ABSTRACT

BROWN, WILLIAM GARRETT. The Use of Near-Infrared Technology to Predict Physical Characteristics of Solid Biofuels. (Under the direction of Dr. Matthew Veal.)

In recent years, U.S. Energy policy has focused on the development of renewable, biomass-derived energy resources to meet national security, economic, sustainability, and rural revitalization goals. While much of the research has focused on the development of liquid transportation fuels, such as cellulosic ethanol, a more direct path towards commercialization would be the combustion of densified biomass products for thermal energy generation. Pelleting and briquetting are two biomass densification strategies that produce compacted, cylindrical-shaped biomass products that are ideal fuel products for industrial hot water, steam, and heat applications. This project specifically investigated the ability of a small briquetting press to produce 5 cm diameter briquettes from coastal Bermuda grass, corn stover, cotton gin trash, and sawdust. Each of these materials is locally-available, found in significant abundance, and have very little economic value to agricultural stakeholders in North Carolina.

In addition to evaluating the ability of the briquetting machine to process these common agricultural wastes, this project focused on the development of near infrared (NIR)-based systems to quickly evaluate the combustion quality of the briquette product. Ash, energy, and moisture content are three of the key physical characteristics of a combustion fuel used to assess economic value and potential applications. Unfortunately, the analytical methods required to quantify these three physical properties can be time consuming, expensive, and require specialized equipment or skilled technicians to complete.
In this study, the four biomass briquette types were scanned using a Foss XDS Rapid Content Analyzer, which is an NIR-based instrument. Additionally, the biomass briquettes were then characterized by determining density, ash content, moisture content, and energy content using analytical laboratory procedures. NIR calibration equations were derived by comparing these values using multiple linear regression techniques. Results of the NIR activity indicated that the uniformity of the briquettes constituents in terms of mixing ratio and particle size are important in the development of robust NIR prediction equations.

Efforts to quantify moisture content in the briquettes with NIR were not successful because the briquette machine produces briquettes of similar moisture content regardless of biomass type. Without sufficient variability in the moisture content of the briquettes it was not possible to develop a calibration equation. Furthermore, it is though the moisture content of the briquettes (generally under 10%) is too low to regularly use NIR to differentiate moisture values.

The ash and energy content calibration equations showed some promise as both relied on identifying wavelengths of chemical bonds or elemental compounds which contribute to these values. These multi-variable regression equations produced moderately accurate prediction equations when the briquette forming material was uniform. But there is need to look at more advanced statistical procedures to develop more refined equations.
The Use of Near-Infrared Technology to Predict Physical Characteristics of Solid Biofuels

by
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DEDICATION

I’d like to dedicate this thesis to my family and my wonderful wife, Natalie Brown. Without all of the support I have received from them, none of this would have been possible.
BIOGRAPHY

William Brown, son of Connie Brown and the late Mike Brown, was born in Winston Salem, North Carolina on August 7th, 1987. He grew up alongside his twin brother in the small community of Pine Hall in Stokes County, North Carolina. Will graduated from South Stokes High School in 2005. While in high school he participated in baseball and Boy Scouts of America. Will was a part of the North Carolina baseball 1A State Champions his junior year (2004). He was also awarded the highest rank in Boy Scouts of America with his Eagle Scout. Will enrolled at Virginia Polytechnic Institute and State University in the fall of 2005 majoring in Biological Systems Engineering with a Land and Water Resources concentration. Will became involved with Virginia Tech’s student branch of the American Society of Agricultural and Biological Engineers as an undergraduate and also became a member of the Virginia Tech chapter of the Farm House Fraternity. Upon graduation in 2009, Will decided to further his education by enrolling in a Master’s program in the department of Biological and Agricultural Engineering at North Carolina State University with an emphasis on solid biofuels. While also attending North Carolina State, Will was an active member of the quarter-scale tractor design team, Pack Pullers.
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Chapter 1 Introduction

Biomass is a critical energy resource that has played a key role in the continued development of human technology, society, and well-being. Energy derived from biomass has been used in many applications including cooking, heating, distilling, and electrical power generation. Energy products derived from biomass are known as biofuels and they can be liquid biofuels, gas biofuels, and solid biofuels. Liquid energy resources such as gasoline and diesel fuel have been the major energy consumable of the industrialized world since the advent of the internal combustion engine. Beginning in the 1970’s, many people began looking for renewable energy resources to displace the consumption of non-renewable resources, thus an emphasis on liquid biofuels like biodiesel and ethanol was created. However, the production of liquid fuels from biomass resources, particularly cellulosic biomass, has been slow to develop as a result of technological challenges. Developing non-liquid fuel markets for biomass energy crops would be an important step to continue the adoption and development of a renewable energy market in the United States.

The use of solid biofuels has not been well-researched or studied although there are numerous applications for the generation of stationary power, heat energy, and potential to operate internal combustion engines. With the expansion of first generation biofuels (grain based), its impacts on food security, food prices, and the environment are not quite understood and have drawn many debates among experts.
For this reason, more research needs to be done on the applicability of solid biofuels which can be used to offset consumption of non-renewable liquid energy resources, such as heating oil and liquid propane.

With approximately 86% of the energy used in the United States coming from nonrenewable fossil fuels, it is easy to see why research efforts are once again focusing on renewable energy sources (Fasina, 2006). With the potential to produce nearly 1 billion dry tons of biomass feedstock per year, the biomass resources of the U.S. are sufficient to supply enough material to warrant solid biofuel production (Perlack et al., 2005). With Perlack’s estimated biomass production, it will be possible to offset about 30% of the United States’ 2010 petroleum consumption. However, while there is considerable promise, it is not fully understood whether these biofuels will be able to perform equally with petroleum based fuels. Unlike nonrenewable hydrocarbons, the energy properties of biomass are highly variable and failure to account for this variability can lead to poor performance from power generation equipment.

This project is focused on rapidly characterizing physical parameters for solid biofuel products. Solid biofuels are primarily used in direct and co-fire boiler and hot water heaters. The three key parameters quantified that determine the value of biomass as a renewable solid fuel resource are ash content, energy content, and moisture content. These three parameters provide information that quickly assesses
the value and potential discounts of biomass resources considered for solid fuel applications.

The form of solid biofuel that has been chosen to research is briquettes. Briquetting is a process of transforming loose biomass into dense pellets of specific sizes for easier handling, transport and storage (Mani, 2007). This study will specifically focus on cylindrical briquettes which are structurally similar to heating pellets but have larger dimensions (Figure 1.1). These briquettes can be burned in heating stoves, boiler systems and in a variety of other applications. Briquettes can be formed from any biomass feedstock as long as the moisture and particle size are within the stated range established by the briquette press manufacturer.

Figure 1.1 Examples of briquettes produced from various biomass types.
To rapidly assess the solid fuel potential of the biomass briquetted, this project utilized Near Infrared Spectroscopy (NIR) to analyze the three key physical parameters previously mentioned within individual briquettes. It is thought that the absorption curves created by a NIR instrument could be used to accurately predict physical characteristics of densified biomass. The use of a NIR instrument to analyze the material facilitated a process that is non-destructive to the sample, simple for the operator, and provided a quick, non-time consuming feedback value. The research hopes to illustrate that a NIR instrument can be placed within a briquette production system to provide real time quantitative data that can be used to manage production operations and to adjust the system on an as-needed basis. Rapid valuation of the biomass by the consumer would be an additional application for NIR-based characterization of biomass samples.

Objectives

The potential of solid biofuels products to provide near-term markets for biomass is significant. However, consumers of the briquettes will most likely provide payment based on the energy content and overall fuel quality of the materials (ash content, moisture content). Completing analytical tests to assess these values would be expensive and a faster method to assess biomass fuel quality would be welcomed. This project is focused on the development of a rapid biomass fuel quality assessment protocol with specific objectives of:
Evaluate the use of a commercially-available briquetting machine to densify biomass for the production of consistent biomass briquettes; and, develop Near-Infrared Spectrometry (NIR) methods to assess fuel quality characteristics including energy content, ash content, and moisture content for four different biomass briquettes.

**Chapter 2 Review of Literature**

In determining which crops and analytical methods to utilize for this research it was necessary to study previous completed research in this field. Most of the prevailing literature discusses briquette production potential as well as general discussion on NIR system applications; however a detailed look at merging the two together is lacking. The existing literature does provide a basis for this investigation; primarily general methodologies and possible prediction capabilities of a NIR system.

For instance, a similar theme in the literature implies that NIR systems can be used to predict moisture and other physical characteristics of grains and other feed components. It is also understood that NIR systems can be used for the evaluation of forage nutrition (McIlwee et. al. 2001), soil fertility (Chang et. al. 2001), and fecal analysis (Landau et al 2006.) An issue that may arise in this investigation is the traditional use of NIR techniques involves quantification of chemical properties and composition and not a physical analysis. The physical differences between various
biomass types and variability in the densification of these biomass types in the briquette press may impact the ability of NIR to differentiate the ash, energy, and moisture contents. The capabilities of the NIR system in this scenario are unknown as relatively little research has been completed involving NIR utilization in the study of solid biofuels. The following chapter describes the importance of each feedstock chosen, the biomass densification process, and the previous applications of NIR systems.

**Feedstocks**

Utilizing agricultural plant wastes/residues that are by-products of harvesting or processing operations can be an effective means of turning unused material into useful commodities (Holt et al. 2006.) These plant wastes can include corn stover, cotton gin trash, peanut hulls, wood processing by-products, and tobacco stalks. An abundance of these currently unused materials is creating economic and environmental issues. The cost associated with disposing of the materials is placing economic stress on processing facilities and producers. Developing solid fuel biofuels markets for these waste materials provides growers a value-added avenue to funnel these crops into a revenue generating enterprise. Re-using these products in on-farm applications is also a very sustainable practice.

Low-value hay and forage crops is another segment of agriculture production that can be exploited as a feedstock for solid biofuels production. The crops include
traditional hay crops such as coastal Bermuda grass and more novel energy grasses such as switchgrass and miscanthus that do not have a viable marketplace. Coastal Bermuda hay is of particular interest in North Carolina has it is grown in abundance on swine production sprayfields. The coastal Bermuda provides a nutrient removal strategy for the hog farmers, but it has virtually no value following harvest. Developing a market for this hay would provide sprayfield managers an opportunity to generate revenue on lands that historically operate at a loss. This project worked with both low value hay crops as well as crop production and processing residues. The four feedstocks that were given consideration in this briquette production study were cotton gin trash, corn stover, bermuda grass hay, and sawdust.

Over the years, research concerning the use of cotton gin by-products as a value added material has been performed to identify markets for this biomass stream. Potential products and markets investigated for cotton gin trash include: fire logs (Karpiscak et. al., 1982), livestock feed (Holloway et. al., 1974), compost (Hills, 1982), and as a raw material in asphalt roofing felt (Kolarik et. al., 1978). The biggest advantage of utilizing cotton gin by-products is the abundance of the material. Assuming that 34 kg of by-products are generated from each bale (Holt et. al., 2006) produced in the United States and using a five year production average of 16.8 million bales produced per year (NASS, 2010,) the amount of cotton gin by-products generated would be 571,200 Mg. With current disposable practices consisting of returning the biomass to the originating cropland, most of the material
generated is not utilized. This disposal event is becoming an economic burden to many of the ginning facilities. In 2001, a gin located in West Texas paid $2.00 per bale to dispose of the gin waste, which calculated to a yearly disposal cost of $110,000 (Holt et. al., 2004.) By capturing the material from the gin process, it can then be densified and used in the generation of on-site power or it can be packaged and sold to residential consumers. Both scenarios would be economically beneficial to the cotton gin operation. Economic and feasibility studies have been conducted that illustrate that fuel briquettes comprised of cotton gin by-products have great potential (Holt et. al., 2003b, 2004b.)

Another crop residue given consideration is corn stover. The term stover refers all of the material left over after grain harvest, i.e. cobs, stalks, leaves, etc. During the process of combining, in which the grain is harvested, waste material is spread back on the field using a rotating disc. Gallagher et. al. estimated that the quantity of corn stover generated in the contiguous 48 states makes up approximately 68 percent of the potential supply of biomass from crop residues. Historically, corn stover has been left in the field as ground cover to reduce erosion and to provide nutrients if not being collected to use as animal feed. Despite already having a useful application, corn stover could provide another biomass feedstock for briquette production. The main aspects to consider when investigating the use of corn stover as a solid biofuel feedstock is consumer location relative to fuel generation, harvesting system, and amount of stover produced in a given region.
Economics would be the driving factor in determining which application to utilize the material.

The third biomass option that has high feasibility potential is Bermuda grass hay. The main advantage with using bermuda grass as a biofuel feedstock is the vast acreage planted in the southern United States. Most often, it is produced as part of a waste management plan to provide crop land that can be irrigated with livestock wastewater. Despite the necessity of moderate amounts of nitrogen for optimal production (Silveira et. al., 2007), bermuda grass has several positive characteristics including persistence, drought tolerance, response to increased fertility, and greater yield potential (Burns and Fisher, 2007.) Another optimistic attribute associated with the utilization of bermuda grass as a solid biofuel feedstock is the possibility of multiple harvests throughout the year. By providing a constant supply of biomass, the briquette production facility can operate continuously, in turn allowing production to be a year round process.

The final feedstock selected for the project was sawdust. Saw dust considered for this study was the leftovers from a wood flooring manufacturer. The conversion of saw dust to a high-energy solid biofuel to be used in a variety of applications has been studied and found to be feasible (Adegoke and Mohammad, 2002.) David Jones, a researcher at the Forest and Wildlife Research Center at Mississippi State University, states that densified wood products have been made in the United States
since the 1970s (Coblentz, 2010.), but the knowledge and technology to create high-energy wood products has been around for centuries. The reason woody biomass has been researched to such great extents is due to the fact that it has much higher heating values when compared to other sources of biomass including ordinary firewood (Osarenmwinda and Imoibe, 2009.) Another consideration involved with the densification of wood waste is the market demand for the product. In the world of heat generation, marketability of the product is driven by heating content per mass of product. Additionally, North Carolina is home to numerous furniture manufacturers that produce tremendous volumes of shavings, sawdust, and other wood residues that are optimal for briquetting. Other factors that influence the price marketability include handling, burning characteristic, and heat intensity. The sawdust and shavings used in the densification process are also demanded in animal bedding markets and in paper production. The four feedstocks used for this study are pictured in Figure 2.1 below.
Briquette Production

To utilize the above mentioned biomass feedstocks as a thermal energy source, the products must be processed and densified to offset problems with handling and storage of the material. Two main methods used to densify material
are pelletizing and briquetting. When comparing the two densification methods, the main difference is size. Briquettes have much higher diameters when compared to pellets. For this research, the briquettes formed were 5.08 cm, while most pellets are approximately 0.635 cm. The densification process investigated for this research project was briquetting. The process of taking loose biomass material for fuel combustion and converting it into a compact product has been around for decades. Only in recent history has emphasis been placed back on this process, mainly driven by environmental concerns and costs associated with energy generation. The advantages of briquettes include easier transport, easier handling of the product, and improved burning characteristics. Other advantages of briquettes are its low sulfur, reduction of dust particles, and ease of use (Osarenmwinda and Imoebe, 2009.) The main advantages of briquettes when compared to pellets are the amount of material located within one unit of product and the unnecessary need of additive binding agents. As stated before, briquettes usually consist of material extruded to a diameter of 5.1 cm while pellets are usually in the 0.6 cm range. Greater pressures and temperatures created by a briquette press cause a natural binding agent described below to be expressed, therefore creating an environment where additional binding agents are not required. Additionally, the briquette process is less harsh on equipment compared to pellet making, generally the residence of the biomass in the equipment is shorter with briquette making and lower machinery operating speeds lessen the harm caused by abrasive components in the biomass.
The densification of biomass, no matter which method (pelleting or briquetting) or equipment is used, follows a similar operating principle. Material is conditioned to achieve an optimal moisture content to allow densification to occur. Moisture conditioning can include hydration or dehydration operations and the optimal moisture content is highly dependent on the type of biomass processed. According to Holt et. al., the energy input involved with the drying of material makes up a majority of the costs associated with the densification process (2004.) Next, the material is reduced in size, depending on material, through a grinding, chopping, or hammering process. After adequate moisture content and particle size is achieved, the material is feed into the machine, usually through a hopper system, before being exposed to the densification process. The compaction process involves mechanical pressure, formed using either a roller mechanism or an oscillating piston, being exposed to the material to reduce the materials volume. This exerted force, causes the material to pass through a die that gives the material a specific shape. The great pressures and temperatures generated as the mechanisms contact the die causes the materials to release lignin, which allows individual particles within the mass to bind to each other (Kers et. al., 2010.) As stated before, this shape can vary from process to process. An important characteristic of both pelleting and briquetting is both methods produce densified products that are uniform in size with consistent densities throughout the final fuel product. This uniformity is an important factor in handling, storage, and ease of use.
**NIR Utilization**

Near infrared spectroscopy is a form of vibrational spectroscopy that employs photon energy in the energy range of $2.65 \times 10^{-19}$ to $7.96 \times 10^{-20}$ J, corresponding to the wavelength region of 750 to 2,500 nm (Pasquini 2003.) This energy range is utilized because it allows for molecules to enter an excited vibrational state without promoting electron excitation within the molecule. The overall objective of the process is to collect qualitative and quantitative information about a given sample. The interaction of the near infrared electromagnetic waves with the sample constituents provide the data used in analytical situations.

NIR analyses were first performed on food and agricultural commodities. The majority of these analyses were performed on samples for constituents such as moisture, protein, and fat because traditional analytical techniques to determine these values were difficult, laborious, and expensive. Analytical, quality control, and research and development laboratories that support industrial manufacturing processes (i.e. commercialized briquette production) share similar needs with the agriculture and food industries. However, the test and measurement requirements in the agricultural feed and food industries differ from an industrial setting. The number of product constituents and physical properties of interest is not as extensive in an industrial setting compared to food/feed applications. (Brimmer and Hall 2001).
Introduction of a NIR analytical methodology to the study of commercialized briquette production systems could be advantageous for both producers and consumers, as a premium would be placed on heating value. The quantitative capabilities of the instrument can be beneficial in terms of quality control and quality assurance. Qualitative NIR methods can also provide significant benefit for the analysis of incoming material at a manufacturing facility (Brimmer and Hall 2001) to ensure the manufacturer is receiving high quality feedstock. This qualitative analysis can be completed in a laboratory, analyzer room, or at the receiving area. The capabilities of the NIR based system make it highly desirable over traditional methods of analysis in terms of cost, throughput, and efficiency.

There are some major advantages to NIR based systems compared to traditional laboratory procedures. The main advantages are the minimal amount of time for sample preparation and the minimal amount of time associated with conducting the analysis. Over time, in an industrial setting, many samples can be studied by the system over a very short period of time. During the initial introduction of the NIR system at a facility a combination of laboratory analysis and NIR scans can be carried out in a few weeks to develop calibration curves and these calibrations can be continuously improved upon with minimal additional costs. Another advantage is that the analysis of the material is non-destructive and no material is lost. The non-destructive nature of the test allows rapid characterization of the source material that will be present in the final fuel production. This is
opposed to destructive testing that may require complex sampling schemes to acquire representative material that may or may not reflect the feedstock used in the final product.

One disadvantage when comparing the two analytical methods is the initial cost of the NIR system. The cost of NIR equipment ranges from $10,000 to over $100,000, and computer systems associated with the equipment ranging from $3,000 to $25,000 (Barton and Kays, 1998.) Currently, commercial laboratories using traditional wet chemistry analysis charge $8-$10/sample for moisture content analysis (DHIA Laboratories), $3-$7.50/sample for ash content (DHIA Laboratories), and $500/sample for calorific value (Kinetica, Inc.) To analyze just one sample for all of three of the parameters would cost around $520 with no accounting for turnaround time, shipping, and sample preparation. Although the equipment costs are quite high, over time the machine would pay for itself. In the previous example, the FOSS XDS System (Foss, Laurel, MD) used in this study has a base price of approx. $60,000. If proper calibration curves were established, the return on investment would occur after 115 samples were analyzed when compared to $520/sample using wet chemistry methods at third party. The utilization of a NIR system would cut down on labor cost, increase quality control measures, and it would allow for more samples to be analyzed much quicker, providing more accurate analytical values.
Previous NIR applications have included pharmaceutical, medical diagnostics, food and agrochemical quality control, and combustion research. Beginning in the 1980s, a major application of the technique was in forage analysis (Marten et al 1985.) Since all of the materials investigated in this project were forage type materials, excluding the cotton gin trash, it was beneficial to focus on the use of NIR in forage analysis.

The variety of biomass types under consideration and their highly variable characteristics stress the need for improved characterization of their chemical and physical properties. With the production of solid biofuels representing a near-term market from biomass with opportunities for widespread commercialized, the demand for rapid characterization methods for in-line measurements is becoming more prevalent. To satisfy this need, the use of a NIR instruments in determining these characteristics has become an accepted system. The use of NIR is of interest to characterize solid biofuels because it quick, non-destructive, user-friendly, and suitable for in-line measurements. Several studies have been completed that show that there is a high potential for NIR spectroscopy to predict moisture content, cellulose, hemicelluloses, and lignin (Lestander and Rhen 2005.) More recent studies illustrate that NIR spectroscopy can also be used to quantify calorific value in shrub species, and ash content in coffee, and soil.

A study of Norway spruce trees, completed by Lestander and Rhen in 2005,
proved that NIR spectroscopy can be used in the creation of models that can be utilized in the prediction of physical properties of biomass materials. The research studied calorific content, ash content, as well as moisture content. Their study was focused on determining which covalent bond overtones accurately described each physical characteristic of the biomass.

For ash content, it was found that interactions of ash forming atom species occurred in C-H overtones sometimes in combination with vibrations of C=C and =CH$_2$ structures. By studying these bond regions, it was found that NIR provided respectably accurate models. The energy content of several covalent bonds contributes to the calorific value found in biomass materials. Lestander and Rhen found that four bonds seemed to contribute to the model more so than the others. Overtones at 2140, 2190, and 2347 nm of the C=C bond should contribute greatly to the calorific value model. The research conducted by Lestander and Rhen, stated that only a slight contribution of these double bonds was discovered at 2190 nm and was not present at any of the other wavelengths. It was found that three other chemical bond overtones played a more critical role in creating the calorific model; C-H, C-O, and O-H. Lestander and Rhen concluded that moisture content, ash content, and calorific value in wood samples could be modeled with fairly high accuracy.

Even though the abovementioned research is promising, it is still not known
whether the same process can be applied to the biomass that was utilized in this research project and similar outcomes obtained. Currently, available research documentation associated with the use of NIR in analyzing physical parameters of biomass is focused on woody materials. The use of NIR in determining forage feed characteristics, i.e. protein, neutral detergent fiber (NDF), acid detergent fiber (ADF), and dry matter has been studied greatly and the associated research documentation is present.

Beginning in the 1960s, researchers began studying the use of NIR spectroscopy as a rapid, inexpensive method to analyze forages for compositional, bioassay, and quality estimates. Research completed between 1960 and the early 1980s illustrates that NIR can be used to accurately predict NDF, ADF, and moisture content in fibrous materials. In 1983, Barton and Burdick produced findings that suggested a NIR instrument does a better job at recognizing identical samples more closely than laboratory analyses. In each instance, the NIR performed better except for crude protein. The researchers attributed the numerical difference in the crude protein analysis to instrumental error. Along with being a more consistent predictor, the NIR system was much quicker; taking only 1 hr to produce results compared to 5 weeks for the laboratory analysis.

With all of the research already completed on NIR implementation as an analytical method, it is easy to see why emphasis is placed on this methodology in
current biofuels research. All of the advantages out-weigh the disadvantages. Even though minimal amounts of research has focused on using NIR directly in solid biofuel applications, this review of literature illustrates how NIR has been used in similar applications.
Chapter 3  Materials and Methods

The tasks executed to complete this investigation can be divided into four distinct categories. First, biomass materials were collected, processed, and densified in an industrial scale briquetting press. Next, briquettes were processed into uniform samples for further analysis. Analytical methods were carried out to quantify NIR reflectance, moisture content, ash content, and heating value for each of the samples. Finally, the NIR calibration curves were developed to find relationships between infrared wavelength reflectance values and the briquette characteristics of interest. The four task sets are described in greater detail below.

Materials Selected

Four distinct biomass materials; cotton gin trash, coastal Bermuda grass, corn stover, and saw dust were selected for analysis. These materials were selected because they can be easily sourced in North Carolina and have very little economic value. All of these materials were derived from industrial facilities or commercial ventures that view the materials as waste.

Cotton gin waste (Figure 3.1) was obtained from Coastal Carolina Gin in Pantego, NC. The gin trash was derived from the 2010 cotton season, stored outside and exposed to the elements prior to briquetting. Approximately, eighty tons was delivered to the briquetting site located in Butner, NC at the Umstead Research Station operated by the North Carolina Department of Agriculture and Consumer Services. The gin trash arrived on two walking floor trailers. The particle size of the material was sufficient for direct feeding into the briquette press; however, the
moisture content was nearly 40% which made the briquetting operation run slowly. The excessive moisture created problems maintaining the die at proper temperature.

Figure 3.1 Cotton gin trash briquetted and the briquette after grinding.

Coastal Bermuda hay (Figure 3.2) was cut and baled on site at the North Carolina State University Beef Unit Field Laboratory in Butner, NC. The hay was round baled and is stored at the Umstead Research Station in the event drought or other adverse climate conditions required its use for animal feed. The Coastal Bermuda grass was cut during the 2009 hay season. Direct round bale feeding into the briquette press is not possible, so the bale was sliced into 50 cm (20 in) segments using a chainsaw and initially fed into a Gehl 170 Mix-All grinder-mixer. The
The corn stover (Figure 3.3) was delivered to the Butner site by Birch Seed Company in Atlanta, IN. This stover was a co-product generated during processing and cleaning seed corn. The stover was primarily comprised of cobs, husks, kernals, and leaves. Unlike traditional corn stover baled in an agricultural field this stover product lacked a significant stalk fraction. The material was the correct size for direct feeding into the briquette machine and had a pre-briquette moisture content of 7%. 

Figure 4.2 Coastal Bermuda hay briquetted and the briquette after grinding.
The sawdust (Figure 3.4) was located using the North Carolina Biomass Trader website (http://www.ncbiomasstrader.com). The material was sourced and delivered by K.R. Snead Trucking, Inc located in Scottsburg, VA. The saw dust was generated by an unnamed laminate floor manufacturing facility in Virginia. Approximately ten tons of saw dust arrived at the Butner facility on a walking floor trailer. The particle size was sufficient to allow direct feeding into the briquette machine and the moisture content was 6% prior to briquetting.
Briquette Press

At the onset of this investigation there were several biomass densification strategies that could have been employed. Pelleting biomass at both the farm- and commercial-scale was considered as was briquetting. Ultimately briquetting was selected as the focus of this project because the briquetting press presented a realistic, industrial scale process that provided the most opportunity to control machine set up and briquetting parameters. Additionally, the throughput and product repeatability were higher for the briquette press compared to similarly priced pelleting systems.

The press chosen for this application was a BP-1500 Automatic Briquette Press from Biomass Briquette Systems, LLC, Chino, CA (Figures 3.5-3.7). A 44 kW
(60 hp) electric motor is the primary power source for the unit. This motor spins two 137 cm (54 in) flywheels which in turn transfer power to a piston. The piston compacts material that is conveyed into briquette’s dye. The unit has a verified output of 544.3 – 680.4 kg/hour. The press produces briquettes with a diameter of .50.8 cm (2 in). The unit was installed under a steel span building that house dairy cows for much of the last half of the twentieth century. The installation included significant upgrades to the flooring and electrical power systems at this former dairy facility. Three-phase 400 Amp service as initiated as well as the addition of a 61 cm (24 in) 5000 psi concrete floor to handle the press’ vibration during operation.

Figure 1.5 Layout of Biomass Briquette Systems BP-1500 automatic briquette press.
In addition to the briquette press, the complete Biomass Briquette Systems unit included a belt conveyor, auger conveyor, and a silo. During operation, material is placed onto the belt conveyor, where metal contamination is removed, and feed into the silo. The silo serves both metering and storage functions. Once in the silo, the material is continuously mixed to prevent bridging. The silo then meters material into an metered feed auger. This feed auger delivers material to the briquette machine. At this point material drops into the briquette forming chamber.
based on the delivery speed of the feed auger. Once in the forming chamber the biomass material comes into contact with the piston.

The piston was attached to a crankshaft in between two parallel, steel flywheels. The press is not equipped with any heating mechanism as the amount of pressure and friction associated with the ramming piston is sufficient to heat the die. When the forming chamber contains enough material to form briquettes, the piston would apply pressure in the die and force the newly created briquette out of the die. A cooling tube was placed at the output of the die to allow the briquettes to cool before being placed in a holding container. The cooling tube had multiple curved sections that could be interchanged to allow for multiple length briquettes. The entire process mentioned above was fully automated; meaning that as long as there was material flowing into the system briquettes could be created on a continual basis.
Figure 3.7 Installed BP-1500 automatic briquette press at the Umstead Research Farm in Butner, NC as viewed from the front.

Preparing Laboratory Samples

Individual briquettes generated by the press had a constant diameter of 5.08 cm (2.00 in) but the lengths varied from 3.18 to 15.24 cm (1.25 to 6.00 in) due to variable particle size within the material. When each briquette was created, stratified layers were formed each time the piston pressed into the die. A single layer in the briquette represented a single sample that would be analyzed. This single layer could be represented as a cylinder with a diameter of 5.08 cm (2.00 in) and a length of 3.18 cm (1.25 in). After running all four materials through the briquette press, a substantial number of irregular briquettes (irregular meaning variability in length) were collected at random. These samples were collected in trash bags and
taken back to Weaver Laboratory on the campus of North Carolina State University for further analysis.

Each briquette was broken at the point of stratification between densified layers to ensure each sample was roughly the same size and shape. Each time the piston struck the biomass material a distinct indentation pattern was left on the briquette. Three prongs on the piston caused three slightly raised areas to appear on the top of each briquette layer. To ensure proper contact between the NIR scanning window and the briquette, the indentions were ground flush with the surface of the briquette. This grinding was completed manually using a file. For the Coastal Bermuda hay, corn stover, and saw dust 120 samples were processed and used in the laboratory analysis. The high moisture content of the cotton gin trash prior to briquetting created significant variability in briquette quality. Therefore, only 75 viable samples of the cotton gin trash briquettes were developed for laboratory analysis.

After processing the samples, they were each placed in a FOSS XDS NIR analyzer (FOSS, Laurel, MD). Each individual sample was placed in the machine to create a specific near infrared reflectance curve that was used to predict physical properties of the individual sample (Figures 3.8, 3.9). The detailed process used to analyze the samples will be covered in the following section. This analysis was done without any further modification of the briquette sample. The NIR scanning is a
non-destructive test which allows for further analysis of the same sample following scanning operations.

To obtain moisture content, ash content, and heating content data the briquette required further reduction. Each briquette sample was ground using a Model 4 Wiley Mill equipped with a 2 mm sieve. After the NIR scan, each sample was placed into numbered and catalogued plastic bags to ensure identity preservation. The sample bags were then individually emptied into the mill. Following the grinding operation for each sample, the mill was cleaned out using an air hose to lessen the opportunity for cross contamination between samples. The ground samples were then stored in the same labeled/catalogued bag where the briquette had been kept.

Figure 1.8 Sawdust briquette segment positioned on Foss XDS NIR instrument.
For a small subset of briquette samples, additional tests to quantify physical properties were conducted prior to grinding. To obtain density data, twenty individual briquette samples were randomly chosen prior to grinding four each of the biomass types. The mass and dimensions of these briquettes were determined so bulk density calculations could be carried out. Bulk density provides a measure of the effectiveness of the briquette press in densifying the material. After bulk density was determined, the 20 sample subset was place in a pycnometer to determine absolute density for all four biomass types. After the density measurements were complete, the samples were ground using the previously mentioned methods and return to the general sample set.
Near Infrared Spectroscopy

The main objective of this research was to determine if it was feasible to use NIR analysis of different densified biomass types to predict the physical and chemical properties of biomass briquettes derived from various materials. The instrument that was utilized was a FOSS XDS Rapid Content® Analyzer (Foss, Laurel, MD) (Figure 3.10). As stated previously, this system allowed the user to take each briquette and place it in the machine with minimal processing. Vision® software (Version 6.0, Foss Laurel, MD) was used to establish a project, calibrated the machine, prompt briquette scanning, catalogue data, and process the results.

The process to obtain sample spectrum using the NIR system is quite simple. There are several components located within the machine, which are not visible, that play an important role in collecting the sample spectrum. These components include a halogen lamp, a mirror, a holographic grid, and infrared detectors. When the machine is commanded to take a sample, the halogen lamp bounces near infrared light onto a mirror. The light then reflects off of the mirror onto a holographic grid. Once the light hits the grid, it then is directed to the measurement window where the sample briquette is positioned. Portions of the light wave are absorbed by the briquette and other portions are reflected. The light that is not absorbed by the sample material is then dispersed back onto two infrared detectors. The amount of light detected by the detectors is recorded internally by the software. The software then quantifies the reflectance data to determine a spectrum curve illustrating the
light absorbance at varying wavelengths. This curve has several peaks indicating high amounts of absorption at given wavelengths.

To begin the process, the XDS system had to be connected to the Vision® software to allow the user to acquire the sample spectrum. Once the system was connected, a reference spectrum was acquired. The reference sample is acquired by performing a scan of a reference material internal to the machine. This reference scan should produce a constant spectrum curve demonstrating the machine is within
calibration. The assessment if the machine’s calibration status is also performed internally with a built in mechanism.

After obtaining a reference spectrum, a briquette was placed on the lens of the scanning system. The Vision® software was then used to acquire the sample spectrum from the specific briquette. The sample number for the briquette (found on the sampling bag) was entered in the Vision software to preserve the identity of the sample. This process was repeated until all samples within a biomass type had been properly scanned and all sample spectrums had been recorded. The reference scan was re-initialized when biomass types were switched or whenever sampling took longer than one day. Foss recommends one reference scan daily or whenever the project type (in this case biomass type) changes.

To keep the entire collection of samples properly organized ‘products’ had to be created in the program. These ‘products’ are the method used by the computer software to differentiate scans and the development of calibration equations. For this project, a ‘product’ was created for each material and its corresponding physical/chemical attribute. For example, products labeled ‘Bermuda Ash’ and ‘Bermuda Heat’ were generated to contain sample spectrum that were used to analyze the coastal Bermuda grass briquette for ash content and heating value, respectively. Within each of these products, constituent values had to be entered to be used in the calibration model creation. These constituents were actual data that
were collected using other analytical devices in the lab. Each product had one set of constituents (i.e. the constituents used for the product titled *Bermuda Ash*, were measured ash content values of the individual Bermuda grass briquettes). Once all of the desired products were created and all constituent values had been input into the software, the next step was to utilize the program in creating calibration models.

For the software to create a calibration equation, some form of regression had to be utilized. For this research it was decided that multi-linear regression would be used to form the desired calibration equations. To accurately predict each physical parameter (ash, moisture, and heating value,) individual equations had to be created for each product. To complete this, the quantitative analysis-regression tool within the software was used. Before this tool could be implemented, a math treatment had to be applied to the sample spectrum to ensure a proper fit of the data. The math treatment chosen was the 2nd derivative. By utilizing the second derivative mathematical treatment, the absorption peaks became more clearly separated for the user. One other important aspect of the calculations is the software’s ability to identify and remove outliers from the validation values used to create the models. This component is very important due to the fact that it ensures outliers and other possibly corrupt data points are not used in complex calibration equations. For the materials which produced 120 briquettes, 100 samples were utilized in the development of the calibration equation. The remaining 20 samples were set aside as an independent validation set. For the gin trash material, 60 samples were used.
with the remaining 15 set aside for validation.

Once the regression process had been completed for each product, the output produced by the software had to be studied to determine which wavelength corresponded to each given constituent. The output graph included a correlation curve, sensitivity curve, and spectra representing the highest entered constituent and lowest constituent values. According to the Vision® 3.50 Tutorials that were provided with the software, the optimal wavelength is one in which there is high correlation and low sensitivity. By selecting an area with low sensitivity the calibration becomes more robust, meaning small changes in absorbance would not result in large relative changes in the reported constituent values. Since the second derivative spectra were used for this analysis, an area of high negative correlation was utilized to provide the optimal wavelength.

After establishing the analysis wavelength, the software calculated the predicted values for each constituent value by using a regression equation. These calculation were determined using ‘new’ wavelengths generated from briquettes that were part of the validation data set and excluded from the development of the calibration equation. These predicted values were exported to Excel to mathematically compare them to the laboratory values calculated from the process listed below. The error term was studied and several statistical values were found including error standard deviation, max error, minimum error, and mean error.
These values were then used to determine how well the NIR system predicted actual physical parameters.

Analytical Methods

In addition to the NIR analysis, several analytical methods were employed to quantify the physical properties of interest, including; moisture content, ash content, and heating value. These analytical methods were carried out using proven procedures on calibrated devices. The analytical methods are generally considered more robust but the time consuming and destructive nature of the test make NIR a more attractive alternative. All of the analytical methods described below were completed after the briquettes were NIR processes and had been ground into a fine powder. Methods and procedures related to the analytical tests are provided below.

Moisture Analysis

Moisture content of the input biomass has been established as a critical factor in briquette development and physical structure as well as the value of the material as a fuel resource. To determine moisture content two parameters need to be known, initial wet biomass mass and final dry biomass mass. It was assumed during these calculations that the aluminum vessels used to hold the samples would remain at a constant mass throughout the process. To obtain moisture values, as well as the ash values and heating content values, the briquettes were separated based on type of biomass used in the fabrication process. For example, moisture content analysis,
ash content analysis, heating content analysis was completed for the briquettes constructed from saw dust before any of the other materials were run. By keeping the materials separate, it helped with organization and also assisted in reducing humidity effects from the surrounding environment.

Aluminum trays were used as the main holding vessels to contain the sample while in the drying oven. The first step was to weigh, on a 0.001 g resolution scale, the empty aluminum trays and then place each tray in a drying oven at 105 °C. The oven used for this analysis was a Fisher Isotemp Oven, Model 6925 (Thermo Fisher Scientific, Inc, Waltham, MA). After one hour of drying, the trays were taken out of the oven and re-weighed to ensure there was no change in weight. This process was repeated until the weight remained constant. The stable dry weight of the tray was recorded as $m_{tray}$. Once the trays were determined to have a static weight, samples were weighed out and placed in the aluminum trays. Initial sample weights ranged from 2.141 g to 8.379 g. The variation in weight was assumed to not be a factor in effecting the measurements since it was given sufficient time to dry down. This weight was recorded as $m_{t+s,i}$. Each sample was placed in the drying oven for a 24 hour time period at 105 °C. To ensure all of the moisture was displaced in the ovens, the samples were removed every six hours and weighed to determine if there was any variation in moisture. The samples were then removed from the oven and allowed to cool down in desiccators before being weighed. Samples awaiting weighing remained in the desiccators to prevent absorption of moisture from the atmosphere.
The final sample weight was recorded once the mass values stabilized (i.e. consistent readings between two weighing periods). This final weight was recorded as \( m_{t+s,f} \).

The following equations describe how moisture content was determined from the measured data.

**Initial Sample Mass Equation**

**Eq. I** \( m_{s,i} = m_{t+s,i} - m_{tray} \)

Where:

\( m_{s,i} \) = initial mass of sample (g)

\( m_{t+s,i} \) = initial mass of sample and tray (g)

\( m_{tray} \) = mass of aluminum tray (g)

**Final Sample Mass Equation**

**Eq. II** \( m_{s,f} = m_{t+s,f} - m_{tray} \)

Where:

\( m_{s,f} \) = final mass of sample (g)

\( m_{t+s,f} \) = final mass of sample and tray (g)

\( m_{tray} \) = mass of aluminum tray (g)
Moisture Content (wet basis) Equation

\[
\text{Eq. III } \text{moisture}_{\%} = \left( \frac{m_{s,i} - m_{s,f}}{m_{s,i}} \right) \times 100
\]

Where:

\( \text{moisture}_{\%} \) = moisture percent mass basis in material

\( m_{s,i} \) = initial sample mass (g)

\( m_{s,f} \) = final sample mass (g)

After calculating the moisture content for each sample, they were then placed back in the oven and held at 105°C until they were used for the ash content and heating content analysis. Keeping the samples in the oven ensured that the ambient moisture in the room would not saturate the ground samples.

Ash Content Analysis

Ash represents the non-combustible components of a fuel that are residues of the combustion process. When burning any kind of fuel, especially biomass fuels, the amount of ash produced during the combustion process is of great concern. Ash can build up in pellet stoves and other types of equipment used to burn these solid biofuels and can adversely affect efficiency and longevity of the equipment. Additionally, ash collection creates a disposal issue that can be costly and time
consuming for the biomass consumer. This investigation followed the ASTM E1755-01 standard to determine the amount of ash present in the four biomass types following the briquetting process. This process involves heating the biomass material at very high temperatures for extended periods of time.

Since moisture content was calculated for the samples previous to this step, it was imperative that the samples remain moisture free as to not interfere with ash content readings. Equipment used for the analysis other than the furnace included two desiccators, 35 porcelain crucibles, and the same 0.001g resolution balance used for weighing samples in the moisture content analysis. The ash content analysis was completed in three to four batch run for each biomass type given the limitations on space in the furnace and the limited number of crucibles. Each batch was processed identically so to not alter the data.

For this project a Fisher Isotemp Muffle Furnace, Model 550-126 (Thermo Fisher Scientific, Inc, Waltham, MA) was utilized. Since the furnace did not have automated temperature ramp capabilities, the standard was modified slightly to accommodate for the available equipment. The first step in the analysis method was to place all of the crucibles in the furnace for 3 h at 575 °C. After being in the oven for the allotted time, the crucibles were removed and cooled to room temperature in the desiccators. Once cooled, the crucible was weighed and then returned to the furnace for another hour at the recommended temperature (575 °C). The crucibles
were then removed from the furnace and placed in the desiccators once again. After allowed to cool, they were reweighed to measure the change in mass. This process was repeated until the mass of the crucible varied by less than 0.3 mg.

The “dried” crucible mass was recorded as the tare mass, $m_{tare}$. Samples already dried out during the moisture content analysis were utilized for this process. Samples were removed from the aluminum pans located in the oven and placed in the “dried” crucibles. Sample masses varied from 0.503 g to 1.484 g. The mass of the crucible combined with the mass of the sample was recorded as $m_{tare+s,i}$. Once each sample was added to each crucible the full crucible was placed in the muffle furnace. According to the standard, the temperature needed to be initially heated to 250 °C at a rate of 10 K/min and held there for 30 min. To accommodate the furnace’s limited heating profile capabilities, the furnace was set to 235 °C for a total time of 40 min. It was assumed that the furnace gained heat at a slow pace as to not cause the material to combust rapidly and blow into surrounding crucibles. Once the initial 40 min was complete, the furnace was set at 575 °C. Depending on the material being analyzed, the amount of time the samples were allowed to be in the furnace varied. This time variation was based on the estimated ash content of the material. The Bermuda grass hay and cotton gin waste were assumed to have significant amounts of ash. Per the published standard, these samples remained in the oven overnight to ensure complete burn of the material and that all of the carbon was eliminated. A ten to twelve hour combustion cycle was required for these high
ash materials. The saw dust and corn stover remained in the furnace for four to five hours as their ash contents were projected to be lower.

Following combustion in the furnace, each sample was removed carefully to avoid any mechanical loss of the test specimen (i.e. ash blowing out of the crucible). The combusted crucibles were stored in a glass desiccator during the cooling phase prior to weighing. Once cooled to a safe handling temperature, each specimen was weighed and the mass recorded. The crucibles were then placed back in the furnace for an additional hour to make certain complete combustion took place. This process was repeated until the mass remained constant after cooling. This final mass of the container and sample mass was recorded as \( m_{\text{tare+s,f}} \). The following equations describe how the ash content was calculated for this analysis.

*Initial Sample Mass Equation*

\[
\text{Eq. IV } \quad m_{s,i} = m_{\text{tare+s,i}} - m_{\text{tare}}
\]

Where:

\( m_{s,i} \) = initial sample mass (g)

\( m_{\text{tare+s,i}} \) = initial crucible mass and sample mass (g)

\( m_{\text{tare}} \) = initial crucible mass (g)
**Final Sample Mass Equation**

\[
\text{Eq. V } m_{s,f} = m_{\text{tare+s,f}} - m_{\text{tare}}
\]

Where:

- \( m_{s,f} \) = final sample mass (g)
- \( m_{\text{tare+s,f}} \) = final crucible mass and sample mass (g)
- \( m_{\text{tare}} \) = initial crucible mass (g)

**Ash Content Equation**

\[
\text{Eq. VI } Ash_{\%} = \left( \frac{m_{s,i} - m_{s,f}}{m_{s,i}} \right) \times 100
\]

Where:

- \( Ash_{\%} \) = percent ash in the material
- \( m_{s,i} \) = initial sample mass (g)
- \( m_{s,f} \) = final sample mass (g)

When each sample had been analyzed for a given material, the crucibles were cleaned out with a soft bristle brush and placed in the desiccators to ensure moisture was not allowed to re-enter any ash material remaining in the crucibles. It was
assumed that any material left in the crucible was pure ash and could not be broken down any further. Before subsequent samples were analyzed, the crucibles were reweighed to obtain an updated tare mass.

**Calorimeter Data**

The energy content of the fuel finished product is one of the most critical parameters when determining the value of a fuel resource for combustion applications. For biofuels to compare favorably with non-renewable fuel sources like coal, natural gas, etc., they must produce comparable heating values on an economic and mass basis. For this project, a Cal2K ECO Isothermal Bomb Calorimeter (Digital Data Systems, Gauteng, South Africa) was used to quantify heating values for each biomass feedstock (Figure 3.11). This calorimeter is a dry jacket, oxygen-bomb system which does not require the use of water when processing a sample. The main components of the system were an aluminum box surrounding a polystyrene insulator and a removable, cylindrical combustion vessel in which the samples were placed. The cylindrical combustion vessel is often referred to as a ‘bomb’. The samples utilized for this procedure were taken from the previous analysis that was completed determining moisture content.
The bomb calorimeter method began by firing a small metal thimble in the furnace for eight hours to ensure any oils used during fabrication of the part were absent during analysis. The thimble is used to hold biomass samples during the actual analysis. The “fired” thimble was then weighed and then the balance was zeroed. Test specimens were then placed in the thimble and their masses were recorded. Sample masses varied from 0.252 g to 0.784 g. This range of sample masses were within manufacturer suggested sample weights for the unit. After the
samples were measured, the thimble containing the material was placed inside the combustion vessel.

A small shaft, which ran through the center of the combustion vessel’s lid, served as the firing electrode. A parallel rod was also affixed to the combustion vessel’s lid and provided a framework to hold the sample containing thimble. A thin metal firing wire was connected between the two shafts described above and cotton thread was tied onto the firing wire. The firing wire allowed for a close circuit between the “hot” electrode and the grounded sample holding rod. A voltage generated by the unit was supplied to the electrode and as the current traveled to the grounded rod, the cotton thread would ignite and cause the biomass material to combust in the presence of a pure oxygen environment. The end of the cotton thread had to be in contact with the sample material in the thimble for complete sample combustion to occur.

Once the combustion vessel was loaded and ready for analysis, pure compressed oxygen was forced into the container until a pressure of 1500 kPa was achieved. By providing an oxygen rich environment, the combustion process was optimized and a complete burn could be achieved. The pressurized vessel was then placed in a cut out region of the polystyrene insulation inside the aluminum control base. Closing the lid on the aluminum control base started the firing process. A set voltage, 22 VDC, was generated by the control base and traveled to the combustion
vessel’s electrode through the control base’s lid. The amount of time to analysis each sample was approximately 30 minutes, which included a ten minute ambient condition check, a ten minute firing procedure and a ten minute cooling period. Additional time to run the samples was necessary if the combustion vessel’s baseline temperature was more than 15% different from ambient conditions. For the vessel to accurately calculate energy content or heating value, it was critical for the combustion vessel’s temperature to be close to room temperature.

The method in which the calorific content was measured was by the temperature rise in the outer aluminum sleeve of the combustion vessel. The combustion vessel is lined with sixteen thermocouples that wirelessly transfer data to the control unit for automated data acquisition and data analysis. The combustion of the material would cause the sleeve to rise in temperature and this temperature difference was used, along with the mass of the material, to calculate the heating content, in BTU/lb. According to the manufacturer, the polystyrene sleeve provided enough insulation to keep surrounding environmental conditions from affecting the sample data.

Density Determination

When putting biomass through a densification process, it is important to minimize the amount of open pore space within the final product. Minimal pore space allows for greater energy production potential in a smaller volume. The denser
the material, the easier it is to store, handle, and transport. Additionally, there were experimental concerns regarding the variability of density in the final briquette product. The surface of the material and its porosity could potentially impact the spectra developed by the NIR device. Insuring consistent densities within the briquettes of a given biomass type was an important step to rule out a source of NIR variability. To determine density characteristics of the briquettes, two key pieces of information were needed; bulk density and absolute density. Both densities were determined for 20 briquettes of each variety. Twenty samples were taken at random from previously NIR scanned briquettes for each of the four biomass types.

Bulk density is defined as the mass of all of the particles present in a given object divided by the total volume occupied by that given mass. This volume includes particle volume, inter-particle void volume, and internal pore volume. For this project, a design protocol was established to ensure all samples were treated equally. The first step in the methodology was to measure the diameter of each briquette using dial calipers. It was found through simple measurements using the calipers, that each briquette was not a perfect circle. When working with variable materials and biological matter in general, these imperfections are expected. To overcome the differences in diameters two measurements were taken, one across the major axis and the other across the minor axis. When these values were determined, they were averaged to give an average diameter measurement. The height of each briquette was measured as the average of three height measurements as well. With
the diameter and height known, the volume of a cylinder formula (Eq. VII) was used to determine the total volume of the briquettes.

**Volume of a Cylindrical Body Equation**

\[
\text{Eq. VII } V = \frac{\pi d^2 h}{4}
\]

Where:

\( V \) = total occupied volume (in\(^3\))

\( d \) = average diameter of the briquette (in)

\( h \) = height of the briquette (in)

Once the volume was determined, the individual briquettes were weighed. This mass was recorded as \( m_b \). With the mass and volume known for a briquette, the bulk density of that material could be determined using the bulk density equation (Eq. VIII) listed below. Before calculating the bulk density, all units were converted to the metric system to match units generated by the pycnometer used to determine the absolute density.
Bulk Density Equation.

\[ \text{Eq. VIII} \quad \rho_b = \frac{m_b}{V} \]

Where:

- \( \rho_b \) = bulk density (g/cm\(^3\))
- \( m_b \) = total mass of briquette (g)
- \( V \) = total occupied volume (cm\(^3\))

An additional bulk density measurement was acquired for the original biomass material prior to its passing through the briquetting press. Approximately, 5 kg of biomass material was randomly collected from the tons of material provided for briquette making. The 5 kg field samples were assessed for moisture content and divided into five 1 kg subsamples. Each subsample had its bulk density assessed using a balance and 1000 mL graduate cylinder. First in this process, the graduated cylinder was weighed and the balance was tared. Next, a funnel placed atop the graduate cylinder was filled with material, then a piece of cardboard between the funnel and graduated cylinder was removed allowing the material to flow through the funnel and into the graduated cylinder. This method minimized material consolidation (i.e. packing) and provided a consistent measure of bulk density. Both the mass of the biomass material was acquired as well as the volume of cylinder filled with material. Using the total biomass mass and total occupied volume values, bulk
density for unprocessed material was determined using Equation VIII.

Absolute density quantification had to take place to gain a thorough understanding of the material. Absolute density refers to the mass of the material divided by the actual volume the material takes up. Pore space is eliminated from the density quantification for the absolute density measurement. For this step, an AccuPyc II 1340 (Micrometrics, Inc, Norcross, GA) was used to calculate the absolute density value. In actuality the pycnometer only measures the volume occupied by a solid; an input mass is then needed to calculate the density. The AccuPyc II 1340 is termed a gas expansion pycnometer and it consists of two separate chambers, one in which the sample is held and a second chamber of known internal volume. The largest sample chamber, 100 cm³, was used in hopes that it would be able to accommodate the biggest briquette.

The samples that were measured for bulk density were placed in catalogued plastic bags to be used in this procedure. Each sample was then placed individually in the chamber intended to contain the sample. This step was completed by carefully slicing the briquette into smaller pieces that could be held completely within the sample chamber. In the cases where the sample would not fit in the chamber, two different runs took place to account for total volume of the particles. In these instances, the sample mass was not entered into the device and the density was calculated within an Excel work sheet. After the briquette was placed in the sample
chamber a gas-tight lid was used to secure the chamber in the pycnometer. Next, the measured sample mass was entered into the device and a complete system purge was performed to vacate all pycnometer chambers of gases. For all samples the pynometer used pure helium as the measurement gas. Helium is both inert and has a small atomic structure allowing it to easily enter and exit pore spaces. These gas qualities are key for safe, efficient absolute density measurements.

After purging the system, the device begins pressurizing the sample chamber. Once pressurized, a valve opens and allows any gas that is being displaced by the present solid material located in the sample to be discharged in the empty second chamber. A transducer measures the pressure in the sample chamber after being pressurized and then measured the overall pressure of the two chambers once the gas was allowed to expand into the reference chamber. The known pressures and known volumes are then used to determine the sample volume (Eq. IX). This process was completed three times for each sample and a standard deviation was calculated.

*Pycnometer Sample Volume Equation*

\[
\text{Eq. IX } \quad V_s = V_c + \frac{V_r}{P_1 - \frac{P_1}{P_2}}
\]

Where:

\( V_s = \text{sample volume (cm}^3) \)
$V_c = \text{volume of empty sample chamber (cm}^3\text{)}$

$V_r = \text{volume of empty reference chamber (cm}^3\text{)}$

$P_1 = \text{pressure of sample chamber only}$

$P_2 = \text{pressure after gas expansion into reference chamber}$

These above calculated data along with bulk density were then used to determine the amount of pore space prevalent in the briquettes. The pore space is measured by a dimensionless value known as porosity. The greater the porosity value, the greater pore volume is present in the material of interest. Since the percentage of pore volume directly correlates to the density of the material, these values can be used to assist in quantifying how well the briquette was constructed. A lower porosity value should directly correspond to denser materials.

*Porosity Equation*

\[
\text{Eq. X } \quad P_t = 1 - \frac{\rho_b}{\rho_s}
\]

Where:

$P_t = \text{porosity (\%)}$

$\rho_b = \text{bulk density (g/cm}^3\text{)}$

$\rho_s = \text{absolute density or density of solids (g/cm}^3\text{)}$
Chapter 4 Results and Discussion

Following the completion of the analytical test, data was analyzed in two distinct sets. First, the analytical data was collected and observed to evaluate the ability of the briquetting press to densify the biomass materials and the potential quality of these four biomass types as solid biofuels. The second results and discussion set is focused on the development of the NIR calibration equations and the robustness of those equations.

Briquetting System Densification Performance

The main objective of the briquette machine is compacting biomass into a more dense package to improve transportation and handling parameters as well as form a better solid fuel product. Table 4-1 summarizes the pre-briquette bulk density and moisture content values and standard deviations. Table 4-2a summarizes the absolute and bulk densities for the briquetted biomass as well as moisture content, ash, and heating value. Table 4-2b provides the corresponding standard deviations for the values in Table 4-2a.
### Table 0-1. Pre-Briquette density and moisture content values and standard deviations.

<table>
<thead>
<tr>
<th>Material Type</th>
<th>Bulk Density (g/cm³)</th>
<th>Moisture (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coastal Bermuda Hay</td>
<td>0.1464 [0.0375]</td>
<td>14.61 [3.63]</td>
</tr>
<tr>
<td>Corn Stover</td>
<td>0.0989 [0.0105]</td>
<td>10.27 [0.34]</td>
</tr>
<tr>
<td>Cotton Gin Trash</td>
<td>0.2578 [0.0973]</td>
<td>38.75 [8.11]</td>
</tr>
<tr>
<td>Sawdust</td>
<td>0.3781 [0.0416]</td>
<td>5.79 [0.88]</td>
</tr>
</tbody>
</table>

### Table 0-1a. Select physical properties values of biomass briquettes.

<table>
<thead>
<tr>
<th>Material Type</th>
<th>Abs. Density (g/cm³)</th>
<th>Bulk Density (g/cm³)</th>
<th>Moisture (%)</th>
<th>Ash (%)</th>
<th>Heating Content (BTU/lbs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coastal Bermuda Hay</td>
<td>1.4360</td>
<td>0.6021</td>
<td>7.28</td>
<td>8.44</td>
<td>7129.45</td>
</tr>
<tr>
<td>Corn Stover</td>
<td>1.4404</td>
<td>0.7972</td>
<td>8.86</td>
<td>4.22</td>
<td>7184.13</td>
</tr>
<tr>
<td>Cotton Gin Trash</td>
<td>1.5743</td>
<td>0.6282</td>
<td>9.65</td>
<td>22.87</td>
<td>6154.45</td>
</tr>
<tr>
<td>Saw Dust</td>
<td>1.4347</td>
<td>0.6261</td>
<td>5.57</td>
<td>1.14</td>
<td>8386.86</td>
</tr>
</tbody>
</table>
Table 0-1b. Select physical properties standard deviations of biomass briquettes (corresponds to values in Table 2a).

<table>
<thead>
<tr>
<th>Material Type</th>
<th>Abs. Density (g/cm³)</th>
<th>Bulk Density (g/cm³)</th>
<th>Moisture (%)</th>
<th>Ash (%)</th>
<th>Heating Content (BTU/lbs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coastal Bermuda Hay</td>
<td>0.014</td>
<td>0.088</td>
<td>0.41</td>
<td>0.91</td>
<td>90.74</td>
</tr>
<tr>
<td>Corn Stover</td>
<td>0.042</td>
<td>0.131</td>
<td>0.22</td>
<td>1.44</td>
<td>86.87</td>
</tr>
<tr>
<td>Cotton Gin Trash</td>
<td>0.047</td>
<td>0.089</td>
<td>0.78</td>
<td>3.30</td>
<td>350.77</td>
</tr>
<tr>
<td>Saw Dust</td>
<td>0.019</td>
<td>0.0751</td>
<td>0.09</td>
<td>0.34</td>
<td>120.74</td>
</tr>
</tbody>
</table>

The tables show a couple of interesting characteristics of the biomass that should be noted. First in the pre-briquette biomass assessment, the cotton gin trash contained a very high level of moisture, average 38.78% moisture content. This moisture content is well outside the 6-15% moisture content recommended by the briquette manufacturer for making briquettes. The gin trash was also the most variable biomass in terms of moisture content and bulk density. These features were attributed to the components of gin trash which include soil, cotton fiber, cotton seed, cotton boll, and cotton leaf/stalk segments. Clearly a sample containing mostly cotton fiber would have considerably different properties than a solid sample of cotton seed or cotton boll.
The variability in the Coastal Bermuda hay’s moisture content is attributed to the outdoor storage of the round bales. Because an entire bale was processed, moisture from the weathered outer section of the bale was mixed with the drier middle creating variability. Another anomaly in the bulk density data is the higher than expected value for sawdust. It was expected that the sawdust would be similar to the coastal Bermuda hay; however, on further inspection of the material additional non-wood materials were found in the sawdust material. Since the source of the sawdust was a laminate floor manufacturer binding agents, polymers, and plastics used to make the flooring were found in the biomass. These dense compounds are the most likely cause of the higher than expected bulk density values.

Within the briquette data tables, the two trends that stand out the most is the recurring variability within the cotton gin trash data and a consolidation of select mean values. The cotton gin briquettes are subject to variable mixing of cotton plant fractions which impact the overall composition of the final product. One briquette could be 50% fiber and the next one could be less than 10% fiber. The variability of the input material affects the physical characteristics of the output materials.

The reason the briquettes of different biomass types begin having consistent physical property values can be explained by the performance of the briquette press. The heat generated in the briquette press die is sufficient to turn water in the biomass to steam. The steam is important as it softens lignin in the plant and
provides an important binding agent for the briquette making process. It appears the heating effect mostly impacts available water in the biomass tissue and moves all biomass types to similar equilibrium moisture content conditions. Additionally, the briquette press applies a fixed force to the die when compacting biomass and this allows similar amounts of compaction to occur in the die as long as particle sizes are roughly the same. Because of this constant compaction effort in a fixed volume die, it would appear density values also achieve similar values. It should be noted that ash and energy content were not evaluated in both pre-briquette and briquette form. There is no evidence in the literature or any other reasoning that would suggest these values would change from densification.

One final point that can be established from Tables 4-2a and 4-2b is the lack of variability in the final, briquette bulk density values. Consistent bulk density is thought to be a critical characteristic that would support the use of NIR to rapidly assess the physical properties of the briquettes. NIR is a light absorbance/reflectance technology and significant variations in material density could impact the infrared light’s ability to penetrate a material’s surface. The coefficient of variation across all biomass types is in the range of 13-17% indicating the briquette press does a good job consistently compacting loose biomass.

The data in Tables 4-1 and 4-2 provide values that can be used to make direct comparisons between pre-briquette and briquetted biomass densities for all four
materials. Comparing the bulk densities of the unprocessed material and briquetted material can provide insight into the performance of the briquette machine. Figure 4-1 shows the comparison between these bulk densities. Compacting the biomass into briquette form increased the bulk density 311%, 706%, 143%, and 65% for the coastal Bermuda hay, corn stover, cotton gin trash, and sawdust, respectively. All four biomass types saw significant increases in their bulk density; however, the magnitude of this increase was varied.

The sawdust is the most obvious underperforming material as it failed to double its bulk density, posting a modest 65% increase. The role of the polymers, plastics, and commercial adhesives used in laminate floor manufacturing on the densification process is unknown. One thought is these materials remain fairly rigid with well-formed until temperatures well above those achieved by the briquette press. While the material's composition played a role in the modest density improvement, the low moisture content of the material is a more likely culprit.
The sawdust was the driest material entering the briquette press and as a result formed the driest briquette. The briquetting process created a very slight 3.8% decrease in sawdust moisture content. Clearly, there was very little available moisture in the sawdust and this lack of moisture harmed the densification process (Figure 4.1). Water in the biomass performs two critical functions. First and foremost, the heat of the die converts the water to steam. The exiting steam is removing moisture from the material and providing a mechanism to improve briquette binding. The steam helps soften the biomass lignin and improve adhesion.
The other critical function of water is providing lubrication between biomass particles under compression. When water is not present, excessive friction between biomass particles will occur and this will cause the particles to resist movement into a more dense form.

The sawdust briquette density and quality suffered from a lack of moisture. The briquettes were the most brittle and were subject to flaking. The briquette machine was able to form a full-size ‘complete’ briquette from the sawdust, but the long term stability of that briquette was questionable. Increasing the moisture content of the sawdust material to 8 – 10% would address the lack of moisture concerns.

While moisture contents below 7% are a concern, minimizing moisture is important to a feedstock procurement manager. Minimal moisture biomass allows the briquette to serve its intended function, densifying biomass. When materials are too wet, the case with the cotton gin trash, excessive amounts of heat in the press die are consumed evaporating water and drying the biomass. This prevents the formation of steam that encourages adhesion of the biomass particles. Another property of water detrimental to briquette formation is its incompressible nature. Because water cannot be compressed, it will fill pore space and essentially make them incompressible. Even if the water evaporates over time, those pore spaces in the briquettes will remain. The only way to fill the pore space with additional solid
mass is to insure water cannot fill the void space first. Keeping the biomass under 16% seems to provide enough moisture for briquetting without impacting the ability to deconstruct pore space. This 16% moisture content threshold is based on the success in briquetting coastal Bermuda hay with similar moisture content values.

Building on the bulk density discussion, porosity can be used to reinforce many of similar themes while advancing the conversation to include particle size and homogeneity. As mention in the methods and materials section, porosity evaluates the ratio of solid particle fraction in the overall bulk volume. Higher porosity values indicate a higher percentage of void space in a given briquette type. The porosity values are represented graphically in Figure 4.2.

![Briquette Porosity Chart]

**Figure Table 0-1b.** Select physical properties standard deviations of biomass briquettes (corresponds to values in Table 2a). Comparison of briquette porosities for four biomass types.
From Figure 4.2 a very noticeable element is the corn stover material has the lowest porosity value. This porosity value indicates corn stover briquettes have the least pore space remaining in the final briquette. The corn stover also had the highest briquette density so this result is in line with density discussions developed earlier. Recalling that this corn stover product is actually a seed corn processing co-product and not a collected field residue may provide some insight regarding this materials superior packing ability. Visual inspection of the raw materials showed the corn stover product to be the most refined and uniform in terms of particle size. This uniformity encouraged compaction and did not allow opportunities for pore spaces to develop when irregular shaped materials came into contact with each other.

Gin trash on the other had was the most heterogeneous material and attempting to compact bolls, stalks, fiber, and soil into a single product allowed significant pore space to develop. Approximately 60% of the gin trash briquette remained pore space following briquetting. In addition to the heterogenous mixture of plant parts, the gin trash contained cotton fiber that did not compress very well and provided a framework for the creation of large pore spaces in the briquette.

Similarly, the sawdust was a mixture of various laminate floor manufacturing compounds and the coastal Bermuda hay was initially in round bale form before passing through a hammer mill operating with a 1.5 cm screen. Both the initial composition in the case of the sawdust and the unrefined processing in the cause of
the Bermuda hay created a mixture of particles sizes in the material stream entering the briquetting press. These results would indicate briquette system managers should put a premium on procuring materials that have uniform composition and particle size. Additional chopping, milling, or grinding should be carried out to make the biomass stream entering the briquette press as homogenous as possible.

Briquette Physical Properties

While the majority of the briquette discussion has been centered on the ability of the briquetting machine to increase the density of the four biomass types, there were other characteristics of the briquettes quantified. Moisture content discussion has already been covered since the moisture content plays a critical role in determining the density of the final briquette product. The two properties that have not been discussed are ash content and energy content. Both of the properties are assumed to remain constant when comparing briquetted material to its original, uncompressed state. However, both properties would be of interest to a consumers and have the potential to be used in economic valuation of the materials.

The ash content values (Table 4-2a) were fairly consistent with the expended trends as the woodiest material contained the lowest ash content value with an average value of 1.14% ash. The herbaceous biomass types had the highest overall ash content values with 4.22%, 8.44%, and 22.87% for the corn stover, coastal Bermuda hay, and cotton gin trash, respectively. The variability within the ash
content for a given biomass also increased with the biomass types. Two potential reasons for these results are evident. Soil contamination of the plant matter will increase ash content values and cotton gin trash is most susceptible to this effect.

The ash content value for the corn stover is similar to ash content values for relatively clean, pure biomass samples (Ververis et al., 2004). Ververis (2004) reports most herbaceous biomass types will produce ash contents between 1% and 5%. The corn stover is a processing residue consisting primarily of husk, cob, and corn leaf components found sufficiently high on the corn plant that soil and debris build-up are minimal. The coastal Bermuda grass and cotton gin trash were both collected with high throughput field operations. Along with plant material, these field operations collect soil that has either accumulated on the plant tissue or been directly disturbed and picked up by the equipment. The ash content analysis method simply tests for non-combustible inorganic matter, which are mostly minerals. For grasses like coastal Bermuda, the amount of silicon minerals in the plant tissue will play a big role in ash content calculations. Even though it is generally assumed the minerals are only found in the plant tissue; one must consider the addition of soil that is on the plant tissue surface will increase these values.

Cotton gin trash is particularly susceptible to the soil contamination phenomenon. The high ash content for the cotton gin trash led to further literature review to determine the ash content of individual components. The literature
suggest cotton fiber has an ash content ranging from 1.0 to 1.5% (Shahbaz, 2001) and cotton stalks have ash content values between 3 and 4% (Verferis, 2004). The only plausible reason for the gin trash repeatedly producing ash content values in the low 20% range is the contamination by external mineral sources. Gin trash is a very low value material with handling and storage operations completed at minimal expense to the gin operator. Combine the poor logistics system with the “dirty” nature of cotton harvest operations and there are ample sources for soil contamination.

The true impact of ash content and moisture content can be observed by careful study of the energy content values (Table 4-2a). An additional figure has been prepared illustrating the energy content of several biomass materials evaluated with the NCSU BAE bomb calorimeter owned by Dr. Matthew Veal’s research program (Figure 4-3). The figure also provides a comparison between these biomass fuels and propane, charcoal, and green wood chips. The later three fuel resources are prevalent heating fuels in North Carolina today.
The average energy contents for the four biomass types studied in this project were 7129.45 Btu/lb, 7184.13 Btu/lb, 6154.45 Btu/lb, and 8386.86 Btu/lb for the coastal Bermuda grass, corn stover, cotton gin trash, and sawdust respectively. Based on observation of Figure 4.3 all of these materials have energy values in line with other biomass types sourced in North Carolina. The impact of moisture and ash content on energy value is also apparent. The sawdust had the highest energy content, but the lowest ash and moisture values. The chemical structure of wood in addition to the advantageous physical properties allowed the sawdust to be the most
energy dense material.

Water in the biomass will rob energy from the material during a combustion process. Energy will be absorbed converting the water to steam, thereby lowering the useful energy content. The wetter the material the more energy consumed drying the material. Ash or mineral content is simply a non-combustible filler in the biomass briquette. A cotton gin briquette is estimated to be 22% ash which indicated nearly a quarter of the briquette contains material that does not contribute to the generation of energy. The high moisture content of the cotton gin briquette (stemming from the high moisture content of the raw, uncompressed material) also plays a role in discounting the material's energy content. As the wettest, highest ash content material, the cotton gin trash produced the lowest energy content value.

Acquiring clean, dry material regardless of the form (loose, pellets, briquettes, etc) is critical when procuring biomass for solid fuel uses. Contamination from soil particles add mass to the biomass being received by a consumer but this material adds no value. Additional excessive mineral deposits present disposal issues and equipment maintenance concerns for the consumer. As a result it is unlikely ‘dirty’ materials such as gin trash will find significant value on the solid biofuel market. The exception to this statement would be the generator of the ‘dirty’ biomass source. Cotton gins are under increasing economic and environmental pressure to find disposal methods for their gin trash. Combusting the material on site to provide
heat, steam, or electricity for their facilities could be a worthwhile venture despite the poor combustion characteristics. Densifying the biomass would then serve two purposes: 1) minimizing the biomass storage footprint and 2) providing a more uniform fuel product.

NIR Calibration Construction and Validation

Initial NIR Analysis

The four biomass types were scanned with a Foss XDS Rapid Content analyzer. The spectra developed from this activity and the second derivative of these associated spectra are shown in Figures 4.4 – 4.11. The second derivative of the spectra was the primary math treatment used to help minimize differences in baseline slope and improves offset between samples.

Second differentiation of NIR spectra is perhaps most common math treatment applied to spectra. The effect of this treatment is the generation of sharp negative peaks that are helpful in identifying wavelengths that may correspond with physical properties. For all four materials, the sharpest negative spike in the second derivative data is observed in the immediate vicinity of 1920 nm. The 1920 nm wavelength corresponds with vibration of O-H bonds (i.e. water). Wavelengths in the immediate area of 1920nm have long been documented as a region to assess moisture content. Figure 4.12 illustrates the ~1920 nm wavelength peak for sawdust and it is evident how the differentiation of these peak values could provide insight
into moisture content differences or a different physical property.

While the second derivative conversion provided some insight into potential wavelengths that could be used to assess physical properties, the actual development of calibration equations required further analysis. Before the calibration equation development initiation, the data was again assessed to identify outliers and redundant wavelengths. Foss Vision® software was used for this purpose. After trial and error, Vision® was configured to examine both wavelength and the physical constituent data (i.e. analytical test results) to find errant datasets.

Figure Table 0-1b. Select physical properties standard deviations of biomass briquettes (corresponds to values in Table 2a)..4 Coastal Bermuda hay NIR spectra from Foss XDS rapid content analyzer.
Figure 0-1b. Select physical properties standard deviations of biomass briquettes (corresponds to values in Table 2a).

5 Second derivative of coastal Bermuda hay NIR spectra.

Figure 0-1b. Select physical properties standard deviations of biomass briquettes (corresponds to values in Table 2a).

6 Corn stover NIR spectra from Foss XDS rapid content analyzer.
Figure Table 0-1b. Select physical properties standard deviations of biomass briquettes (corresponds to values in Table 2a).

7 Second derivative of corn stover NIR spectra.

Figure Table 0-1b. Select physical properties standard deviations of biomass briquettes (corresponds to values in Table 2a).

8 Cotton gin trash NIR spectra from Foss XDS rapid content analyzer.
Figure Table 0-1b. Select physical properties standard deviations of biomass briquettes (corresponds to values in Table 2a).

9 Second derivative of cotton gin trash NIR spectra.

Figure Table 0-1b. Select physical properties standard deviations of biomass briquettes (corresponds to values in Table 2a).

10 Sawdust NIR spectra from Foss XDS rapid content analyzer.
Figure Table 0-1b. Select physical properties standard deviations of biomass briquettes (corresponds to values in Table 2a). Second derivative of sawdust NIR spectra.
For all four data sets, the number of outliers and redundant data points was relatively small. The sawdust had 4% of the data eliminated from calibration equation development with concerns regarding spectral development being the primary criteria for elimination. This is not surprising given the heterogeneous nature of the sawdust and the complex compounds (polymers and adhesives) contained in the material. These complex chemical compounds can generate very strong NIR response and the heterogeneous nature of the sawdust exposed the NIR to variable ‘doses’ of the compounds. Viewing the spectra for the sawdust in Figure 4.10 shows some fairly obvious candidate spectrum for elimination based on outlier concerns. For the other biomass types, 2-3% of the data was removed from
calibration equation development consideration. Spectral outliers were the primary culprit again, although occasionally an errant constituent data provided the justification for removal. Constituent data concerns were usually the result of correctable data entry errors.

Once the datasets were refined to remove errant constituent data and suspected outliers in the spectra, the development of the calibration equations through regression analysis began. Development of the calibration equations is not overly precise and can be very subjective depending on the user. The Vision® software provides analysis of the spectra and identifies potential wavelengths that may correspond with variations in a physical property. However, it is up to the user to make specific selection of the wavelengths to be considered in the calibration equation and the selection criteria are entirely left to the user.

Finally, Figure 4.13 illustrates the selection of the wavelengths to include in a calibration equation. Both correlation and sensitivity values are plotted and used as selection criteria. Generally, wavelengths that express high absolute correlation (brown line) and very low sensitivity (orange line) are ideal for inclusion. The sensitivity value is important because a robust correlation equation should not generate large changes in the predicted constituent value when there are slight variations with the absorbance values. Wavelengths with very sharp peaks in the correlation data should also be avoided.
Wavelengths of interest were manually selected and Vision would generate regressions statistics ($R^2$, F-ratio, and residual plots) to assist in the evaluation of a wavelengths value in predicting the physical property of interest. Initially, wavelengths were selected, judged individually, and ranked based on their apparent contribution to the development of a robust calibration equation. The ranked wavelengths were then combined one at a time, adding new terms to the linear regression equation. As terms were added the regression statistics were monitored. Primarily, a increasing $R^2$ value along with a decreasing F-ratio were used to justify the addition of a term. If $R^2$ remained static or the F-ratio suddenly increased, then the model equation reverted back to a reduced number of terms.

A total of twelve unique regression equations were developed for this project. For each of the four biomass briquette types; ash, energy, and moisture content regression equations were develop. The specific coefficients, wavelengths, residual
plots, and sensitivity/correlation plots for all twelve equations are in Appendix A.

Moisture Content Calibration

The most surprising result of this entire project was the inability to develop a robust, significant prediction equation for briquette moisture content. Moisture content quantification with NIR has long been established and many commercially-available technologies that rely exclusively on NIR to determine moisture content in biomass. The results of this project indicated that for three term regression equations coastal Bermuda hay had an $R^2=0.568$, cotton gin trash $R^2=0.239$, corn stover $R^2=0.443$, and sawdust $R^2=0.384$. A three term model produced best results for all four biomass types. While the correlations were weak, all models made use of wavelengths in the immediate proximity to 1450 nm and 1920 nm which have been traditionally used by NIR instruments for the detection of water.

Perhaps this result is not very surprising after looking through the analytical data once again. First, the moisture content values are at the very low end of the range where NIR can be applied. The highest moisture content of the 439 samples analyzed for moisture was 11%. The average moisture content for all samples combined was 7.67% with a standard deviation of 1.62%. In addition to relatively dry samples, the moisture contents were remarkably consistent in their moisture content value. This lack of variability hindered the development of a calibration equation. Ideally, a range of moisture contents from 10% to 50% would be used in
the development of a moisture calibration curve. Due to lack of material options and
time constraints, these ideal moistures could not be utilized.

To address the lack of moisture variability, the only plausible solution would
be to grind the briquettes to a powder and rehydrate the material to varying moisture
contents. While this effort would be effective in developing a moisture content
calibration curve for the four biomass types, the modification in material density
may affect the applicability of the calibration curve to briquettes. Additionally, the
robustness of the calibration equation at low, single digit moisture contents would
remain a concern.

On further inspection, the failure to develop a strong moisture content
prediction equation for the various briquettes may not be a problem. As stated
earlier, the briquette system will dehydrate the material as part of the production
process. It appears the briquette machine is very consistent in driving moisture out
of the biomass to a consistent level regardless of biomass type. From a consumer
standpoint, if a well-form, solid briquette is being delivered, it could be assumed the
biomass is at a moisture content of less than 10.5%. Only one briquette of the 438
briquettes sampled had a moisture content over this threshold. In all likelihood, a
briquette with a high moisture content would be ill formed and have inconsistent
dimensions, so a visual inspection may be sufficient to guard against excessive
moisture in the fuel product.
Ash Content Calibration

The development of a NIR calibration curve for ash content is very difficult and complex. While moisture content can be purely determined from the absorption characteristics of the O-H bonds at well-known wavelengths, ash is more variable in terms of constituents and amounts of the varying constituents. Ash is comprised of various elements, minerals, and compounds that are incombustible. Key components of ash can include Al, Ca, K, Mg, Na, P, and Si. However, the amount of the various components will vary both between and within biomass types based on climatic conditions, soil fertility, rainfall, and nutrient use efficiency.

Because of the variability of ash, the development of the calibration/prediction equation relies heavily on indirect measure of the constituents to assess ash. Literature (Lestander and Rhen, 2005) suggests that much of the inference regarding ash content occurs in the carbon chains, C-H, C=C, and C=CH₂. This provides additional framework to identify and rank the potential wavelengths to predict ash content.

Due to the multiple constituents contained in the ash, regression equations with four to seven terms were used to establish calibration equations. For coastal Bermuda hay, a seven term equation was developed with an $R^2=0.68$. The development of an ash content calibration equation for the corn stover lead to a four term linear regression equation with an $R^2=0.81$. Cotton gin trash had a five term
regression equation with an $R^2=0.388$. Finally, the sawdust ash calibration consisted of a seven term regression equation with an $R^2=0.5147$.

Both calibration equations for the coastal Bermuda hay and corn stover were better than expected. These two biomass types were the most homogeneous and had been processed to fairly consistent particle size prior to briquetting. Because the NIR device was scanning briquettes comprised of the same material repeatedly, a somewhat robust prediction equation was developed. Both the cotton gin trash and sawdust had greater heterogeneity in terms of particle size and constituents.

The gin trash suffered from a combination of varying particles sizes of different plant components. The NIR device may view a stalk or boll segment of 4% ash on one scan and a large lint fiber patch on the next scan with an ash content of 1%. Meanwhile the entire briquette was processed for ash content analysis which may have led to an analytical result of 3.5% ash content. Grinding the gin trash ahead of briquetting to equalize the particle size for all components might have improved the prediction equation development. However, that is a costly and unjustifiable process if the sole purpose is allowing NIR analysis of the final product.

The sawdust also showed poor results when developing a prediction equation for ash content. There were two issues with the sawdust, first like moisture content the ash value was very low and fairly consistent. The other issue is the addition of foreign laminate flooring materials such as plastics, polymers, and adhesives. The
foreign compounds have strong chemical signatures when NIR is used. Because these materials were randomly dispersed throughout briquettes a consistent scan of similar constituents was not achieved. One scan might contain 90% sawdust, 10% foreign matter and the next scan might have 50% sawdust, 50% foreign matter. Like the gin trash exercise, the ash content of each of the constituent varies affect the readings.

Ash content prediction follows a similar them that has been seen throughout this project. Maintaining regular particle size and a homogeneous briquetting material is critical for formation of briquettes and the analysis of the briquette with NIR. Grinding, milling, and mixing operations to make particle size more consistent cannot be justified for the sake of improving NIR measurements. However, these operations would most likely improve briquette quality and density so they should be considered from that standpoint.

*Energy Content Calibration*

For the consumer, energy content may have the greatest meaning and implications in developing price schedules for biomass fuels. Having an energy dense material would improve storage, delivery, and combustion parameters. Lestander and Rhen (2005) again provide guidance on potential covalent bonds that contribute to the gross caloric value of biomass spruce. C=C, C-H, C=O, and O-H which have peaks at the 2190 nm, 1738 nm, 2270 nm, and 1936 nm were the primary
bonds that can be used to predict the energy content of the biomass. As with ash content, these values were used as guidelines to initiate the selection and ranking of wavelength.

Multiple C, H, and O bonds were studied in the development of the energy content calibration equation. Typically, the best fit equation had fewer terms than the ash content equation. All equations had between three and 5 terms in the calibration/prediction equation. For coastal Bermuda hay, a five term equation was developed with an $R^2=0.50$. The development of an energy content calibration equation for the corn stover lead to a three term linear regression equation with an $R^2=0.52$. Cotton gin trash had a five term regression equation with an $R^2=0.567$. Finally, saw dust ash calibration consisted of a five term regression equation with an $R^2=0.5144$.

Overall the results of the energy content calibration were encouraging, although robust, strong correlations were not found. The correlations were found using a surprisingly small number of terms. While the correlation values were marginal, studying the residuals provided some hope NIR scanning to assess energy content is a viable methodology. For all biomass types, the maximum absolute error was in the range of 350 Btu/lb ± 50 Btu/lb. This error value was sufficient to drive down the goodness of fit statistics, but even these maximum residual values are only a 3.5% to 6% departure from the analytically acquire energy content value.
Based on the residual values it is evident there is room for refinement to improve the prediction, but the NIR methods maybe used for screening purposes. It appears that energy content can be predicted with enough certainty to determine a “good” briquette from a “bad” briquette if the difference between those two arbitrary categories was greater than 500 Btu/lb. It is unlikely a payment strategy for solid biomass fuels would be based on the exact energy content. A more likely scenario would be similar to grain trading which discounts grain once it passes certain thresholds for damage, foreign matter, or moisture content.

A final point to consider is all of the calibration equations could be improved if more advanced statistical methods were used. Partial least squares and non-linear regression analysis are other statistical methodologies used to develop NIR calibration equations. However, both of these methods require significant statistical knowledge, experience analyzing NIR spectra, and understanding of the underlying chemistry behind NIR methodology. For this project, it was decided multi-variable linear regression would be used exclusively given the time, financial, and scope of the degree program.

**Chapter 5 Conclusions**

This research focused on implementing a prototype fuel briquette production system and utilizing this system to gain insight into the possible use of an in-line NIR component to provide real time feedback. Multiple research goals were
identified and outlined in previous sections. These objectives were incorporated into the design objectives. These objectives included: implementing a commercial grade briquette press, collecting briquettes formed by the press that were created from four different biomass materials, analyzing these briquettes in a laboratory setting to determine several physical constituents, and then taking these actual constituents and comparing them to predicted values computed by the NIR software. The briquette system was constructed on the Umstead Research Farm in Butner, NC. The system was then utilized to create fuel briquettes during the Fall 2010 and Spring 2011. The system consisted of two material conveying components, a metering silo, and the briquette press.

**Briquette Production**

The creation of fuel briquettes using the briquette press was the most strenuous portion of this research. Much time was required to get the briquette press operational due to extensive electrical wiring and component location requirements. After the initial site work was completed the briquette making process had to be fine tuned as this machine is a prototype and the only one operating in the United States. The metering rate into the compression chamber and material quality (particle size, moisture content, soil contamination) were the main factors affecting briquette production. If the material was forced into the compression chamber too quickly the machine would bind up and no briquettes were created. If the material was forced in too slowly, the briquette produced would be
loose and flakey, rendering it valueless.

Of the four materials used, it was found that corn stover and bermuda hay worked the best for this system. These materials were the most homogeneous. No bridging occurred in any of the hoppers and little problems were encountered involving clogging of the die. The reason these materials performed favorably could have been due to moderate moisture contents and material structure. The coastal Bermuda hay and corn stover varied greatly in material structure but the coastal Bermuda hay contained a substantial lignin. Once this lignin started breaking down due to the heat in the die it begin acting like a binding agent resulting in a strong, tightly bound briquette. Sawdust possessed adequate lignin amounts but had excessively low moisture content resulting in loose and weak bounded briquettes. The lack of moisture prevented steam generation and the lignin could not ‘melt’.

The cotton gin trash was the poorest performing material. This poor performance can be explained by its high moisture content and variable composition. Initially, the flow of the cotton gin waste material into the compression chamber caused the die to become clogged. Each time this occurred, the die had to be cleaned and the system had to be restarted. The time required to clean the die allowed further cooling of the die causing production rates to decrease greatly. Another significant issue involving the cotton gin waste was the amount of bridging that took place in the orifices of every hopper or holding tank. This bridging
problem was attributed to the concentration of cotton fiber present in the material. The presence of fiber, hull, stalks, and soil provide opportunities for pore space to develop in the briquette lowering the densification efficiency. Overall, successful briquetting depends heavily on uniform particle size, moisture contents between 7 and 15%, and homogenous materials.

NIR Calibration Equations

The Foss XDS Rapid Content was employed to scan briquettes from the four biomass types in an attempt to provide a rapid, non-destructive evaluation of ash, energy, and moisture content. The spectra generated by the Foss device demonstrated peak and characteristics that have been historically found in NIR application with biomass. However, the effectiveness of NIR to characterize fuel briquettes is marginal as a result of variable particle size and variations in constituents forming the briquette.

The attempt to develop a prediction equation for moisture content yielded no useful equation. The briquette machine did an excellent job producing consistent moisture contents in the final briquette production regardless of biomass type. The lack of variation in the moisture profile as well as the very low moisture contents observed in the fuel briquettes are conditions not conducive to the development of calibration equations. Hydrating the briquettes artificially to create a moisture profile would probably not help the situation. The moisture contents are so low, they
are at the very edge of NIR’s capabilities to detect moisture. Ultimately it was decided if a solid briquette is formed; the moisture content would probably not be a concern for the consumer.

Ash and energy content calibration equations were developed using indirect sensing of components thought to contribute to each attribute. Because ash and energy are determined by the elemental bonding structure and elemental/mineral make-up of the briquette it was necessary to look at multiple wavelengths that were associated with each of the suspected contributors. For briquetted materials that were consistent in particle size and constituents the results were promising with regards to ash content. The maximum ash content calibration $R^2=0.81$ for coastal Bermuda grass. The energy content calibration equations were similar for all four biomass types in terms of their goodness of fit statistics. Energy content prediction by NIR is sufficient to allow gross assessment of the briquette but probably not strong enough to allow definitive statements about an individual briquette’s energy content.
Bibliography


Mani, S. 2007. Life Cycle Analysis of biomass pelleting technology. AIChE Annual Conference, Salt Lake City, UT, USA.


APPENDIX
Figure A1. Calibration equation development for coastal Bermuda grass ash content.
Figure A2. Calibration equation development for coastal Bermuda grass energy content.
Figure A3. Calibration equation development for coastal Bermuda grass moisture content.
Figure A4. Calibration equation development for corn stover ash content.
Figure A5. Calibration equation development for corn stover energy content.
Figure A6. Calibration equation development for corn stover moisture content.
Figure A7. Calibration equation development for cotton gin trash ash content.
Figure A8. Calibration equation development for cotton gin trash energy content.
Figure A9. Calibration equation development for cotton gin trash moisture content.
Figure A10. Calibration equation development for sawdust ash content.
Figure A11. Calibration equation development for sawdust energy content.
Figure A12. Calibration equation development for sawdust moisture content.