Rapid Prediction of Wood Constituent Composition and Energy Traits Using Near-Infrared Spectroscopy

by

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Abstract

There is increasing interest in producing energy from renewable biomass resources. These resources, however, tend to be highly variable in nature and this heterogeneity can complicate their effective utilization. Rapid prediction of energy and chemical characteristics of biomass could assist in optimizing its conversion to biofuel and bioenergy. Loblolly pine (*Pinus taeda*) is the most common woody biomass in the southern U.S. and the most promising renewable resource for bioenergy. Near infrared spectroscopy (NIR) has been of great interest as a rapid, cost-effective and nondestructive technique for quantitative and qualitative analyses. This research aims at developing NIR calibrations for rapid measurement of constituent and energy properties of biomass, which can be applicable to large-scale assessment of forest resource properties and consequently assist efficient process control of large-scale conversion of heterogeneous feedstock to energy outputs.

In particular, the objectives of this research were: (1) develop NIR calibrations for prediction of lignin, extractives, ash, moisture content, and energy content (calorific value) of loblolly pine biomass; and (2) compare the NIR calibrations based on spectra from wood powder and chips and reveal the potential of calibrations based on a single spectrum per chip to predict the properties of loblolly pine.

The calibrations based on spectra of wood powder, averaged spectra per chip (25) and single spectrum per chip for constituents and calorific value were established. Good calibration

were obtained based on spectra from powder with coefficients of determination (R^2) of 0.93 (SEC=0.28%) for lignin, 0.91(SEC=0.14%) for extractives, 0.85 (SEC=0.025) for ash, 0.96 (SEC=0.32) for moisture, and 0.91 (SEC=0.05 MJ/kg) for calorific value. The calibrations based on averaged spectra per chip also presented good correlation with an R^2 ranging from 0.8 to 0.9 for composition and calorific value. Calibrations based on a single spectrum per chip gave an R^2 of 0.81 (SEC=0.4%) for lignin, 0.84(SEC=0.18%) for extractives, 0.72 (SEC=0.03) for ash, 0.87 (SEC=0.33) for moisture, and 0.74 (SEC=0.34 MJ/kg) for calorific value.

The results indicate that for all properties in the current study, the calibrations based on spectra from the powder gave the highest R^2 and relatively lower standard error. Furthermore, good correlations between measured and predicted values were also acquired from the calibrations based on averaged spectra per chip, exhibited a slightly lower R^2. Although not as good as powdered or average chip tests, relatively strong calibrations were possible for even the single spectrum treatment when predicting chip properties. With RPD values ranging from 1.3 to 2.9, the calibrations based on single spectrum per chip met the requirement for initial screening. The simplicity and rapidity of calibrations based on a single spectrum from a solid wood chip may outweigh the slightly greater precision achieved when analyzing ground, bulk samples. This study reveals that NIRS in combination with multivariate analysis has the potential to predict the bioenergy and chemical characteristics of biomass in an industrial conversion.

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Chapter1 INTRODUCTION

With a growing concern of economic stability and environment issues, the use of renewable resource to replace fossil fuels has attracted great attention. Because they are clean burning, have lower net CO_2 emission, have a short cycle of growing and are presumed sustainable, biomass energy has been attracting more and more attention worldwide (Kumar *et al.*, 2009; Broek *et al*., 1996). After the bioconversion through direct combustion, biological and thermochemical processes, biomass can be utilized as three end-products: heat and power, transportation fuels such as ethanol, and chemical intermediates. The production of biofuel and generation of electrical power are currently the two main markets for bioenergy (Zhang *et al*., 2010; Cantrell *et al*., 2008; McLaughlin *et al*., 1999). At present, biomass accounts for 14% of the world's primary energy consumption and it is estimated that, by 2025, biomass sources will provide up to 30% of raw materials for the chemical industry, about 38% of the world's direct fuel use and 17% of the world's electricity (Kamm, 2007; Demirbas, 2000; Demirbas, 2001a).

Due to the rapid attainment of maturity and widespread availability in southern U.S., loblolly pine is developing as a promising renewable energy resource (Baker and Balmer, 1983; Sannigrahi *et al*., 2008). Consequently, the investigation of factors that influence the bioconversion of loblolly pine is becoming increasingly necessary. Quantity of specific chemical constituents and calorific value are the main characteristics of biomass thought to impact conversion of biomass to non-thermal energy products and could play an important role in

biological and thermochemical processes for conversion (Dinus, 2000; Ragland *et al*., 1991; Demirbas, 2004; Demirbas, 2001b).

The methods for measurement of chemical composition of wood are conventional wet chemical analyses, plus calorific value is obtained using a bomb calorimeter. These methods are cost prohibitive and time consuming, destructive, sample throughput limited and require specific sample preparation. Thus, there is a need for a rapid, reliable and cost effective method for measurement of properties of biomass.

Recently near infrared spectroscopy (NIR) combined with multivariate analysis has been demonstrated to be a rapid, cost effective and reliable method for measuring wood properties (Via *et al*., 2003; Taylor *et al*., 2008; Hein *et al*., 2010; So and Eberhardt, 2010; Poke *et al*., 2007). Most of these studies were based on milled wood sample. Milling of samples is felt to improve results in these studies by overcoming a specific limitation inherent in the application of NIR diffuse reflectance mode in heterogeneous materials. Because NIR measurements are typically made over relatively small areas, irregularities in surface properties of woody material can lead to significant variation in results and a strong dependence on sample size (Yeh *et al*., 2004). Nevertheless, in most biomass and bioenergy applications wood chips will likely be the main feedstock and the ability to effectively characterize them using NIR could lead to improved on-line and process control monitoring capabilities. The exclusion of the grinding step will also simplify the development of NIR calibrations for lab applications, provided accuracy of measurements can be maintained.

Some studies have reported NIR calibrations of solid wood chips or strips and obtained encouraging results (Poke and Raymond, 2006; Jones *et al*., 2008; Jones *et al*., 2006; Kelley *et al*., 2004). However, the research mentioned above were all based on multiple, averaged spectra of solid wood chips or strips, to date nobody has investigated the NIR calibrations established from a single spectrum per chip. This situation might be more realistic in an online process in which chips were moving rapidly past an NIR sensing device that was providing real-time control information to a conversion system.

The objectives of this research were: (1) develop NIR calibrations for prediction of lignin, extractives, ash, moisture content, and energy content (calorific value) of loblolly pine biomass; and (2) compare the NIR calibrations based on spectra from wood powder and chips and reveal the potential of calibrations based on a single spectrum per chip to predict the properties of loblolly pine.

The present study seeks to develop the NIR calibrations based on wood powder and chips for a rapid, cost-effective measurement of chemical composition and energy content of loblolly pine, which could assist and optimize the biological, thermochemical processes and direct combustion of large-scale heterogeneous feedstock to energy outputs.

Chapter 2 LITERATURE REVIEW

2.1 Introduction

The characteristics of softwood especially loblolly pine wood are presented in the review. The chemical components, energy traits and the relationship between these two are reported. The relationship reveals the contribution of different composition to energy traits, which can lead to the efficient measurement and optimization of bioconversion process. Finally, the principle, instrument, limitation and application of near infrared spectroscopy and multivariate analysis are presented.

2.2 Wood chemical composition

Loblolly pine is the fastest growing and widely cultivated softwood pine species in the southeastern United States. Normally the major chemical components in wood contain carbohydrate (65-75%), lignin (18-35%) and minor components such as extractives, minerals, and trace components, which account for 4-10% of the dry biomass weight (Pettersen, 1984). The components studied in the current research were reviewed in detail. A good understanding of chemical components of wood facilitates a further study of wood energy outputs and utilization in different areas.

2.2.1 Lignin

Lignin is the third major component of the wood cell wall and acts as a cementing material bonding the cells together (Farmer, 1967). The word lignin is a derived name from the latin word *lignum*, meaning wood but is present in most non-wood plants (SjÖstrÖm, 1981). The basic structural unit of lignin molecule is the phenylpropane unit which is an aromatic ring with a three-carbon side chain (Farmer, 1967). Normally softwood and hardwood contain 26-32% and 20-28% lignin respectively. Lignin is an amorphous polyphenolic polymer that is synthesized by coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, which is shown in Figure 2.1 and Figure 2.2 (Ragauskas *et al.,* 2006; Pettersen, 1984).

White (1987) determined the lignin content of four species softwoods: Engelmann spruce (26.9%), Western redcedar (30.8%), Southern pine (26.8%) and Redwood (33.8%). Demirbas (2001) also reported lignin content of 32.5 and 21.89% for softwood and hardwood. So *et al.* (2012) measured lignin content from the extracted longleaf pine and the values ranged between 26.6 and 31.5%. Via *et al.* (2007) measured Klason lignin content of longleaf pine at different tree heights and horizontal ring numbers, and the values ranged from 26.5 to 30.8%.

The lignin content of loblolly pine ranged from 24.1 to 32.63% as presented by Sykes *et al.* (2005) in which the lignin content was determined for different ring numbers and for earlywood and latewood. Ferraz *et al.* (2004) and Sannigrahi *et al*. (2008) also observed lignin content for loblolly pine of 28.2 and 29.4%, respectively.

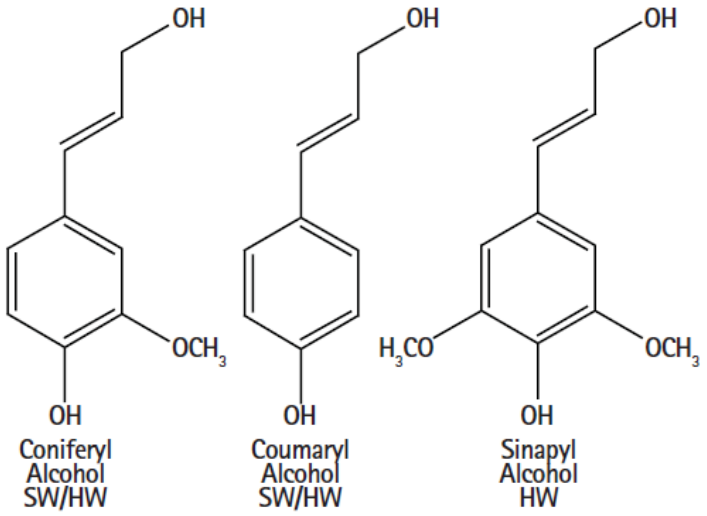


Figure 2.1. Precursors of lignin biosynthesis for softwood (SW) and hardwood (HW)

(Ragauskas *et al.*, 2006)

2.2.2 Extractives

In addition to polysaccharides and lignin, wood contains smaller amounts of components called extractives which can accounts for 4– 10% of the dry weight of normal wood species.

Extractives include many different kinds of organic compounds, such as tannins, starch, waxes, fats, proteins, phenolics, resins, essential oils, simple sugars and alcohols (Farmer, 1967). The extractives are mostly present in the heartwood while smaller amounts exist in the sapwood. Extractives protect wood against fungi and insect damage, can be a supply of energy reserves, and can be intermediates in tree metabolism. They also contribute to other properties of wood such as color, decay resistance, taste and flammability (Pettersen, 1984).

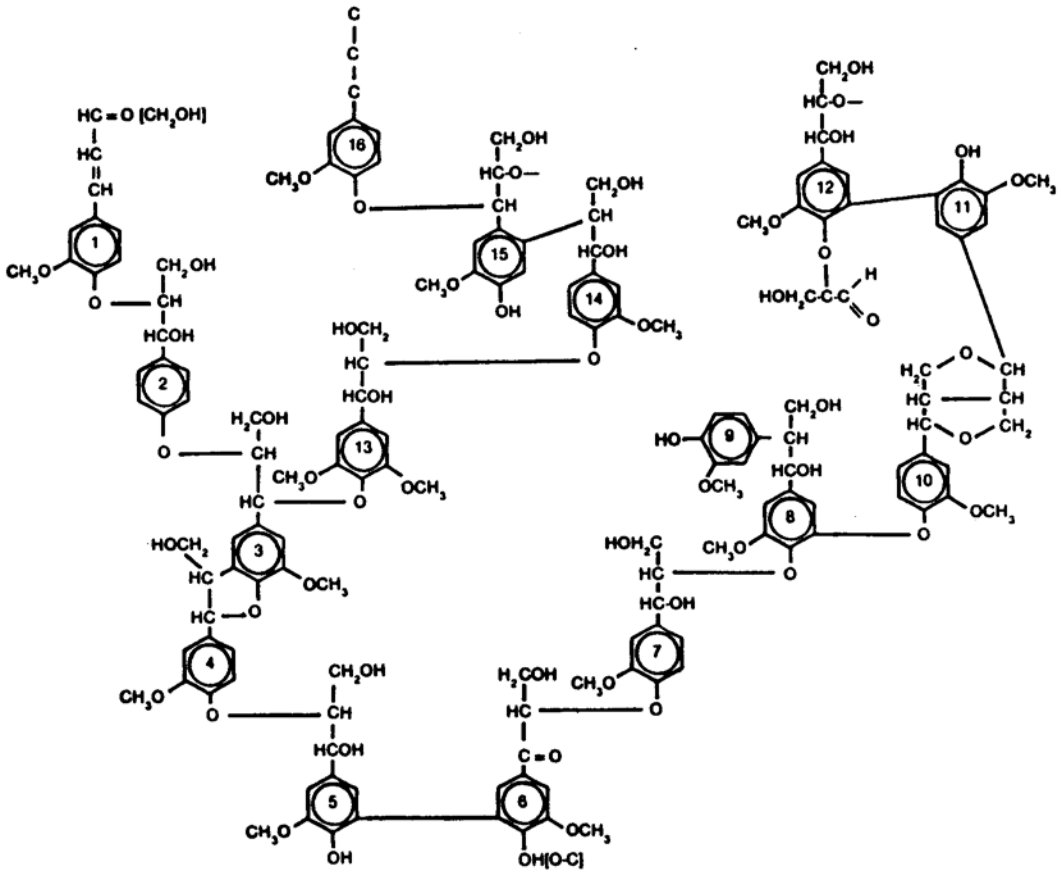


Figure 2.2. A partial structure of softwood lignin (PETTERSEN, 1984)

So *et al.* (2012) measured extractives content of 40 longleaf pine samples with a wide range from 0.0 to 20.6%. Extractives content ranging from 2.8 to 26.9% was presented by Kelley *et al.* (2004) with the measurement of extractives content of different tree, height, and growth ring combinations of loblolly pine. Via *et al.* (2007) determined extractives content of longleaf pine samples of different tree height and ring number and the values ranged from 1.7 to 30.5%. White (1987) also reported extractives content of four species softwoods: Engelmann spruce

(2.4%), Western redcedar (7.8%), Southern pine (5.4%) and Redwood (8.2%). Shupe *et al.* (1997) observed the extractives content of innerwood and outerwood from five silviculturally different loblolly pine stands with the alcohol-benzene extractives content from 2.5 to 4.53% for outerwood and 5.23 to 6.98% for innerwood.

2.2.3 Moisture content

Moisture content of wood is the amount of water contained in the wood sample, which can be expressed on dry basis or wet basis. Water can be held in wood by two ways: bound water and free water. Moisture content is calculated as the weight loss after drying, which is normally ranged between 8 to 14% on dry basis. Hearmon (1948) determined moisture content of 10% for Scots pine and ranged from 6.8 to 12% for Sitka spruce. Wood (1955) also reported moisture content ranged from 7.1 to 21.6% for Sitka spruce. Ragland *et al*. (1991) presented that fresh wood has a moisture content of 35-60% on a wet basis, dried wood used for fuel has a moisture content of 5-20%.

2.2.4 Ash content

Ash content is the solid residual remaining after ignition of wood sample. The ash content of wood is measured by combustion a weighted sample in a crucible until all carbonaceous matter is gone (Farmer, 1967). Ash is a product of the minerals present in the structure of trees, such as calcium, potassium and magnesium (Pettersen, 1984). And the ash content can typically account for 0.2-2% of wood on dry basis.

Lestander and Rhén (2005) observed an ash content of 0.3 to 2.2% for Norway spruce samples. Etiégni (1991) found that ash yield decreased by approximately 45% as the combustion temperature increased from 538 to1093°C, while the metal content increased with the

temperature increased. Rhén *et al.* (2007) also presented that based on the different tree species, ash content was approximately 0.4-0.6% in stem wood, 2.5-3.5% in stem bark and 2.2-8.7% in foliage. McMillin (1969) reported that ash content of early wood was 0.43%, which decreased with distance from the pith, and increased with increases in rate of tree growth rate for loblolly pine. The ash content of latewood of loblolly pine was 0.39% that was unrelated to distance from pith, specific gravity and growth rate.

2.3 Wood calorific value

The gross calorific value (GCV) or higher heating value (HHV) of a substance is defined as the amount of heat released by the combustion of a specific quantity of this substance after it have returned to the original pre-combustion temperature (normally at 25°C). The GCV subtracted by the latent heat of vaporization of water in the combustion substance becomes the lower heating value (LHV) (So and Eberhardt, 2010; Sheng and Azevedo, 2005). The GCV is measured in a bomb calorimeter, in which the combustion of the mixture of sample and oxidizer is initiated by an ignition device. After a complete combustion of the sample, the HHV is calculated with water in its liquid phase while LHV is calculated with water in vapor phase, which is calculated as the difference of heat of the sample and the product. GCV of biomass was found to relate to its proximate, ultimate analysis composition which can be calculated with a formula: HHV=-1.367+0.3137C+0.7009H+0.0318O (Sheng and Azevedo, 2005). The GCV of biomass was also considered related to the amount of fixed carbon: GCV=0.196(FC) +14.119 (Demirbas, 1997).

GCV is a crucial property of biofuel and biomass because of the impact on utilization of any material as a fuel, so there have been a lot of studies focused on this energy trait. Gillon *et al.* (1997) determined the GCV of a wide variety of biomass including conifer, broadleaved trees,

shrubs, twigs, fern and grasses in which the value ranged from17.1 to 24.6 MJ/kg. GCV for a variety of biomass including leaf, corncob, straw, wood, stalk, hazelnut shell was also reported by Demibaş (2001b) and the value ranged from 17.8 to 21.53 KJ/g.

A lot of studies focused on the GCV of softwood and the relationship between GCV and the characteristics of biomass. Lestander and Rhén (2005) tested the GCV of stem and branch wood of 36-year-old Norway spruce samples and the values ranged from 20.2 to 21.7 KJ/g.

White (1987) reported GCV for four softwoods and four hardwoods which ranged from 8600 to 9260 Btu/lb and from 8410 to 8880 Btu/lb, respectively. That study also found that softwoods generally have higher GCV values due to the higher resin and extractives content.

The similar results also reported by Jain (1992) with the determination of calorific value of 26 hardwood species and 16 *Pinus* species on an ash-free dry-weight basis in which the calorific value ranged from 11.61 to 22.67 KJ/g for hardwoods and ranging from 16.91 to 23.35 KJ/g for softwoods. Maranan and Laborie (2007) determined the calorific value between 18.71 and 19.68 KJ/g for hybrid poplar wood, and the study also indicated that there was no relationship between GCV and the age and location of the population evaluated.

Singh and Kostecky (1986) tested the GCV of 10 tree species (6 softwoods and 4 hardwoods) and different parts of the tree including stump, stem, branches, foliage, and bark. The results showed that the mean calorific values of oven-dry softwoods and hardwoods were 20.178 and 19.146 MJ/kg, and the calorific values of different parts of tree were in descending order: treetop, branches, foliage, bark, stump and stem.

Kryla (1984) also measured the GCV of different species and different parts of softwood, in most cases the GCV from this study were slightly higher than those reported by Singh (1986)

and the order of GCV of different parts of the tree is almost the same with those reported by Singh (1986).

Nurmi (1997) investigated the influence of different species and different parts on GCV by measurement of Scots pine, Norway spruce, silver birch and black alder. This study showed that they were both significant factors for GCV, the conifers determined to have the highest GCV and crown material had a higher GCV than stems or whole tree material.

2.4 Relationship between chemical composition and energy trait

Gross calorific value, which is one of the most important properties of biomass affecting utilization of material as a fuel, is highly dependent on the chemical components of biomass. Demirbaș (2001a) examined the chemical composition and calorific value of 14 biomass fuels including leaf, straw, softwood, hardwood, shell, bark, stalk and olive. The results showed that GCV had no obvious relationships with holocellulose, but there were good correlations between GCV and lignin contents and mathematical equations were also developed to calculate GCV from lignin content of biomass.

Similarly, based on the measurement of chemical composition and GCV of biomass samples, Demirbaș (2002) also obtained that moisture and ash generally decrease GCV, extractives make biomass more desirable as fuel, and there were no direct relations between GCV and holocellulose.

Based on the plot of regression coefficients of twenty longleaf pine samples, So and Eberhardt (2010) observed a strong relationship between GCV and extractives content and an weaker relationship between GCV and lignin content. So *et al.* (2012) also obtained a strong relation between GCV and extractives content based on the plot of regression coefficients of 40 longleaf pine samples using both MIR and NIR. By determination of chemical components and

GCV of four hardwoods and four softwoods, White (1987) reported that GCV was correlated with lignin and extractives content.

The results above are consistent with the GCV of individual wood components. Rhén *et al.* (2007) found that on the basis of hydrogen of 6% of biomass, the calorific value were 36.9-39.4 MJ/kg for extractives, 26.8 MJ/kg for lignin and 18.7-19.5 MJ/kg for cellulose. It was also found that owing to the inorganic components of ash, which has lower calorific values and may cause problems of higher deposits during burning, the biomass material with lower ash content are preferred in energy crops. Fuels characteristics of different biomass species were also presented by Demirbaș (2002) that cellulose and hemicelluloses have a GCV of 18.6 MJ/kg, lignin has a GCV ranging from 23.26 to 25.58 MJ/kg.

The GCV of holocellulose, extractives and lignin are also in accordance with their carbon content and other elemental composition, in other words, the GCV of biomass is consistent with the carbon content and other elemental composition of biomss. There has been a lot of research focused on the correlation between ultimate and proximate analyses of biomass and GCV.

Demirbaș (2004) found that carbon content and hydrogen content increased the GCV and oxygen and nitrogen decreased the GCV of biomass. The study also found that GCV relates to the oxidation state of the biomass in which carbon atoms generally dominate and overshadow small variations in hydrogen content.

Similarly, Annamalai *et al.* (1987) also demonstrated an empirical equation, which was originally developed to estimate the GCV of fossil fuels, can be used for accurately estimate the GCV of biomass fuels. The equation showed that the higher the carbon and hydrogen content are, the lower the oxygen content is and the higher the GCV will be.

Sheng and Azevedo (2004) obtained a formula based on ultimate analysis that GCV has a positive correlation with C, H as well as O content which is on the contrast with the conclusion reported by Annamalai *et al.* (1987).

2.5 Near infrared spectroscopy

Near infrared spectroscopy (NIR) is a rapid and nondestructive technique for quantitative and qualitative analyses in various industries. Historically, in 1800 the NIR region was discovered by Herschel who separated the electromagnetic spectrum with a prism and found out that the temperature increased towards and beyond the red near infrared region (Reich, 2005).

NIR refers to the region ranging from 12500 to 4000 cm^{-1} (800 to 2500 nm) of the electromagnetic spectrum. The absorption bands mainly arise from overtones and combination bands of fundamental vibrations which were generated by the molecular vibrations in the mid-infrared region ranging from 4000 to 400 cm^{-1} (Bokobza, 2002). The near infrared radiation absorbed by a molecule give rise to vibrations of individual bonds in a manner of diatomic non-harmonic oscillator, which is different from that of the fundamental vibrations in mid-infrared region modeled according to vibrations of the harmonic motions based on Hook's law (Heigl *et al.*, 2007).

The key issues determining the band occurrence and spectral properties such as frequency and intensity of NIR bands are anharmonicity and Fermi resonance (Reich, 2005). In wood, the C-H, O-H, N-H mainly account for the fundamental vibrations which produce a series of complex, broad and overlapping bands. These overtones and combination bands in the near-infrared region are much weaker than the absorptions of the corresponding fundamental vibrations in the mid-infrared region (Borchert, 2003).

NIR analyses can be carried out in transmission or diffuse reflection mode. While the former one requires a more specific sample preparation such as the KBr pellet made of milling sample or wood wafer of certain size by using microtome or razor blade, and the latter one involves a limitation of small penetration depth into the samples (Tsuchikawa *et al.*, 2005; Yeh *et al.*, 2005; Fackler *et al.*, 2007; Poke and Raymond, 2006; Sykes *et al.*, 2005).

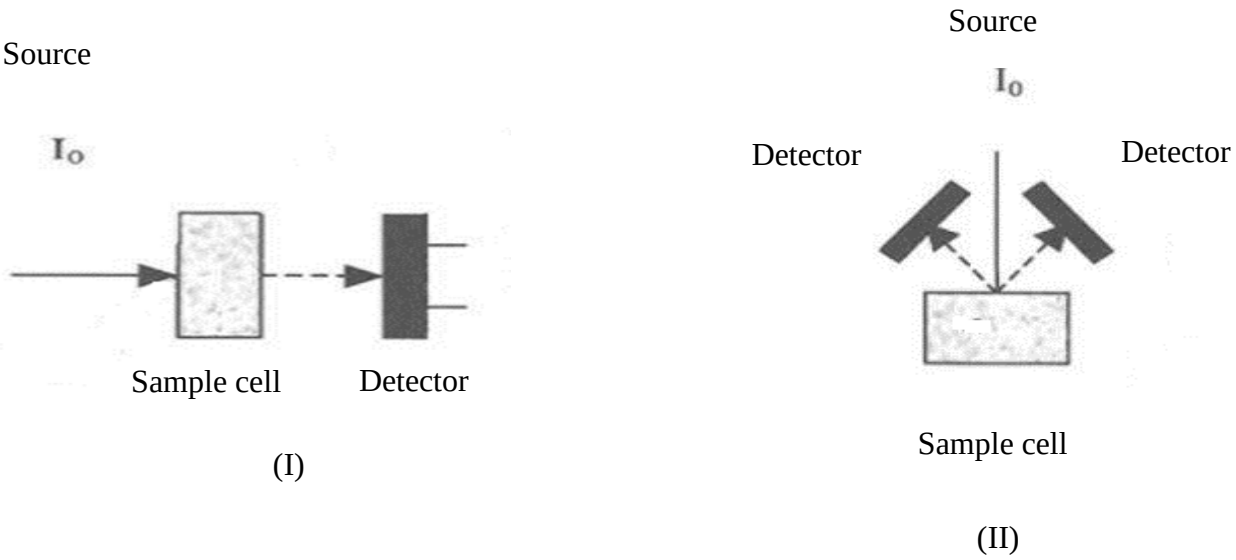


Figure 2.3.The transmittance (I) and reflectance (II) mode of NIR (Murray and Cowe, 2004)

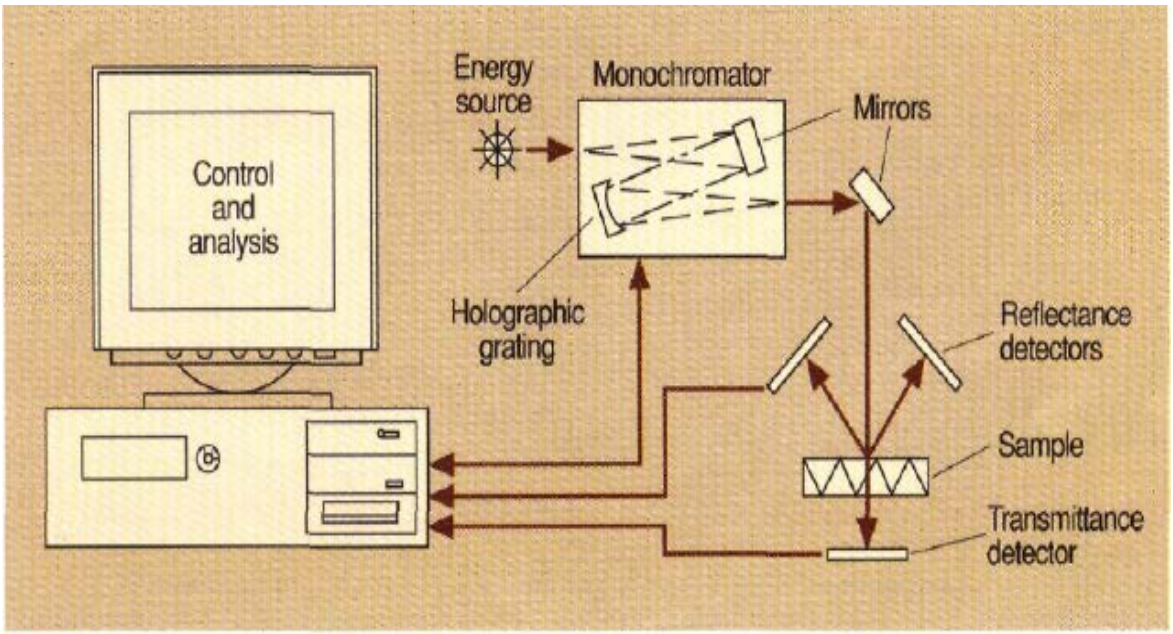


Figure 2.4.The configuration of NIR spectrometer (McClure, 1994)

In transmission mode, the sample is placed between the beam source and the detector, which measures the decrease in radiation intensity when the radiation is passing through the sample. For reflectance mode, the detector is located between the source and sample to measure the intensity of light reflected from the sample (Figure 2.3). In diffuse reflectance mode, the sample is illuminated by low-energy NIR radiation, according to the interaction between the radiation and chemical components of the sample, the radiation is transmitted through the sample, where it can be absorbed by the overtones and vibrational combinations of the analyte species in the sample, or scattered in the sample before some of them diffusely reflected back to the detector (Malin *et al*., 1999; McCarty *et al.*, 2002). NIR reflectance spectra are recorded and

accessed by calculating log (1/R) which is normally used for ordinate as absorbance, where R is the ratio of the reflectance of the sample to that of a nonabsorbing standard (Burns and Ciurczak, 1992).

Figure 2.4 presents the configuration of the NIR spectrometer which is normally composed of an energy source, monochromator, mirrors, sample presentation interface, reflectance detectors, transmittance detector and the control and analysis systems.

The light source is generally a tungsten halogen lamp or light emitting diodes (LEDs) (Bokobza, 2002). The light is first monochromated by a monochromator which is classified as filter and scanning type. In the scanning monochromator, a grating or a prism is applied to separate the individual frequencies of the radiation, and the filter monochromator is a wheel holding a number of absorption or interference filters (Nicolai *et al.*, 2007).

The detectors most commonly used in NIR spectrometer include lead sulphide detectors (PbS) and lead selenide detectors (PbSe), silicon detectors, indium gallium arsenide detectors (InGaAs). Compared with other detectors, the PbS and PbSe are with higher detection capability and faster response speed, the silicon detectors are fast, sensitive and low cost, and the InGaAs detectors are most expensive, high sensitive and with good signal-to-noise performance and stability (Satoshi, 2002).

The application of NIR was started in the early 1950s in agricultural industry, then in 1960s the utilization of multivariate analysis to NIR resulted in an increased acceptance of NIR in the food and agricultural industries (Schwanninger *et al*., 2011; So *et al*., 2004). Since the 1980s, NIR associated with chemometrics and multivariate analysis led to an upsurge of interest in NIR in diverse areas of academic study and various industrial fields such as biology, pharmaceutical, pulp and paper industries (Burns and Ciurczak, 2001; Roggo *et al*., 2007;

Pasquini, 2003; Karoui and Baerdemaeker, 2007; Santos *et al*., 2005; Antti *et al*., 1996). There were also a number of studies evaluating the potential of NIR for measurement of biomass properties.

Mclellan (1991) observed desirable correlations between laboratory measured and NIR predicted results for a wide variety of biomass including 18 species fresh and senescent foliage (6 needle-leaved conifers and 12 broad-leaved deciduous) collected from 5 locations. The correlation coefficients of calibrations for nitrogen, lignin and cellulose were 0.98, 0.88 and 0.90, respectively. The analytical error was examined by the randomly selected duplicate samples measured by different labs which showed that the analytical errors of NIR analysis was dramatically lower than those of wet chemistry methods. The relative mean error of NIR method was 1.4% for nitrogen, 2.1% for lignin and 0.6% for cellulose, while for laboratory measurements ranged from 3.9-6.1% for nitrogen, 6.9-14.1% for lignin, and 4.3-5.1% for cellulose. An interlaboratory comparison was also made to test the precision and relative accuracy of using NIR and the wet chemistry analyzed in five different labs. The results showed that because of the existence of important biases between laboratory measurements, the substitution of standardized NIR procedures could improve the intercomparability of the results between studies.

Similarly, Fagan *et al.* (2011) established the NIR calibrations for two dedicated bioenergy crops. Samples of Miscanthus and two varieties of SRCW i.e. Tora and Karin were fertilized with different levels of waste water before harvesting, the bottom 1.5 m of the stem were harvested for the determination of moisture content, calorific value, ash content and carbon content and the collection of spectral data of 164 samples with NIR. The NIR spectral data were pretreated with different methods including multiplicative scatter correction (MSC), standard

normal variant (SNV), first and second derivatives and application of different spectral range from 400 to 2500 nm. Partial least squares regression (PLS) was applied for developing NIR calibrations and full cross-validation were used for confirming the calibrations. The coefficients of determination (r^2) for calibrations of moisture content, calorific value, ash and carbon content were 0.99, 0.99, 0.58 and 0.88, respectively.

The chemical compositions of a diverse source of biomass were predicted by NIR calibrations reported by Kelley *et al*. (2004). Perennial crops (e.g., sugar cane, flax, sisal and hemp), pure fiber (e.g., cotton) and tropical monocotyledons (e.g., palm and banana) were subjected to a wide variety of extraction and chemical treatments before laboratory measurements and NIR analysis. NIR calibrations were constructed with PLS and confirmed for prediction precision using cross-validation. Good correlations between the measured and NIR predicted results were obtained for three major components, lignin, glucose and xylose with r ranging from 0.87 to 0.94, a weaker but promising results were presented for four minor sugars, mannose, galactose, arabinose and rhamnose with r ranging from 0.72 to 0.87.

The correlations between laboratory measured and NIR predicted chemical composition of longleaf pine were reported by So and Eberhardt (2010). Forty samples were collected from breast and mid height of 20 longleaf pine trees. The calibrations for extractives and lignin were developed by PLS then tested with a validation set. The results for extractives provided strong statistics with an r^2 of 0.88 and 0.78 for the calibration and validation set, respectively and when employing only two principle components. A poorer result was found for lignin content with an r^2 of 0.71 and 0.33 for calibration and validation set using 3 principle components. When 5 principle components were used, the result was improved with r^2 of 0.92 and 0.71 for calibration and validation set.

Physical and mechanical properties of biomass were also measured by NIR. Hein *et al*. (2011) developed NIR calibrations for biomass products i.e. agro-based particleboards which were made of different contents of *Eucalyptus* and *Pinus* wood particles with sugar cane bagasse. The properties of modulus of elasticity (MOE), modulus of rupture (MOR), internal bond (IB), water absorption (WA24H) and thickness swelling (TS24H) after immersion for 24h were examined and the spectral data collected with NIR were pretreated with 1^{st} or 2^{nd} derivatives prior to NIR calibration. The PLS calibrations presented satisfactory correlation between NIR spectral data and reference data with r^2 of 0.70 for IB, 0.46 for MOE, 0.74 for MOR, 0.72 for WA24H, and 0.82 for TS24H, respectively.

Density, MOR and MOE of longleaf pine samples were also predicted by NIR presented by Via (2003). Different parts of 10 longleaf pine trees were collected for conventional measurements and NIR prediction. Multiple linear regression (MLR) and principal component regression (PCR) were employed in calibration construction. The correlation between laboratory measurement and NIR prediction were good with the treatment of MLR, which with r^2 of 0.76 for density, 0.86 for MOE and 0.88 for MOR. With PCR the similar calibrations obtained if only wavelengths known to associate with lignin and cellulose were utilized. This study also revealed that MOE and MOR were poorly correlated with NIR spectral data in the pith wood region while density was strongly correlated, which may arise from the low range of variation in MOE and MOR in pith wood and the presentence of high amount of resinous extractives near the pith.

All these studies mentioned above illustrate that near infrared spectroscopy in combination with multivariate analysis is a powerful tool to predict the physical, mechanical, chemical and energy properties of the biomass.

2.6 The applications of NIR to biomass

Due to feedstock variation, the chemical, physical and energy characteristics of the biomass are crucial to process control. Rapid measurement of characteristics of biomass can be applicable to large-scale nondestructive forest resource properties assessment and consequently assist efficient process control for large-scale conversion of heterogeneous feedstock to energy outputs. In most cases of biomass industry, it is more practical to make a large number of biomass chip samples rather than milled samples screened which is a prerequisite for on-line and in-line monitoring. The exclusion of the grinding step will also simplify the development of NIR calibrations.

Nevertheless, there are few studies developing NIR calibrations for chip sample for biomass properties. Near infrared radiation can just penetrate to depths of several millimeters into the sample. The penetration depths are further dependent on the size and shape of the particles of the materials, the voids between the particles, and the arrangement of particles (Chang *et al.*, 2001). For heterogeneous material such as wood, this small penetration depth may result in variation in the spectral signal and thus there is a strong dependence on sample size and preparation technique (Yeh *et al*., 2004). In spite of this limitation, there are still some investigations explore the calibrations based on solid wood chip or strip obtaining some encouraging results.

The properties of loblolly pine samples harvested from three plantations in Georgia were analyzed with NIR by Jones *et al.* (2005). Totally, radial strips of 120 loblolly pine trees were measured in terms of air-dry density, microfibril angle (MFA), and stiffness. NIR calibrations were established based on the averaged spectra of different sections of the wood strips and pretreated with the MSC, first and second derivative. The NIR calibrations with spectra

pretreated by MSC presented the best statistics overall for density, MFA and stiffness with r^2 of 0.83, 0.90 and 0.91, respectively. When tested by validation set, the calibration treated with second-derivative provided the best results with r^2 of 0.81, 0.80 and 0.87 for density, MFA and stiffness. This study also demonstrated that the transfer of one sample from the prediction set to the calibration set greatly improved the accuracy of predictions and minimized the difference between mathematical treatments.

NIR calibrations for *Eucalyptus delegatensis*, *Pinus radiate* D. Don and loblolly pine wood generated from averaged spectra of wood strips for a variety of wood properties were reported by Schimleck *et al.* (2001, 2002, 2005). For *Eucalyptus delegatensis*, the NIR spectra were collected from the radial–longitudinal face of each sample which was also determined for density, MFA, E_L and MOR. The original and second-derivative spectral data were analyzed by PLS for construction of NIR calibrations which were validated with a test set. The correlation between laboratory measurement data and NIR fitted data were good in all cases, with r^2 of 0.93 for density, 0.77 for MFA, 0.90 for $E_{L,}$ and 0.78 for MOR, respectively.

A series of *Pinus radiate* D. Don samples were characterized in terms of density, MFA and E_L. Fifty NIR spectra were obtained from radial/longitudinal face of each sample then averaged into one spectrum. The relationships were good in all cases, which were based on PLS and second-derivative spectral data, and coefficients of determination ranging from 0.68 for MFA through 0.82 for E_L to 0.94 for density.

Similarly, air-dry density, MFA, stiffness and several tracheid morphological characteristics of the radial-transverse (RT) face and radial-longitudinal (RL) face of 20 loblolly pine samples were analyzed. NIR diffuse reflectance spectra obtained from the RL- and RT-faces of strips were converted to second derivative spectra and then were subjected to the modified

partial least squares regression. In general, calibrations based on spectra from RL-face provided the strongest statistics with r^2 ranging from 0.86 to 0.97, exceptions were tracheid perimeter and tracheid radial and tangential diameters. Difference between the two set were small which reveal that either face could be used for NIR analysis.

Jones *et al.* (2008) compared the calibrations of basic specific gravity and lignin content based on the spectra obtained by using a variety of sampling options including whole-tree wood chips, core holes, core samples and drill shavings. Second derivative spectral data were analyzed by PLS to develop the calibrations. The results indicated that calibrations based on spectra from dried and green whole-tree chips (milled and intact) present the strongest statistics with r^2 ranging from 0.45 to 0.74 for basic specific gravity and from 0.50 to 0.73 for lignin. Similar results observed from milled increment cores, while poorer calibrations generated from intact increment cores. The other sampling options i.e. drill shavings produced errors that were too large for practical applications.

The chemical compositions of wood strips were also predicted with NIR by Jones *et al.* (2006). Seventeen loblolly pine of variable age representing seven sites were selected for the wet chemistry measurements including cellulose, hemicellulose, lignin (acid soluble and insoluble), arabinan, galactan, glucan, mannan, and xylan contents. NIR spectra were collected in 12.5 mm sections from the pre-record positions that represent wood close to the pith (juvenile wood), close to bark (mature wood) and the transition zone between juvenile and mature wood. The averaged spectra of fifty scans were converted to second derivative spectra analyzed by PLS regression. Calibrations were developed from full set of all 40 samples and split set of 28 samples for calibration and 12 samples for prediction. For full set, calibrations of cellulose, glucan, mannan, xylan, insoluble, and total lignin content were desirable with r^2 greater than 0.80.

The r^2 of calibration for arabinan was 0.72 while for acid-solube lignin, hemicellulose and galactan were poorer with r^2 ranging from 0.18 to 0.57. The results based on the calibration set with 28 samples were similar with that of full set with good r^2 ranging from 0.75 to 0.98 for cellulose, glucan, mannan, xylan, insoluble, and total lignin content. A weaker r^2 was also obtained for arabinan of 0.75 and for acid-solube lignin, hemicellulose and galactan ranging from 0.25 to 0.66. However, when the calibrations were validated by the prediction set, the r^2 were noticeably low which may be a consequence of the diverse origins of the samples in the test set.

However, the researches mentioned above all based on the averaged spectra of solid wood chips or strips, to date hardly one research investigate the NIR calibrations established from a single spectrum per chip of samples.

2.7 Multivariate Analysis

Just as mentioned previously, the NIR technique was not widely applied until the utilization of multivariate analysis to NIR which resulted in an increased acceptance of this technique. Because of the highly overlapping spectra and difficult interpreting overtones, the application of multivariate analysis to NIR technique simplify the calculation of regression models and enable the interpretation of overtones. Multivariate data are data with many variables ranging from six to millions including factors and responses. And multivariate data analysis, including partial least squares (PLS) regression and principal component analysis (PCA), are involved to model factors and responses, find relationship between all factors and responses and extract useful information from multivariate data (Hair *et al*., 1995).

The principle of PCA is that the reduction of dimensionality of a data set that contain a large number of intercorrelated variables and meanwhile retain as much as possible of the

information of original data (Kemsley, 1996). The mechanism of PLS is to predict or analyze a set of dependent variables from a set of independent variables by extracting a set of orthogonal factors, called principal components, from the independent variables (Abdi, 2007). PLS is a regression extension of PCA, with the former presents some advantages including: superior prediction results, fewer principal components, more readily interpreted loadings and better capability for handling nonlinearities (Wentzell and Montoto, 2003). Because of its merits, PLS has become a powerful tool applied to analyses of ultraviolet, NIR, chromatographic and electrochemical data (Haland and Thomas, 1988).

In PLS, the variation in **X** is X-scores called **t**, the variation in **Y** is Y-scores called **u**. The relationship between **X** and X-scores is described by X-loadings called **p**, while the corresponding relationship between **Y** and Y-scores is given by Y-loadings called **q**. The **X**-decomposition is first influenced by the $\mathbf{u_1}$, which result in the calculation of the X-loadings that

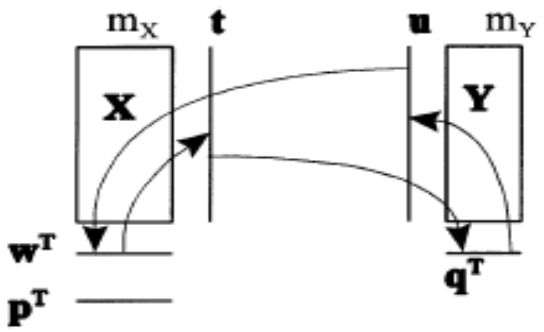


Figure 2.5. The arrow scheme for PLS regression (Westerhuis *et al*., 1998)

termed as **w** (loading-weights). **E** and **F** represent the error matrices for the X-scores and Y-scores, respectively. The arrow scheme for PLS regression is shown in Figure 2.5. The

interdependent **u→t** and **t→u** substitutions are repeated until convergence of **t**. The decomposition of **X** and **Y** can be described by the equations below (Esbensen, 2000; Maranan, 2006; Yeniay and Göktaş, 2002).

$$\mathbf{X}=\boldsymbol{\Sigma}\mathbf{t}\cdot\mathbf{p}^{\mathbf{T}}+\mathbf{E}$$

$$\mathbf{Y}=\boldsymbol{\Sigma}\mathbf{u}\cdot\mathbf{q}^{\mathbf{T}}+\mathbf{F}$$

$$\mathbf{B}=\mathbf{w}\,(\mathbf{p}^{\mathbf{T}}\mathbf{w})^{-1}\mathbf{q}^{\mathbf{T}}$$

$$\mathbf{Y}=\mathbf{X}\,\mathbf{w}\,(\mathbf{p}^{\mathbf{T}}\mathbf{w})^{-1}\mathbf{q}^{\mathbf{T}}=\mathbf{XB}$$

Chapter 3 RAPID PREDICTION OF CONSTITUENT COMPOSITION AND ENERGY TRAITS OF LOBLOLLY PINE WOOD USING NEAR INFRARED SPECTROSCOPY

3.1 Abstract

Near infrared spectroscopy (NIR) was applied to determine the extractives, lignin, ash, moisture, and calorific value of loblolly pine. Calibrations for these properties were established based on NIR spectra collected from milled sample and chip samples. The chip samples were further subdivided into groups including calibrations derived from multiple averaged spectra per chip (25) and a single spectrum per chip. Calibrations were developed from 2/3 of 72 total randomly selected samples using partial least squares (PLS) regression and a variety of pretreatments for raw spectral data, then validated using the remaining 1/3 of samples. Calibrations for all properties developed from milled samples showed the strongest correlation between laboratory measurement and NIR predicted values with coefficient of determination for calibrations (R_c^2) ranging from 0.85 to 0.96 for the calibration set, and for predictions (R_p^2) of from 0.56 to 0.89 for the validation set. Properties were moderately predicted by the calibrations developed from multiple spectra per chip, achieving R_c^2 higher than 0.8 and R_p^2 varied from 0.4 to 0.77. Good results were also obtained from the calibrations based on a single spectrum per chip, achieving R_c^2 ranging from 0.72 to 0.87. Some properties, however, including ash, extractives and calorific value, were poorly predicted for the validation set with an R_p^2 of 0.33, 0.42, and 0.41, respectively. This study revealed the potential of NIR in combination with multivariate analysis

to predict the chemical composition and energy trait of loblolly pine wood in process control settings.

3.2 Introduction

Economic stability, environmental issues and uncertain supplies of fossil fuels at both the national and global scale have resulted in an increased interest in finding an alternative source to fossil fuels (Orts *et al*., 2008). Because it is clean-burning, has lower net emission of CO_2 into the atmosphere, and can be grown relatively quickly and sustainably biomass energy has been attracting more and more attention worldwide as a more desirable source of energy (Kumar *et al.*, 2009; Broek *et al*., 1996). As the only renewable organic resource that can fixes carbon dioxide in the atmosphere by photosynthesis, biomass has been extensively utilized worldwide, which accounts for approximately 14% of world's primary energy consumption (Parikka, 2004; Demirbas, 2007). The conversion of biomass to liquid transportation fuels could significantly decrease world dependency on fossil fuel. As a primary energy source, biomass (43%) is just behind hydropower (51%) among renewable resources (Chum and Overend, 2001). Currently, over 3 percent of the total energy consumption in the U.S. is supplied by biomass, most resulting from industrial heat and steam production by the pulp and paper industry and electrical generation with forest industry residues and municipal solid waste (Perlack *et al*., 2005). It is also estimated that by 2025 resource will provide up to 30% of the raw material for the chemical industry, about 38% of the world's direct fuel use, and 17% of the world's electricity (Kamm, 2007; Demirbas, 2000). As a result, there is a great need of high yield biomass production

systems and bioconversion technologies which can convert biomass into forms of bioenergy and chemicals usable in industry efficiently.

Biomass refers to all plant, plant-derived materials and animal manure including forest residues, wood product residues, agricultural field residues, processing waste, animal wastes, agricultural and woody crops grown for fuels (Simpkins, 2006; McKendry, 2002). Biomass is a stored source of solar energy which can be released by conversion though biological (biochemical) and thermochemical processes and direct combustion (Zhang *et al*., 2010). The conversion processes of biomass can produce three main kinds of end-products: heat and power, transportation fuels such as ethanol, and chemical intermediates. The production of biofuel and generation of electrical power are the two main markets for bioenergy (Cantrell *et al*., 2008; McLaughlin *et al*., 1999).

Currently, the biofuels industry of U.S. is primarily (95.6%) based on the conversion from corn to ethanol. However, because of the competing demands for corn in other industries, it is not possible that corn output can fulfill the future biofuel demand (Petrulis, *et al*., 1993). Furthermore, combustion is the most widely used process for biomass conversion and accounts for over 97% of bioenergy generation in the world. However, in many cases the limited availability and high costs are key problems for conversion of biomass to higher-valued bioenergy outputs such as transportation fuels and electrical power (Dornburg and Faaij, 2001; Zhang *et al*., 2010). As a result, sources of renewable biomass that are abundant, cost-effective and can be stored in large quantities are in demand. In particular, because of the large biological forestlands of U.S. (29.1-34.6 billion cubic feet per year), woody biomass is an important potential source of renewable biomass in the U.S. In particular, the energy produced from woody

biomass accounts for the majority of biomass energy (64%) currently produced, followed by municipal solid waste (24%), agricultural waste (5%) and landfill gases (5%) (Demirbas, 2007).

Loblolly pine is the most common and fast-growing forest species in the southern U.S., where it is dominant on about 29 million acres and constitutes over one-half of the standing pine volume (Schultz, 1999). It ranges across 14 states extending from southern New Jersey to central Florida and west to eastern Texas. Loblolly pine is also an adaptable species that has been introduced on other continents (Baker and Balmer, 1983; Li *et al.*, 1999). Because of its rapid growth and positive traits such as stem straightness and wood quality, loblolly pine wood has been accepted and widely used in forest products and some related industries.

Normally the major chemical components in wood contain carbohydrates (65-75%), lignin (18-35%) and minor components such as extractives, minerals, and trace components, accounting for 4-10% of the dry biomass weight. Each of the constituent has some impact on the bioconversion of biomass to some form of energy. Lignin is a heterogeneous biopolymer based on phenol propane units. It is difficult to dehydrate and is a residual product in current process used to convert biomass to ethanol. Some compounds of extractives such as tannins and phenolics interfere with activity of hydrolytic and fermentative enzymes in bioconversion even if present in low concentrations. Similarly, lower ash and moisture content is preferred because they also interfere with enzymatic and acid hydrolysis and decrease the carbohydrate content, respectively (Dinus, 2000). On the other hand, biomass of low moisture content and high carbon content is desirable for combustion of biomass into biopower. The variation of carbon content in biomass is reflected in variation of lignin and extractives content (Ragland and Aerts, 1991). As a result, the determination of relative concentrations of constituents influencing efficiency of biomass conversion, including extractives, lignin, ash and moisture, is crucial for designing and

optimizing the bioconversion of woody biomass to biofuel. Additionally, biomass, as a combustion resource has outstanding advantages including high volatility of fuel and high reactivity of both fuel and resulting char (Demirbas, 2004). Nevertheless, compared to fossil fuels, biomass fuels have relatively low heating values that arise from high moisture content and high oxygen content (Zhang *et al*., 2010). Consequently, it is also crucial to evaluate biomass feedstock for their combustion properties prior to conversion, among which the calorific value is of greatest significance.

The traditional methods for determination of chemical composition and calorific value of woody biomass are time and cost consuming, destructive and have limited sample throughput. Recently near infrared spectroscopy (NIR) has been demonstrated as a rapid, cost effective, reliably accurate method for measuring chemical components and energy trait of wood (So and Eberhardt, 2010; Via *et al*., 2007; Maranan, 2006; Poke *et al*., 2007). Sample preparation when employing NIR techniques has been found to significantly influence repeatability and precision of results.

Among studies using NIR to predict wood properties, most were based on samples of ground material. In production situations that might arise in a large-scale biomass energy conversion industry, however, feedstock are likely to arrive in chipped, rather than ground, form. It could be more practical in that situation to measure characteristics of unprocessed biomass chip samples for optimizing conversion processes instead of taking the time required to mill samples. The delay required for grinding and sample preparation might be lengthy enough to render the process unsuitable for control of continuous bioconversion processes. The exclusion of the grinding step will also simplify the development of NIR calibrations. There have been some studies having investigated NIR calibrations of solid wood chip or strip and obtained some

encouraging results (Poke and Raymond, 2006; Jones, *et al*., 2008; Jones, *et al*., 2006; Kelley, *et al*., 2004).

These studies mentioned above were all based on multiple averaged spectra obtained from solid wood chips or strips and to date no one has investigated NIR calibrations based on a single spectrum per sample. For on-line, continuous conversion processes, however, large quantities of feedstock would likely be moving towards conversion reactors at high speeds, rendering it impractical to sample multiple spectra from a single entity. More likely, estimates of bulk properties will be derived from single samples of multiple chips, rather than multiple samples of single chips. It is important, therefore, to understand the potential differences in prediction capabilities of the two approaches. If the feedstocks are moving at a high rate of speed into the conversion process, it is also likely it will be necessary to predict bulk properties from relatively infrequent sampling. It will therefore be important to understand errors associated with predicting bulk properties from intermittently derived measurements on relatively small volumes of feedstock. The present study seeks to: 1) develop predictive models for chemical constituents of loblolly pine, including extractives, lignin, ash, calorific value and moisture, using NIR spectroscopy, and 2) compare the accuracy of calibrations based on the spectra of milled samples, averaged spectra per single chip, plus a single spectrum per chip. The goal is to understand the potential of infrequent NIR sampling of a continuous stream of feedstock material to reliably predict properties of loblolly pine that are of potential importance in its conversion to energy products.

3.3 Materials and methods

3. 3. 1 Materials

Sixty samples were obtained from the top and bottom of 30 loblolly pine trees that were harvested from 3 different places including Cusseta, GA (10 trees), Greenville, AL (10 trees) and Fort Gaines, GA (10 trees), and fourteen samples of mixed pine chips were obtained from a paper mill chip pile in Cottonton, AL. The tree samples were from a clean chipping operation, and each sample was taken as a single stem was sent through the chipper. A 10-inch PVC pipe topped with an elbow was inserted into the stream of chips, a portion of which were diverted into a bucket. This procedure was repeated twice for each stem, once while chips from the bottom portion of the stem were being blown into the van, and once while chips from near the top. All the samples were bagged separately, labeled, and received as wood chips of 1-4 g. The wood chips were air dried for one week under ambient conditions. Eight (8) chips for each sample were randomly selected for spectra collection with near-infrared spectroscopy (NIR) and the remaining wood chips were oven-dried at 105°C for 24h to determine moisture content. After spectra collection, the selected chips were milled to 20 mesh with a Marathon mill equipped with 20 mesh screen plate, and the milled sample were also used to collect NIR spectra and subsequently oven-dried for moisture content. The milled samples were then kept under ambient conditions until wet chemistry analysis.

3. 3. 2 Chemical Analysis

The moisture content of dried chips and milled samples was determined as weight loss after drying at 105 ± 2°C for 24h using a convection oven. Wood meal samples were extracted with acetone in a Soxhlet apparatus for 6 h. The extracts were transferred to a small plate and

evaporated in a ventilation hood for 3h. The extracts were then concentrated at 40°C for 12 h in a vacuum drying oven. Extractive-free sample was treated with Klason method for measurement of acid insoluble lignin content. The sample was pre-hydrolyzed with 72% sulfuric acid at 30 °C water bath for 2 h and stirred every 15 min, then diluted to 4% H_2SO_4 and autoclaved at 121°C for 1h. The solid residue was filtered off, dried and weigh to calculate lignin content. Ash content was measured as the residue remaining after dry oxidation at 575 °C in muffle furnace. Moisture content was also determined to adjust the extractives, lignin and ash content to a dry weight basis and all the measurements were performed in duplicate.

3.3.3 Calorific value analysis

The calorific value was determined using a IKA oxygen bomb calorimeter C200. Pellets of 0.5g sample were prepared with a hand press, placed in the calorimeter and pressurized with oxygen, then the bucket filled with 2000ml 22°C water. Then the sample combustion was initiated an ignition device. After the combustion, calorific value was read from the display. The calorimeter was calibrated with benzoic acid pellets. Moisture content was measured to adjust the calorific value to a dry weight basis and energy content determination was carried out in duplicate.

3. 3. 4 NIR Analysis

NIR spectra were acquired using a PerkinElmer spectrum model 400 (Perkin Elmer Co., Waltham, MA) FT-NIR spectrometer (Figure 3.1) operating in a diffuse reflection mode. The chip and milled samples were placed on the scanning window of approximately 0.8 cm in diameter and background correction was performed with a white disk. Thirty-two scans were averaged for every spectrum between 4000 and 10000 cm^{-1} at a resolution of 4 cm^{-1}. The spectra of each milled sample were collected 3 times then averaged to one spectrum. For chip samples,

five points from both sides of each chip were randomly selected and for every point five spectra were collected. In total, 25 spectra were averaged for each chip.

3. 3. 5 Multivariate Analysis

Approximately two-thirds of the samples were randomly selected to represent the NIR calibration set and one-third a validation set. Spectrum Quant+ 4.6.0 software was used for multivariate analysis. Because of the noise in the spectral measurements and experimental instrumentation, the effects of scatter and particle size, the raw NIR spectra were always complicated, broad and overlapping. So prior to modeling, spectral data were subjected to pretreatments including Savitzky-Golay smoothing and derivatives to reduce noise, and multiplicative scatter correction (MSC) and standard normal variate transformation (SNV) to remove the effect of baseline height and slope.

Savitzky-Golay smoothing and derivatives are algorithms performed using a polynomial regression on a range of values around each raw data point in a spectrum to estimate a spectral value free from noise. The derivatives of a spectrum are computed using Savitzky-Golay polynomials (Schwanninger *et al*., 2011; Savitzky and Golay, 1964). Figure 3.1 shows the difference between the spectra before and after 1^{st} derivative processing with 49 smoothing points.

MSC, proposed by Geladi *et al*. (1985), uses linear regression of spectral variables to average replicate spectra and simultaneously corrects for both multiplicative and additive scatter effects. MSC based on correcting the scatter level of all spectra of a group of samples to the level of the average spectrum, each spectrum is fitted to the average spectrum as closely as possible using least squares (Isaksson and Naes, 1988).

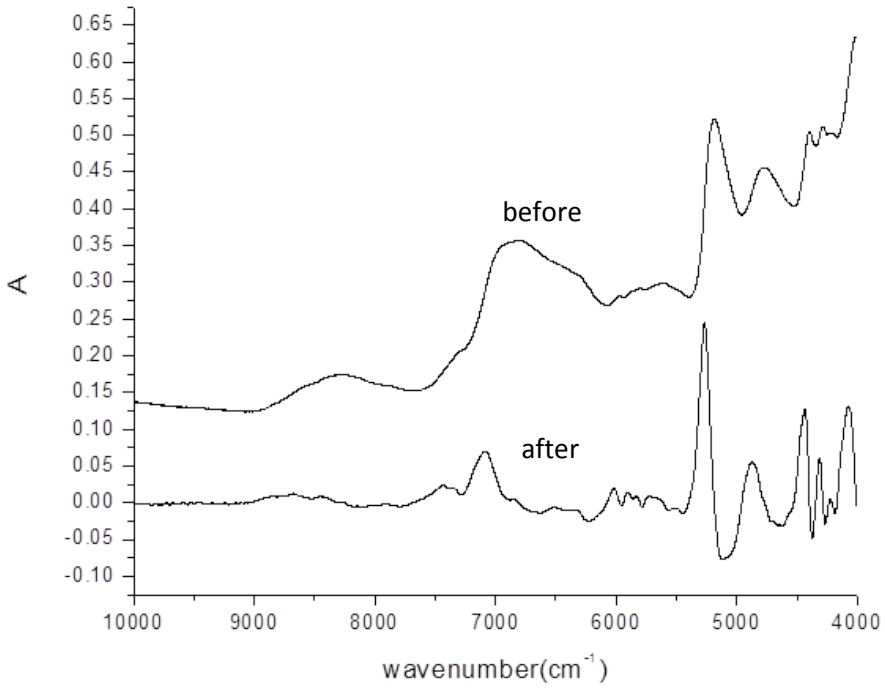


Figure 3.1 NIR spectra before and after 1st derivatives with 49 smoothing points

For each digitized spectrum, the row vector $\mathbf{x}_i$, is fitted by regressing it against the average spectrum of the training set, ***m*** (Wold *et al*.,1998):

$\boldsymbol{x}_{ik}=a_i + b_i\boldsymbol{m}_k + \boldsymbol{e}_{ik}$

The average training set spectrum has the elements:

$$\boldsymbol{m}_k=\frac{\sum x_{ik}}{N}$$

Then, from each row, $\mathbf{x}_i$, one subtracts the intercept (a_i) and divides by the multiplicative constant (b_i):

$$\boldsymbol{x}_{i,MSC}=(\boldsymbol{x}_i-a_i)/b_i$$

SNV is a mathematical transformation of the log (1/R) spectra by calculation of the standard normal variation at each wavelength removes slope variation on an individual sample basis by subtracting the spectrum mean and scaling with the spectrum standard deviation (Barnes *et al*., 1989). The algorithm is as follows, **x** is a row vector containing the original spectrum, $\mathbf{x_o}$ is the mean of **x** (Guo *et al*., 1999):

$$\boldsymbol{x}_{ij,\,SNV}=\frac{(xij-xo)}{\sqrt{\frac{\sum_{i=1}^{p}(xij-xo)^2}{p-1}}}$$

Partial least-squares regression (PLS) was performed on preprocessed spectra to transfer a large number of original independent variables to a small number of factors (latent variables) that are linear combinations of original variables (Wold *et al*., 2001; Theodora and MacGregor, 1995). The calibration models consisted of these orthogonal variables with a maximum is 10. The number of principal components plays an important role in the development of calibrations. Exclusion of key components results in missing information while inclusion of excessive components leads to overfitting that the calibration represents not just the true correlation between reference data and predicted data but also random noise and individual features of the calibration set. The optimal number of principal component depends on the response of residual Y-variance with changing number of principal components (Kelley *et al*., 2004). Additional iterations were terminated when the addition of new factor did not substantially decrease the residual Y-variance.

The coefficient of determination (R^2) and standard error of calibration (SEC) were used to assess the calibration models. Standard error of prediction (SEP) was used to examine the accuracy of a calibration to predict a set of unknown samples that are different from the calibration set (Wu *et al*. 2011).

R^2 is calculated as:

$$R^2=1-\frac{\sum_{i=1}^{n}(\hat{y}_i-y_i)^2}{\sum_{i=1}^{n}(y_i-\bar{y})^2}$$

Where, $\hat{y}_i$ and y_i are the predicted and measured values of sample i, $\bar{y}$ is the mean of the measurement values, and n is the sample size.

SEC is calculated as:

$$\text{SEC}=\sqrt{\frac{\sum_{i=1}^{n}(y_i-\bar{y})^2}{n-1}}$$

Where, $\bar{y}$ is the mean of the measurement values, y_i is the measured value of sample i,

n is the sample size.

A further evaluation of the performance of calibrations was assessed by RPD, which is the ratio of the standard deviation of reference data to the standard error of prediction (Williams and Sobering, 1993). An RPD value greater than 8 is good for process control, development and applied research, a value of 5-8 is adequate for quality control, a value of 2.5-5 is satisfactory for screening, while values more than 1.5 can be used for initial screening (Williams and Norris, 2001).

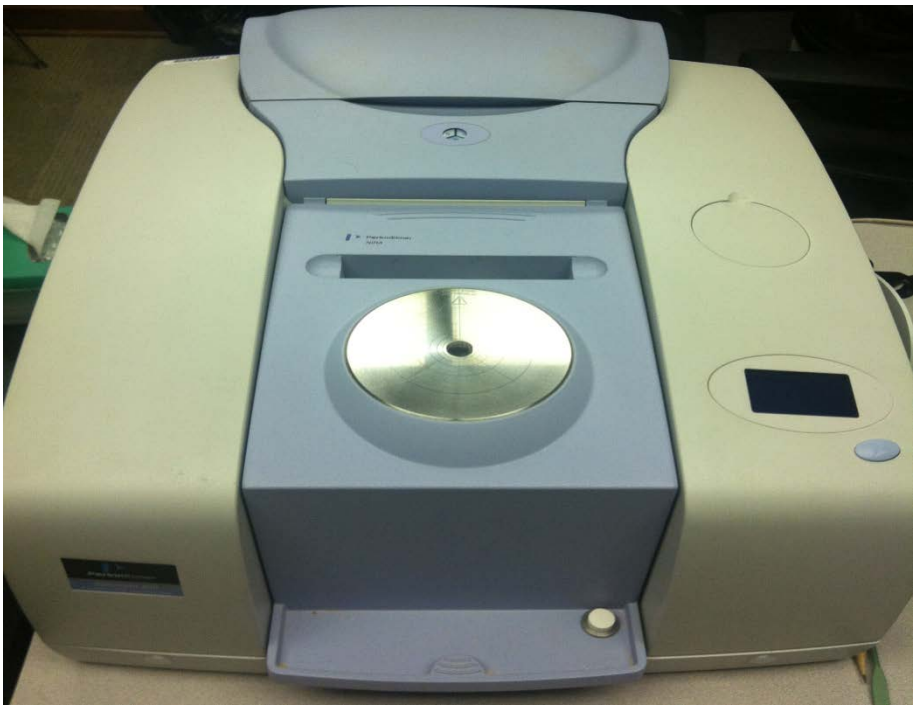


Figure 3.2 PerkinElmer spectrum model 400 FT-NIR spectrometer

3.4 Results and Discussions

3. 4. 1 NIR spectra

The NIR spectra of 5 milled samples and 5 averaged spectra of chip samples are shown in Figure 3. 2. The pattern of these spectra were very similar except for the baseline differences. Spectra from the chip samples exhibited more severe than those of the powder, an expected result that is likely attributable to the heterogeneous reflection of light from the chip surface.

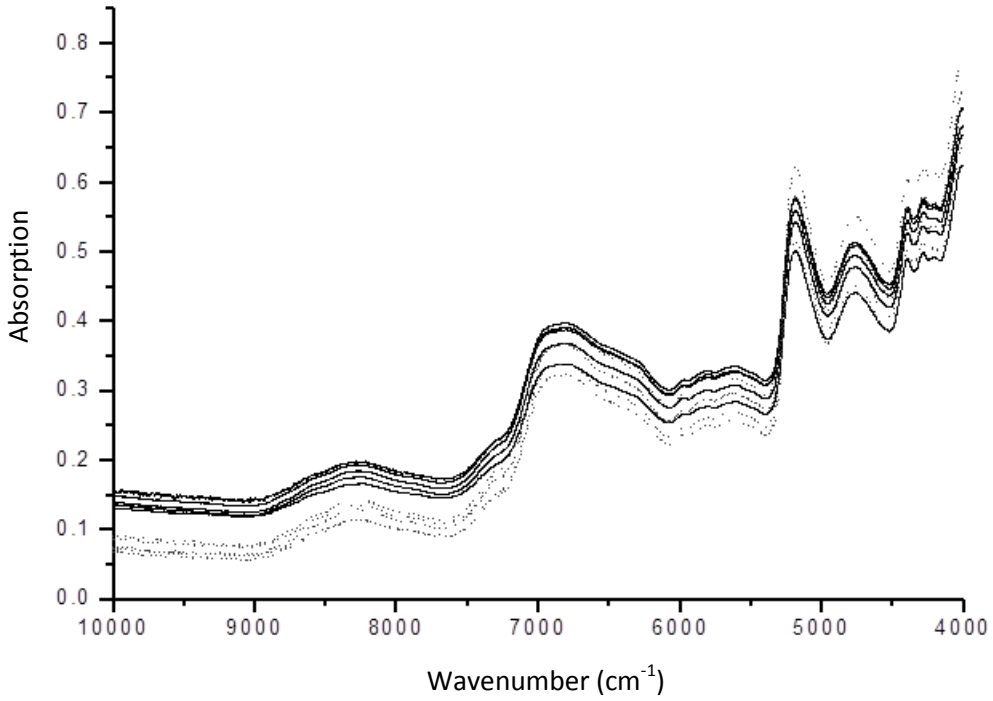


Figure 3.3 5 spectra (dotted line) and 5 averaged spectra of chip (solid line) of loblolly pine sample.

Several spectral peaks can be detected visually. The peak at 8250 cm^{-1} is assigned to the 2nd overtone of C-H stretching vibration in cellulose (Michell and Schimleck, 1996).The absorption at 6825 cm^{-1} is due to the 1st overtone of O-H stretching vibration in lignin and hemicellulose (Schwanninger *et al*., 2011). Bands appearing at 5473-5984 cm^{-1} are associated with 1st overtone C-H stretching in cellulose, lignin, hemicellulose and 1st overtone C-H_2 stretching in cellulose (Schwanninger *et al*., 2011; Ali *et al*., 2001). The peak at 5185 cm^{-1} is attributed to a combination of O-H stretching vibration and O-H deformation of H_2O (Sun *et al*., 2011). Absorption at 4769 cm^{-1} is related to a combination of O-H and C-H deformation and O-H stretching vibration in cellulose and xylan (Bassett *et al*., 1963). Bands at 4394 cm^{-1} and 4283 cm^{-1} correspond to O-H stretching vibration and C-C stretching in cellulose and C-H stretching

and C-H deformation in cellulose and hemicellulose respectively (Schwanninger *et al*., 2011; Ali *et al*., 2001).

3. 4. 2 Calibrations of lignin content

The mean of lignin content of chipped and milled samples in the calibration set were 26.13 and 25.94% and ranged from 23.9 to 27.8% and 24.2 to 27.6%, respectively. The validation set also presented a similar range from 24.5 to 27.9% and 24.55 to 27.44% with average value of 26.2 and 26% (Table 3.1 and Table 3.2). These values were consistent with those reported by White (1987), who reported lignin content from 26.8 to 33.8% from four different softwoods. Figure 3.4 shows the correlation between laboratory-measured lignin content and the values predicted by calibrations using the spectra of milled sample (a), averaged spectra per chip (b), single spectrum per chip (c). The calibration based on milled sample with pretreatment of MSC plus a 1st derivative with 13 smoothing points over the frequency range from 4000 to 10000 cm^{-1}, and 4 principal components selected for the model, provided the strongest correlation with R_c^2 of 0.93. When the validation set was used to evaluate this calibration, it also displayed good correlation with R_P^2 of 0.64 and SEP of 0.39% (Table 3.3). This result is similar to the result obtained by Üner *et al*. (2011) with R^2 of 0.909, SEC of 1.51% and SEP of 3.28% (w/w) by using a much larger reference data set ranging from 19.93 to 36.7%. These values are also consistent with those reported by So and Eberhardt (2010) using 5 principal components with R_c^2 of 0.92, SEC of 0.34%, R_P^2 and SEP of 0.71 and 0.83%, respectively.

The calibration based on averaged spectra per chip, with frequency range from 4000 to 10000 cm^{-1}, pretreated with MSC and 1st derivative plus 13 smoothing points, afforded R_c^2 of 0.86, SEC of 0.33%, R_P^2 and SEP of 0.55 and 0.53%, respectively (Table 3.3). Jones (2006) also

presented a similar calibration for 12.5×12.5 mm strip sample of loblolly pine with lignin content ranging from 25.84 to 30.86%, reporting R_c^2 of 0.85 (SEC=0.47%) and R_p^2 of 0.51 (SEP=1.26) with 4 principal components. The result for chip samples was not as desirable as the calibration based on milled samples. Variability in raw spectra were the likely cause for poorer results, the variation a product of the heterogeneous structure of intact wood materials, and this result was expected. Averaging 25 spectra for each chip tended to minimize the variation, but did not eliminate it.

By contrast, the calibration based on single spectrum per chip has increased limitations as explained earlier, so it is not unexpected that by using similar pretreatment (MSC plus a 1st derivative with 25 smoothing points in the frequency range 4000 to 10000 cm^{-1}), a calibration with R_c^2 of 0.81, SEC of 0.4%, R_P^2 of 0.6, SEP of 0.68% was obtained (Table 3.3). It is not as good as the calibrations developed using averaged spectra, especially the SEP and SEC were high, but the RPD of 2.1 was still satisfactory for initial screening. This result is comparable to that reported by Jones *et al*. (2008) in which the calibration for lignin content of solid wood with R^2 of 0.70, SEC of 0.45%, SECV of 0.59%. They captured the spectra of chips by using a FOSS NIR Systems fitted with a large transport module and the same systems were also applied by Jonsson *et al*. (2004) for moisture content of wood chips. This method enables the on-line process control for a large amount of chip samples but it also has the same limitation of spectra from wood chips mentioned earlier. In addition, for all three calibrations, the R^2 of the calibration set was higher than those of the validation set, and in reverse the standard error of validation set was higher than those of calibration set, which may partly arise from the fewer data points and narrower data range of validation set.

3. 4. 3 Calibrations of extractives content

The extractives content of loblolly pine chip and milled wood samples are presented in Table 3.1 and Table 3.2. The overall mean was 3.25 and 3.23% with a range from 2.19 to 4.09% and 2.4 to 4.02%, respectively, which corresponds to the values reported by Poke *et al.* (2004) with a mean value of 3.22% ranging from 3.03 to 3.37%. Figure 3.5 shows the calibrations for extractives content based on different spectral data.

Predicted and measured values of the milled samples were correlated with R_c^2 of 0.91, SEC of 0.14% using the spectral region from 4500 to 10000 cm^{-1} , MSC and 2^{nd} derivative plus 25 smoothing points (Table 3.4). R_P^2 of 0.56 and SEP of 0.22% were obtained from the validation set. Üner *et al*. (2011) also observed a consistent calibration for extractives content of Turkish pine with R^2 of 0.8679 and SEC of 0.86% by using a wider reference data span from 2.05 to 16.12%.

Pretreatment of averaged chip sampling spectra differed slightly from the milled preparation set, with MSC and 2^{nd} derivative plus 9 smoothing points achieving maximum R_c^2 of calibration and prediction sets of 0.86, SEC of 0.16%, R_P^2 and SEP of 0.4 and 0.32%, respectively. Similar correspondence between calibration and prediction sets for extractives from averaged spectra were also reported by Poke and Raymond (2006) with R^2 of 0.84 and SEC of 1.37% for wood radial strip of 20 × 20 mm of *Eucalyptus globulus.* Kelley *et al*. (2004) also built the calibration for extractives based on averaged spectra collected from the surface of intact wood of loblolly pine using 4 principal components, the same R^2 of 0.86 and a higher RMSEC of 2.3% was obtained and it was partly due to the wider range of reference data from 2.8 to 26.9%.

For the calibration based on single spectrum per chip, R^2 and standard error of calibration and validation set were both not as good as those of the calibrations above (Table 3.4), which was predominantly due to the inhomogeneous material structure of chip sample just as mentioned earlier. Nevertheless the RPD value of 2.2 indicates that the calibration was still satisfactory for initial screening. Furthermore, it is noticeable that the correlation of the calibration based on single spectrum per chip is just slightly weaker, especially between the calibrations based on averaged spectra per chip and single spectrum per chip, however, the development of the latter is more simple and rapid than the former.

3. 4. 4 Calibrations of ash content

The ash content of meal and chip sample for calibration and validation set had a similar range from 0.19 to 0.43% with a similar mean value around 0.3% (Table 3.1 and Table 3.2). The values are consistent with the values presented by Rhén *et al.* (2007) with ash content of 0.34% and 0.36% for stem wood of Norway spruce and Scots pine. Figure 3.6 shows the calibrations of ash content based on different spectral data. By using the pretreatment of 1^{st} derivative plus 25 smoothing points and 5 principal components, the calibration based on spectra from milled sample produced R_c^2 of 0.85, SEC of 0.025%, R_P^2 and SEP of 0.61 and 0.037%, respectively (Table 3.5). The correlation coefficient was higher than that obtained by Maranan (2006) on hybrid poplar wood with R_c of 0.794, which may arise from a limited sample size and different pretreatment of spectral data.

For the calibration based on averaged spectra per chip, measured and predicted ash content were correlated with R_c^2 of 0.80, SEC of 0.028% by using the spectral region from 4000 to 10000 cm^{-1}, 2^{nd} derivative plus 37 smoothing points and 4 principal components (Table 3.5).

When the calibration was used to estimate ash contents for the validation set, R_P^2 of 0.51 and SEP of 0.044% were obtained. It is noteworthy that the calibration based on spectra from milled sample was only slightly better than that based on averaged spectra per chip, which may be due to a larger population of chip sample was applied. The predicted and measured ash content correlated fairly with the calibration based on single spectrum per chip, with R_c^2 of 0.72, SEC of 0.03% by using the pretreatment of 1st derivative plus 25 smoothing points and 4 principal components (Table 3.5). However, the measured and predicted value correlated poorly for validation set with R_P^2 of 0.33, there is still a need for a wider range of samples to increase the correlation of prediction.

3. 4. 5 Calibrations of moisture content

All samples were received as green chips with moisture content ranging from 44.1 to 63.8%. There is a limitation of NIR applied to high moisture content samples that the presence of several strong and broad absorption bands arise from water may obscure spectral information derived from other components (Schimleck *et al*., 2003; Abrams *et al*., 1988). Schimleck *et al*. (2003) demonstrated that the calibrations based on spectra from dried wood with around 7% moisture content were superior to those developed using spectra from green wood. Therefore, in the current study, the determination of the chemical components was based on the samples after one week air-dried and the moisture content ranged from 6.7 to 12.22%.

Good correlations between measured and predicted moisture content were obtained from the calibrations based on spectra from milled sample, averaged spectra per chip and single spectrum per chip, which with R_c^2 ranging from 0.87 to 0.96, R_P^2 ranging from 0.7 to 0.89 (Table 3.6). The calibrations were comparable to those reported by Fagan *et al*. (2011) for two dedicated

bioenergy crops with R^2 of 0.99. Hoffmeyer and Pedersen (1995) also presented a similar calibration for moisture content of Norway spruce. Additionally, it is noticeable that the SEC and SEP of calibrations based on chip sample were both lower than those based on the milled sample, which may arise from a larger population of chip sample and a wider range of moisture content of milled wood. The similar case was also illustrated by Üner *et al.* (2011) that higher SEP and SEC values were obtained from the data set with larger ranges.

3. 4. 6 Calibrations of calorific value

The overall mean of calorific value of chip and milled sample was 19.28 and 18.64 MJ/kg, it varied from 18.2 to 20.7 MJ/kg and from 18.3to 18.9 MJ/kg, respectively (Table 3.7), which is similar to the range evaluated by Maranan and Loborie (2007) varied from 18.71 to 19.68 MJ/kg, and also corresponds to the values determined by So *et al*. (2012) ranged from 19.5 to 20.6 MJ/kg. In contrast, a wider range from 17.05 to 24.59 MJ/kg was presented by Gillon *et al*. (1997) using different parts of plants including living leaves, needles, twigs, bark, leaf and needle litter. The correlations of calibration for calorific value based on spectra of milled sample (a), averaged spectra per chip (b), and single spectrum per chip (c) are shown in Figure 3.8. The calibration based on milled sample presented R_c^2 of 0.91 and SEC of 0.05 MJ/kg, which was pretreated with 2^{nd} derivative plus 19 smoothing points in the spectral region of 4000-9000 cm^{-1}. When the calibration was evaluated with validation set, R_P^2 was 0.85 with SEP of 0.08 MJ/kg. The R^2 for calibration and validation set are slightly higher while SEP is lower than those reported by Maranan and Loborie (2007), which correlated with R_c^2 of 0.82, R_P^2 of 0.81and SEP of 0.12 MJ/kg. The lower SEP maybe arise from a narrower data range applied in the current study. With RPD value of 3.12, the calibration based on milled sample is satisfactory for prediction of calorific value.

NIR predicted values based on the averaged spectra per chip correlated moderately with the measured values, by using 1st derivative plus 19 smoothing points and 5 principal components, R_c^2 of 0.87, SEC of 0.22 MJ/kg, R_P^2 of 0.52 and SEP of 0.29 MJ/kg were obtained (Table 3.7). The R^2 of calibration developed from single spectrum per chip was 0.74, when the calibration was evaluated with validation set, the R_P^2 and SEP were 0.37 and 0.43MJ/kg, respectively. The calibration based on single spectrum may need more samples and wider data range to improve the quality of validation set with R_P^2 of 0.37. And the RPD value of 1.3 also indicated that a larger population was needed to make the calibration good enough for initial screening. It should be noted that the range of reference data of milled sample was much narrower than that of chip sample, which results in the SEC and SEP for chip sample was several times of those of milled sample. The similar result was also illustrated by Üner (2011) that higher SEP and SEC values were obtained from the data set with larger concentration ranges.

3.5 Conclusions

This study illustrates the potential of NIR to predict the constituent compositions and calorific value of loblolly pine wood. The calibrations based on spectra from milled wood, averaged spectra from single chip and single spectrum from single chip were compared. The best calibrations were all developed from milled samples with coefficient of determination (R^2) values of 0.93 (SEC=0.28%) for lignin, 0.91 (SEC=0.14%) for extractives, 0.85 (SEC=0.025%) for ash content, 0.96 (SEC=0.32%) for moisture content, and 0.91 (SEC=0.05 MJ/kg) for calorific value, respectively. Furthermore, the calibrations for all these properties based on averaged spectra per chip are slightly better than those based on a single spectrum per chip. In addition, it also revealed strong calibrations were possible for even the single spectrum treatment when predicting chip properties. The simplicity and rapidity of calibrations based on a single spectrum from a solid wood chip may outweigh the slightly greater precision achieved when analyzing ground, bulk samples. However, the calibrations should be further developed with a wider range of samples to improve the accuracy prior to application in industry.

Table 3.1.Statistical summary of chemical composition and calorific value of chip sample for calibration set and validation set.

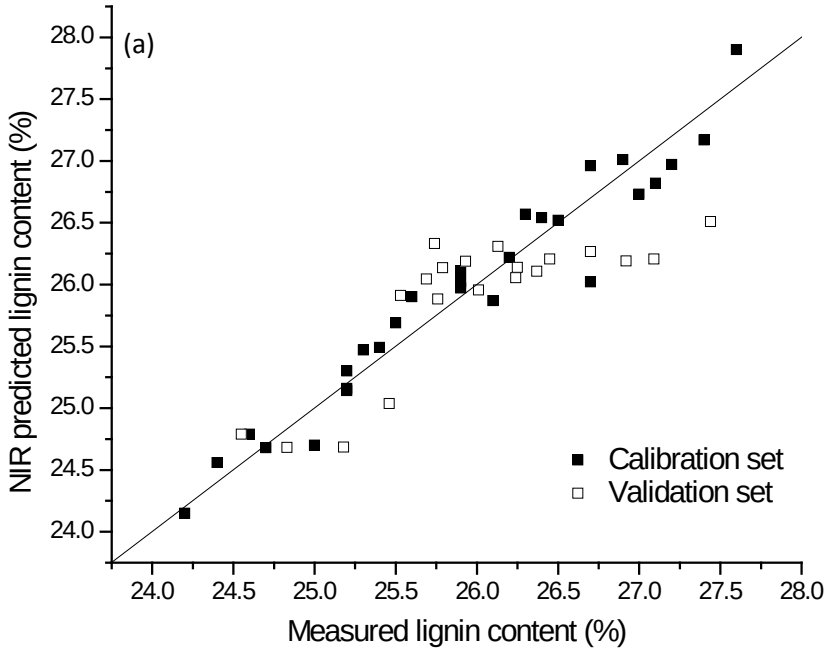
Properties	Calibration set					Validation set				
	Min	Max	Mean	SD	n	Min	Max	Mean	SD	n
Lignin (%)	23.9	27.8	26.13	1.8	48	24.5	27.9	26.2	1.45	24
Extractives (%)	2.19	4.09	3.25	0.72	48	2.42	3.97	3.19	0.68	24
CV (MJ/kg)	18.2	20.7	19.2	0.57	48	18.42	20.65	19.36	0.56	24
Ash (%)	0.19	0.43	0.3	0.093	48	0.22	0.43	0.31	0.08	24
Moisture (%)	6.9	10	9.13	1.4	48	7.1	10	8.97	1.26	24

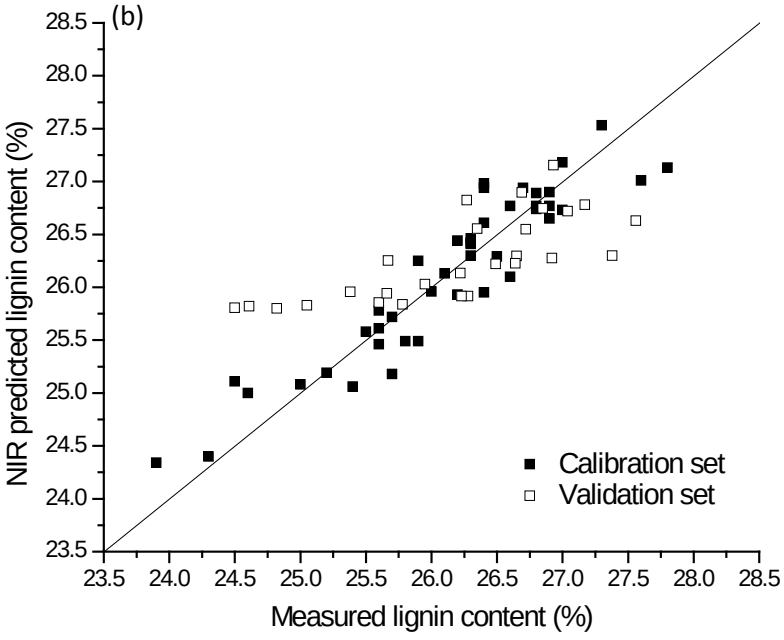
Min, minimum value; Max, maximum value; SD, standard deviation of measurement; n, sample number; CV, calorific value.

Table 3.2. Statistical summary of chemical composition and calorific value of milled sample for calibration set and validation set.

Properties	Calibration set					Validation set				
	Min	Max	Mean	SD	n	Min	Max	Mean	SD	n
Lignin (%)	24.2	27.6	25.94	1.42	34	24.55	27.44	26	1.3	17
Extractives (%)	2.4	4.02	3.23	0.82	34	2.4	4.0	3.24	0.77	17
CV (MJ/kg)	18.3	18.9	18.61	0.31	34	18.3	18.8	18.67	0.25	17
Ash (%)	0.19	0.41	0.29	0.086	34	0.24	0.39	0.31	0.073	17
Moisture (%)	6.7	12.22	9.11	1.76	34	7.25	12.2	9.4	1.64	17

Min, minimum value; Max, maximum value; SD, standard deviation of measurement; n, sample number; CV, calorific value.


(a)
NIR predicted lignin content (%)
Measured lignin content (%)
Calibration set
Validation set
28.0
27.5
27.0
26.5
26.0
25.5
25.0
24.5
24.0


(b)
NIR predicted lignin content (%)
Measured lignin content (%)
Calibration set
Validation set
28.5
28.0
27.5
27.0
26.5
26.0
25.5
25.0
24.5
24.0
23.5

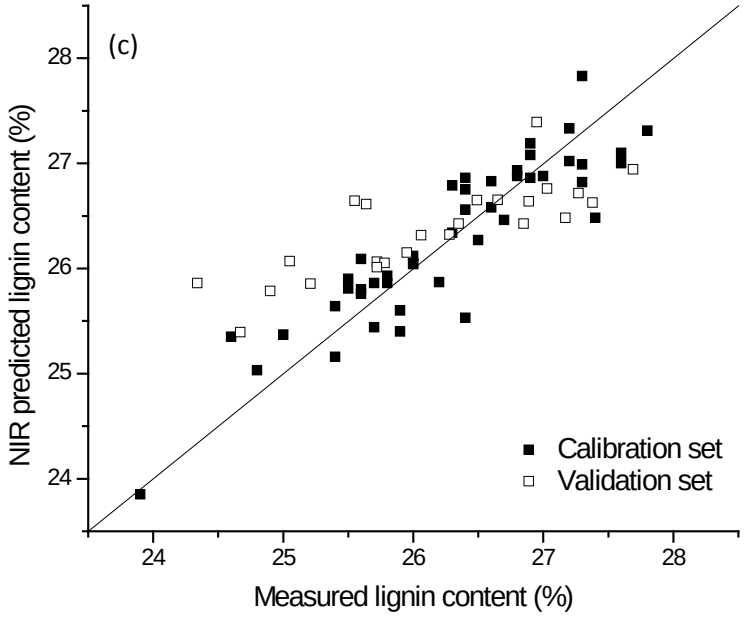
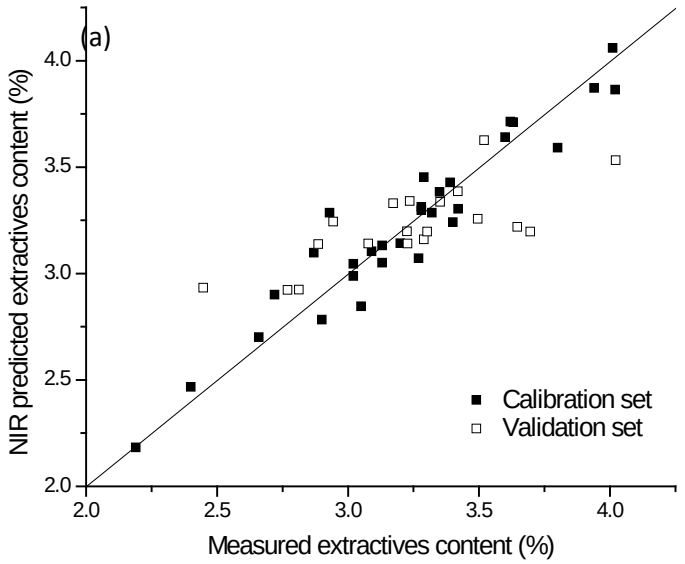
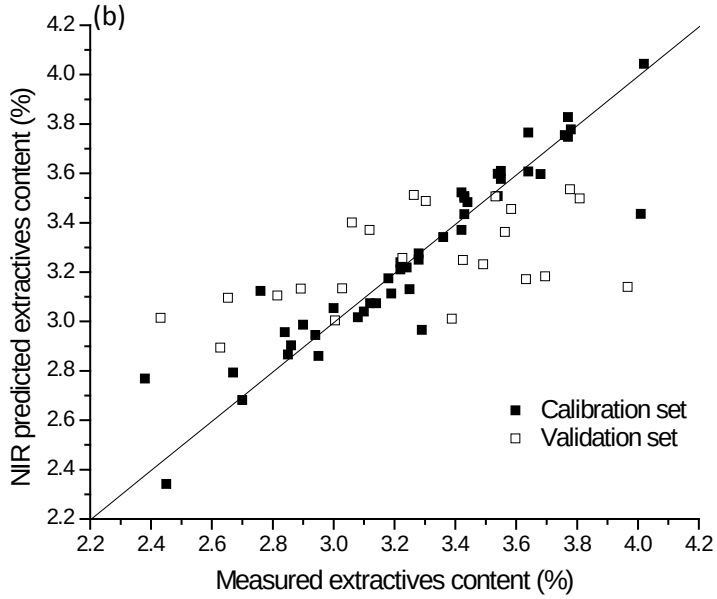


Figure 3.4 Correlation between the measured lignin content and the value predicted by calibrations using the spectra of milled sample (a), averaged spectra per chip (b), single spectrum per chip (c).

Table 3.3. Summary of pretreatment methods and quality of the PLS calibrations for lignin content.

Parameter	Spectral region (cm^{-1})	Treatment	No. of PCs	R_c^2	SEC	R_p^2	SEP	RPD
Spectra of meal	4000-10000	MSC 1der13	4	0.93	0.28	0.64	0.39	3.3
Averaged spectra of chip	4000-10000	MSC 1der13	6	0.86	0.33	0.55	0.53	2.7
One spectrum of chip	4000-10000	MSC 1der25	5	0.81	0.4	0.6	0.68	2.1


(a)
NIR predicted extractives content (%)
Measured extractives content (%)
Calibration set
Validation set
2.0
2.5
3.0
3.5
4.0


(b)
NIR predicted extractives content (%)
Measured extractives content (%)
Calibration set
Validation set
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2

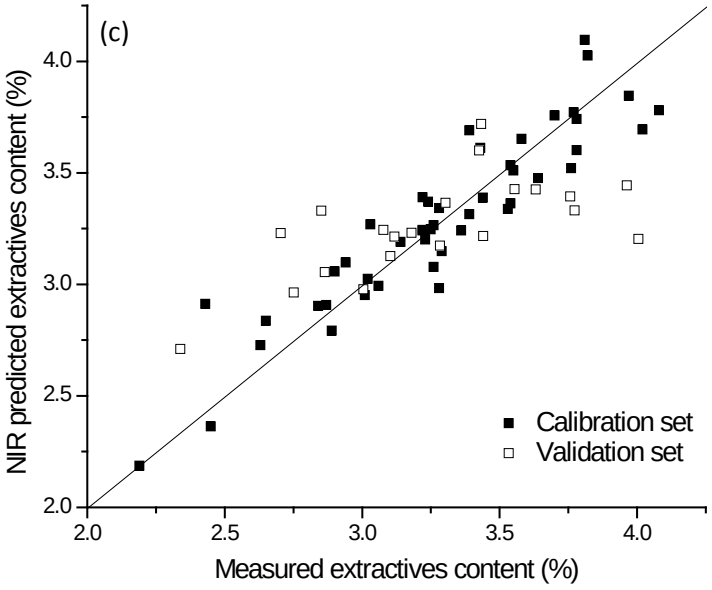
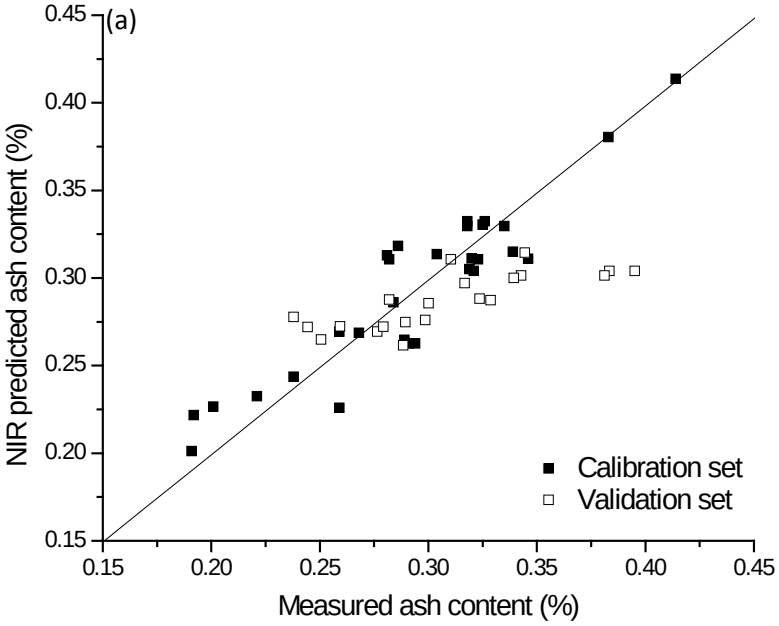
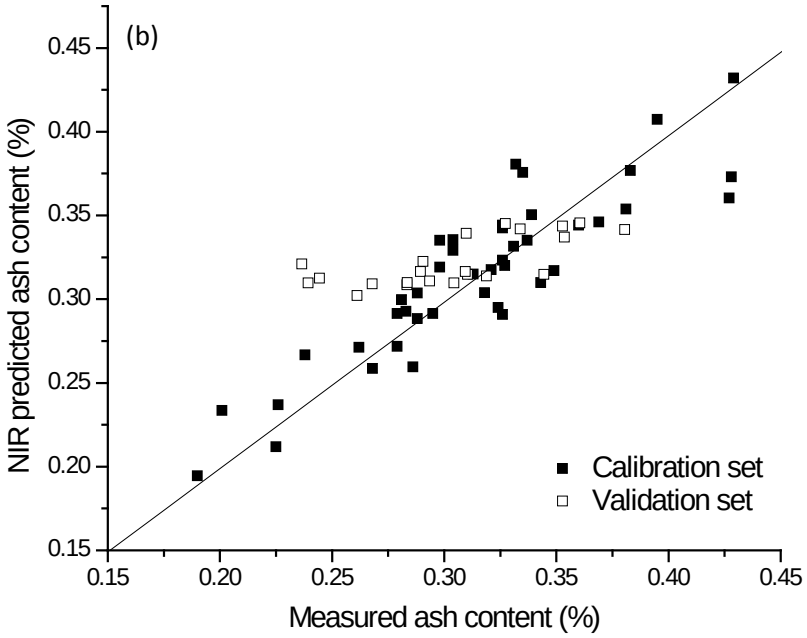


Figure 3.5 Correlation between the measured extractives content and the value predicted by calibrations using the spectra of milled sample (a), averaged spectra per chip (b), single spectrum per chip (c).

Table 3.4. Summary of pretreatment methods and quality of the PLS calibrations for extractives content.

Parameter	Spectral region (cm^{-1})	Treatment	No. of PCs	R_c^2	SEC	R_p^2	SEP	RPD
Spectra of meal	4000-10000	MSC 2der25	3	0.91	0.14	0.56	0.22	3.5
Averaged spectra of chip	4000-9000	MSC 2der9	4	0.86	0.16	0.4	0.32	2.1
One spectrum of chip	4000-10000	2der49	4	0.84	0.18	0.42	0.3	2.2


(a)
NIR predicted ash content (%)
Measured ash content (%)
Calibration set
Validation set
0.15
0.20
0.25
0.30
0.35
0.40
0.45


(b)
NIR predicted ash content (%)
Measured ash content (%)
Calibration set
Validation set
0.15
0.20
0.25
0.30
0.35
0.40
0.45

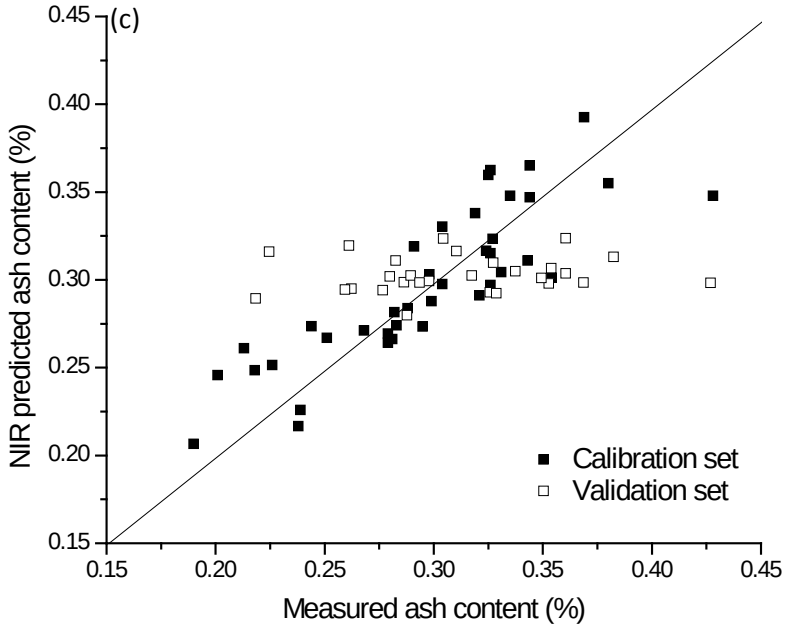
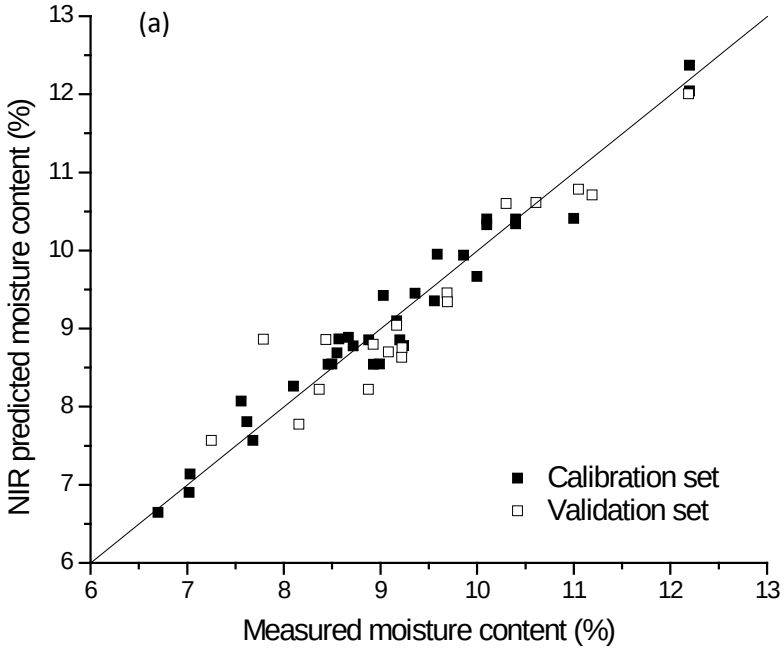
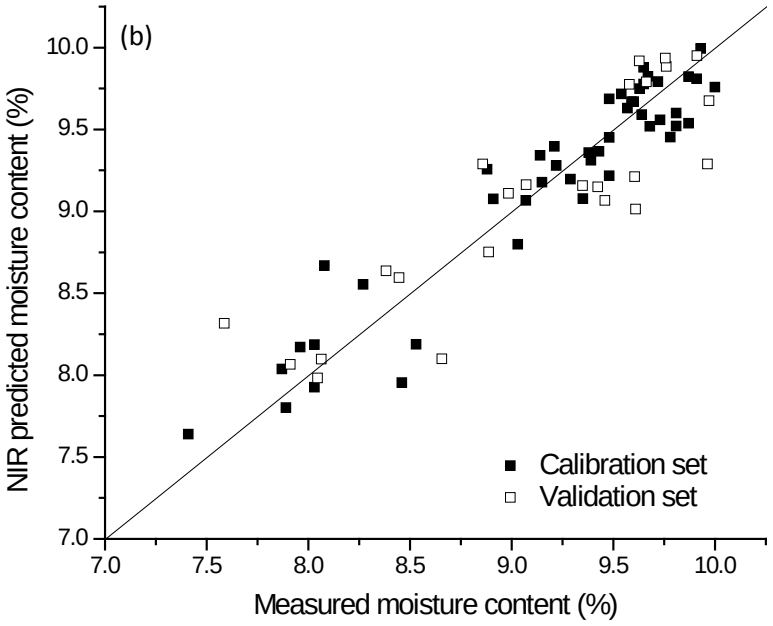


Figure 3.6 Correlation between the measured ash content and the value predicted by calibrations using the spectra of milled sample (a), averaged spectra per chip (b), single spectrum per chip (c).

Table 3.5. Summary of pretreatment methods and quality of the PLS calibrations for ash content.

Parameter	Spectral region (cm^{-1})	Treatment	No. of PCs	R_c^2	SEC	R_p^2	SEP	RPD
Spectra of meal	4000-10000	1der25	5	0.85	0.025	0.61	0.037	1.97
Averaged spectra of chip	4000-10000	2der37	4	0.80	0.028	0.51	0.044	1.9
One spectrum of chip	4000-10000	1der25	4	0.72	0.03	0.33	0.052	1.6


(a)
NIR predicted moisture content (%)
Measured moisture content (%)
Calibration set
Validation set
6
7
8
9
10
11
12
13


(b)
NIR predicted moisture content (%)
Measured moisture content (%)
Calibration set
Validation set
7.0
7.5
8.0
8.5
9.0
9.5
10.0

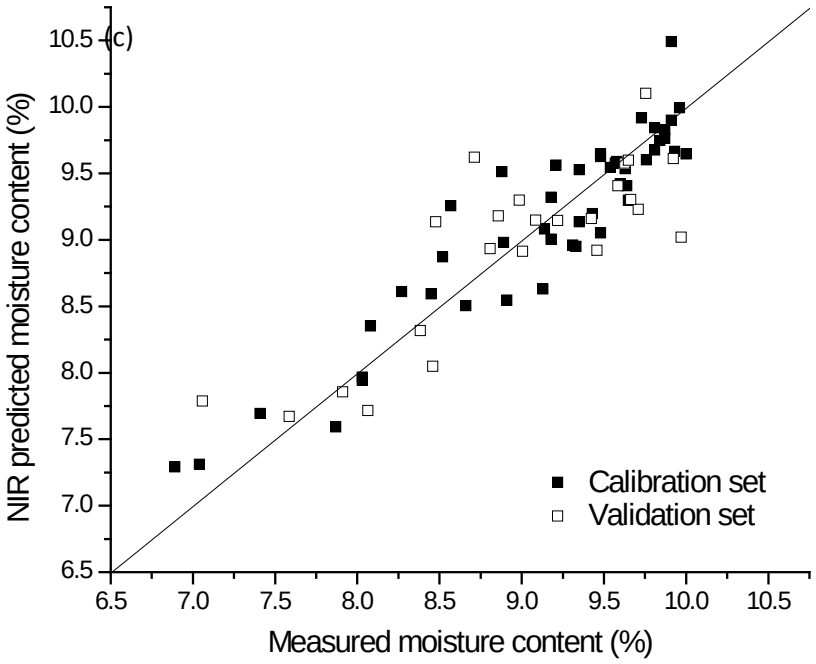
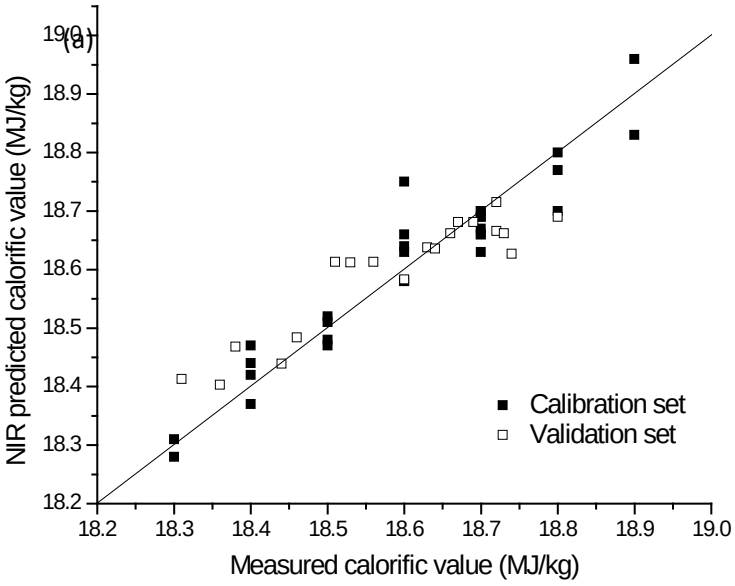
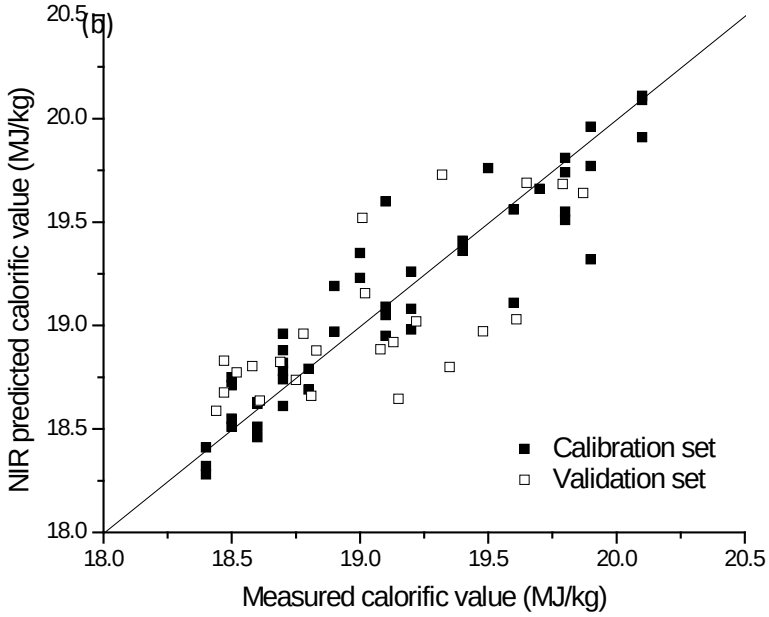


Figure 3.7 Correlation between the measured moisture content and the value predicted by calibrations using the spectra of milled sample (a), averaged spectra per chip (b), single spectrum per chip (c).

Table 3.6. Summary of pretreatment methods and quality of the PLS calibrations for moisture content.

Parameter	Spectral region (cm^{-1})	Treatment	No. of PCs	R_c^2	RMSEC	R_p^2	RMSEP	RPD
Spectra of meal	4000-8000	1der5	5	0.96	0.32	0.89	0.45	3.6
Averaged spectra of chip	4000-10000	1der37	6	0.90	0.25	0.77	0.34	3.7
One spectrum of chip	4000-9000	1der37	7	0.87	0.33	0.70	0.43	2.9


(a)
NIR predicted calorific value (MJ/kg)
Measured calorific value (MJ/kg)
Calibration set
Validation set
18.2
18.3
18.4
18.5
18.6
18.7
18.8
18.9
19.0


(b)
NIR predicted calorific value (MJ/kg)
Measured calorific value (MJ/kg)
Calibration set
Validation set
18.0
18.5
19.0
19.5
20.0
20.5

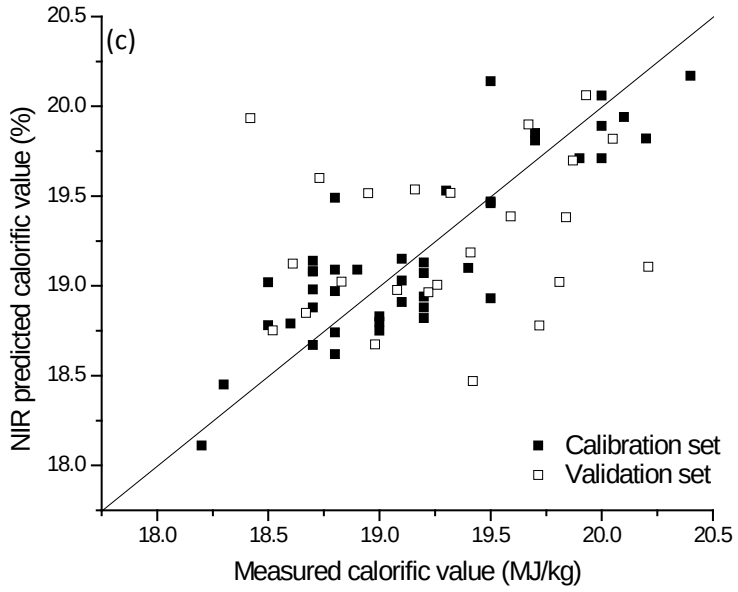


Figure 3.8. Correlation between the measured and the predicted calorific value by calibrations using the spectra of milled sample (a), averaged spectra per chip(b), one spectrum per chip (c).

Table 3.7. Summary of pretreatment methods and quality of the PLS calibrations for calorific value.

Parameter	Spectral region (cm^{-1})	Treatment	No. of PCs	R_c^2	SEC	R_p^2	SEP	RPD
Spectra of meal	4000-9000	2der19	3	0.91	0.05	0.85	0.08	3.12
Averaged spectra of chip	4000-10000	1der19	5	0.87	0.22	0.52	0.29	1.9
One spectrum of chip	4000-10000	1der37	6	0.74	0.34	0.37	0.43	1.3

Table 3.8 Summary of pretreatment methods of calibrations for chemical composition and energy content based on spectra of meal, averaged spectra per chip, single spectrum per chip.

properties	spectra of meal	averaged spectra per chip	single spectrum per chip
Lignin	4000-10000 cm^{-1} MSC 1der13	4000-10000 cm^{-1} MSC 1der13	4000-10000 cm^{-1} MSC 1der25
Extractives	4000-10000 cm^{-1} MSC 2der25	4000-9000 cm^{-1} MSC 2der9	4000-10000 cm^{-1} 2der49
Ash	4000-10000 cm^{-1} 1der25	4000-10000 cm^{-1} 2der37	4000-10000 cm^{-1} 1der25
Moisture	4000-8000 cm^{-1} 1der5	4000-10000 cm^{-1} 1der37	4000-9000 cm^{-1} 1der37
CV	4000-9000 cm^{-1} 2der19	4000-1000 cm^{-1} 1der19	4000-10000 cm^{-1} 1der37

CV, calorific value; MSC, multiplicative scatter correction; der, derivative.

Chapter 4 Conclusions and further studies

4.1 Conclusions

The calibrations based on spectra from wood powder, averaged spectra per chip and single spectra per chip for chemical compositions and calorific value of loblolly pine were established. Good calibrations were obtained based on spectra from powder with coefficients of determination (R^2) values of 0.93 (SEC=0.28%) for lignin, 0.91(SEC=0.14%) for extractives, 0.85 (SEC=0.025) for ash, 0.96 (SEC=0.32) for moisture, and 0.91 (SEC=0.05 MJ/kg) for calorific value. With the RPD values ranged from 1.97 to 3.6, the calibrations were all satisfied for the initial screening. The calibrations based on averaged spectra per chip also presented good correlation with R^2 ranging from 0.8 to 0.9 for chemical composition and calorific value. Calibrations based on single spectrum per chip gave R^2 of 0.81 (SEC=0.4%) for lignin, 0.84(SEC=0.18%) for extractives, 0.72 (SEC=0.03) for ash, 0.87 (SEC=0.33) for moisture, and 0.74 (SEC=0.34 MJ/kg) for calorific value.

The results indicate that for all properties in the current study, the calibrations based on spectra from powder gave the highest R^2. Furthermore, good correlations between measured and predicted values were also acquired from the calibrations based on averaged spectra per chip with slightly lower R^2. It's most encouraging that strong calibrations were possible for even the single spectrum treatment when predicting chip properties. However, when the calibrations based on single spectrum per chip were validated by prediction set, the correlations were

disappointed for extractives, calorific value and ash with R^2_p lower than 0.5. With the RPD values ranged from 1.3 to 2.9, the calibrations based on single spectrum per chip still meet the requirement for initial screening, which could facilitate large-scale forest resource properties assessment and consequently assist the efficient process control for large-scale conversion of heterogeneous feedstock to energy outputs. In most cases of biomass industry, it is more practical to make a large number of biomass chip samples screened rather than milled samples, which is a prerequisite for on-line and in-line monitoring. The simplicity and rapidity of calibrations based on a single spectrum from a solid wood chip may outweigh the slightly greater precision achieved when analyzing ground, bulk samples. This study reveals that NIRS in combination with multivariate analysis has the potential to predict the bioenergy and chemical characteristics of biomass in industrial conversion.

4.2 Further studies

The results showed the potential of calibrations based on single spectrum per chip to predict the characteristics of biomass. However, the calibrations may need more samples with more variability to improve the prediction correlation and accuracy, which with relatively low R_p^2 and high standard error in the current study. Furthermore, more biomass species can be applied to make the calibrations more robust and powerful.

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