% (Farmer, 1967). In practice, pure cellulose which consists entirely of glucose residues is not easily prepared from wood (Farmer, 1967). Instead, α-cellulose is commonly determined by wet chemistry analysis of wood. α -cellulose is the insoluble residue that remains when crude cellulose preparations are treated with strong alkali under prescribed conditions (Farmer, 1967). In other words; it is the sodium-insoluble cellulose.

On the other hand, hemicelluloses account for 25 to 35% of dry wood mass: 27 ± 2 % in softwoods and 30 ± 5 % in hardwoods (Goldstein, 1977). Hemicelluloses differ from cellulose; in that they are constituted of several sugar units, assembled into shorter branched chains (Fengel and Wegner, 1984). Glucose, mannose, galactose, xylose, arabinose, 4-*O* – methylglucuronic acid and galacturonic acid residues are the sugar units of hemicelluloses (Pettersen, 1984). The individual hemicelluloses are named according to the sugar units of which they are built up, thus, we have xylan (xylose units), mannan (mannose units), arabinogalactan (arabinose and galactose units) etc. (Farmer, 1967). For hardwood; arabinogalactan, glucuronoxylan, glucomannan and pectin are the most common components of hemicellulose (Petersen, 1984). Moreover, glucuronoxylan content varies from 15% to 30% of dry wood depending on the hardwood species (Sjöström, 1981). Besides xylan, hardwood contains 2-5% of a glucomannan (Sjöström, 1981), 1-5% of arabinogalactan and pectin (Petersen, 1984).

The chemical composition of various poplars has been reported in the literature. For instance, Blankenhorn *et al.* (1985a) determined α-cellulose and hollocellulose content of hybrid poplar woods that varies from 38.2 % to 45.5% and 64.3% to 80.2% respectively. The poplars examined in this study were *maximowiczii* x “Berolinensis’, ‘Angulata’ x deltoides, ‘Angulata x *trichocarpa*, *nigra* x *laurifolia*, ‘Betulifolia’ x *trichocarpa*, *deltoides* x *trichocarpa* (DxT) and *maximowiczii* x *trichocarpa* (MxT). Klasnja *et al*. (2003) reported a mean value 75.3% (72.4% -78.1%) of hollocellulose contents from 40 clones of eastern cottonwood (*P. deltoides).* Olson (1985) reported an α-cellulose content ranging from 48.2% to 55.8% of oven dry, extractive-free wood with an average of 51.1% for seventy-five eastern cottonwood (*P.* deltoides) clones. In another study, mannan, arabinan and xylan contents from hybrid poplar woods averaged of 2.7%, 0.5% and 17% respectively (Tuskan *et al.,* 1999).

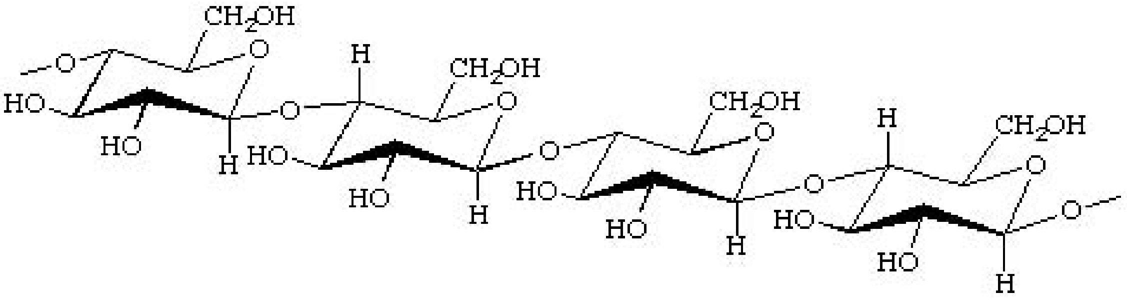

Figure 2.1. Chemical structure of cellulose (Eero Sjöström, 1981)

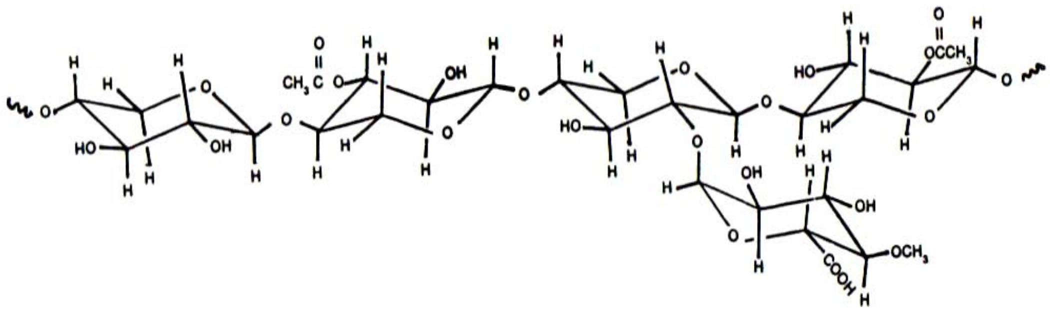

Figure 2.2. Partial molecular structure of glucuronoxylan (Pettersen, 1984)

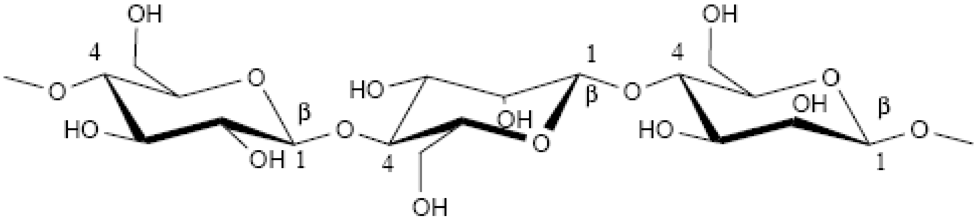

Figure 2.3. Partial molecular structure of glucomannan (Laine, 2005)

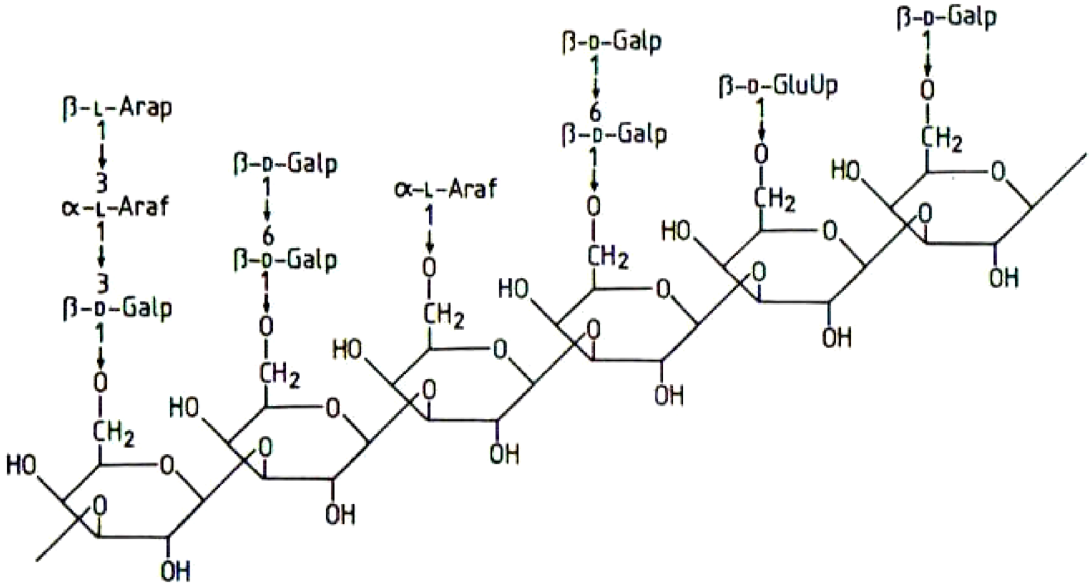

Figure 2.4. Partial molecular structure of arabinogalactan (Fengel and Wegner, 1984)

2.2.2 Lignin

Lignin, a complex polymer, accounts for 25% to 31% of softwood mass and 16% to 24% of hardwood mass (Goldstein, 1977). It is the binder that holds cellulose fibers and hemicellulose together. The three basic building units of lignin are parahydroxyl, guaiacyl and syringyl alcohol. Hardwood lignin is built essentially on syringyl and guaiacyl units, present in one to one ratio (Goldstein, 1977).

Blakenhorn *et al.* (1985b) measured an average lignin content of 18.6% in three *populus* hybrid clones (*maximowiczii* x 'Berolinenses', 'Angulata' x *trichocarpa* and *maximowiczii* x *trichocarpa*). White (1987) reported an acid-soluble lignin content of 4.5, 5.8, 5.0 and 4.7% of oven-dry wood for maple, yellow poplar, red oak and basswood, respectively. In addition, average klason lignin content of 18.1 to 22.5% from the four hardwood species was determined (White, 1987). Mészáros *et al.* (2004) also measured a 24 to 30% klason lignin content from young poplar wood shoots (*Populus* x *euramericana* and *Populus* x intermericana).

2.2.3 Extractives

In addition to the hollocellulose and lignin components, wood contains varying amounts of substances called extractives. Although wood extractives are usually considered minor components by mass, they are believed to play an important role in determining energy content in biomass (Kenney *et al.,* 1990). Extractives include tannins, fats, starch, waxes, proteins, phenolics, simple sugars, alcohols, resins, and essential oils. Extractives function as intermediates in tree metabolism, as energy reserves, and as internal defense against microbial attack. They also contribute to properties of wood such as color, odor, taste, decay resistance, density, flammability, and moisture absorption. Blakenhorn *et al.* (1985b) reported average 9.9% extractive contents in various *Populus* hybrids clones. In White's study (1987), the extractive content of yellow poplar wood was determined to be 3.8%.

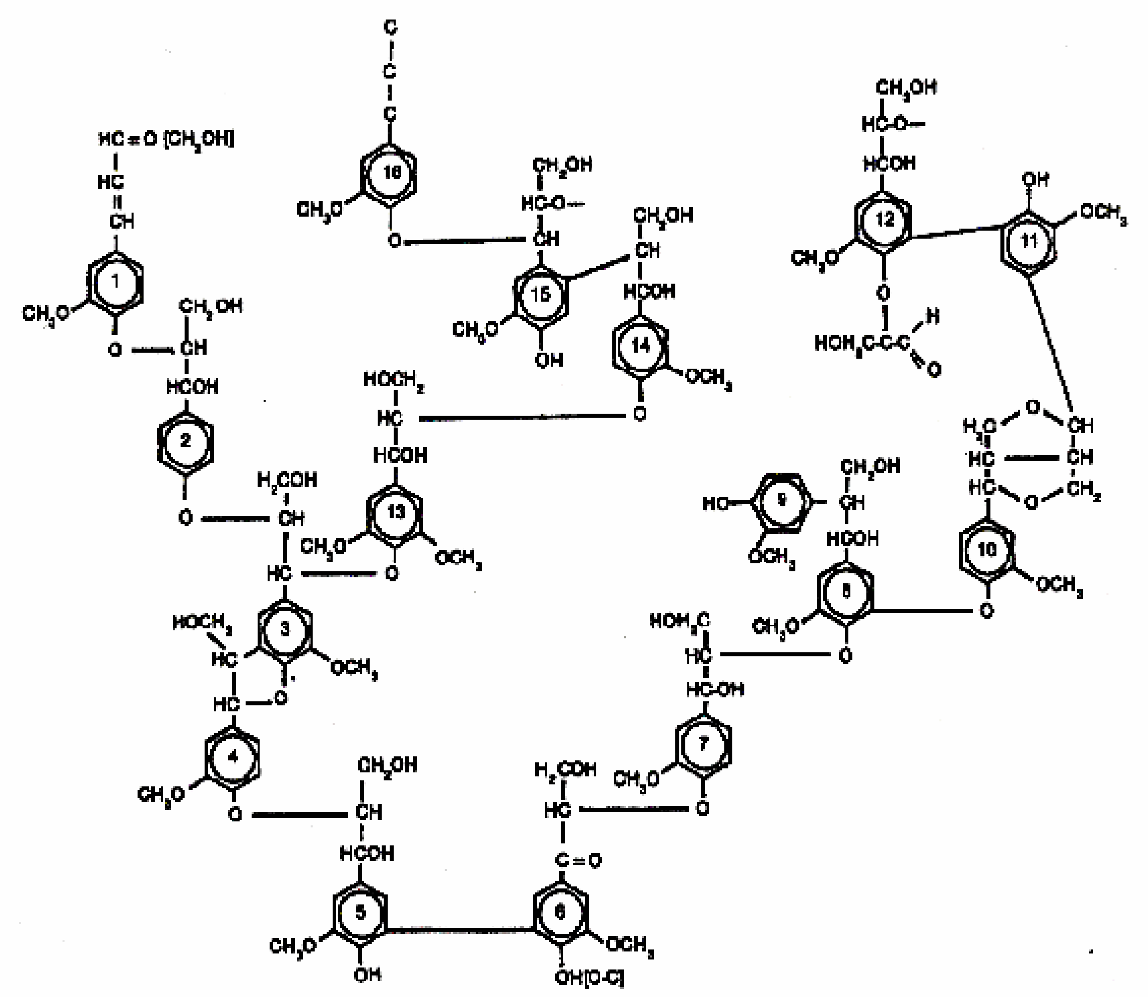

Figure 2.5. Partial molecular structure of lignin (Pettersen ,1984)

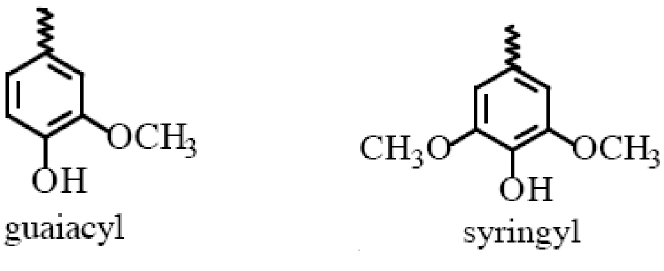

Figure 2.6. Partial molecular structure of guaiacyl and syringyl units (Fengel and Wegner, 1984)

2.2.4 Ash Content

Following a complete combustion of wood, ashes remain as the solid residue. Ash is made of inorganic materials, mostly calcium, potassium and magnesium (Panshin and de Zeeuw, 1970). Klasnja *et al*. (2002) reported an ash content for clone poplar wood (*P. deltoides* and *P. euramericana*) between 0.47% and 1.16%, whereas Bowersox *et al.* (1979) measured average ash contents of 0.8% from seven hybrid poplar clones (*maximowiczii* x "Berolinensis', 'Angulata' x deltoides, 'Angulata' x *trichocarpa*, *nigra* x *laurifolia*, 'Betulifolia' x *trichocarpa*, *deltoides* x *trichocarpa* and *maximowiczii* x *trichocarpa*).

2.3 Wood Calorific Value

Calorific value is defined as the amount of energy released from the combustion of a unit mass of a combustible material. Two calorific values are generally defined; these are the higher heating value (HHV) and the lower heating value (LHV) (ASTM E711-87, 2004). The HHV, or gross calorific value or gross heat of combustion, is the amount of heat or energy produced by the complete combustion, in a bomb calorimeter, of a unit mass of a sample in an oxygen atmosphere such that all water in the products remain in liquid form. This is the value frequently reported in the literature (Kenney *et al*., 1990). On the other hand, LHV is the amount of heat or energy produced by complete combustion, assuming that water remains as vapor. HHV is easily converted to LHV (Kenney *et al*., 1990, Nunez-Riguerra *et al*., 1996). Different calorimeters have been used to determine gross calorific value. Harada (2001) used a cone calorimeter to determine the heat release rate and time of ignition of nine wood species. Nunez-

Riguerra *et al.* (1996) used a static bomb calorimeter to determine HHV of forest wastes. Krigstin *et al.* (1993) used a differential scanning calorimeter (DSC) to evaluate the energy characteristics of hybrid willow. The authors argue that compared to conventional adiabatic oxygen calorimeter, a DSC gives more accurate measurement as it accounts for heat dissipation, incomplete combustion and heat of vaporization. However, standard methods (ASTM E870-82) recommend the use of an oxygen-bomb calorimeter to measure gross calorific values of wood. Based on these methods, calorific values of wood vary between 15 and 25 KJ/g (Harada, 2001; Krigstin *et al.,* 1993).

Several studies have focused on evaluating the calorific value of poplar wood and its dependency on tree characteristics. For instance, for *P. deltoides* and *P. euramericana*, the HHV of age 1, 2 and 12 year old oven dry poplar was measured in the 16KJ/g to 24KJ/g range (Klasnja *et al*., 2002). In this study, the highest calorific value was measured in 2 year old trees compared to 1 year and 12 year old trees; also the HHV of bark was lower than with that of wood (Klasnja *et al*., 2002). Therefore, the study suggests that tree age is an important factor of HHV in hybrid poplars and wood itself is more favorable in HHV compared to bark. Blankenhorn *et al.* (1985a) measured the HHV of seven *Populus* hybrid clones from age 1 to 8. These clones include wood, bark and wood/bark specimens that exhibited variations from 17.7 to 20 KJ/g. The study showed that the heat of combustion within and among clones was significantly different for some wood, bark and wood/bark specimens. However, no apparent trends were found in these clones with regards to their ages. Seven yellow poplar woods were also evaluated by Harris (1984) and the effect of location in the tree was determined. The average HHV of stem wood was 19.40KJ/g and branch wood had an HHV of 19.37KJ/g.

The result of this study showed that there was no significant difference in HHV due to position in tree. In the study of energy values of nine *populus* clones by Strong (1992), calorific values of wood were found to vary based on location. Strong (1992) measured a mean calorific values of nine *populus* clones ranging from 19.41KJ/g to 19.91KJ/g. The calorific values increased up the stem in this study and branch calorific values were always higher than those other components. In addition, Strong (1992) did not find any significant different between clones. This result agrees with the study of Bowersox *et al.* (1979). While in the study of Neenan *et al*. (1979), the calorific value of yellow poplar for wood, bark, branches, twigs and leaves was on the range of 19.39 KJ/g to 21.21 KJ/g but no significant difference was found among wood parts. Geyer *et al*. (2000) reported that the HHV of hybrid poplar wood was on the order of 18.90 KJ/g. In this study, no significant difference was found between clones. Movessessian (2003) also found no significant difference in energy content between clones. However, this study observed that growing sites had a significant impact on energy content of branch wood ($p = 0.003$). In addition, it was also detected that there were significance difference in energy content between various tree fractions, including trunks, branches and leaves.

Based on the studies presented above, clones seem to be a minor factor of calorific value. Wood locations within the tree, tree age and growing sites, on the other hand, affect the HHV of hybrid poplar. In connection with these, we will investigate if there is a variability of HHV in terms of parentages, ages and growing sites.

2.4 Wood specific gravity

Wood specific gravity is one of the important factors in wood combustion. High specific gravity is important regardless of end-product use because there is greater mass of material for a given volume, which lowers transportation costs. Combining high specific gravity with high biomass production maximizes feedstock output on an area basis (Tharakan *et al.,* 2003). Thakaran *et al.* (2003) studied seven hybrid poplar clones and found that the specific gravity was on the range 0.33 to 0.37 g cm^{-3}. For three year old *P. deltoides* clones, Olson *et al,* 1985 a wide range in specific gravity among clones from 0.27 to 0.39 g cm^{-3}, revealing a relatively wide range in specific gravity among clones. Moreover, Thakaran *et al.* (2003) stated that wood specific gravity increases with age. These studies warrant further study on the effect of parentages, ages and growing sites on the specific gravity.

2.5 Correlations between chemical composition and wood energy potential

A number of measurable wood traits have been suggested as being important to improving the quality of biofuel feedstock, and some of these traits may correlate with one another. Two end products that will be addressed in this review are combustible feedstock and feedstock for ethanol conversion. In several instances, a high level of a particular component may be better for one or another end product, but usually not both. On the other hand, certain traits may be good for one end product while neutral for the other. In terms of tree breeding approach to plan specific traits, it will be necessary to at least screen and separate them based on the end-product use.

Several correlations between wood calorific value and chemical composition in terms of polymeric and elemental composition have been established. For instance, Demirbas (2001) established a highly significant linear correlation between HHV of the biomass fuel and the lignin content. The biomass fuels included were generally from straw, leaf, wood, stalks, bark, olive, and nut shell. Higher lignin contents therefore lead to higher HHV. Similarly, White (1987) correlated the HHV of wood (4 softwood and 4 hardwood species) with lignin and extractives contents. It was found out that extractives raised the higher heating values of the wood samples tested in addition to higher lignin content; softwoods are considered to have greater HHV because of their resin or extractive contents. These observations are consistent with the individual calorific value of wood polymers. According to Fuwape (1989), the gross heat of combustion for lignin and extractives of Gmelina (*Gmelina arborea*) is on the order of 25 KJ/g. On the other hand, cellulose and hemicellulose exhibit a lower heat of combustion, in the 17-20KJ/g range.

According to Kenney *et al.,* (1990), hollocellulose (cellulose and hemicellulose) is also the raw material upon which ethanol production using wood feedstock is based. Cellulose consists of 6-carbon (6-C) sugars while hemicellulose contains a mixture of 5- and 6-C sugars. Based on the report of Dinus (2000), efficient conversion to ethanol requires 6-C sugars, whereas 5-C sugars inhibit the conversion process. Dinus (2000) added that higher cellulose content translates to greater ethanol production and reduction of hemicellulose would allow an increase in the amount of cellulose available. In addition, the study performed by Kenney *et al.,* (1990), the lignin content of a particular species, family, or clone may have an impact on its value as a feedstock for energy conversion, pulping or chemical extraction process. From an energy standpoint, lignin has the energy content similar to coal (Dinus, 2000), so selecting and breeding for high lignin clones would be advantageous for the use as a combustible feedstock. However, wood with low lignin content is easily converted to ethanol. Moreover, although ash represents only minor proportion by weight, it is believed to be major determinant of the combustion behavior of a material (Krigstin, *et al*., 1993). Additionally, low ash content has also been suggested as important in conversion to ethanol (Dinus, 2000). High ash content of wood is less desirable for fuelwood as it is characterized as non combustible products and reduces heat of combustion (Klasnja *et al.*, 2002). Since ash contains the inorganic elements in the biomass which are important macronutrients to the trees, biomass production strategies will need to consider removal of these micronutrients and their replenishment on the site (Blakenhorn *et al*., 1985a). Furthermore, small quantities of tannins or phenolics from extractives can inhibit enzymatic breakdown of cellulose during the conversion to ethanol (Dinus, 2000).

Based on the aforementioned research, it is expected that high lignin and extractive contents and low levels of ash and hollocellulose of wood offer a higher gross calorific value. However, the ideal feedstock for conversion to ethanol should have high levels of cellulose content and low levels of lignin, hemicellulose, extractives and ash.

2.6 Near Infrared Spectroscopy

Infrared spectroscopy measures the wavelength and intensity of the absorption of near infrared light by a sample. This is commonly obtained by passing an infrared radiation through the sample and determining the amount of radiation that is absorbed at a particular energy or wavelength. In near-infrared spectroscopy, the wavelength extends from 780 nm (12, 800 cm^{-1}) to 2,500 nm (4,000 cm^{-1}) (Antii, 1999). It is energetic enough to excite overtones and combinations of molecular vibrations to higher energy levels. When the infrared (IR) radiation is absorbed by organic molecule, the energy is converted into molecular motions called vibrations. These molecular vibrations would allow the absorption bands to give rise throughout most of the infrared region of the spectrum. The absorbance, A, at each wavelength is measured with a spectrometer. The most common and significant advances of NIR techniques is based upon in mathematical process of Fourier transformation (FT).

NIRS is particularly effective at revealing absorption bands relevant of C-H, O-H, and N-H chemical functional groups (Skoog D. A. *et al.*, 1998). For this reason, NIRS has shown promise as a nondestructive evaluator of the properties of wood-based materials (Kludt, 2003*)*.

Figure 2.7 represents the typical components of Fourier Transform-Infrared (FT-IR) spectrometer. From the source, radiation containing all IR wavelengths emerges. It is split into two beams, one of fixed length (via fixed mirror) and the other of varying length (via movable mirror). Both beams are recombined and pass into constructive and destructive interferences through the sample. When the recombined beam hits the sample, the sample absorbs frequencies, so that their intensities are reduced. The interferogram, that contains information on all frequencies of the beam, is Fourier transformed from the time domain to the frequency domain. (Silverstein and Webster, 1998). This operation is reiterated from each wavelength of the beam so as to give rise to the complete IR spectrum. The detector also produces signal noise in response to the infrared beam. Liquid nitrogen is used to cool down and reduce the amount of noise that develops in the detector. The detector's output is converted from the analog to digital form and transferred to the computer for a complete IR absorption spectrum.

In the 1980s, Near-Infrared (NIR) techniques transformed from being considered an ambiguous characterization tool to a well-defined qualitative and quantitative analysis with broad uses in numerous fields of science (Antii, 1999). Recent work has demonstrated the usefulness of the technique for the forest products industry. Together with the multivariate analysis, NIR has become a powerful chemometric tool for modeling properties of materials, wood and wood-based products in particular.

Of particular interest, Gillon *et al.* (1997) used near infrared spectroscopy as a fast estimation technique of the calorific value of forest fuels. In this study, fifty fuel samples, such as broad-leaved trees, conifers, shrubs, fern and grasses from the Mediterannean forest, (17.1 – 24.6 MJ/kg) were used to establish a calibration model between NIR spectra (1100-2500 nm) and calorific values. The second derivative NIR spectra were used in the calibration model. The calibration equations were calculated using the modified partial least squares regression (PLS) method (Martens and Jensen, 1982 ; Shenk and Westerhaus, 1991). The calibration model was validated on two sets of 15 samples of shrub species, belonging to *Arbutus undeo L* and *Erica arborea L*. The coefficients of determination (r^2) of the regression between the predicted and measured calorific value were 0.79 and 0.76, respectively.

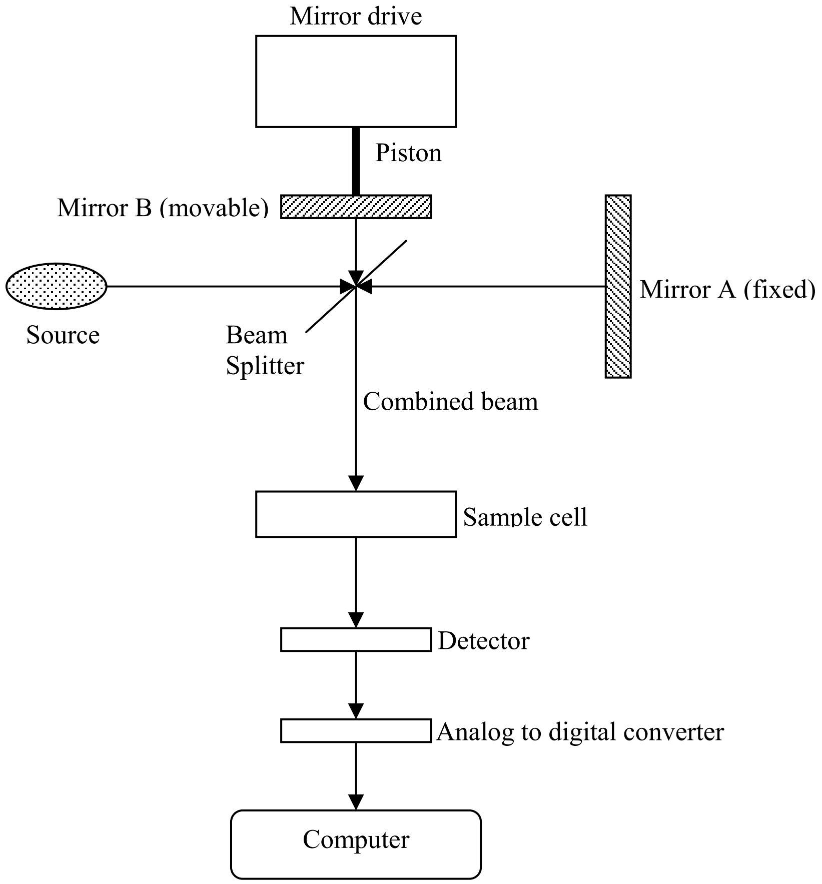

Figure 2.7. Schematic diagram of an FT-IR spectrometer

Similarly, Kelley *et al.* (2004a) predicted the chemical composition of 27 solid loblolly pine woods with the use of near infrared spectroscopy. Forty-two samples were used in the calibration model. Full near infrared spectral range (500 nm – 2400 nm) and the reduced range 650 nm – 1150 nm were both considered to build the model. The spectra were averaged over 10-nm interval. Lignin, glucose, xylose, mannose, galactose and extractives content were measured using traditional wet chemistry techniques. The chemical composition was then correlated with the NIR spectra using PLS methods. The correlations were very strong with correlation coefficients generally above 0.80.

The chemical composition of a variety of agricultural biomass samples was also analyzed by Kelley *et al.* (2004b) with near infrared spectroscopy. The analysis showed that NIR spectroscopy with multivariate analysis could be used to accurately predict the chemical composition of agricultural biomass samples. The correlation coefficients (R) between the measured and predicted values were high for the three major components such as lignin ($R = 0.71$), glucose ($R = 0.87$) and xylose ($R = 0.71$) while the other four minor sugars (mannose, galactose, arabinose and rhamnose) gave weaker results ($R < 0.57$).

Bailleres *et al*. (2002) also demonstrated that NIR spectroscopy and PLS method can be used effectively to predict the lignin content, extractive content and S/G ratio of eucalyptus wood. Coefficient of determination (r^2) was good between the wet chemistry measurements of the constituents and the predicted values ranging from 0.78 - 0.90.

Ferraz *et al.* (2000) estimated the chemical composition of biodegraded pine and eucalyptus wood by NIR spectroscopy together with multivariate analysis. PLS models were able to predict glucan, lignin and polyoses content with r^2 values higher than 0.86 in most cases.

NIR spectroscopy has also been examined by Schimleck *et al.*, (1997) as a rapid means of determining carbohydrates, cellulose, glucan, hemicellulose and xylan content of eucalyptus woods. In this study, the second derivative of NIR spectra was used to develop the models with very good coefficients of correlation ($R > 0.92$).

NIRS techniques have also been used to predict the physical and mechanical properties of wood. For instance, Schimleck *et al.* (2003a) attempted to predict stiffness, air-dry density and microfibril angle (MFA) of *eucalyptus nitens* wood from NIR spectra over a range of 1100 nm – 2500 nm. The coefficients of determination (r^2) ranged from 0.69 for MFA to 0.93 for density. For *Pinus taeda*, good predictions were also possible for density ($r^2 = 0.87$) and stiffness ($r^2 = 0.95$) (Schimleck, *et al.,* 2003b). Moreso, Hauksson *et al.,* 2001 predicted wood density of Norway spruce and found good correlations with a minimum root mean square error of prediction (RSMEP) of 0.82 to 0.94 based on NIR spectra of wood samples. This result is comparable with the study of Hoffmeyer and Pedersen, 1995, where they showed that the wood densities of Norway spruce are easily detectable by NIR. Kludt, 2003 conducted also a study to predict modulus of rupture (MOR) and modulus of elasticity (MOE) of clear wood specimens of common Inland Northwest species. Spectra were collected over 1000 nm – 2500 nm and they were pre-treated to 1st and 2nd derivative prior to statistical analysis. MOR and MOE were well predicted from the NIR spectra with R ranging from 0.88 to 0.92. It was concluded that 1st derivative spectra were the best choice in the calibration model compared with the raw and 2nd derivative spectra. Furthermore, more studies have been conducted to use NIRS to predict the physical and mechanical properties of wood (Thumm & Medder 2001, Gindl *et al.* 2001, Hoffmeyer and Pederson 1995).

NIRS techniques had been also used for pulp and paper applications (Sefara *et al.,* 2000). Calibration models were developed using normal spectra and 2nd derivative spectra to evaluate the difference in the spectral treatment. The 2nd derivative spectra resulted in an improved correlation model with $r^2 = 0.912$. The results imply that the pulp yield is well modeled by the NIR spectra.

With all of these studies, NIRS techniques coupled with multivariate analysis proved to be a powerful tool for modeling various properties of certain wood species.

2.7 Multivariate Analysis

Projection to latent structures (also known as partial least squares), PLS, is a very effective method for calculating the regression models from multivariate data. PLS is a regression extension of principal component analysis (PCA) designed to find the latent structure in the predictor block X and in the responses Y and to maximize the covariance between the two blocks (Antti, 1999). In the PLS method, the variation in the predictor block is described by the X-scores, T, while the corresponding variation in the response block is described by the Y-scores, U. The matrix of X-loadings, P, is calculated for each dimension. The X-loadings, P, gives the relationship between the X matrix and the X-scores matrix, T. There is also a set of Y-loadings called Q, which relates the Y-variables with the Y-scores, U. However, the loadings weights, W, represents the contribution in building the regression relationship between the X-variables and the Y-variables. The residual variances (error) matrices, E and F, are computed for the X-scores and Y-scores, respectively.

The decomposition of X and Y can be described by the equations (Esbensen, 2000):

Equation 2.1 $\mathbf{X = TP^T + E}$

Equation 2.2 $\mathbf{Y = UQ^T + F}$

The set of PLS regression coefficients can then be calculated by:

Equation 2.3 $\mathbf{B = W(P^TW)^{-1}Q^T}$

The estimated/predicted $\hat{Y}$ from new predictor X variables is then given by:

Equation 2.4 $\mathbf{\hat{Y} = XW(P^TW)^{-1}Q^T = XB}$

This step-by-step PLS regression modeling can be calculated using Non-linear Iterative Partial Least Squares (NIPALS) algorithm. Further details on NIPALS algorithm can be found elsewhere (Esbensen, 2000).

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CHAPTER 3

PREDICTING THE CHEMICAL COMPOSITION OF HYBRID POPLAR WOOD USING NEAR INFRARED SPECTROSCOPY

3.1 Abstract

Near infrared spectroscopy (NIRS) was used to develop chemometric models of hybrid poplars. In particular, lignin, glucan, galactan, mannan, xylan, arabinan, extractives and ash contents along with lignin syringyl/ guiacyl (S/G) ratio were considered. Partial Least Squares (PLS) method was applied to correlate chemical composition of wood with NIR spectral data. Calibration models were thus developed using the original NIR spectra along with the 1st and 2nd derivatives of the NIR spectra. For the chemical traits measured in this study, the 1st derivative spectral treatment provided the best calibration models. The correlation coefficients (R) for lignin, galactan, and mannan contents were high, generally above 0.90, while the xylan content, ash content and S/G ratio, provided lower correlations. The calibration models for extractives, glucan and arabinan contents were poor. This study demonstrates that NIRS coupled with multivariate analysis can be used to predict some specific chemical traits of hybrid poplars.

3.2 Introduction

Renewable energy resources are increasingly considered as an source to fossils fuels. Accordingly, the biomass program at DOE aims to develop technologies for converting biomass into biofuels and bioproducts so as to lessen the US dependence on foreign oil. Today, ethanol productions, biodiesel, biomass power and industrial process energy are the primary means to extract energy from biomass (DiPardo, 2002; Perlack *et al.,* 2005, Wu *et al.,* 2005). Biomass energy is also the only renewable alternative for liquid transportation fuel. In particular, cellulosic ethanol is gaining more and more attention (C & EN, 2006). Cellulosic ethanol is obtained by first hydrolyzing the biomass into sugars and then fermenting these sugars into ethanol using microbial conversion (Badger, 2002). For microbial fermentation, hexoses or 6-carbons such as glucose are the preferred sugars. On the other hand, pentoses or 5-carbon sugars are not easily converted into ethanol by naturally occurring organism (Dipardo, 2002). They can be converted to ethanol by genetically engineered yeast, but the ethanol yield is not high enough to make it the process economically attractive.

Wood primarily comprises three polymers, lignin (15 – 25%), cellulose (40 – 45%) and hemicellulose (25 – 35%). In addition, a variety of organic compounds is present in small amounts, the extractives along with minerals or ash (5 – 10%). Lignin is based on phenyl propane units and as such is not desirable for ethanol conversion (Dinus, 2000). Ashes and extractives are also detrimental to ethanol conversion. For instance, tannins and phenolics can inhibit the enzymatic breakdown of cellulose during the conversion to ethanol (Dinus, 2000). Cellulose consists of 6-carbon sugar units, glucose, while hemicellulose contains a mixture of 5 and 6-carbon sugars. Among hemicellulose C-6 sugars are the glucoses, galactoses and mannoses that make up galactoglucomannans in hardwoods. Xyloses and arabinose on the other hand are C-5 sugars. Higher cellulose content therefore currently translates into higher ethanol yield with currently available microorganisms. With advances in the bioprocess, hemicellulose and C-5 sugars may be as appropriate for ethanol conversion. In fact, some ethanol conversion processes consider the use of two populations of microorganisms to process the C-5 and C-6 sugars respectively.

As a result, an ideal biomass feedstock for conversion to ethanol should have high levels of cellulose and possibly hemicellulose while having low levels of lignin, extractives and ash (Dipardo, 2002)

Due to the high growth rate and ease of clonal propagation of hybrid poplars, these crops hold promises for utilization as biomass energy (Balatinecz and Kretschmann, 2001; Blankenhorn *et al.*; 1985; Dinus *et al.*, 2000; Movessessian, 2003). Provided that chemical composition is a heritable trait, hybrid poplar trees could be hybridized and optimized for high yield in sugars and low yields in lignin, ash and extractives. In this endeavor, the ability to rapidly determine the chemical composition and the specific sugar contents in hybrid poplar wood would greatly assist in optimizing tree selection and hybridization for energy crop. Unfortunately, chemical composition of wood is traditionally determined with wet chemistry analyses that are time-consuming and expensive. Over the last decade however, near infrared spectroscopy (NIRS) has emerged as an efficient technique for rapidly estimating the chemical composition of wood using empirical chemometric models (Bailleres *et. al*., 2002; Ferraz *et al.,* 2000; Kelley *et.al.,* 2004a, 2004b; Schimleck *et al.,* 1997). NIRS is a non destructive technique which requires minimal sample preparation. NIRS measures the absorption of NIR light by an organic material consisting of functional groups such as C-H, O-H and N-H (Ciurczak, 2001). Coupled with multivariate analysis, NIR spectral information can be used to develop calibration models of a chemical property of interest. Such calibration models relate the NIR spectra of a large number of specimens to their known chemical properties. The calibration model is then used to predict the chemical properties of wood for further samples based on their NIR spectra.

The present study fits within the broader program to optimize hybrid poplar plantations for biomass conversion into cellulosic ethanol. This project is collaboration with Greenwood Resources Inc., a large producer of hybrid-poplar in the Pacific Northwest. This particular study focuses on optimizing the chemical composition of hybrid poplar woods for conversion into ethanol. In that objective, this study seeks to develop and estimate NIRS calibration models for predicting the chemical properties of hybrid poplar wood that are relevant to ethanol conversion, namely the lignin, ash, extractives, C-6 sugars (glucose, galactose and mannose) and the C-5 sugars (xylose and arabinose).

3.3 Materials and Methods

3.3.1 Chemical Analysis

Forty hybrid poplar wood samples spanning a large range of chemical compositions were characterized for chemical composition at the National Renewable Energy Laboratory (NREL). Specifically, total lignin content, structural sugars, extractives and ash were measured based on protocols described by Browning (1967). In particular, C6 sugars, glucans, galactans and mannans, and C5 sugars, xylans and arabinans were measured. In addition, the syringyl/guaiacyl (S/G) ratio of lignin was determined by analytical pyrolysis techniques (Evans and Milne, 1987; Tuskan *et. al*., 1999a). The data summary is shown in Table 3.1.

3.3.2 NIR Analysis

Solid bark free specimens of the 40 hybrid poplar woods were received from NREL. Each specimen was milled to mesh #40 using a Wiley mill machine and subsequently oven-dried to constant weight. The specimens were then kept in a desiccator under drierite until near infrared scanning analysis. For NIR measurements, one gram of each samples were placed in a glass bottle and sealed by cap in order to maintain dryness. Near infrared spectra were collected on a Nicolet Nexus 670 FT-IR spectrometer, equipped with a white light source, XKBr beam splitter, liquid nitrogen cooled Thermo Nicolet MCT-A detector, and the Nicolet Smart Near-IR UpDrift probing port. Spectral absorbance values were collected over the range of 1000 to 2500 nm at 1 nm interval. Two spectral measurements were performed and averaged per specimen, each consisting of 40 scans. A background correction was accomplished on a white ceramic standard at 10- minute intervals during the NIRS spectra scanning process.

3.3.3 Multvariate Analysis

Approximately two-thirds of the samples were randomly selected for developing the NIR calibration model and one-third for validating the model (Table 3.1). To establish calibration models, the spectral data were considered in three different ways; original spectra, 1st spectral derivative and 2nd derivative. The Savitsky-Golay differentiation method was used to generate the 1st and 2nd derivatives of the spectra (Esbensen, 2000; Kludt, 2003). This method calculates derivatives of any order based on a polynomial approximation of the curves. Calibration between the NIR spectral measurements (raw data, 1st and 2nd derivative) and the various chemical constituents were developed using the software package Unscrambler® 7.6 CAMO for the multivariate analysis, partial least square (PLS) analyses. For PLS analysis, the NIR spectra (predictor) were combined into X-matrices while the information of the chemical properties (response) were established as the Y-matrices. Prior to PLS analysis, the X-matrix and Y-matrix were mean centered variance normalized. The Y-matrix was scaled by multiplying the original value by the inverse of the standard deviations to make up the large difference in magnitude. However, the X-matrix was not scaled by the inverse of the standard deviation to avoid over-emphasis of noise wavelengths (Esbensen, 2000). Two algorithms, the PLS-1 and PLS-2 were used in the calibration models. The PLS-1 permits only one Y-variable to be projected against the X-matrix at a time. On the other hand, PLS-2 allows several Y-variables to be projected against the X-matrix at once. Both PLS-1 and PLS-2 models were constructed for different response variables. The specimens in the validation set were used to evaluate the quality of the PLS models. They were assessed based on the correlation coefficient (R) between predicted and measured value and based on the root mean square error of predictions (RMSEP). In addition, the number of PLS components or factors used to form the calibration model was determined by observing the response of the residual of the Y-variance with added factors (Kelley *et al.,* 2004b). The model was considered complete when the addition of a new factor no longer decreased the residual Y-variance.

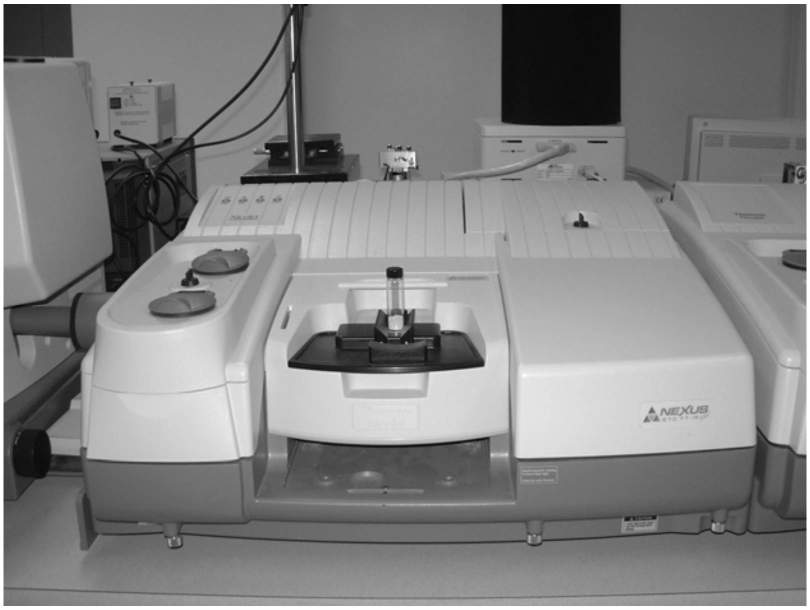


Figure 3.1. Nicolet 670 FT-IR Spectrometer with Smart Near-IR UpDRIFT installation.

3.4 Results and Discussions

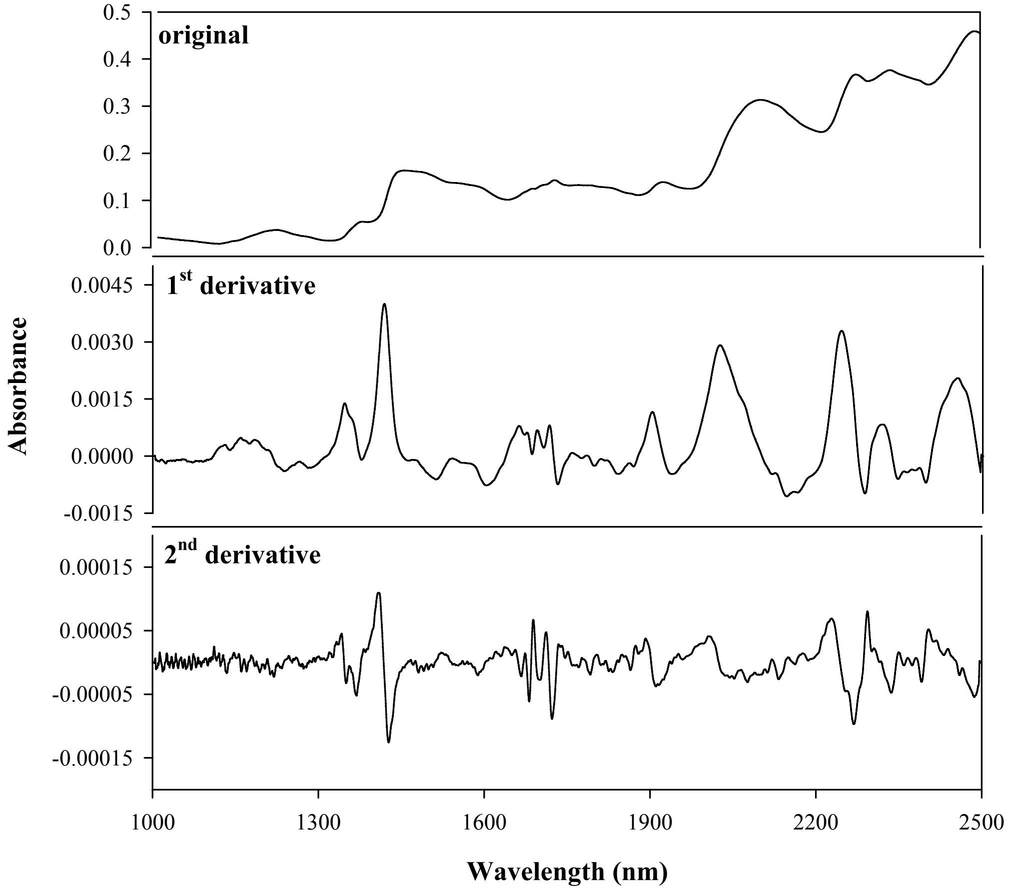
The hybrid poplar samples displayed a wide range of chemical traits (Table 3.1 and Table 3.2). Extractives, ash and lignin content ranged between 1.1 – 6.5%, 0.3 – 2.4% and 21.1 – 28.2% respectively. Glucan, xylan, galactan, arabinan and mannan contents ranged between 40.3 - 48.6%, 12.8 – 18.9%, 0.6 – 2.5%, 0 – 1.2% and 1.4 – 3.3% respectively while the S/G ratio varies from 1.1 – 2.5. The lignin contents were high while the extractives content were low compared to the study reported by Blankenhorn *et. al*. (1985). However, the ash contents displayed large variations compared to those of previous studies (Klasnjan *et. al*. 2002, Bowersox *et al.*, 1979). Furthermore, values of some sugar units were measured in a similar range than previous studies (Tuskan *et al.,* 1999b).

Table 3.1. Descriptive statistics of the chemical composition of hybrid poplar woods.

Chemical Composition	Calibration set No. of samples	Validation set No. of samples	Min.	Max.	Average
Extractives	27	13	1.13	6.54	3.04
Ash	27	13	0.27	2.43	0.85
Lignin	27	13	21.09	28.24	24.55
Glucan (6-C)	27	13	40.25	48.6	43.75
Xylan (5-C)	27	13	12.83	18.87	16.5
Galactan (6-C)	27	13	0.59	2.5	1.28
Arabinan (5-C)	27	13	0.00	1.19	0.58
Mannan (6-C)	27	13	1.38	3.79	2.68
S/G ratio	14	7	1.11	2.54	1.91

In Figure 3.2, a typical NIR spectrum along with its 1st and 2nd derivatives is presented. The NIR spectrum of wood has absorption bands that can be attributed to specific wood components (Michelle and Schimleck, 1996; Kelley *et al.*, 2004a) (Figure 3.1). Carbon/hydrogen (C-H) vibrations occur on the peak 1200 nm, the vibration bands of cellulose and hemicellulose hydroxyls are seen between on 1400 nm and 1650 nm, that of lignin hydroxyl around 1700 nm and finally strong vibrations of the cellulose hydroxyl are also observed around 2100 nm. Note also the absence of water hydroxyl absorption around 1920 nm, which confirms that the wood specimens were dry. The assignments provide some insights into the chemical structures present in the material, but the overlapping bands limit the information available from simple, visual inspection of NIR spectra (Kelley *et al.*, 2004a). This is why NIR spectroscopy combined with multivariate analysis (MVA) techniques has the capacity to manage the absorbance from many wavelengths and then correlate it with the chemical components of hybrid poplars.

Figure 3.2. Typical spectra of hybrid poplar wood.



A multivariate analysis (PLS methods) was used to develop calibration models for predicting the chemical components of hybrid poplar woods. PLS-2 analysis was primarily conducted for screening with multiple Y-variables (e.g. chemical components). However, on this study, PLS-2 method failed to properly model most of the chemical components implying that some of the chemical components were not correlated to each other. Conversely, PLS 2 method was presented in the study of Kelley *et al* (2002) and provided good correlations for predicting the chemical components of pine woods. However, ash, and arabinan were not included in their study. In this case, a series of PLS-1 methods can be used on the set of Y-variables (Esbensen, 2000). Therefore, all the results presented in this study were based on PLS-1 method. Through the PLS-1 method, the calibration model is formed as a function of the regression coefficients and absorbance at each wavelength.

Results of the original, 1st and 2nd derivative spectra are shown in Table 3.2. For all the chemical traits modeled in this study, the 1st derivative of the NIR spectra gave the highest correlations and the lowest RMSEPs compared to the original and 2nd derivative spectral data. Using the 1st derivative, the correlation coefficients between predicted and measured contents for lignin, galactan, and mannan were very good, above 0.90. Good correlations, above 0.70 were also found for the predictions of xylan content, ash content, and S/G ratio. Figure 3.3-6 shows the NIR-predicted values versus the actual / measured values of chemical composition from the 1st derivative spectra. In spite of the limited sample size good models were clearly obtained. In fact, the correlation coefficients for predicting lignin (R = 0.95), mannan (R = 0.92), galactan (R = 0.93) and xylan (R = 0.79) contents of hybrid poplar obtained in this study were higher than those obtained by Kelley *et al.,* (2004a) on pine wood with R values ranging from 0.75 – 0.86 for the same constituents. Accordingly, lower RMSEP (0.21 - 2.05) were measured in the present study compared to the previous results on pine wood that ranged from 0.6 to 2.70. The lower quality of the models for these constituents may arise from the choice of the raw spectra and from the reduced spectral range used to formulate the calibration models for pine. In addition, the variation of the species may also influence the calibration models. On the other hand, the correlation coefficients obtained in this study were somewhat lower than those reported for eucalyptus by Schimleck *et al.* (1997). In their study, very high correlation coefficients, above 0.92, were measured for carbohydrates, cellulose, glucan, hemicellulose, and xylan contents of eucalyptus from models based on the 2nd spectral derivative. The S/G ratio was also well correlated with NIR data (R = 0.87), in accordance with the report of Bailleres *et al.* (2002). Additionally, the calibration model for ash was good (R = 0.79). Overall, this shows that the NIR analysis could predict most of the chemical components of hybrid poplar wood with high correlations using 1st derivative spectral treatments. This may have been due to the 1st derivative pretreatment technique being a "baseline correction" between spectra where the relative shift in the original spectra are normalized and only changes in slope (derivative) are reflected (Kludt, 2003) to reduce the noise from original spectra. On the other hand, the calibration models for extractives (R = -0.41), glucan (R = 0.41) and arabinan (0.30) contents were poor. These results are surprising considering that these components were well modeled with NIR methods for other wood species (Axrup *et al.,* 2000; Kelley *et al.,* 2004a, 2004b; Schimleck *et al.,* 1997). Poor results on this study may arise from variation in the wet chemistry analyses performed in the different laboratories. It is noteworthy that in a preliminary investigation conducted by NREL with another analytical technique (analytical pyrolysis) on the same samples, the calibration models failed similarly for these components.

Since ethanol conversion principally occurs from C-6 sugars, good predictability of galactan and mannan contents, both C-6 sugars, from NIR spectra supports the idea that NIR could be used for assessing the propensity of hybrid poplar clones for ethanol conversion. In addition, good calibration models for lignin, xylan (C-5 sugar) and ash contents can also provide valuable quick assessment of hybrid poplar adequacy for ethanol conversion. Unfortunately, there is still a need for improving the accuracy of

NIRS calibration models for glucans, wood's most abundant C-6 sugars, upon which ethanol conversion is primarily done. This is a major limitation in using NIR methods alone for quickly assessing the adequacy of hybrid poplar woods for conversion into ethanol.

Table 3.2. Correlations coefficients (R) and root mean square error of prediction (RMSEP) of PLS models for chemical components of hybrid poplar woods.

Chemical Composition	*Original spectra*			*1st derivative spectra*			*2nd derivative spectra*		
	# PC	R	RMSEP[1]	# PC	R	RMSEP	# PC	R	RMSEP
Extractives	3	0.316	1.09	4	-0.408	1.26	4	0.187	1.09
Ash	8	0.752	0.31	3	0.794	0.30	4	0.69	0.30
Lignin	8	0.863	1.26	4	0.953	0.80	4	0.845	0.98
Glucan	5	0.434	1.96	3	0.410	2.05	5	0.15	2.18
Xylan	6	0.761	0.89	5	0.787	0.81	5	0.563	1.12
Galactan	3	0.723	0.39	4	0.926	0.26	5	0.818	0.36
Arabinan	6	0.34	0.26	4	0.300	0.26	5	0.001	0.28
Mannan	7	0.882	0.25	4	0.920	0.21	5	0.643	0.41
S/G ratio	6	0.787	0.33	6	0.868	0.30	8	0.797	0.38

[1] percent except for S/G ratio

Figure 3.3. Relationship between measured weight percent lignin and NIR predicted value. 1st derivative spectra.

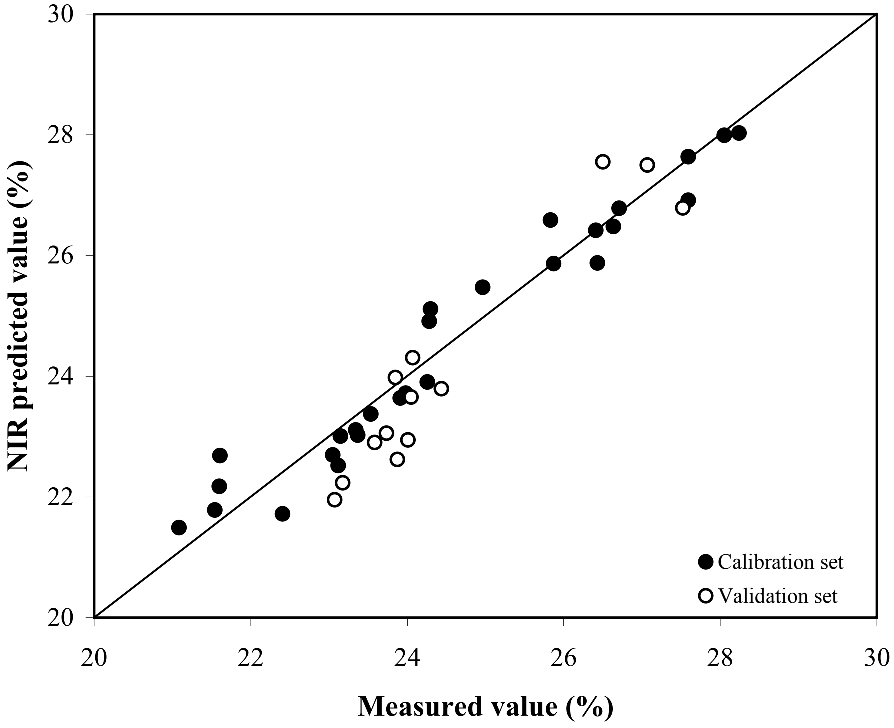


Figure 3.4. Relationship between measured weight percent galactan and NIR predicted value. 1st derivative spectra.

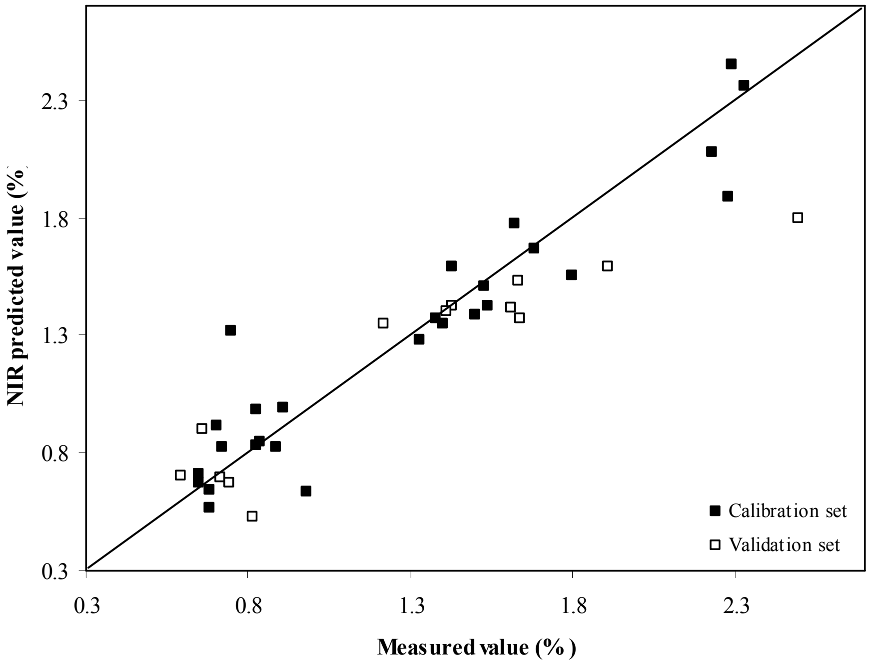


Figure 3.5. Relationship between measured weight percent mannan and NIR predicted value. 1st derivative spectra.

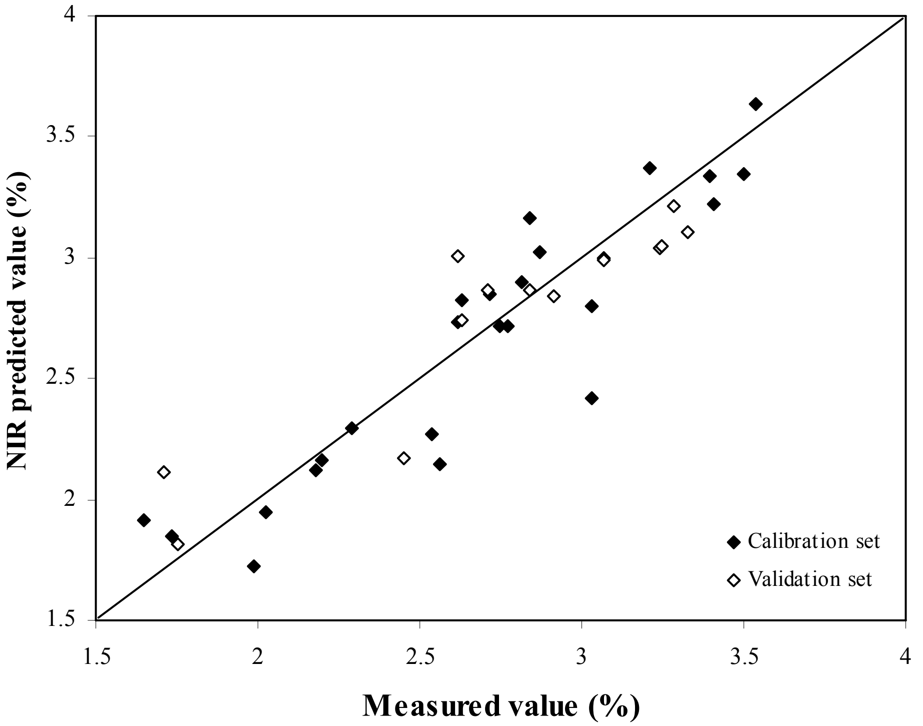
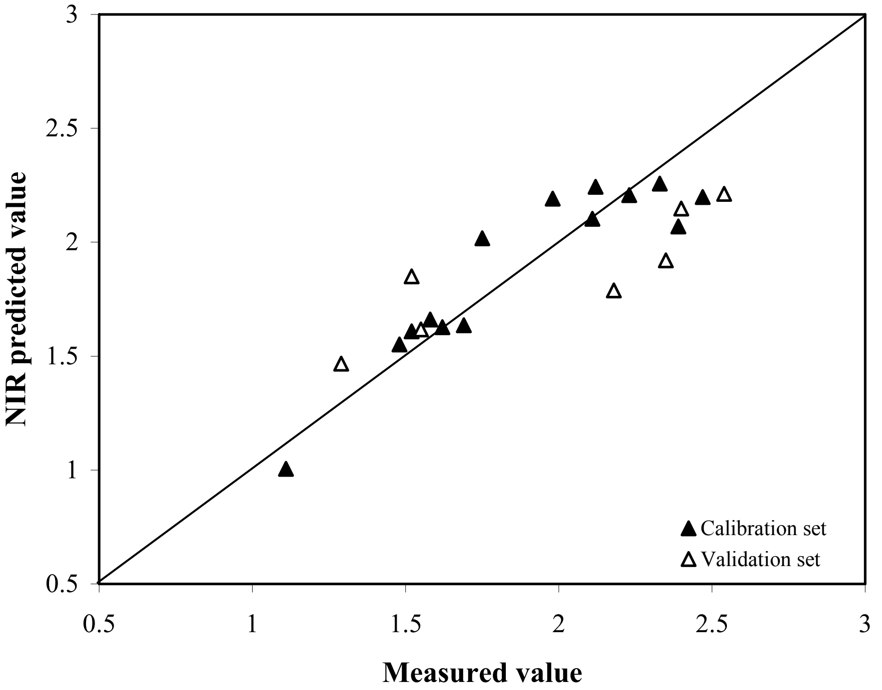


Figure 3.6. Relationship between measured S/G ratio and NIR predicted value. 1st derivative spectra.



3.5. Conclusions

This study demonstrates that NIR spectra can be used to predict some chemical traits of hybrid poplar woods, lignin content (R = 0.95), galactan content (R = 0.93) and mannan content (R = 0.92) in particular as shown be the high correlation coefficients between the predicted and measured values. In addition, good correlations were obtained for xylan content (R = 0.79), ash content (R = 0.79) and S/G ratio (R = 0.87). In all cases, it was noticeable that the 1st derivative of the spectral data was the best choice in building NIR calibrations model compared to the original spectra. The 2nd derivative always gave the poorest calibration models. NIR could therefore be utilized as a rapid screening tool for some chemical traits of hybrid poplars, thereby assisting in low cost, selective tree hybridization programs. However, the poor prediction of glucan content from NIR spectra precludes the use of NIR as the sole technique to characterize wood traits that are relevant to ethanol conversion.

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CHAPTER 4

PREDICTING THE CALORIFIC VALUE AND SPECIFIC GRAVITY OF HYBRID POPLAR WOOD USING NEAR INFRARED SPECTROSCOPY

4.1 Abstract

The potential application of near infrared spectroscopy for determining the calorific value and specific gravity of hybrid poplar woods was assessed. Two calibration sets were used for establishing a calibration model between near infrared (NIR) spectra (1000-2500nm) and wood properties (calorific value and specific gravity) and an additional two validation sets were used to validate the calibration models. In addition, two mathematical pretreatments of NIR spectra were performed and compared with the original spectra. The results gave good correlation coefficients(R) of 0.812 and 0.839 for calorific value and specific gravity respectively on the 1st derivative spectra with minimum root mean square error of prediction (RMSEP) compared to the other two spectra. Furthermore, ANOVA test was performed to examine the effect of parentage, age and growing site on hybrid poplar calorific value and specific gravity.

4.2 Introduction

Hybrid poplars are among the fastest-growing trees in North America and hybrid poplar plantations are increasing. In the last decade, the Pacific Northwest, specifically Oregon and Washington, has established approximately 45,000 acres towards the production of hybrid poplars with a projection of an additional 5,000 acres within the next few years (Chastagner and Hudak, 1999). Faster growing hybrid poplars have been produced through cross-fertilization to meet the increasing demand of the forest products industry. Poplar wood is used for the manufacturing of a wide variety of forest products including pulp and paper, lumber, veneer and plywood, composite panels, structural composite lumbers, pallets, furniture components, fruit baskets, containers and chopsticks (Ballatinecs and Kretschmann, 2001). With the increasing interest for renewable energy, hybrid poplar plantations offer a possible source of renewable biomass for conversion into energy (Ballatinecs and Kretschmann, 2001; Klasnja, 2002; Movessessian, 2003; Kenney *et.al.,* 1990). In this perspective, selective tree hybridization can assist the optimization of hybrid poplar plantations as energy crop. Such hybridization programs should not only consider the biomass yield as measured by the tree growth rate and the specific gravity of the wood but also its calorific value; calorific value is the amount of energy released from the combustion of a unit mass of a combustible material. The higher heating value (HHV) which is frequently reported in the literature is obtained from the gross calorific value or the gross heat of combustion (Kenney *et al.*, 1990). The HHV is the amount of heat measured in a bomb calorimeter from the complete combustion of a unit mass in an oxygen atmosphere in which all water remains in liquid form. Nunez-Riguerra *et al.* (1996) used a static bomb calorimeter to determine the HHV of forest wastes. Harada (2001) used a cone calorimeter to determine the heat release rate and time of ignition of nine wood species. Krigstin *et al.* (1993) used a differential scanning calorimeter (DSC) to evaluate the energy characteristics of hybrid willow. Based on these methods, the calorific values of wood vary between 15 and 25 KJ/g (Harada, 2001; Krigstin *et al.,* 1993). Yet the standard method (ASTM E870-82, 2004) suggests the use of an oxygen-bomb calorimeter to measure the gross calorific value of wood.

Wood specific gravity is also an important aspect of biomass production of an energy crop (Thakaran *et al.,* 2003). Combining high specific gravity with high biomass production would allow for maximized feedstock output. Wood specific gravity can be measured using the water displacement method based on TAPPI standards. This method requires the samples to first be debarked and kiln dried; one then measures the water displacement caused by immersion in water of a green wood and kiln-dried wood samples. The specific gravity is then calculated by the ratio of the displacement values of green wood and kiln-dried wood (Thakaran *et al.,* 2003).

Both of these conventional methods in determining wood calorific value and specific gravity of wood require extensive work, sample preparation, and time to perform. An optimal methodology could measure both the calorific value and the wood specific value effectively, reliably and affordably which in turn would optimize and assist hybridization programs of poplar woods for biomass production and bioenergy.

Recently, near infrared spectroscopy (NIRS) in combination with multivariate analysis has shown promise as a method for rapid and accurate field measurements of wood properties (Schimleck *et al.,* 2003a, 2003b; Hauksson *et al.,* 2001; Hoffmeyer and Pedersen, 1995; Gillon *et al.* 1997). NIRS is particularly effective at revealing absorption bands relevant of C-H, O-H, and N-H chemical functional groups (Skoog D. A. *et al.,* 1998). For this reason, NIRS has shown promise as a nondestructive evaluator of the properties of wood based materials (Kludt, 2003). Utilizing a strong calibration model, the cheaper NIR data can be used to rapidly predict a desired property. Gillon *et al.* (1997) used various fuel components from the Mediterranean forest such as twigs, leaves, needles, and bark from different species (broad-leaved trees, conifers, shrubs, fern and grasses) to establish a calibration model between NIR spectra and biomass calorific value. Using the calibration model, the r^2 between the NIRS-predicted and measured values were 0.79 and 0.76 for two sets of shrub species, *Arbutus unedo* L. and *Erica arborea* L, respectively (Gillon *et al.,* 1997). The study demonstrated the potential use of NIRS for field measurements of wood calorific value. More so, recent studies have concluded that the use of NIRS for predicting wood density is feasible (Hauksson *et al.* 2001; Hoffmeyer and Pedersen, 1995; Schimleck *et al.,* 2003a, 2003b). Hauksson *et al.* (2001); and Hoffmeyer and Pedersen (1995) found good correlations on the order of $r^2 \geq 0.90$ in predicting Norway spruce wood density using NIRS. Hoffmeyer and Pedersen (1995) concluded that NIR method is very versatile in the non-destructive evaluation of wood. In addition, Schimleck *et al.* (2003a, 2003b), showed the application of NIRS to predict air-dry density of *Eucalyptus nitens* and *Pinus taeda* wood. Relationships between measured values and NIR estimates were good with $r^2 = 0.87$ for *Pinus taeda* and 0.93 for *Eucalyptus nitens*. Similarly, NIRS calibration models could be developed for predicting both calorific value and specific gravity of hybrid poplar woods. NIRS could then provide a rapid non-destructive method that would require minimal sample preparation and allow for rapid field measurements of hybrid poplar wood calorific value and specific gravity. Such a tool would assist hybridization programs aimed at enhancing the desirable energy traits of hybrid poplar woods, high calorific value and specific gravity in particular. Furthermore, it could assist in screening sylvicultural and genetic factors that determine these properties in hybrid poplar. In particular, several studies indicate a variation of calorific value and specific gravity of hybrid poplar based on clone, tree age, and growing sites. For instance, Klasnja *et al.,* (2001) conducted a study of ovendry poplar wood (*P. deltoides* and *P. euramericanaI)* to determine the gross calorific value at tree ages 1, 2 and 12 year. The calorific values measured had large variations between 16 KJ/g to 24 KJ/g. The highest calorific value was measured in 2 years old trees compared to one year and 12 years old trees. Bowersox *et al.* (1979) found that the HHVs of seven oven dry *Populus* clones were not significantly different. Likewise, Strong (1992) detected no significant difference between the mean calorific values of nine *populus* clones, within the small range of 19.4 -19.9 KJ/g. Similar results were reported by Geyer *et al*. (2000) and Movessessian (2003). The latter study further indicated that hybrid poplar clones grown in different sites had different energy contents. These results somewhat differ from that of Blankenhorn *et al.* (1985a) which measured small but significant differences in the HHV (17.70 KJ/g to 20.04 KJ/g) of seven hybrid poplar clones. In this study, the authors report that tree age has no influence on HHV. Calorific values of stems and branches of woods have also been evaluated (Harris 1984). Harris concluded that there was no significant difference in HHV between stemwood and branchwood for sweetgum and yellow poplar, but a significant difference in HHV was found in white oak tree.

As for the specific gravity values, Thakaran *et al.* (2003) studied seven poplar clones and found that for three year old *P. deltoides* clones, the specific gravity was on the range of 0.33 – 0.37 g cm^{-3}. They also studied willow clones with a range of 0.35 – 0.48 g cm^{-3} and stated that wood specific gravity increases with age. Olson *et al.* (1984) found that the specific gravity of several *P. deltoides* clones varied significantly among clones with specific gravity ranging from 0.27 – 0.39. Altogether these studies suggest that clone selection may have a minor impact on wood calorific value and a large impact on specific gravity. Sample location within the tree, tree age and growing site may have a greater effect on HHV of hybrid poplar.

In this perspective, the primary aim of this study is to develop calibration models using NIRS and multivariate analysis to predict the calorific value and specific gravity of hybrid poplar woods. A second objective is to evaluate if parentage, tree age and growth site impact the calorific value and specific gravity of hybrid poplar woods.

4.3 Materials and Methods

4.3.1 Hybrid poplar sample selection and preparation

For calorific value modeling, a total of seventy eight hybrid poplar samples were obtained, 58 samples from Greenwood Resources Company (GRC), 16 from National Renewable Energy Laboratory, and 4 from Washington State University Extension Program. Of the seventy eight samples, 51 samples were used as the calibration set for modeling calorific value and 27 samples were used for the validation set. For specific gravity modeling, the 58 samples from GRC were used, among which 36 were utilized for building the calibration model and the remaining 22 samples served to validate the model. Sample selection in the calibration or validation set was based on a stratified random sampling technique that included several factors; parentage, age, and site of growth (Table 4.1). For each clone, 5 to 20 grams of sample were received in sealed plastic bags in the form of a wood core or flour. The specimens were milled to mesh #40 using a Wiley milling machine for uniformed size particles and subsequently ovendried to a constant weight. They were kept in a desiccator under drierite until calorific and NIR measurements. Each sample was divided into two parts, one for bomb calorimetry and the other for near infrared spectroscopy. For NIR measurements, one gram of sample was placed in a glass bottle and sealed by cap to maintain dryness.

4.3.2 Determination of specific gravity

Specific gravity was determined at Greenwood Resource Company using vacuum saturation and water immersion method on the 58 wood core samples provided for the study. Specifically, the wood cores were saturated in water by immersion in water followed by a three step vacuum application. The water-saturated wood core was connected on a needle probe and submerged into a graduated cylinder containing 100 ml of water, securing that the core was covered with about 1cm of water. At the end of 30 seconds immersion, the weight was recorded to be equivalent to the volume of the core. The wood core was then dried in the oven at 105 degrees C for 24 hours and the dry weight was recorded. Wood density was calculated by dividing each weight by its volume. Finally, the specific gravity of each wood core was calculated to be equivalent to the density of wood divided by the density of water.

4.3.3 Calorific value measurement

Gross calorific value was determined in tri-replicates according to ASTM Test Method E711 using a Parr Bomb calorimeter 6200. Approximately 1± 0.1 gram of sample was pelletized using an hydraulic press. A 10 centimeter nickel alloy fuse wire was attached between the ignition terminals of the bomb. One gram of type II deionized water was added to the calorimeter bomb, the wood pellet was placed and the bucket was filled with 2000 grams of type II DI water, which was $3^{o}C - 5^{o}C$ below the jacket temperature. The bomb was pressurized with oxygen to 30 atm, immersed into the bucket and the charge was fired. At the end of combustion, the bomb was rinsed with type II DI water and the remaining length of the fuse wire was measured for fuse correction. Preliminary acid titrations of the bomb washings indicated that a fixed value of 8 calories was adequate for acid corrections. The gross heat of combustion was determined after the corrections were applied. Samples that exhibited a variation of more than 5% were eliminated and the bomb calorimetry experiment was repeated until three valid samples were obtained.

Figure 4.1. Parr 6200 Oxygen Bomb Calorimeter installation.

4.3.4 NIRS analysis

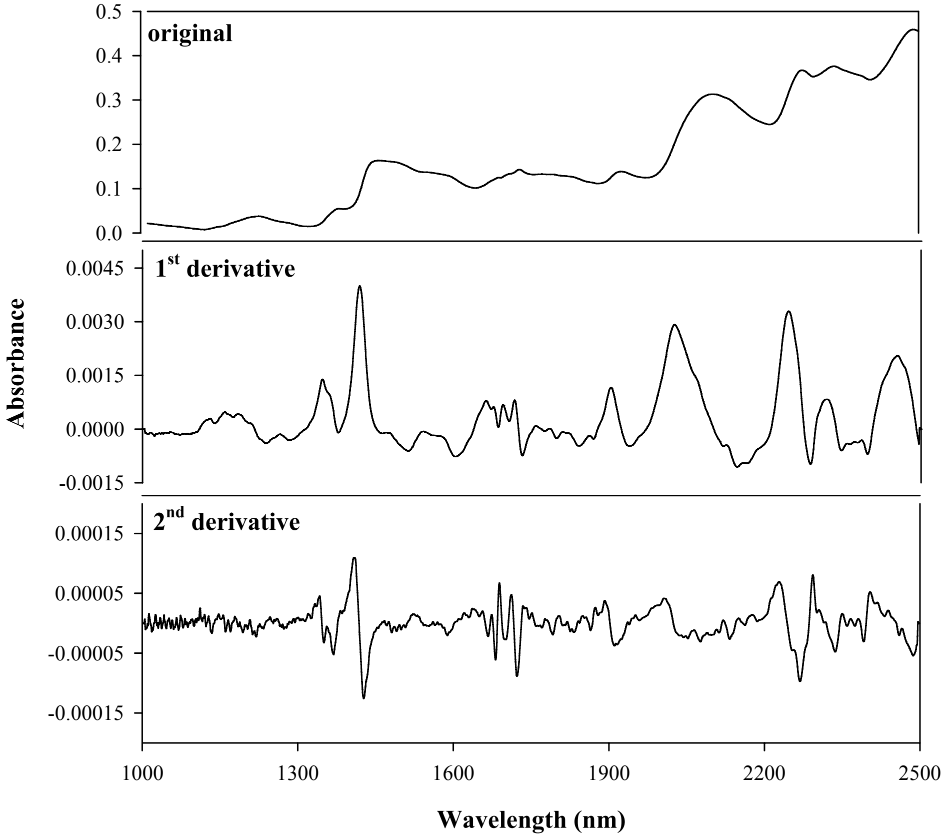
Near infrared spectra were collected on a Nicolet Nexus 670 FT-IR spectrometer, equipped with a white light source, XKBr beam splitter, liquid nitrogen cooled Thermo Nicolet MCT-A detector, and the Nicolet Smart Near-IR UpDrift probing port. Spectral absorbance values were collected over the range of 1000 to 2500 nm at 1 nm interval. Two spectral measurements per sample were performed and average, each consisting of 40 scans. A background correction was accomplished on a white ceramic standard at 10-minute intervals during the NIRS spectra scanning process. To establish calibration models, the spectral data were considered in three different ways; the original spectra, 1st spectral derivative, and 2nd derivative. The Savitsky-Golay differentiation method was used for the 1st and 2nd spectral derivatives of the spectra (Esbensen, 2000; Kludt, 2003). This method calculates derivatives of any order based on a polynomial approximation of the curves.

Calibrations between the NIR spectral measurements (raw data, 1st and 2nd derivative) and the gross calorific value and specific gravity were developed using the software package Unscrambler® 7.6, CAMO for the multivariate analysis, partial least square (PLS) analyses. For PLS analysis, the NIR spectra (predictor) were combined into X matrices while the information from calorific value and specific gravity (response) were established as the Y-matrices. Prior to PLS analysis, the X and Y matrices were mean centered variance normalized. The Y-matrix was scaled by multiplying the original value by the inverse of the standard deviations to make up the large difference in magnitude. However, the X-matrix was not scaled by the inverse of the standard deviation to avoid over-emphasis of noise wavelengths (Esbensen, 2000). All samples in calibration set from both wood properties were used to construct PLS models.

The calibration models were then assessed by predicting both properties using samples from validation set. Correlation coefficient (R) and root mean square error of prediction (RMSEP) were used to describe the effectiveness and robustness of each calibration model. Furthermore, the number of PLS components (factors) required for the calibration model was determined by observing the response of the residual Y-variance with added factors (Kelley *et al.*, 2004). The model was deemed complete when the addition of a new factor did not further decrease the residual Y- variance. Too few factors can result in a less accurate models while too many factors can lead in over fitting or "over prediction" of the model.

For the evaluation of significant difference in calorific value and specific gravity in terms of parentage, age, and site growth, analysis of variance (ANOVA) was used at $\alpha = 0.05$. A one-way fixed effect model was used for each factor due to the limitations of the availability of the samples.

Figure 4.2. Typical spectra of hybrid poplar wood.



4.4 Results and Discussions

4.4.1 Calorific measurements

Table 4.1 summarizes the properties of hybrid poplar clones used for the calibration and validation sets for modeling calorific value. The calorific value of the hybrid poplar samples averaged at 19.3KJ/g, and varied within a very limited range from 97 to 102% of the mean (18.7 to 19.7 KJ/g). Those values are in accordance with the literature and so are the very small variations observed (Blankenhorn *et. al*., 1985b; Harris, 1984; Strong, 1992).

The typical FTIR spectrum of hybrid poplar is shown in Figure 4.2. It is complex and contains numerous broad overlapping bands. The spectral matrix, X, described by the 1,500 spectral variables or wavelengths (1000 nm – 2500 nm) comprises some properties of the sample (e.g. calorific value). Figure 4.3-4 shows the 1st and 2nd derivative spectra. Through the PLS methods, calibration models of calorific value were built from the raw spectral data and the first and second derivatives. Using these calibration models, the calorific values of the 27 hybrid poplar samples in the validation set were predicted. The quality of the calibration models obtained from the various spectral data is summarized in Table 4.5 with the correlation coefficients and root mean square errors of prediction. Although the calorific content of the hybrid poplar samples used in this study did not span a large variation, the NIR spectra could be related to the calorific value. The correlation coefficient (R) of the 1st derivative spectra was measured at 0.812 with a low RMSEP of 0.12 KJ/g. The 1st derivative mathematical pretreatment method considerably improved the prediction of wood calorific value compared to the original spectra and the second derivative. This may have been due to the 1st derivative pretreatment technique being a "baseline correction" between spectra where the relative shift in the original spectra are normalized and only changes in slope (derivative) are reflected (Kludt, 2003) to reduce the noise from original spectra. Moreover, 2nd derivative spectra demonstrated relatively poor results among the three spectra. This is somewhat surprising, since the second derivative mathematical pretreatment method showed good results of calorific value of forest fuels in a previous study conducted by Gillon, *et al.* (1997).

Analysis of variance was also conducted to evaluate the effect of parentage, tree age and growing site on the calorific value. Table 4.3 shows the ANOVA results for differences in calorific value between parentages of hybrid poplar. For groups A and C, the results show that there were no difference in calorific values with p-values of 0.17 and 0.13 respectively. These hybrids, grown in Westport, Oregon, include *deltoides* x *maximowizcii* (D x M), *deltoides* x *trichocarpa* (D x T), *trichocarpa* x *deltoides* (T x D), *deltoides* x *trichocarpa-maximowizcii* (D x TM), and *deltoides* x *trichocarpa-nigra* (D X TN) evaluated at ages 4 and 5 years. From analysis of the group B samples, no significant difference (p = 0.40) was found between the T x D and D x N hybrids grown in Boardman, Oregon, and evaluated at age 6. Altogether, these analyses indicated that parentage had no effect on the calorific value of hybrid poplars. Such a result is consistent with previous studies that detected no difference in the calorific value of various hybrid poplar clones (Bowersox *et al.* 1979, Blankenhorm *et al.* 1985b, Strong 1992, Geyer *et al*. 2000, Movessessian 2003). Furthermore, Table 4.4-5 demonstrate that within the hybrid poplar samples evaluated here, age and growing sites had no significant effect (p = 0.40 and 0.80 respectively) on calorific value. These results differ from those of Klasnja *et al*., (2001) and Movessessian (2003), where calorific value varied due to age and site growth. This discrepancy is easily explained by the limited range in ages (4 and 5 years old) and growth sites that were available in the current study.

Table 4.1. Mean calorific value and specific gravity of hybrid poplar

Parentage	Age(yr)	Location of trees	Calorific Value - KJ/g n = 3	Specific Gravity n = 1- 6
Calibration set				
DxD	5	Fitler, MS	19.35 (0.18)[a]	0.3428 (0.0147)
DxD	5	Fitler, MS	19.11 (0.19)	0.3488 (0.0102)
DxD	5	Fitler, MS	19.47 (0.04)	0.3437 (0.0221)
DxD	5	Togo Island, MS	19.18 (0.08)	0.3305 (0.0162)
DxD	5	Togo Island, MS	19.53 (0.14)	0.3503 (0.0101)
DxD	5	Togo Island, MS	19.32 (0.08)	0.3778 (0.0104)
T	10	Westport, OR	19.10 (0.35)	0.3041 (0.0212)
T	10	Westport, OR	18.81 (0.30)	0.2867 (0.0010)
T	10	Westport, OR	19.11 (0.17)	0.3097 (0.0036)
TxD	6	Boardman, OR	19.13 (0.14)	0.3167 (0.0062)
TxD	6	Boardman, OR	19.29 (0.17)	0.3191 (0.0075)
TxD	6	Boardman, OR	19.31 (0.10)	0.3120 (0.0076)
TxD	5	Westport, OR	19.48 (0.07)	0.3007 (0.0094)
TxD	5	Westport, OR	19.41 (0.05)	0.3285 (0.0115)
TxD	5	Westport, OR	19.39 (0.12)	0.2875 (0.0133)
TxD	4	Westport, OR	19.46 (0.17)	0.2870 (0.0158)
TxD	4	Westport, OR	19.29 (0.08)	0.2855 (0.0106)
TxD	4	Westport, OR	19.22 (0.20)	0.2797 (0.0079)
DxT	5	Westport, OR	19.47 (0.10)	0.2910 (0.0217)
DxT	5	Westport, OR	19.37 (0.05)	0.3110 (0.0076)
DxT	5	Westport, OR	19.30 (0.04)	0.2947 (0.0086)
DxT	4	Westport, OR	19.39 (0.07)	0.2900 (0.0087)
DxT	4	Westport, OR	19.22 (0.19)	0.2945 (0.0132)
DxT	4	Westport, OR	19.22 (0.07)	0.3025 (0.0200)
DxN	6	Boardman, OR	19.40 (0.02)	0.3474 (0.0061)
DxN	6	Boardman, OR	19.30 (0.12)	0.3251 (0.0075)
DxN	6	Boardman, OR	19.20 (0.13)	0.3138 (0.0085)
DxM	4	Westport, OR	19.19 (0.16)	0.2968 (0.0047)
DxM	4	Westport, OR	19.29 (0.14)	0.2815 (0.0029)
DxM	4	Westport, OR	19.16 (0.07)	0.2653 (0.0100)
TxM	6	Westport, OR	19.25 (0.23)	0.2920 (0.0144)
TxM	6	Westport, OR	19.25 (0.06)	0.3319 (0.0330)
TxM	6	Westport, OR	19.37 (0.07)	0.3074 (0.0044)
DxTM	5	Westport, OR	19.63 (0.04)	0.2703 (0.0096)
DxTN	5	Westport, OR	19.26 (0.23)	0.2670 (0.0102)
TDxM	5	Clastkaine, OR	19.20 (0.13)	0.3092
M x M	15	Puyallup, WA	18.71 (0.62)	
M x M	15	Puyallup, WA	19.06 (0.42)	
u[b]			19.10 (0.32)	
u			19.18 (0.57)	
u			19.32 (0.27)	
u			19.36 (0.36)	
u			19.35 (0.25)	
u			19.68 (0.02)	

u			19.58 (0.03)	
u			19.57 (0.02)	
u			19.54 (0.02)	
u			19.62 (0.01)	
u			19.41 (0.17)	
u			19.57 (0.03)	
u			19.50 (0.03)	
u			19.01 (0.10)	
u			19.11 (0.03)	
u			19.25 (0.06)	
Validation set				
DxD	5	Fitler, MS	19.56 (0.03)	0.3340 (0.0090)
DxD	5	Fitler, MS	19.59 (0.03)	0.3375 (0.0136)
DxD	5	Togo Island, MS	19.51 (0.07)	0.3853 (0.0135)
DxD	5	Togo Island, MS	19.40 (0.15)	0.3312 (0.0057)
T	10	Westport, OR	19.39 (0.02)	0.3167 (0.0012)
T	10	Westport, OR	19.31 (0.09)	0.3004 (0.0025)
TxD	6	Boardman, OR	19.43 (0.04)	0.3252 (0.0089)
TxD	6	Boardman, OR	19.32 (0.13)	0.3398 (0.0111)
TxD	5	Westport, OR	19.56 (0.04)	0.3290 (0.0046)
TxD	5	Westport, OR	19.66 (0.02)	0.2878 (0.0039)
TxD	4	Westport, OR	19.65 (0.04)	0.2908 (0.0118)
TxD	4	Westport, OR	19.48 (0.06)	0.2642 (0.0094)
DxT	5	Westport, OR	19.34 (0.26)	0.2882 (0.0102)
DxT	5	Westport, OR	19.56 (0.19)	0.2770 (0.0098)
DxT	4	Westport, OR	19.46 (0.07)	0.3227 (0.0195)
DxT	4	Westport, OR	19.44 (0.12)	0.3022 (0.0077)
DxN	6	Boardman, OR	19.52 (0.03)	0.3275 (0.0097)
DxN	6	Boardman, OR	19.38 (0.03)	0.3325 (0.0225)
DxM	4	Westport, OR	19.31 (0.43)	0.2650 (0.0092)
DxM	4	Westport, OR	19.33 (0.18)	0.2690 (0.0076)
TxM	6	Westport, OR	19.42 (0.03)	0.3229 (0.0094)
TxM	6	Westport, OR	19.43 (0.10)	0.2808 (0.0051)
MxM	15	Puyallup, WA	19.13 (0.32)	
u			19.38 (0.09)	
u			19.61 (0.03)	
u			19.37 (0.07)	
u			19.06 (0.11)	

[a] Standard deviation, n: number of replicates [b] unknown

Table 4.2. Correlation coefficient (R) and root mean square error of prediction (RMSEP) of PLS models for calorific value of hybrid poplar woods.

Spectra	Factors	RMSEP (KJ/g)	R value
Original	4	0.13	0.689
1st derivative	3	0.12	0.812
2nd derivative	4	0.12	0.614

Table 4.3. ANOVA summary for differences in calorific value between parentages of hybrid poplar

Source of Variations	Degrees of Freedom	Total Sum of Squares	Mean Square	F	P-level
Group A					
Between parentages	2	0.0675	0.0337	2.09	0.166
Within parentages	12	0.1936	0.0161		
Total	14	0.2611			
Group B					
Between parentages	1	0.0102	0.0102	0.79	0.399
Within parentages	8	0.1031	0.0129		
Total	9	0.1133			
Group C					
Between parentages	3	0.0897	0.0299	2.53	0.130
Within parentages	8	0.0945	0.0118		
Total	11	0.1842			

A: hybrids include DxM, DxT and TxD at age 4 years old in Westport, OR.
B: hybrids include TxD and DxN at age 6 years old in Boardman, OR.
C: hybrids include DxT, TxD, DxTM and DxTN at age 5 years old in Westport, OR.

Table 4.4. ANOVA summary for differences in calorific value between ages of hybrid poplar

Source of Variations	Degrees of Freedom	Total Sum of Squares	Mean Square	F	P-level
Group D					
Between ages	1	0.0096	0.0096	0.77	0.407
Within ages	8	0.1002	0.0125		
Total	9	0.1098			
Group E					
Between ages	1	0.0160	0.0160	0.78	0.404
Within ages	8	0.1648	0.0206		
Total	9	0.1808			

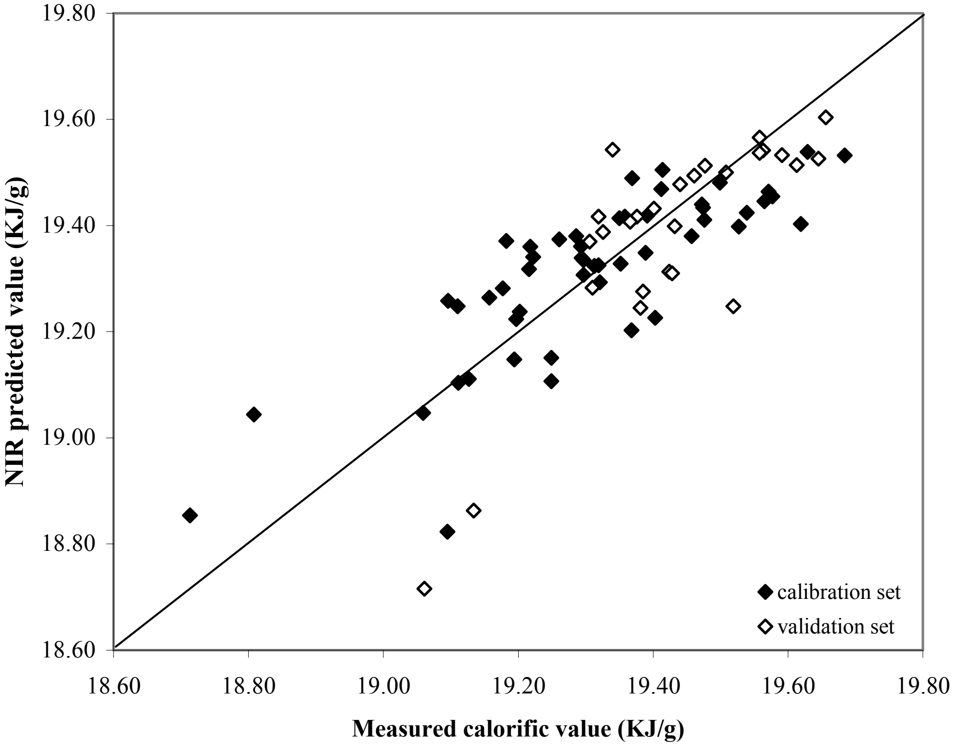
D: hybrids include DxT at ages 4 and 5years old in Westport, OR.
E: hybrids include TxD at ages 4 and 5years old in Westport, OR.

Table 4.5. ANOVA summary for differences in calorific value between growing sites of hybrid poplar

Source of Variations	Degrees of Freedom	Total Sum of Squares	Mean Square	F	P-level
Group F					
Between sites	1	0.0020	0.0020	0.07	0.803
Within sites	8	0.2350	0.0294		
Total	9	0.2370			

F: hybrids include DxD at ages 5 years old in Togo Island and Fitler, OR.

Figure 4.3. Relationship between calorific values measured using a bomb calorimeter and NIR predicted calorific values. 1st derivative spectra.



4.4.2 Specific Gravity

A summary of the calibration and prediction data set is given in Table 4.1. The specific gravity of hybrid poplar wood was on the range 0.2642-0.3853 with an overall mean of 0.3092; comparable with previous results of studies of poplar clones (0.27-0.39) (Olson *et.al,* 1984; Tharakan *et al.* 2003).

Table 4.6 compares the quality of the calibration models obtained from the three spectral data. The calibration model of specific gravity gives the best correlation coefficient (R = 0.839) and minimum RMSEP (0.02) for the 1st derivative spectra. In addition, an outlier having a specific gravity of 0.3853 was found in the validation set and was discarded. The 2nd derivative spectra still gave the poorest calibration models among all three spectral data. This finding agrees with the wood calorific value where the 1st derivative spectra gave better results on this study. The RMSEP value is slightly lower than that obtained in predicting the density of Norway spruce wood with NIR calibration models (Hauksson *et al.* 2001). However, the correlation coefficient on this study is slightly lower than that obtained by Schimleck *et. al* (2003a, 2003b) and Hoffmeyer and Pedersen (1995). In these studies the wood density of green *Pinus taeda*, *Eucalyptus nitens* and Norway spruce were predicted from NIR models respectively and found correlation coefficients in the 0.85-0.93 range.

Table 4.7 presents the results of the analysis of variance that was performed for detecting significant differences in specific gravity between parentages. Group A shows that the specific gravity of hybrid poplars was significantly different (p = 0.01) between parentages. No significant difference was detected for the specific gravity of the hybrid-poplars pertaining to the Group B with a p-value of 0.14. The effect of age was also examined based on the available data. No significance difference (p = 0.24) in the specific gravity was detected between ages 4 and 5 for the DxT hybrid poplars. On the other hand, the DxT poplars of age 4 and 5 had significant differences in specific gravity (p = 0.04). In spite of the limited sampling available in this study, those results have similarities with the study of Thakaran *et al.* (2003) where wood specific gravity was found to vary with age. All these findings show that some hybrid poplars display a significant difference in specific gravity between parentages and ages while others do not. Finally, no significant difference in specific gravity of hybrid poplar was detected based on growth site (Table 4.9).

Table 4.6. Correlation coefficient (R) and root mean square error of prediction (RMSEP) of PLS models for specific gravity of hybrid poplar woods.

Spectra	Factors	RSMEP	R value
Original	4	0.03	0.605
1st derivative	4	0.02	0.839
2nd derivative	3	0.03	0.229

Figure 4.4. Relationship between measured specific gravity and the NIR predicted value. 1st derivative spectra.

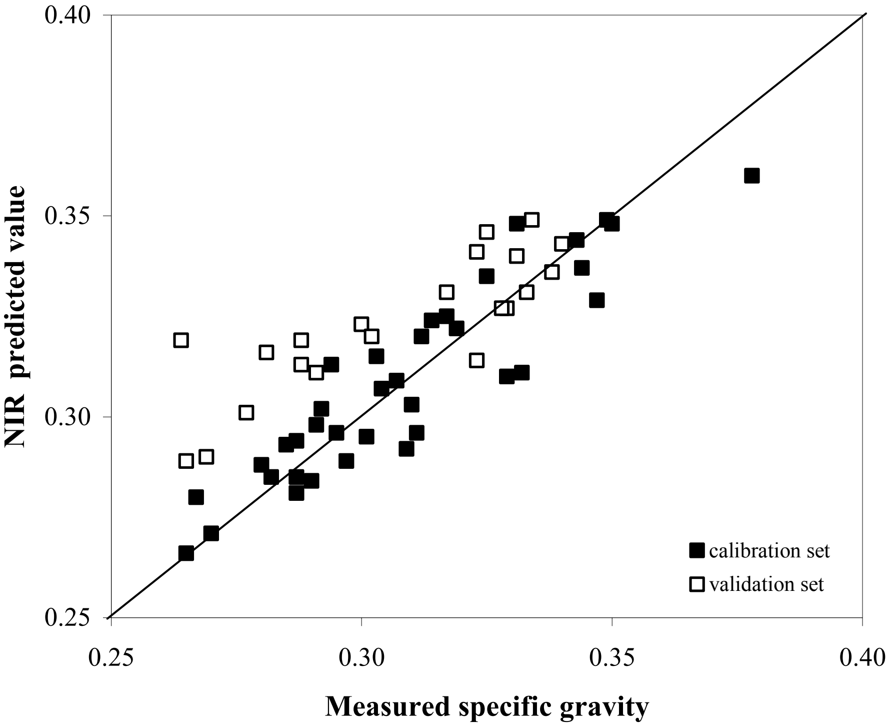


Table 4.7. ANOVA summary for differences in specific gravity between parentages of hybrid poplar

Source of Variations	Degrees of Freedom	Total Sum of Squares	Mean Square	F	P-level
Group A					
Between parentages	2	0.001992	0.000996	6.60	0.012
Within parentages	12	0.001810	0.000151		
Total	14	0.003801			
Group B					
Between parentages	1	0.000112	0.000112	0.85	0.385
Within parentages	8	0.001061	0.000133		
Total	9	0.001173			
Group C					
Between parentages	3	0.002109	0.000703	2.40	0.143
Within parentages	8	0.002342	0.000293		
Total	11	0.004451			

A: hybrids include DxM, DxT and TxD at age 4 years old in Westport, OR.
B: hybrids include TxD and DxN at age 6 years old in Boardman, OR.
C: hybrids include DxT, TxD, DxTM and DxTN at age 5 years old in Westport, OR.

Table 4.8. ANOVA summary for differences in specific gravity between ages of hybrid poplar

Source of Variations	Degrees of Freedom	Total Sum of Squares	Mean Square	F	P-level
Group D					
Between ages	1	0.000250	0.000250	1.62	0.239
Within ages	8	0.001236	0.000155		
Total	9	0.001486			
Group E					
Between ages	1	0.001595	0.001595	5.88	0.042
Within ages	8	0.002170	0.000271		
Total	9	0.003765			

D: hybrids include DxT at ages 4 and 5years old in Westport, OR.
E: hybrids include TxD at ages 4 and 5years old in Westport, OR.

Table 4.9. ANOVA summary for differences in specific gravity between growing sites of hybrid poplar

Source of Variations	Degrees of Freedom	Total Sum of Squares	Mean Square	F	P-level
Group F					
Between sites	1	0.000466	0.000466	1.35	0.278
Within sites	8	0.002759	0.000345		
Total	9	0.003225			

F: hybrids include DxD at ages 5 years old in Togo Island and Fitler, OR.

4.5 Conclusions

For wood calorific value and specific gravity, NIRS calibration models were developed. The correlation coefficients of the calibration models from the 1st derivative spectra, between the predicted and measured values, gave good results (R>0.80), better than those obtained with the two other spectral pretreatments. The results from the 1st derivative spectra also gave the lowest root mean square of error of prediction (RSMEP) for calorific value (0.12 KJ/g) and specific gravity (0.02). Because the traditional methods of bomb calorimetry and specific gravity measurements can be laborious and time consuming, NIRS afford a better method to measure calorific value and specific gravity of hybrid poplars. This rapid tool will enable quick assays of hybridizing and clones for future crops.

In addition, for the 78 hybrid poplars evaluated here and having different ages (4, 5, 6, 10 and 15 years old), parentages (16 different parents) and growing sites (6), a limited variation of calorific value was measured. Age and growing sites had no significant effect on wood calorific value. However, in some cases parentage had a significant effect on the calorific value of some hybrid poplars. For specific gravity of hybrid poplar, in some cases parentage and age had a significant impact. On the other hand, there was no apparent influence from the growing sites on specific gravity.

4.6 Reference

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APPENDIX A

CHEMICAL DATA OF HYBRID POPLAR WOOD

Table A.1. Calibration set – chemical compostion

	Identity	Extractives	Ash	Lignin	Glucan	Xylan	Galactan	Arabinan	Mannan
1	331-1780	3.12	0.50	22.41	42.37	18.55	2.29	0.56	3.54
2	93-968	3.26	0.40	21.61	48.60	17.02	2.33	0.53	3.21
3	998-069	2.94	0.57	21.60	43.76	16.18	1.62	0.16	3.07
4	148	4.04	0.80	26.71	45.33	14.13	1.40	0.50	1.65
5	351	2.11	0.33	26.41	47.08	14.83	1.50	0.64	3.03
6	238	2.79	0.52	27.59	44.65	14.07	1.33	0.57	2.56
7	135	3.13	1.42	28.24	42.67	16.46	1.80	0.42	1.38
8	212	1.85	0.77	27.59	44.13	15.40	1.43	0.57	2.29
9	80-1	2.94	0.46	24.26	42.37	18.87	1.53	0.72	3.41
10	73-2	2.97	0.46	23.05	43.45	18.46	1.54	0.76	2.84
11	N-3	3.62	0.45	24.30	43.46	17.99	1.38	0.83	2.62
12	352	2.94	0.27	25.83	46.84	14.69	1.68	0.64	2.54
13	50181	4.09	0.62	23.15	42.85	17.68	2.28	0.53	3.40
14	50188	3.00	0.37	23.12	43.63	18.07	2.23	0.64	3.50
15	900-050	6.54	1.57	24.28	41.05	13.37	0.89	0.75	2.02
16	900-062	2.31	2.43	26.64	42.86	16.95	0.70	1.19	1.42
17	900-063	3.44	2.03	25.87	41.47	13.00	0.98	0.94	1.73
18	901-100	4.81	1.92	24.96	41.18	12.83	0.84	0.77	2.18
19	901-101	2.51	1.94	28.05	41.13	14.52	0.83	0.67	1.99
20	901-099	3.29	1.31	26.43	42.39	15.17	0.91	0.69	2.20
21	998-066	3.14	0.81	23.34	42.18	17.31	0.68	0.58	2.72
22	998-068	4.47	0.56	21.54	45.08	15.98	0.65	0.66	3.03
23	998-071	4.08	0.94	23.54	43.67	16.55	0.65	0.54	2.77
24	998-072	1.62	0.63	23.98	43.14	17.65	0.75	0.63	2.87
25	998-065	3.22	0.85	23.91	44.65	18.55	0.82	0.59	2.63
26	998-069	3.74	0.52	21.09	47.32	16.55	0.72	0.56	2.81
27	998-073	2.34	0.68	23.37	45.67	17.26	0.68	0.48	2.75

all units are in percent weight (%)

Table A.2. Calibration set – chemical compostion

	Identity	Extractives	Ash	Lignin	Glucan	Xylan	Galactan	Arabinan	Mannan
1	998-071	2.62	0.86	24.44	40.69	16.95	1.61	0.02	2.84
2	998-070	1.93	0.76	23.85	42.29	16.95	1.63	0.00	2.62
3	73-1	3.09	0.54	24.05	42.83	18.30	1.43	0.87	3.33
4	144	1.21	2.08	27.07	47.44	15.22	1.91	0.51	1.75
5	214	2.43	0.68	26.50	44.85	15.22	1.22	0.35	3.79
6	80-3	3.36	0.35	24.07	42.00	18.46	1.41	0.70	3.24
7	147	1.13	0.60	27.52	46.4	15.21	1.64	0.52	1.71
8	998-063	3.35	0.56	23.74	40.25	17.61	0.71	0.59	3.07
9	53246	3.81	0.43	23.18	44.63	17.71	2.50	0.60	3.29
10	998-070	2.62	0.69	23.58	45.52	16.97	0.66	0.41	2.71
11	998-062	2.94	0.72	24.01	42.85	17.40	0.81	0.52	2.63
12	998-064	2.09	0.80	23.87	43.72	17.37	0.59	0.59	2.91
13	998-067	3.07	0.77	23.07	43.65	18.71	0.74	0.54	3.25

all units are in percent weight (%)

Table A.3. Calibration set – S/G ratio

	Identity	S/G ratio
1	14-129	1.98
2	331-1917	2.11
3	331-1657	2.23
4	331-1784	2.12
5	998-063	1.69
6	998-069	1.75
7	900-050	1.11
8	998-067	1.58
9	998-066	1.52
10	998-071	1.48
11	50188	2.39
12	998-072	1.62
13	331-1087	2.33
14	53246	2.47

Table A-3. Validation set – S/G ratio

	Identity	S/G ratio
1	331-1780	2.40
2	93-968	2.54
3	998-065	1.29
4	998-064	1.52
5	998-073	1.55
6	998-070	2.18
7	50181	2.35

APPENDIX B

COMPLETE DESCRIPTION OF HYBRID POPLAR WOOD

(CALORIFIC VALUE & SPECIFIC GRAVITY)

Table B.1. Calibration set – calorific value

	Accession no.	Identity	Parentage	Age(yr)	Location of trees
1	5513	53-90-851	DxD	5	Fitler, MS
2	5587	19-89-688	DxD	5	Fitler, MS
3	5600	39-89-595	DxD	5	Fitler, MS
4	5489	34-89-500	DxD	5	Togo Island, MS
5	5523	60-90-982	DxD	5	Togo Island, MS
6	5528	41-89-643	DxD	5	Togo Island, MS
7	1922	GS-007-02	T	10	Westport, OR
8	1944	GS-009-05	T	10	Westport, OR
9	2045	GS-017-06	T	10	Westport, OR
10	567	180-370	TxD	6	Boardman, OR
11	636	189-436	TxD	6	Boardman, OR
12	587	181-389	TxD	6	Boardman, OR
13	7849	581-96-18287	TxD	5	Westport, OR
14	7855	581-96-18302	TxD	5	Westport, OR
15	7856	588-96-18404	TxD	5	Westport, OR
16	7239	421-95-12839	TxD	4	Westport, OR
17	7253	449-95-13093	TxD	4	Westport, OR
18	7254	449-95-13094	TxD	4	Westport, OR
19	7944	529-96-16924	DxT	5	Westport, OR
20	7951	534-96-16967	DxT	5	Westport, OR
21	7970	539-96-17026	DxT	5	Westport, OR
22	7174	413-95-12672	DxT	4	Westport, OR
23	7171	413-95-12667	DxT	4	Westport, OR
24	7161	413-95-12617	DxT	4	Westport, OR
25	860	DN 2 (BADEN 431)	DxN	6	Boardman, OR
26	897	NE 224	DxN	6	Boardman, OR
27	906	I78 (JACOMETTI)	DxN	6	Boardman, OR
28	7388	386-95-11567	DxM	4	Westport, OR
29	7414	391-95-11724	DxM	4	Westport, OR
30	7419	391-95-11742	DxM	4	Westport, OR
31	990	262-5	TxM	6	Westport, OR
30	1015	265-208	TxM	6	Westport, OR
33	1065	270-86	TxM	6	Westport, OR
34	7803	541-96-17087	DxTM	5	Westport, OR
35	7908	523-96-16806	DxTN	5	Westport, OR
36	971	233-3	TDxM	5	Clastkaine, OR
37	*	294-048	M x M	15	Puyallup, WA
38	*	301-237	M x M	15	Puyallup, WA
39	900-050	Caudina, DN-34	u[a]		

40	900-062	Caudina, DN-34	u
41	901-100	Caudina, DN-34	u
42	901-101	Caudina, DN-34	u
43	901-099	Caudina, DN-34	u
44	998-063	DN-34	u
45	998-064	DN-34	u
46	998-066	DN-182	u
47	998-067	DN-17	u
48	998-068	NC-5260	u
49	998-070	DN-182	u
50	998-071	DN-17	u
51	998-073	DN-34	u

[a]unknown

Table B.2. Validation set – calorific value

	Accession no.	Identity	Parentage	Age(yr)	Site Growth
1	5492	34-89-496	DxD	5	Fitler, MS
2	5472	58-90-941	DxD	5	Fitler, MS
3	5577	45-89-728	DxD	5	Togo Island, MS
4	5620	20-89-626	DxD	5	Togo Island, MS
5	2551	GS-049-04	T	10	Westport, OR
6	2345	GS-038-01	T	10	Westport, OR
7	595	183-396	TxD	6	Boardman, OR
8	661	190-461	TxD	6	Boardman, OR
9	7853	581-96-18295	TxD	5	Westport, OR
10	7824	573-96-18087	TxD	5	Westport, OR
11	199	15-29	TxD	4	Westport, OR
12	7288	434-95-13094	TxD	4	Westport, OR
13	7938	539-96-16903	DxT	5	Westport, OR
14	7922	525-96-16875	DxT	5	Westport, OR
15	7183	413-95-12713	DxT	4	Westport, OR
16	7184	413-95-12714	DxT	4	Westport, OR
17	868	DN 177 (SPIJK)	DxN	6	Boardman, OR
18	900	NE 389	DxN	6	Boardman, OR
19	7416	391-95-11729	DxM	4	Westport, OR
20	7427	391-95-11766	DxM	4	Westport, OR
21	1003	263-20	TxM	6	Westport, OR
22	1052	269-72	TxM	6	Westport, OR
23	*	290-006	MxM	15	Puyallup, WA
24	900-063	Caudina, DN-34	u[a]		
25	998-062	DN-34	u		
26	998-069	NC-5260	u		
27	184-411		u		

[a]unknown

Table B.3. Calibration set – specific gravity

	Accession no.	Identity	Parentage	Age(yr)	Site Growth
1	5513	53-90-851	DxD	5	Fitler, MS
2	5587	19-89-688	DxD	5	Fitler, MS
3	5600	39-89-595	DxD	5	Fitler, MS
4	5489	34-89-500	DxD	5	Togo Island, MS
5	5523	60-90-982	DxD	5	Togo Island, MS
6	5528	41-89-643	DxD	5	Togo Island, MS
7	1922	GS-007-02	T	10	Westport, OR
8	1944	GS-009-05	T	10	Westport, OR
9	2045	GS-017-06	T	10	Westport, OR
10	567	180-370	TxD	6	Boardman, OR
11	587	181-389	TxD	6	Boardman, OR
12	636	189-436	TxD	6	Boardman, OR
13	7849	581-96-18287	TxD	5	Westport, OR
14	7855	581-96-18302	TxD	5	Westport, OR
15	7856	588-96-18404	TxD	5	Westport, OR
16	7239	421-95-12839	TxD	4	Westport, OR
17	7253	449-95-13093	TxD	4	Westport, OR
18	7254	449-95-13094	TxD	4	Westport, OR
19	7944	529-96-16924	DxT	5	Westport, OR
20	7951	534-96-16967	DxT	5	Westport, OR
21	7970	539-96-17026	DxT	5	Westport, OR
22	7174	413-95-12672	DxT	4	Westport, OR
23	7171	413-95-12667	DxT	4	Westport, OR
24	7161	413-95-12617	DxT	4	Westport, OR
25	860	DN 2 (BADEN 431)	DxN	6	Boardman, OR
26	897	NE 224	DxN	6	Boardman, OR
27	906	I78 (JACOMETTI)	DxN	6	Boardman, OR
28	7388	386-95-11567	DxM	4	Westport, OR
29	7414	391-95-11724	DxM	4	Westport, OR
30	7419	391-95-11742	DxM	4	Westport, OR
31	990	262-5	TxM	6	Westport, OR
30	1015	265-208	TxM	6	Westport, OR
33	1065	270-86	TxM	6	Westport, OR
34	7803	541-96-17087	DxTM	5	Westport, OR
35	7908	523-96-16806	DxTN	5	Westport, OR
36	971	233-3	TDxM	5	Clastkaine, OR

Table B.4. Validation set – specific gravity

	Accession no.	Identity	Parentage	Age(yr)	Site growth
1	5492	34-89-496	DxD	5	Fitler, MS
2	5472	58-90-941	DxD	5	Fitler, MS
3	5577	45-89-728	DxD	5	Togo Island, MS
4	5620	20-89-626	DxD	5	Togo Island, MS
5	2551	GS-049-04	T	10	Westport, OR
6	2345	GS-038-01	T	10	Westport, OR
7	595	183-396	TxD	6	Boardman, OR
8	661	190-461	TxD	6	Boardman, OR
9	7853	581-96-18295	TxD	5	Westport, OR
10	7824	573-96-18087	TxD	5	Westport, OR
11	199	15-29	TxD	4	Westport, OR
12	7288	434-95-13094	TxD	4	Westport, OR
13	7938	539-96-16903	DxT	5	Westport, OR
14	7922	525-96-16875	DxT	5	Westport, OR
15	7183	413-95-12713	DxT	4	Westport, OR
16	7184	413-95-12714	DxT	4	Westport, OR
17	868	DN 177 (SPIJK)	DxN	6	Boardman, OR
18	900	NE 389	DxN	6	Boardman, OR
19	7416	391-95-11729	DxM	4	Westport, OR
20	7427	391-95-11766	DxM	4	Westport, OR
21	1003	263-20	TxM	6	Westport, OR
22	1052	269-72	TxM	6	Westport, OR

APPENDIX D

DETERMINATION OF THE ACID CORRECTION

B.1. Experimental Procedure:

ASTM Test Methods E775-87 was used for bomb washing procedures to measure the acid correction. After the bomb was fired, the bomb was allowed to stand for 5 minutes. It was removed from the water bucket and the residual gases were released in no less than one minute. The bomb was opened and examined for the traces of the unburned material. If nothing was found, all parts of the interior of the bomb including the capsule was carefully washed with fine jet of type II DI water containing methyl orange until no acid reaction was observed. The washings were collected in a 250-ml beaker and titrated with standard sodium carbonate solution to obtain acid correction for the heating value as specified in calorimetric determination of Test Method ASTM E711. One bomb washing in every combination of the calibration and validation sets was selected to measure the average acid corrections.

B.2. Discussion and Recommendation:

27 bomb washings were selected from the calibration set and the validation set matrix to measure the average acid correction. The average value that was obtained from bomb washings method was approximately 8 calories which is less than with the value of 10 calories that was used as recommended in the manuals of 6200 oxygen bomb calorimeter (Parr Instrument).

In the ASTM treatment, the correction for acid formation assumed that all acid titrated is nitric acid. If sulfur is present in the sample, which in turn produced sulfuric acid, part of the correction for the sulfuric acid was already included in the nitric acid correction. For most work, it is recommended to set acid value to nitric acid only. This will make the experiments more time efficient.

Based on the results, 8 calories will be used in the acid correction for all experiments.

Table B.1. Acid corrections of hybrid poplar

Accession no.	Identity	Taxon	Age	Location of trees	Acid Corrections (Calories)
Calibration set					
5513	53-90-851	DxD	5	Fitler, MS	7.1654
5489	34-89-500	DxD	5	Togo Island, MS	7.6431
1922	GS-007-02	T	10	Westport, OR	8.1208
567	180-370	TxD	6	Boardman, OR	8.1208
7849	581-96-18287	TxD	5	Westport, OR	7.6431
7239	421-95-12839	TxD	4	Westport, OR	8.1208
7944	529-96-16924	DxT	5	Westport, OR	7.6431
7174	413-95-12672	DxT	4	Westport, OR	8.1208
860	DN 2 (BADEN 431)	DxN	6	Boardman, OR	8.1208
7388	386-95-11567	DxM	4	Westport, OR	7.6431
990	262-5	TxM	6	Westport, OR	8.1208
7803	541-96-17087	DxTM	5	Westport, OR	7.6431
7908	523-96-16806	DxTN	5	Westport, OR	7.6431
971	233-3	TDxM	5	Clatskine, OR	8.1208
*	294-048	M x M	15	Puyallup, WA	8.1208
Validation set					
5492	34-89-496	DxD	5	Fitler, MS	7.6431
5577	45-89-728	DxD	5	Togo Island, MS	7.6431
2551	GS-049-04	T	10	Westport, OR	7.1654
595	183-396	TxD	6	Boardman, OR	8.1208
7853	581-96-18295	TxD	5	Westport, OR	7.6431
199	15-29	TxD	4	Westport, OR	7.6431
7938	539-96-16903	DxT	5	Westport, OR	7.1654
7183	413-95-12713	DxT	4	Westport, OR	8.1208
868	DN 177 (SPIJK)	DxN	6	Boardman, OR	8.1208
7416	391-95-11729	DxM	4	Westport, OR	8.1208
1003	263-20	TxM	6	Westport, OR	7.6431
*	290-006	MxM	15	Puyallup, WA	7.1654
Average value					***7.7846***

B.3. Reference:

ASTM E775-87 (Reapproved 2004) Standard Test Methods for Total Sulfur in the Analysis of Refuse-Derived Fuel

ASTM E711-87 (Reapproved 2004) Standard Test methods for Gross Calorific Value of Refuse-Derived Fuel by the Bomb Calorimeter.

APPENDIX D

PLS ALGORITHMS

C.1. PLS-2 Algorithms (Esbensen, 2000)

1. Center and scale (if necessary) both the X and Y matrices appropriately:

   Index initialization, f: f=1; $X_f = X$; $Y_f = Y$
2. for u_f choose any column in Y (initial proxy u-vector)
3. $w_f = X^T u_f / | X^T u_f |$
4. $t_f = Xw_f$
5. $q_f = Y^T t_f / | Y^T t_f |$
6. $u_f = Yw_f$
7. check for convergence: if $| t_{f,new} – t_{f,old} |$ < criterion, stop; else go to step 2
8. $p_f = X^T t / t^T t$
9. $b = u^T t / t^t t$ (inner relation)
10. $X_{f+1} = X_f - t_f p_f^T$; $Y_{f+1} = X_f - b t_f q_f^T$; updating
11. f := f +1
12. Repeat 2 through 11 until f = A (optimum no. of PLS-components)

C.2. PLS-1 Algorithms (Esbensen, 2000)

1. Center and scale (if necessary) both the X and Y matrices appropriately:

   Index initialization, f: f=1; $X_f = X$; $Y_f = y$
2. $w_f = X^T y_f / | X^T y_f |$
3. $t_f = Xw_f$
4. $q_f = t^T y_f / | t^T t_f |$
5. $p_f = X_y^T t_f / t_f^T t_f$
6. $X_{f+1} = X_f - t_f p_f^T$; $y_{f+1} = y_f - b_f t_f$
7. f := f +1
8. Repeat 2 through 7 until f = A (optimum no. of PLS-components)

C.3. Reference:

Esbensen, K. H., 2000. Multivariate Data Analysis – in practice (4th edition). Olso, CAMO ASA.

APPENDIX E

REGRESSION COEFFICIENT PLOTS (1^{ST} DERIVATIVE SPECTRA)

Figure D.1. Regression coefficients for the calibration model for predicting extractives content of hybrid poplar wood.

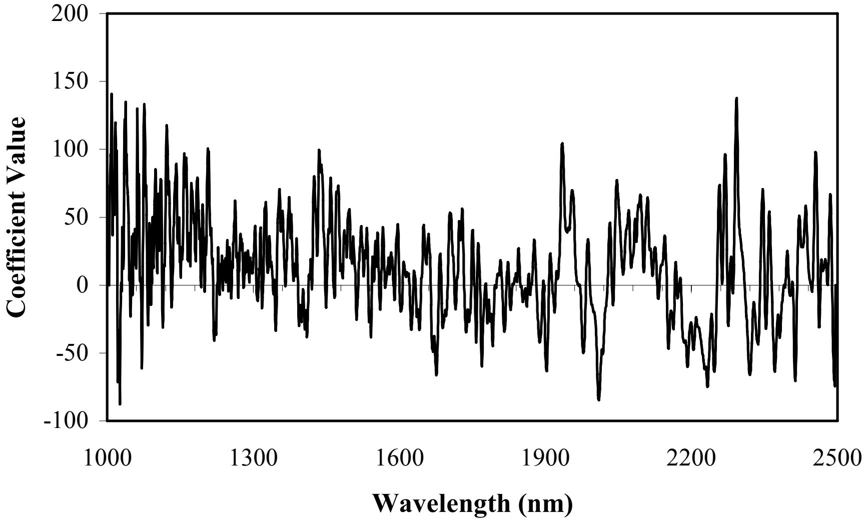

Figure D.2. Regression coefficients for the calibration model for predicting ash content of hybrid poplar wood.

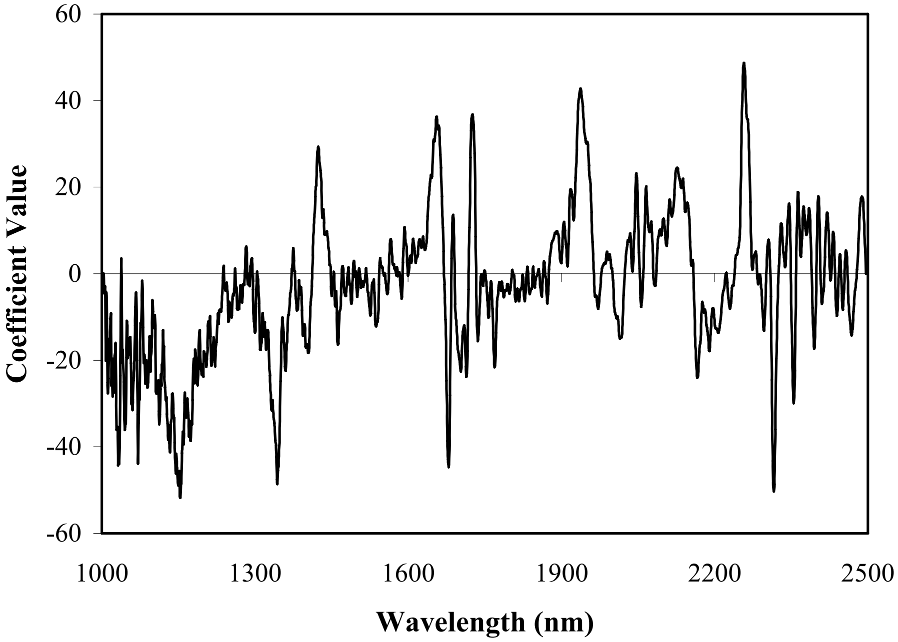

Figure D.3. Regression coefficients for the calibration model for predicting lignin content of hybrid poplar wood.

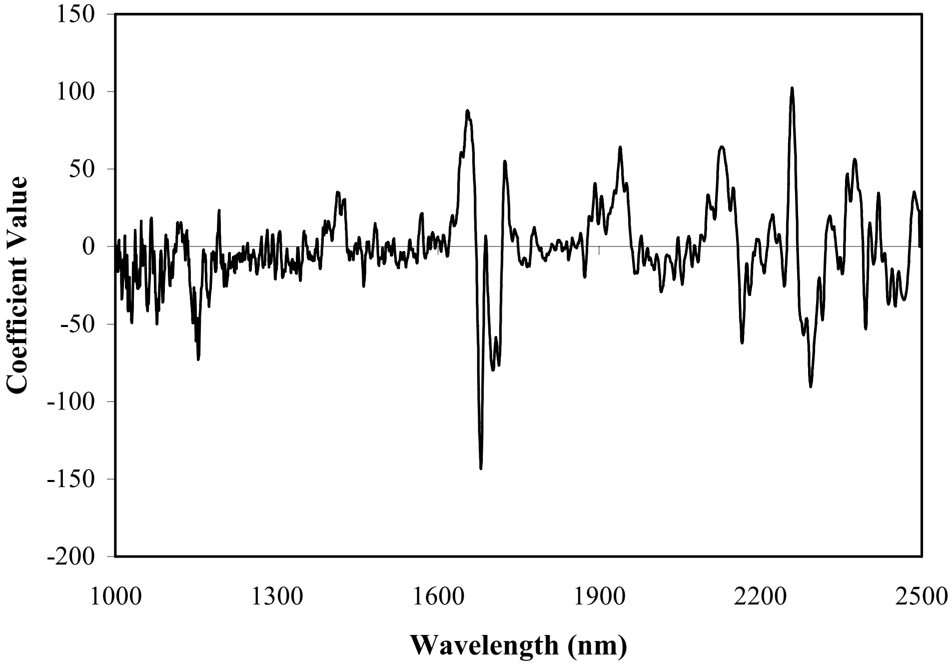

Figure D.4. Regression coefficients for the calibration model for predicting glucan content of hybrid poplar wood.

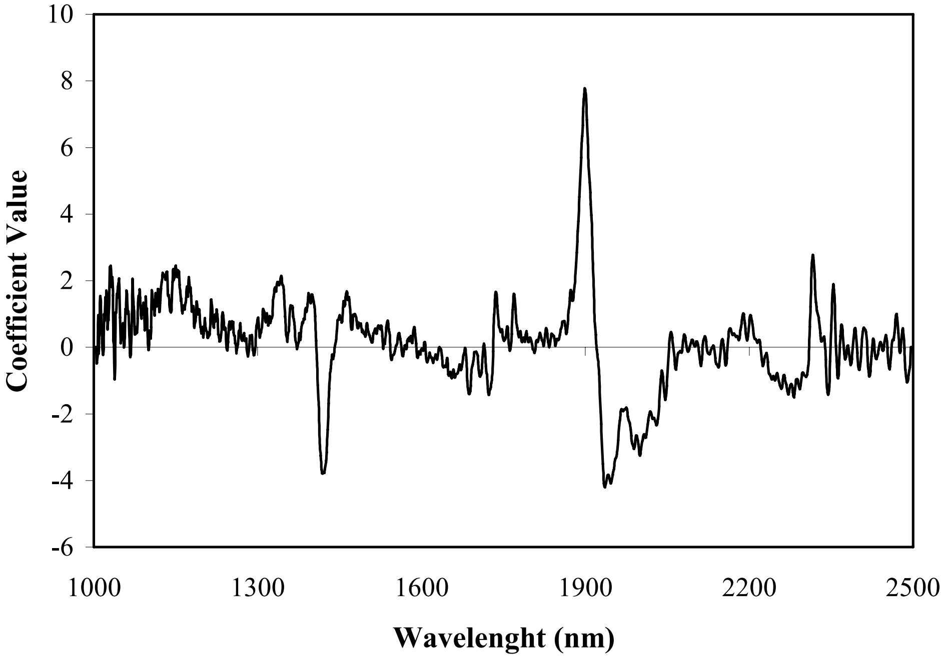

Figure D.5. Regression coefficients for the calibration model for predicting xylan content of hybrid poplar wood.

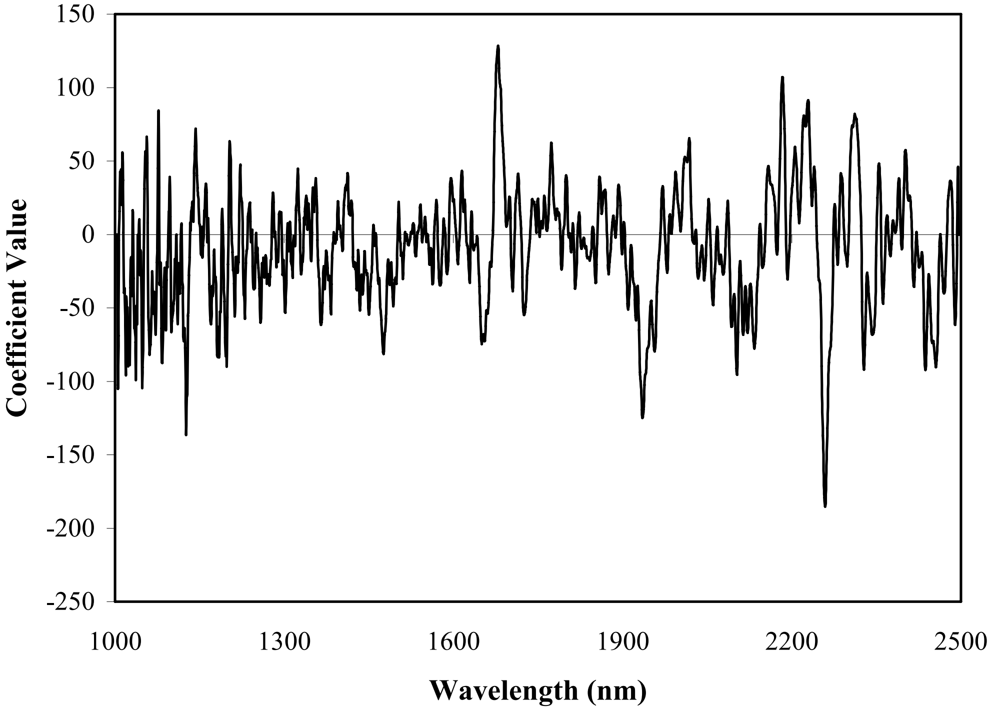

Figure D.6. Regression coefficients for the calibration model for predicting galactan content of hybrid poplar wood.

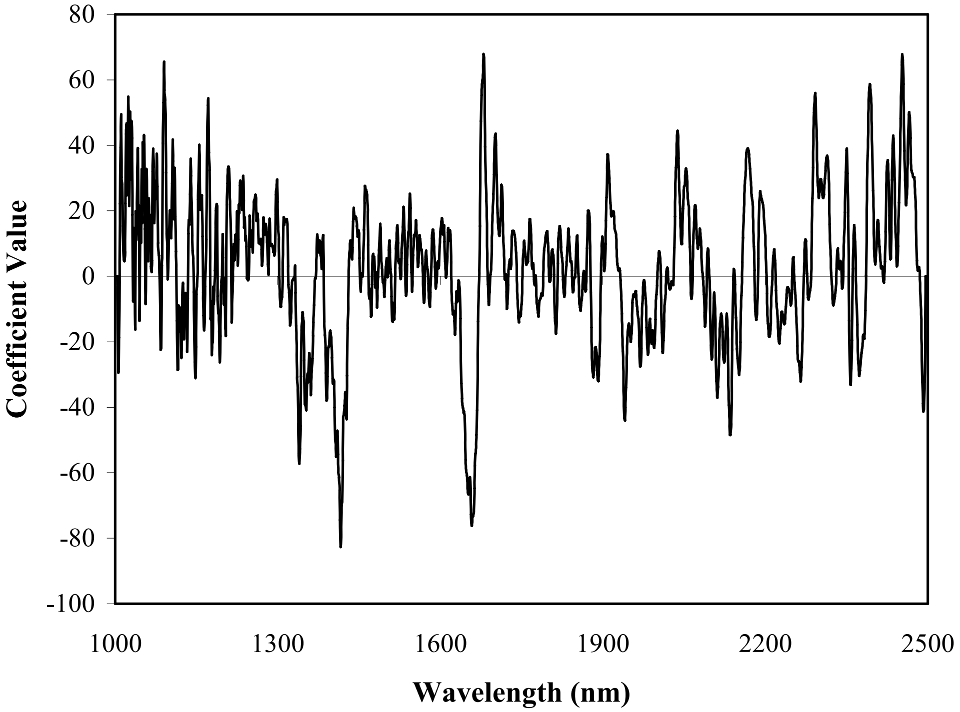

Figure D.7. Regression coefficients for the calibration model for predicting arabinan content of hybrid poplar wood.

Figure D.8. Regression coefficients for the calibration model for predicting mannan content of hybrid poplar wood.

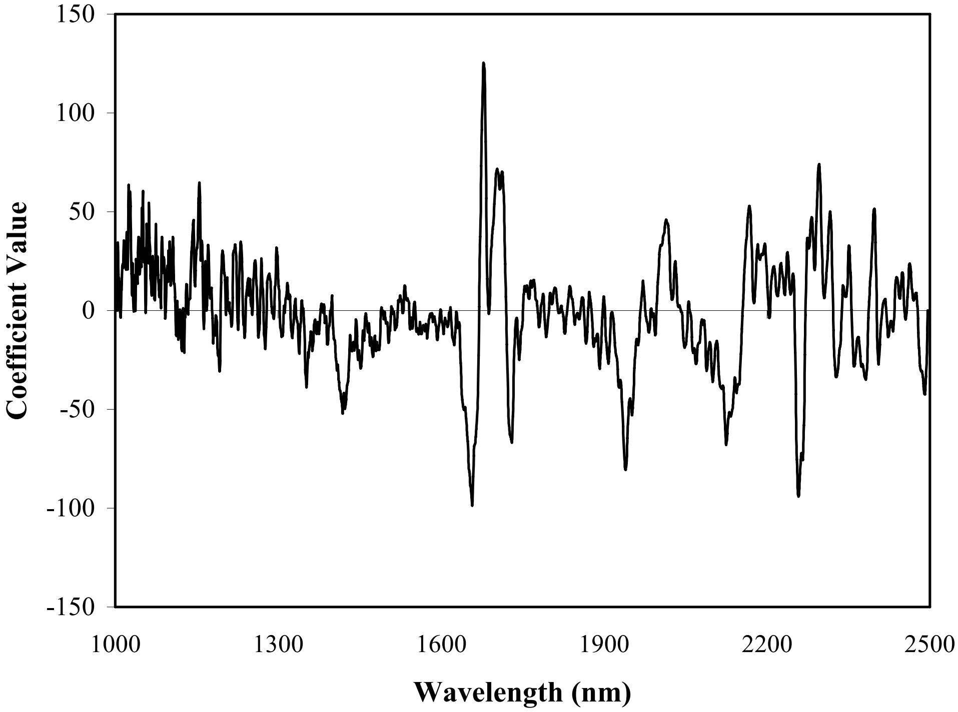

Figure D.9. Regression coefficients for the calibration model for predicting S/G ratio of hybrid poplar wood.

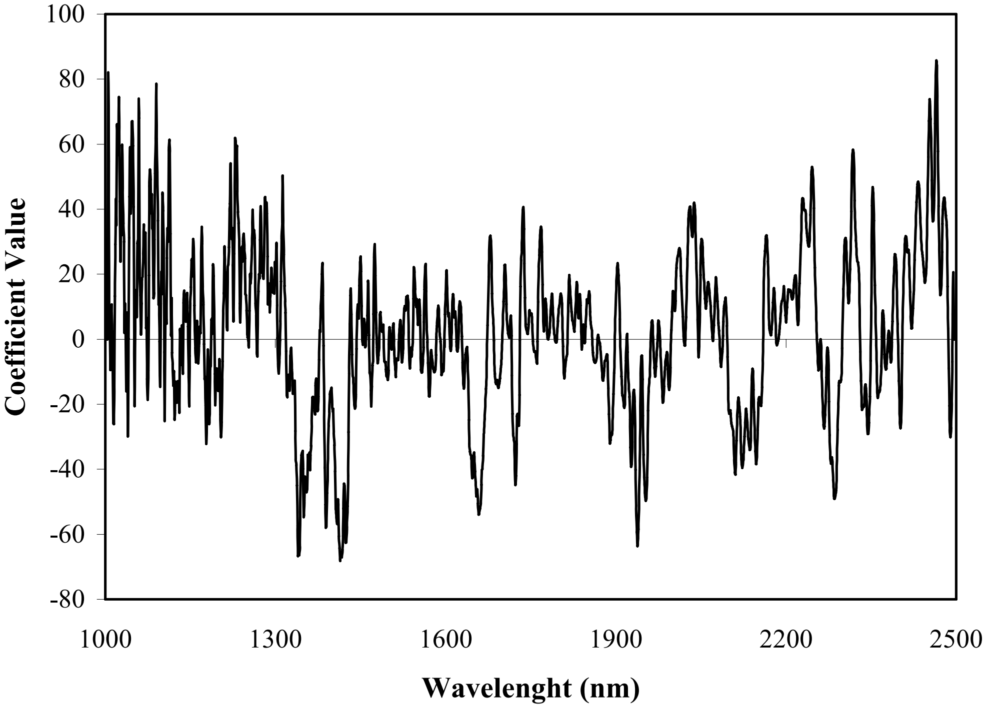

Figure D.10. Regression coefficients for the calibration model for predicting calorific value content of hybrid poplar wood.

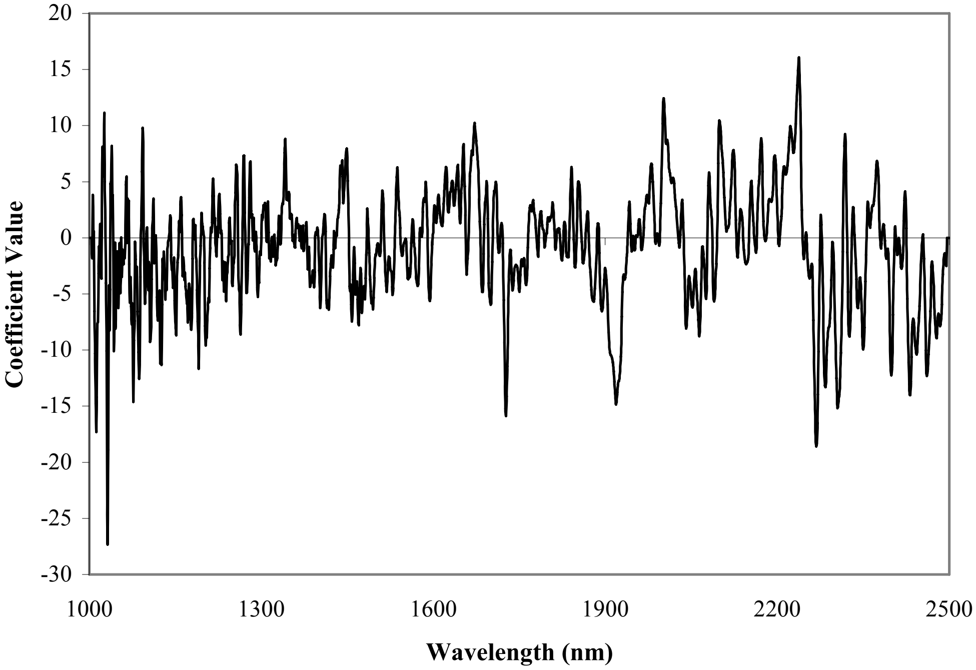

Figure D.11. Regression coefficients for the calibration model for predicting specific gravity of hybrid poplar wood.