2015

OPTIMAL USES OF BIOMASS RESOURCES IN DISTRIBUTED APPLICATIONS

Joshua J. Jackson
University of Kentucky, joshjjackson85@gmail.com

Joshua J. Jackson, Student

Dr. Michael Montross, Major Professor

Dr. Donald G. Colliver, Director of Graduate Studies

OPTIMAL USES OF BIOMASS RESOURCES IN DISTRIBUTED APPLICATIONS

DISSERTATION

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the College of Engineering at the University of Kentucky

By

Joshua J. Jackson

Lexington, Kentucky

Director: Dr. Michael Montross, Professor of Biosystems & Agricultural Engineering

Lexington, Kentucky

2015

ABSTRACT OF DISSERTATION

OPTIMAL USES OF BIOMASS RESOURCES IN DISTRIBUTED APPLICATIONS

Biomass production is spatially distributed resulting in high transportation costs when moving dedicated biomass crops and crop residues. A multifaceted approach was taken to address this issue as the low bulk and energy density of biomass limits transportation efficiency. Two systems were analyzed for the conversion of biomass into a denser feedstock applicable to on-farm use. Pelletization was able to densify the material into a solid fuel. Using a pilot scale flat ring pellet mill, the density of the material was able to be increased to at least 4.4 times that of uncompressed material. Pellet durability was found to be strongly related to the moisture content of the material entering the mill. Unlike with ring roller pellet mills, a higher durability was typically seen forbiomass materials with a preconditioned moisture content of 20% (w.b.).

From a liquid fuel standpoint, the conversion of lignocellulosic material into biobutanol on-farm was the second method investigated. For the pretreatment of biomass, alkaline hydrogen peroxide spray was demonstrated to be an effective enhancer of saccharification. The viability of on-farm biobutanol preprocessing bunker facilities within Kentucky was analyzed using Geographic Information systems (GIS) to specifically address transportation related factors. The spatial variability of corn field production, size, and location were resolved by utilizing ModelBuilder to combine the various forms of data and their attributes. Centralized and Distributed preprocessing with Centralized refining (DC) transportation systems were compared. Centralized was defined as transport of corn stover directly from the field to a refinery. Distributed-Centralized was specified as going from the field to the biobutanol bunker with corn stover and from the bunker to the refinery with a dewatered crude biobutanol solution. For the DC design, the location of the field and refinery were fixed with the biobutanol bunker location being variable and dependent upon differing maximum transportation (8-80 km) cutoffs for biomass transport from the field to biobutanol bunkers. The DC designs demonstrated a lower (38 - 59%) total transportation cost with a reduced fuel use and CO_2 emissions compared to the centralized system.

KEYWORDS: biomass transport, pelletization, alkaline hydrogen peroxide spray pretreatment, GIS location-allocation, distributed biomass collection

Joshua J. Jackson

July 13, 2015

OPTIMAL USES OF BIOMASS RESOURCES IN DISTRIBUTED APPLICATIONS

By

Joshua J. Jackson

Dr. Michael D. Montross

Director of Thesis

Dr. Donald G. Colliver

Director of Graduate Studies

July 13, 2015

To my wife Rebecca, and parents James and Elda, I could not have done it without you. Thanks for all the love and support along the way.

ACKNOWLEDGMENTS

I would like to extend my gratitude to the numerous people who helped me along the way to this milestone. First and foremost, I would like to thank my advisor, Dr. Mike Montross, for his support, advice, and mentorship over the course of this project. Without his encouragement there is no telling how long it would have taken me to finish.

To my committee members, thanks for the insight and comments.

To my fellow graduate students, thanks for the friendship and welcome distractions that made my graduate school experience memorable. Specifically, thanks to Aaron Turner, Nicole Koeninger, and Will Adams for their support in conducting this research.

To Zac Hammond, Nathan Bush, Thomas Loxley, Matt Fogle, and all of the other undergrads, thanks for your time and effort preparing samples, pelleting, and all of the other tedious tasks that went into this research.

Finally, I would like to thank my family for their love support and encouragement. To Justin and Joey, I appreciate the effort you all put into the farming operations when I was unable to help due to my research activities. To Mom and Dad, thank you for instilling in me the desire to learn and understand the world around me from a young age.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF EQUATIONS

CHAPTER 1: INTRODUCTION

The utilization of biomass for energy is becoming increasingly important since biomass can be used for electricity, heat, and biofuels (primarily liquid transportation fuels). Due to concerns related to national security, energy independence, and sustainability, the government has mandated in the Energy Independence and Security Act that 36 billion gallons of biofuels be produced annually by 2022 (Grabber, Quideau et al., 1996). Approximately 10 billion gallons of biofuels are currently being produced as corn ethanol, but in order to meet the stated goal the remaining 26 billion gallons will need to utilize a variety of feedstocks. Corn stover, wheat straw, miscanthus, and switchgrass are example feedstocks that could be produced from farms in the US and used as biofuels. These biomass feedstocks could be utilized to produce liquid fuels such as butanol or as pellets for heating applications. Nonetheless, a continued push for biofuels produced from lignocellulosic materials (agricultural residues, perennial herbaceous crops, and woody material) will likely continue due to governmental mandates.

While the focus has begun to shift toward the collection of agricultural residues, the production of grains and other commodities will always be a driving factor on farms with the production of residues being a secondary goal from the current economic perspective as the ratio of the value of the grain to stover is 7.47:1 (Luo, van der Voet et al., 2009). Greater than 80% of the agricultural residues are accounted for by corn stover and wheat straw, making efficient harvest and storage of these two biomass materials essential (U.S. Department of Energy, 2011). Additionally, the use of dedicated biomass crops, such as switchgrass and miscanthus which have potential yields of over 5 tons per acre, could also have a major impact on the production of cellulosic biofuels.

Biofuels production is heavily dependent upon the cost associated with harvest, transport, and storage (Hess, Wright et al., 2007). The transportation costs of getting biomass to a biorefinery becomes significant as transportation costs increase linearly with distance but can decrease with increased bulk and/or energy density. The primary difficulty of cellulosic biomass is that there is a high volume of a material that manifests a low energy and bulk density characteristic and variable moisture content. Densifying or processing the biomass on-farm would minimize the difficulties in transporting and handling biomass.

The standard model for biomass to biofuel transport consists primarily of a centralized biorefinery that either accumulates the biomass directly or has satellite locations that collect, store, and preprocess the material (You and Wang, 2011). There are two options for densifying biomass on-farm: pelletization or conversion to a crude biofuel. Pelletization of biomass, which itself requires an energy input, is able to mechanically increase the bulk density and amount of energy transported per truck. Pellets are also more uniform and flowable than raw biomass. A recently proposed improvement on this model is on-farm crude butanol production (Nokes, Lynn et al., 2013). In this system, preprocessing and concentration would take place on-farm. This would allow the material's energy density to be increased at the beginning of the supply chain, and it would allow existing infrastructure to be used to transport the crude butanol to the biorefinery, thus increasing transportation efficiency.

In addition to deciding what crops should be grown, producers will need information on the benefits and costs of pelletization versus biofuel production versus forage production. Pelleted biomass could have advantages relative to storing forages in bales. On-farm biofuel production would require pretreatment to improve the digestibility of the biomass. Mechanical, physico-chemical, chemical, and biological types of pretreatment exist, and one or a combination of these methods could be used to improve the subsequent digestibility for biofuels (Kumar, Barrett et al., 2009, Galbe and Zacchi, 2012). This pretreated biomass could also be utilized alternatively for livestock production (Kerley, Fahey et al., 1986, Atwell, Merchen et al., 1991, Willms, Berger et al., 1991).

One way in which differing production and transport models could be accounted for is by utilizing Geographic Information System (GIS) (Graham, English et al., 2000, Haddad and Anderson, 2008, You and Wang, 2011, You, Tao et al., 2012). GIS is ideal for the representation of biomass accumulation, storage, and transport as it allows for the theoretical yield, spatial distribution, and transportation network to be accounted for simultaneously. There are economies of scale for biomass processing facilities, yet the spatial variability of biomass production limits the benefits (Panichelli and Gnansounou, 2008, Jack, 2009, Bowling, Ponce-Ortega et al., 2011). Thus the overall spatial distribution and cost would dictate whether the processing facilities' location is organized in a centralized, distributed, or distributed-centralized fashion (You and Wang, 2011). The impact of biomass production and transport (bales vs. pellets vs. crude butanol), models would have to be analyzed in GIS. Information provided by GIS can be combined with Life Cycle Analysis (LCA) and Life Cycle Costing (LCC) to determine which production model would limit the overall environmental impact and cost (You, Tao et al., 2012). From an environmental perspective, each would need to be compared in the context of overall production of greenhouse gases (CO_2, CH_4, NO_X, etc.). The economic perspective would allow for the comparison of market and potential income and cost associated with each system.

1.1 Project Objectives

The overall goal of the project is to quantify the changes in biomass (corn stover, wheat straw, switchgrass, and miscanthus) due to pelleting and alkaline hydrogen peroxide pretreatment for conversion to biofuels. On-farm pelleting versus on-farm conversion to biofuels will be compared with a GIS model to evaluate the potential impacts of distributed biomass processing. The specific objectives and hypotheses are:

1. *Evaluate the energetic value of pelleted biomass (corn stover, wheat straw, switchgrass, and miscanthus) from a flat ring die system appropriate for on-farm use and determining the Higher Heating Value (HHV), production rate, percentage of pellets produced, specific energy, and durability based on treatment (moisture preconditioning).*

Hypothesis: Appropriate moisture contents for a ring die system will be different than traditional pelleting systems and will govern production rate, pelleting performance and durability.

2. *Quantify the effect of alkaline hydrogen peroxide spray pretreatment on lignocellulosic material (corn stover, wheat straw, switchgrass, and miscanthus) in terms of compositional changes (cellulose, hemicellulose, and lignin) and*

subsequent enzymatic hydrolysis to sugars. The treatments will include three concentrations of NaOH and three concentrations of H_2O_2.

Hypothesis: The spray AHP treatment will allow for the increased digestion of biomass for potential on-farm butanol production. Increased H_2O_2 concentration with extended pretreatment times will improve enzymatic saccharification.

3. *Develop a model for comparing alternative on-farm processing of biomass into liquid fuels (distributed preprocessing with centralized refining) and centralized, within a GIS framework.*

Hypothesis: The distributed preprocessing of on-farm processing facilities will allow for an increased cost saving and improved environmental impact associated with reduced transportation requirements as indicated by the GIS model.

Justification – Distributed processing of biomass will allow farmers to capture additional value in the product and reduce the overall environmental burden of biofuel production. Farmers could utilize a number of processing options for biomass that is harvested and stored on-farm. These include pelleting, animal feed, or conversion to a crude butanol stream. The most appropriate end-use of the biomass will be a function of a wide range of variables. However, this investigation will evaluate the potential benefits in terms of compositional changes of the biomass due to pretreatment and changes in energy density relative to transportation costs using a GIS approach.

1.2 Organization of Thesis

Chapter 1 establishes the general rationale and justification of this research and identifies the specific objectives that will be addressed within this dissertation. Chapter 2 explores prior research that is germane to the transformation of raw lignocellulosic material into a more usable product from a conversion and transportation standpoint. Pelleting performance by varying moisture content for a pilot scale flat ring die will be addressed in Chapter 3. Chapter 4 discusses the methodology and findings from the use of high solids alkaline hydrogen peroxide spray of pretreatment upon several different biomass types. Chapter 5 examines the feasibility of using on-farm biobutanol bunkers using a GIS case study to evaluate how the distributed processing would affect the system. Chapter 6 provides a general summary and conclusion. Chapter 7 discusses future work. The appendix possesses additional tables and graphs relevant to the dissertation but not included within the main body.

CHAPTER 2:LITERATURE REVIEW

Within the Unites States and other parts of the world, a paradigm shift is taking place with respect to energy production, and renewable fuels are gaining increasing interest in comparison to fossil fuels. Concerns about climate change, energy independence and security, and sustainability are driving the emphasis of renewable energy sources. While there are many different forms of renewable energy such as wind, solar, geothermal, and hydroelectric, one renewable energy source of particular importance is lignocellulosic material. Lignocellulosic material, or biomass as it is commonly referred, is composed of plant tissue of which the cellulose, hemicellulose, and lignin fractions are specifically germane to the bioenergy fuel development. In the United States, the majority of the biofuel produced to date has been ethanol derived from corn (Shinners, Boettcher et al., 2010). Lignocellulosic material is preferred to corn based ethanol or soybean based biodiesel as lignocellulosic material does not directly compete with food and feed supplies. This is not to say that biomass would not have any impact on food production since shifts in land management strategies for the production of biomass could inherently impact other types of agricultural production. Nonetheless, the type of lignocellulosic material grown is related to the production characteristics specific to each location within a region but is typically derived from three different sources: agricultural residues, dedicated biomass crops and woody residues.

2.1 Agricultural Residues

Agricultural residues are composed of any of the byproducts of a commodity, or grain, produced such as corn, wheat, barley, oats, pearl millet, sorghum and rice straw to name a few. World-wide, wheat straw is the most abundant renewable feedstock and possesses a low lignin content which makes it more acceptable for enzymatic hydrolysis and fermentation than other crops (Qi, Chen et al., 2009). However within the US, corn stover was estimated to be the largest source of agricultural residue (U.S. Department of Energy, 2011).

2.2 Dedicated Biomass Crops

The use of dedicated energy crops (cellulosic biomass that would be utilized for non-food or feed purposes) would be needed to supplement corn grain used for the production of 36 billion gallons of renewable fuels (Larson, Yu et al., 2010, Shinners, Boettcher et al., 2010). Dedicated biomass crops are typically perennial grasses that are high yielding and efficient with nutrients. These crops can be harvested in the late fall or early spring depending upon condition and can be produced upon marginal crop ground. Miscanthus and switchgrass are considered to be the two most likely crops for dedicated biomass (U.S. Department of Energy, 2011).

2.2.1 Miscanthus

Miscanthus giganteus is the most common hybrid proposed as an energy crop (Heaton, Dohleman et al., 2008). Miscanthus, a non-native grass, is a non-wood rhizomatous tall grass originating in Eastern Asia and pacific islands (Lewandowski, Clifton-Brown et al., 2000, Brosse, Dufour et al., 2012). Originally used as an ornamental plant, the Miscanthus genus is composed of 17 species and also utilizes the more efficient C_4 photosynthetic pathway (Naidu, Moose et al., 2003) and has been shown to have a potential yield greater than switchgrass.

2.2.2 Switchgrass

Established via seed and a native grass, switchgrass (*Panicum virgatum*) has numerous advantages as a bioenergy crop. Switchgrass, a warm season grass, produces a large quantity of biomass (Mulkey, Owens et al., 2006) and can be harvested multiple times during the growing season or after the first heavy frost. The more frequent harvest of switchgrass can result in greater yields (Thomason, Raun et al., 2005, Fike, Parrish et al., 2006). However, these increased yields come at an increased cost. Thomason, Raun et al. (2005) showed that three harvests and the addition of 488 kg N/ha resulted in the highest yield (18 Mg/ha), but no fertilization resulted in 16.9 Mg/ha. The additional yield of 0.5 US ton cost approximately $500. Thus, high N fertilization rates do not appear to have a viable economic return. However, the plant uptake of K increases with yield so this nutrient may be more important to add (Thomason, Raun et al., 2005).

2.3 Biomass Recalcitrance

Biomass recalcitrance, the attributes of the plant cell wall that make the plant more resistant to degradation by enzymatic and catabolic means (Li, Foster et al., 2012), is one of the primary challenges facing the biofuels industry and livestock producers desiring to use alternative fodder (agricultural residues or switchgrass) as a feedstuff. Two major factors with biomass recalcitrance are cellulose crystallinity and lignin. Cellulose crystallinity is the result of numerous polymers of cellulose arranged in a crystalline structure held together by intra and intermolecular hydrogen bonds. Lignin's physiological role within the plant cell wall is to provide structural strength, supply a protective barrier against pathogens, and impair water transport through cell types. The inability of biomass to be digested directly is why pretreatment of the material must take place.

2.4 Pretreatment

The pretreatment of lignocelluosic material is essential for the efficient conversion of biomass into monomers of carbohydrates readily available for enzymatic hydrolysis/fermentation (Kumar, Barrett et al., 2009, Galbe and Zacchi, 2012). The primary goal of pretreatment is to maximize the amount of carbohydrates available for hydrolysis and minimize the energy demand, cost, and potential downstream inhibitors. Four general methodologies exist for the pretreatment of biomass (Figure 2-1): physical, chemical, physico-chemical, and biological.

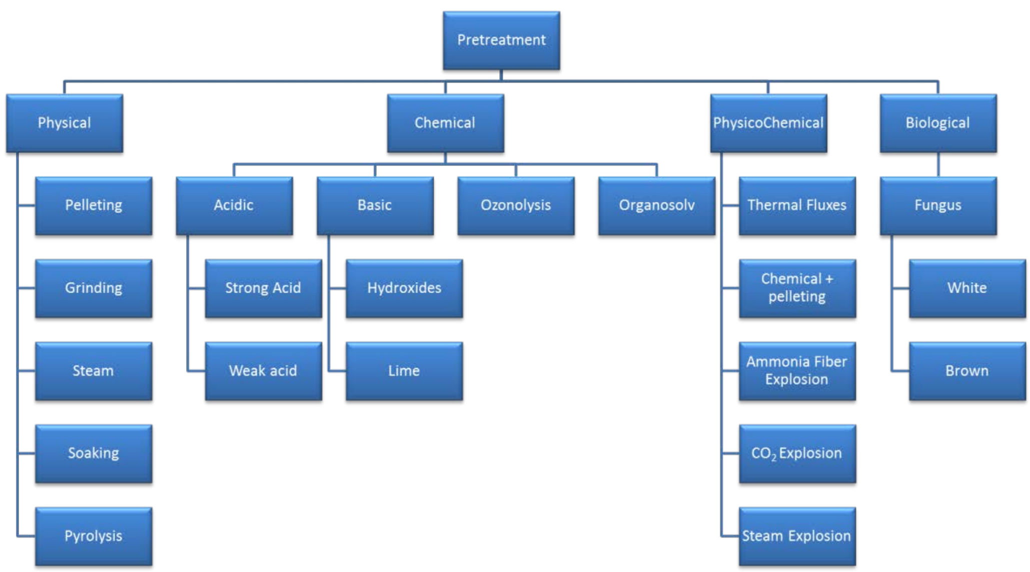


Figure 2-1 Visual breakdown of pretreatment strategies

2.4.1 Physical/Mechanical

Mechanical pretreatment consists of grinding, chipping, or milling to a reduced particle size which would decrease the crystallinity of the cellulose and increase the surface area for enzymatic reactions to take place (Kumar, Barrett et al., 2009, Silva, Couturier et al., 2012). The energy and time required for grinding biomass is related to the final particle size, biomass type, and the type of grinder (tub grinder, chipper, hammer mill, knife mill, ball mill, etc) (Kumar, Barrett et al., 2009, Silva, Couturier et al., 2012). Milling of the material is also advantageous to pelletization as the reduced biomass size allows for the material to pack together more densely and improve the durability of the pellets.

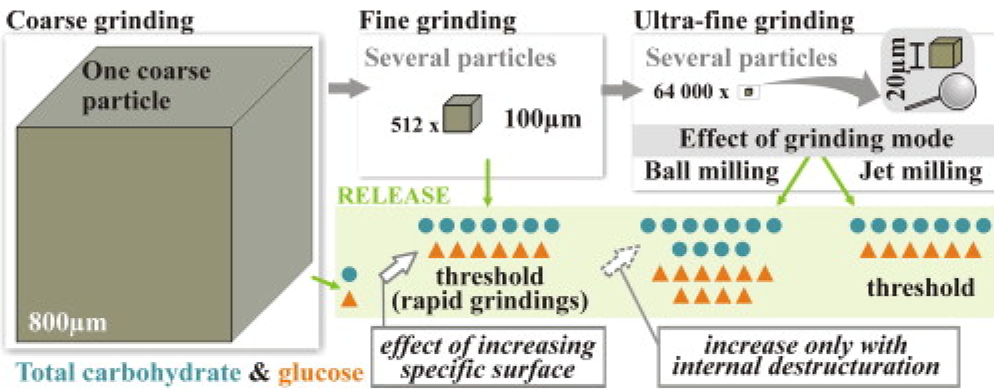


Figure 2-2. Reducing particle size increases surface area and downstream yield by enzymatic reactions (Silva, Couturier et al., 2012)

2.4.2 Chemical

Chemical pretreatment is dependent upon the pH of the compounds being applied and the compounds used can be acidic, neutral, or basic (Keith and Daniels, 1976, Jackson, 1977, Klopfenstein, 1978, Chen, Chen et al., 2012). Acid hydrolysis can utilize either concentrated or dilute acid. The implementation of concentrated or dilute acid (H_2SO_4 and/or HCl) in the pretreatment phase results in effective downstream enzymatic hydrolysis. However, the cost of recovery and corrosion resistant reactors will likely limit the application for on-farm processes. The alkaline treatment of biomass has been demonstrated to effectively increase enzymatic hydrolysis and can use NaOH, lime, and other basic compounds to increase fiber digestion (Pavlostathis and Gossett, 1985, Kaar and Holtzapple, 2000, Kim, Kim et al., 2003, Kim and Lee, 2007).

2.4.3 Physico-Chemical

Physico-chemical pretreatment uses a combination of both physical (temperature, pressure, or both) and chemical methods to improve the digestibility of cellulosic material (Sewell, Berger et al., 2009, Brodeur, Yau et al., 2011). One example is ammonia fiber explosion (AFEX) which uses ammonia at high temperatures and pressures to make biomass more susceptible to enzymatic degradation and fermentation (Bals, Murnen et al., 2010). Although effective on low lignin material, this method requires the use of high energy inputs and pressurized vessels.

2.4.4 Biological

The biological pretreatment of lignocellulosic material typically utilizes fungus (i.e. *Phanerochaete chyrsoporium*) to breakdown the structure. Although biological treatments are relatively safe and environmentally friendly, they are time intensive (weeks) and some dry matter losses from the forage would occur (Streeter, Conway et al., 1982, Hatakka, 1983, Jung, Valdez et al., 1992, Zadrazil, Kamra et al., 1996, Shrivastava, Thakur et al., 2011).

2.4.5 H_2O_2 Oxidative Delignification

Hydrogen peroxide is a potential chemical used in pretreatment that is assumed to be an environmentally safe compound that is stable and decomposes slowly at a rate of 1% per year into water and oxygen (Hart and Rudie, 2007). Alkaline hydrogen peroxide (AHP) treatment, also referred to as oxidative delignification (Kumar, Barrett et al., 2009), has been demonstrated to increase the digestibility of many different lignocellulosic materials (Gould, 1984). This method classically uses a combination of NaOH and H_2O_2 to improve subsequent enzymatic saccharificaiton by either ruminal bacteria or processes for biofuel production (Kerley, Fahey et al., 1986, Qureshi, Saha et al., 2008). For this type of pretreatment to be effective, a pH greater than or equal to 11.5 is required for partial solubilization of hemicelluloses, lignin and silica and a pH below 10 results does not allow for improved cellulose digestibility (Gould, 1984). Ambient temperatures of 20 - 25 °C are acceptable for AHP pretreatment to result in increased cellulose hydrolysis (Gould, 1984). The use of ambient or near ambient temperatures at atmospheric pressure allows for minimal costs and energy inputs for pretreatment.

2.4.5.1 Mode of Action

The effect of AHP treatment is twofold as both the sodium hydroxide and H_2O_2 act upon the biomass. The use of NaOH to treat lignocellulosic material is not a new concept and has been utilized for nearly a century to increase the digestibility of wheat straw (Jackson, 1977). The alkalinity of the NaOH impairs the intermolecular hydrogen bonds between cellulose and this causes swelling. The swelling allows for more accessibility to the cellulose structure. Furthermore, the lignin, hemicellulose, and silica are dissolved by hydrolysizing the acetyl moieties attached to hemicellulose (Jackson, 1977).

AHP is most effective when the pH is close to the pka of H_2O_2 pka of 11.5 so that a perhydroxyl anion (OOH- can be formed)

$H_2O_2 \leftrightarrow H^+ + HOO^-$

The perhydroxyl from this reaction leads to the formation of hydroxyl and superoxide radicals which can lead to the solubilization of lignin.

$H_2O_2 + HOO^- \rightarrow HO^{-}\cdot + O^{-}\cdot + H_2O$

The hydroxyl radical species causes alkyl –ester scission in lignin which at the alkaline pH would allow for the improved solubilization of lignin which would further propagate delignification (Li, Foster et al., 2012). Gould (1984) found that 45-55% of the lignin could be solubilized with the AHP treatment. Uncertainty remains as to the effectiveness of AHP treatment upon cellulose crystallinity.

2.4.5.2 Lab Scale AHP Pretreatment

The initial research performed by Gould and Freer (1984) demonstrated that the majority of the cellulose was utilized after AHP pretreatment. This method used 1 g biomass (2% (w/volume pretreatment solution) biomass loading), an H_2O_2 loading of 0.5 g/g biomass (1% w/v), and 24 hours residence time. Variations of this have been performed to ascertain the optimum conditions. The concentration has been altered to 0.125, 0.25, and 0.5 g H_2O_2/g biomass (Banerjee, Car et al., 2011). Compared to 0.25 and 0.5 g/g biomass, the lowest concentration AHP 0.125 g/g biomass exhibited the lowest percentage yield of glucose and xylose. Nonetheless, this could be compensated for by increasing the residence time to 48 hours for the AHP pretreatment and continually adjusting the pH to the optimum level of 11.5 during the pretreatment period. The biomass loading was evaluated from 2% to 20% and a concentration of 20% was found to the most effective for subsequent enzymatic saccharification (Banerjee, Car et al., 2011). Most of the research has been conducted on a gram scale with ground material. A more scalable method must be developed if AHP pretreatment is going to be used on a large scale. To-date, most experiments have utilized lab scale methodologies.

2.4.5.3 Field Scale AHP Pretreatments

For the process to be commercially viable for animal feed and biofuels, other application options for AHP pretreatment were developed (Atwell, 1990, Cameron, 1990). The high solids or"dry" method of AHP treatment was developed and can be utilized to process whole round bales. The procedure involves grinding the biomass in a tub grinder with a 10 mm to 100 mm screen size. For most forage operations, this would most likely involve the use of a silage baler or a forage chopper that has the ability to reduce particle size. The biomass material is then mixed with a solution of 5% NaOH, and 2% H_2O_2 to obtain a moisture content of 37%. However, the dry method does not allow for the loss of solubilized hemicelluloses due to the lower moisture level.

2.4.5.4 Timing of H_2O_2 Application

The addition of H_2O_2 to treat biomass can take place either simultaneously with the alkaline solution (NaOH) or application of H_2O_2 can be delayed. The concomitant addition and 12 hour delayed addition of H_2O_2 demonstrated equivalent ($p > 0.05$) dry matter disappearance (DMD) of 62.4 and 63.7%, respectively after 24 hours (Lewis, Holzgraefe et al., 1987). Nonetheless, after 36 hours of reaction time, the delayed addition of H_2O_2 resulted in a DMD that was 17% greater that exhibited by the simultaneous addition of AHP solution. The delayed addition allowed more time for the NaOH to react and open up the lignin.

2.4.5.5 Concerns

The use of NaOH to reduce the pH has caused some concerns due to the fact that the additional Na would cause a reduction in the formation of butanol downstream (Qureshi, Saha et al., 2008). This type of pretreatment could allow for all other processes (enzymatic hydrolysis and fermentation) to be carried out without washing, but pH adjustments would have to take place (Banerjee, Car et al., 2012). It has been proposed that field chopped corn stover could be used (unpublished work by Banerjee, Car et al.

(2012)), but this variable may need further validation. The addition of hydrogen peroxide has been performed in many different ways (Gould, 1984, Kerley, Fahey et al., 1985, Lewis, Holzgraefe et al., 1987, Chaudhry and Miller, 1996, Banerjee, Car et al., 2011, Chen, Chen et al., 2012). The method used by (Willms, Berger et al., 1991) is preferred as it could be modified for use in a bunker silo. For their analysis, the particle size of wheat straw was reduced using a tub grinder and fed into a mixer where NaOH, H_2O_2, and water were added. The treated material was sequentially stored until use.

2.4.6 Hornification

The drying of samples after pretreatment for storage or other processes can negatively influence the formation of glucose monomers after enzymatic hydrolysis. Hornificaiton is the irreversible changes in plant structure that occurs as a result of drying. Prior to drying, the water sorption capacity is higher than it is after drying and rewetting. The loss of this sorption capacity is specifically related to reductions in pore volume, which have been observed to decrease from 35 Å to 25 Å, and pore numbers related as a result of initial water loss (Kato and Cameron, 1999). Temperature is surmised to have a dominating influence as oven, or heated drying, results in greater hornificaiton than air drying, which impact lignocellulosic material to a lesser extent (Luo and Zhu, 2011). Time is a factor that is inversely correlated with temperature. As time increases, the temperature to reach an equivalent degree of hornification decreases. The collapse of pore space is thought to occur in one of two ways. For one, the drying creates void space which brings the microfibers closer together and allows them to form H-bonds which propogates and closes the pores. The other method assumes that as water leaves the pore space, the surface tension of the remaining water pulls the walls and fibers together. The larger pores will collapse first and are more susceptible to collapse than smaller pores. The goal of pretreatment is to remove or alter barriers to enzyme hydrolysis such as hemicellulose and lignin. Typically in successful pretreatment, pores are created and swelling occurs. Thus the drying of pretreated samples is thought to reduce the effectiveness of pretreatment.

2.5 Transportation Costs

The major goal of processing biomass on-farm is to allow for decreased transportation costs, which can account for 30% of the feedstock cost with current biomass handling systems (Hess, Wright et al., 2007). Increasing the bulk density of bales will decrease the collection and transportation cost, and if the material is in the form of pellets, transportation costs to a biorefinery will be the lowest. Reducing transportation costs would likely require densification at distributed locations – either by pelleting or processing to liquid fuels.

Geographic Information Systems (GIS) have been used in many different studies and in varying capacities to evaluate biomass quantities and transportation models (Ayoub, Martins et al., 2007, Haddad and Anderson, 2008, Larson, Yu et al., 2010, Cattafi, Gavanelli et al., 2011, Martinez and Maier, 2011). These researchers used similar tools, but employed differing methodologies for their studies. The Network Analysis Extension of ArcMap has proved to be a powerful tool in determining the optimum location of biomass collection points (Martinez and Maier, 2011). Instead of inaccurately using a linear distance between the farm and the biomass collection point, GIS can calculate the actual distance using existing roads from the farm to the biomass collection point or other points of interest.

A main objective of utilizing biofuels is to reduce energy consumption and the associated environmental impacts, in terms of CO_2, NO_x, SO_2, and N_2O emissions, from fossil fuel consumption. Life Cycle Analysis (LCA) is used to ascertain the environmental impact of different production systems. In addition to determining the environmental impact with LCA, Life Cycle Costing (LCC) can also be used to determine the cost associated with the various production options (Luo, van der Voet et al., 2009). Commonly, the transportation of raw biomass over large distances is assumed to require more energy than what is actually produced (Cattafi, Gavanelli et al., 2011). The location of the processing facility for biomass is of extreme importance. Oftentimes, economies of scale dictate that the processing facility for biomass must be high-tonnage and require expansive supply areas (Bowling, Ponce-Ortega et al., 2011). However, this assumption will be challenged by the use of distributed on-farm biomass processing facilities.

As previously stated, the transportation of the feedstock from the field to the processing plant has numerous costs associated with it, including costs in terms of dollars and energy. De and Assadi (2009) accounted for the monetary costs in the examination of co-firing biomass in coal plants by assuming a biomass distribution density around the plant and determining the total distance that would need to be traveled annually to supply the plant. Kumar and Sokhansanj (2007) evaluated the feasibility of supplying switchgrass to a biorefinery with a capacity of 1814 dry tonnes per day. Energy expended in the transportation of the biomass was estimated at 4.8% to 6.3% of the total energy content of the material. At an assumed yield of 11 dry metric tons/ha, the plant required a transportation range of 77 km and the analysis showed transport costs increased or decreased with plant size because of increased travel distance to supply larger facilities.

Steffe (1996) examined transport scenarios for supplying agriculture residues and wood chips for conversion to biofuels or direct combustion to produce electricity. The study examined standalone trucking; and trucking in combination with rail, ship, and pipeline transportation. The study noted that the low density of baled biomass often made volume the limiting factor for transportation, and found rail transport was economical after 500 km, whereas shipment via pipeline and ship were economical after 1500 km and 3000 km, respectively.

2.6 Geographic Information System GIS

Over the past two decades, improvements in GIS software, hardware, and computer networks have made geospatial data more readily available and complete. Geospatial data is generally composed of the following: mapsheet and plans, aerial/remote sensed images, surveys, or digital data products (Graham, English et al., 2000, Malczewski, 2004). GIS has been used in varying capacities to evaluate biomass quantities and transportation models (Ayoub, Martins et al., 2007, Larson, Yu et al., 2010, Cattafi, Gavanelli et al., 2011, Martinez and Maier, 2011). The use of GIS to identify bioenergy crop yield dates back to studies performed by Ramsey and Cushman in the 1980's and biomass facility location optimization back to 1996 with the Biomass Resource Assessment Version One (BRAVO) model (Noon and Daly, 1996).

2.7 Yield/Acreage Estimations for GIS Biomass Studies

The accurate determination of crop production areas and yield is essential to the determination of subsequent transportation costs. The United States Department of Agriculture (USDA) National Agriculture Statistics Service (NASS) collect information pertaining to both crop area and yield though surveys and provides this annual data for crop production on a county and state level. The NASS crop area and yield data, however, does not provide the distribution or variation in production that can occur and a uniform production distribution has been assumed in most studies.

Cropland data layer (CDL) is a land cover data set that specifically relates to agriculture and is derived from satellite imagery with a 30 by 30 meter pixel resolution. Originally developed in 1997, CDL has allowed researchers to examine crop rotation, crop expansion, crop distribution, bioenergy potential, ecological impact, and yields within a geospatial format (Mueller and Harris). With CDL identifying the area of production, the total yield from a production area of interest can be determined using a number of different methods. A constant yield can be assumed for all the areas identified by the study, a yield factor could be based upon soils data, or remotely sensed data could be used. Each one has inherent advantages and drawbacks. A constant yield allows for the quick and easy calculation to be performed; however, the constant yield assumption would not take into account known spatial variations in production. Data layers containing the geospatial soils information would allow for the spatial variance in crop production potential to be accounted for in studies. Remote sensing could also be used to predict the yield but the satellite resolution may not be ideal for field less than 25 hectares (Doraiswamy, Hatfield et al., 2004). The use of drones could ameliorate the resolution issue, but the commercial use of unmanned aerial vehicles is still problematic. Soil properties can account for 30% of the expected yield variation (Kravchenko and Bullock, 2000), yet temporal yield variation has been shown to be 1.1 to 3.9 times greater than spatial variation (Bunselmeyer and Lauer, 2015). While models may predict the potential yield, numerous exogenous factors (planting date, harvest date, precipitation, nutrient and pest management, and climate) ultimately influence the final yield (Lobell, Cassman et al., 2009).

2.7.1 Candidate Site Selection for Biomass Facilities

The location of biomass processing facilities and satellite collection/preprocessing facilities has typically been refined using two differing mechanisms: suitability and optimization. Suitability analysis ascertains what spatial factors would be favorable (proximity to power grid, water resources, and other distribution networks) and unsatisfactory (proximity to schools, environmentally sensitive areas, etc) to implement siting of biomass facilities. Thus, suitability of a biomass processing facility can be evaluated as either exclusionary or preferential site development (Dong, 2008). From the optimization of biomass perspective, mixed integer linear programming (Xie, Zhao et al., 2009), location-allocation (Möller, 2003, Sultana and Kumar, 2012), and other methods have been used to optimize biomass facility size and location.

2.7.2 Network Analysis

The use of Network Analysis for transportation applications has become ubiquitous as the ability to analyze multiple modes of transportation separately or simultaneously exists (Curtin, 2007). Within network analysis, ArcGIS possesses many different features for transportation analysis: routing, vehicle routing, service area, origin to destination (O-D) cost matrix, and location-allocation. For the transportation analysis options listed, Dijkstra's algorithm (Dijkstra, 1959) or a modified version is to determine the shortest path for transport given a defined road network with the exception of location-allocation (Environmental Systems Research Institute (ESRI)).

Routing and vehicle routing has been used in studies that deal with transport between the field and processing facilities as well as models which have processing equipment that need to be moved from location to location such as harvesting and preprocessing equipment (Simpson, Hamann et al., 2007, Perpina, Alfonso et al., 2009, Cavalli and Grigolato, 2010) (Dean, 1997, Chiueh, Lee et al., 2012). Furthermore, routing can be an effective tool for analyzing and minimizing the cost of transport using either a time or distance parameter. Routing is used when there are relatively few or specific routes that need to be analyzed. The movement of mobile biomass processing equipment was specifically analyzed with routing as it allows for the minimization of travel distance overall (Ha, Munster et al., 2011, Ha, Munster et al., 2014).

Service area has also been used in GIS biomass supply chain management studies (Haddad and Anderson, 2008, Martinez and Maier, 2011). The service area can be defined by either a distance or travel time from a point of interest. The service area can be combined with the use of concentric rings (annuluses) to ascertain how much biomass is within a specified boundary of the biomass plant. Service area is ideal when the location of the biomass plant has been predefined or hypothetical. Although not part of the service area feature, many researchers have used the buffer tool to create areas of interest around potential biomass locations (Velazquez-Marti and Annevelink, 2009, Nolan, Donnell et al., 2010, Stephen, Sokhansanj et al., 2010).

Origin to destination (OD) cost matrices can be used by GIS to evaluate transport costs between origin and destination points within a spatial analysis (Parker, Tittmann et al., 2010). OD cost matrixes are effective when there are a large number of locations which need to have routes developed. The development of a matrix allows for the manipulation of the distance to be performed in spreadsheets outside of ArcGIS.

Using metaheuristics, location-allocation has been used to identify potential sites for bioenergy plants (Möller, 2003). Transport costs based on either distances or times between the biomass source points (demand points) and bioprocessing facilities are minimized with most of these analyses. Suitability and optimization are typically combined using this format (Wilson, 2009). Demand at the bioprocessing facility can be designated as either capacitated or uncapacitated for the analysis (Dong, 2008). Within location-allocation there are many differing types of problems: p-median, maximize coverage, minimize facilities, maximize attendance, maximize market share, and target market share.

2.7.3 Transportation Assumptions

The maximum one-way transportation distance for biomass to a collection hub, pre-processing facility, or processing facility has been used as a variable (varying between 5 and 200 km) in most studies (Shi, Elmore et al., 2008, Rentizelas, Tatsiopoulos et al., 2009, Alex Marvin, Schmidt et al., 2012). The traveled distance has been measured both using Euclidean distances and GIS road networks (Shi, Elmore et al., 2008, Rentizelas, Tatsiopoulos et al., 2009, Alex Marvin, Schmidt et al., 2012, Yu, Wang et al., 2012). Euclidian measurement for overall distance traveled requires an assumption on the tortuosity of the road. Tortuosity is typically surmised to range from 1.2 - 3 for straight and curvy roads, respectively (Overend, 1982, Jack, 2009). The use of GIS road networks allows for the inference to be more accurate (Sultana and Kumar, 2014). In other trials, the estimated duration of transport has been used to ascertain a practical level of transport distance given current producer sentiment. A maximum transport distance of 50 km (or 30 miles) is typically assumed according to Miranowski (Overend, 1982, Jack, 2009).

Trucking costs are defined in different ways and can be based upon time or distance. The distance dependent costs can be broken down into fixed and variable costs (Mahmudi and Flynn, 2006). The fixed transportation costs ($/Mg) are the expenses that are incurred at any distance, examples include the cost associated with loading and unloading biomass, taxes, and insurance. The variable cost ($ / Mg-km) is dependent upon the miles traveled and includes: fuel use, labor, transport vehicle payments, maintenance, and other costs. Costs have also been assumed to vary given the distance traveled (Petrolia, 2008).

The average speed of transportation vehicles for biomass has been defined by whether the vehicle is loaded or unloaded (Rentizelas, Tatsiopoulos et al., 2009), by type of road (Haddad and Anderson, 2008), and by the specified road statute within GIS shapefiles (Sultana and Kumar). The speed of the vehicle can then be used to ascertain the time and/or labor required for transportation.

Biomass crops possess a low volumetric energy content and low bulk density which makes the transportation of biomass less desirable than the transportation of coal or liquefied energy products. Nonetheless the transportation efficiency has been improved using a number of different mechanical densification technologies to make bales, cubes, pucks, briquettes, or pellets.

Baling of biomass can be performed using either a large round or square baler with each method having inherent advantages and disadvantages. Round balers are owned by the majority of farmers who accumulate forage for livestock hay. In areas of high rainfall, such as the Southeastern US, round bales are advantageous due to the fact that they can “shed” water (Amit, Carol et al., 2010, Larson, Mooney et al., 2010). Round bales can be wrapped using several different methods such as the following: sisal twine, plastic twine, mesh net wrap, plastic wrap, and breathable non-woven film (Shinners, Boettcher et al., 2010). Net wrapping is preferred since twine wrap takes considerably more time to perform and takes on more water than net wrap (Shinners, Boettcher et al., 2010). However, round bales are considerably more difficult to transport than large square bales since they deform under a static load and cannot stack as easily (Sokhansanj, Mani et al., 2009).

Compared to round bales, large square bales produce more dense bales with bulk densities of approximately 149 kg/m^3 (9.3 lb/ft^3) and 109 kg/m3 (6.8 lb/ft^3) for square and round bales, respectively (Amit, Carol et al., 2010). Furthermore, square bales are easier to handle and stack than round bales which results in a lower transportation cost (Sokhansanj, Mani et al., 2009). The production of bales is also expedited when using a square baler as compared to round baler since the operator of the square baler does not have to stop to wrap or tie the bale (Larson, Mooney et al., 2010). However, large square balers manifest a higher initial cost than round baler which could result in in a purchasing price that is greater than three times that of a large round baler (Larson, Mooney et al., 2010). Square bales are also more susceptible to spoilage and dry matter losses when compared to round bales as square bales lack the ability to shed water. Even though each baling system has advantages and disadvantages, both round and square baling will have to be utilized until either another accumulation method is developed or one baling system is selected as the preferred method.

Baled biomass presents challenges associated with handling and transportation (specifically, energy density and bulk density of the product). The low bulk density (40-200 kg/m^3) of baled material can cause trucks to “cube out”. Volume as opposed to weight limits the total amount of biomass that is able to be transported. The density of the bale is affected by baler type, baler age, biomass material, bale size, shape, crop, moisture content, travel speed, and baler settings. Approximately 14% of the weight capacity of the truck is lost due to limitation with volume (Turner, 2014). Efforts have been made on a laboratory setting to increase the bale density to the minimum desired bale density of 256 kg/m^3 by altering structural components of biomass material by subjecting bulk samples to further compression to break the plant nodes and reduce elastic response of the baled material (Turner, 2014).

2.8 Pelleted Biomass

Pelletization of biomass creates a more uniform product and allows for biomass to be handled, transported, and stored with greater ease than baled biomass. Handling of the material is improved by the fact that pelleted material possesses greater flowability and bulk density. Logistically speaking, pelleted biomass transport is dependent upon the distance traveled as the cost will determine the preferred mode of transport (tractor, truck, rail, and ship) (Forsberg, 2000). Additionally, pelleted biomass is easier to move between the different modes of transport, enhancing handling efficiency. With regard to truck transport, the improved bulk density of pelleted biomass allows for the weight of the biomass to become the limiting factor in transport as opposed to volume. Storage of the biomass can also be moved from outdoor or under tarp to inside a grain bin. Ideally when the solid biomass leaves the farm gate, it would need to be in a pelleted form for ease and efficiency of transport and distribution. Again, this is another process that could take place on-farm to produce a denser, flowable product.

The quality of pellets formed has been based on a number of different factors. The bulk density of the final pellets formed is essential since pelleted biomass can possess three times the density of ground material. A second quality factor is pellet resilience. Assessing the pellet resilience against breaking due to handling, transport, and storage is assessed with the pellet durability index (PDI). Pellet durability can be measured in a number of different ways (tumbling, Holmen tester, and Ligno tester), but the Kansas tumbling test which eventually became the American Society of Agricultural and Biological Engineers (ASABE) Standard for Densified Products for Bulk Handling – Definition and Method (ASAE S269.5 OCT2012) is generally regarded as the industry standard for feed mills. The Pellet Fuel Institute (PFI) uses the ASABE standard as one of the characteristics to certify their three different grades of pellets with the minimum standard for the durability being 95% of pellets remaining intact after the test. The formation of fines is undesirable to the consumer as that part of the product is generally lost in handling.

2.8.1 Pellet Mill Characteristics

Different types of pellet mills and operational scale allow for many variations in quality and performance characteristics to exist. Within the solid biofuels industry and research community, there are three types of pellet mills. Used primarily within academia on a lab scale, the single piston pellet mill allows for the compressive strength of each individual pellet to be assessed. Commonly used within the feed industry, the other two types of pellet mills use either a flat ring or ring roller dies. Ring roller dies are more common with a large industrial setting typically while flat ring dies are used for research trials or smaller volumes of material (Tumuluru, 2014). Flat ring dies are known for their compact design and robustness for pelletizing different materials. The feed input from the top allows for quick access to the pellet chamber and pellet production can be visibly monitored. However, the ring roller die create more friction which increases die temperature and allows for better pellets to be produced. The extra fiction increased the energy consumption of the pelleting process (Garcia-Maraver and Carpio, 2015). The investment cost of flat and ring dies vary with the price depending upon the scale and availability (Thek and Obernberger, 2004, Garcia-Maraver and Carpio, 2015).

The die properties have been shown to influence pellet quality as well. Carbon steel alloy, stainless steel alloy, and high chrome alloy are typically used to make the die as they must be durable enough to allow for pellet formation (Garcia-Maraver and Carpio, 2015). As the thickness of the die increases the durability of pellets produced increases, however throughput of material was reduced because of it. With alfalfa, the larger diameter die was able to handle higher moisture contents but resulted in less durable pellets than the smaller die diameter (Tabil and Sokhansanj, 1996). The shape and number of holes in a mill influence the quality of pellets as well. Die speed has been shown not to influence pellet production for a ring roller die (Tabil and Sokhansanj, 1996). For a flat ring die increasing the speed increased the throughput of pellets reducing the specific energy but the bulk density and PDI remained the same (Hoover, Tumuluru et al., 2014). The temperature of the die is very important as 90°C is generally regarded as the minimum temperature required for pelletization (Stelte, Sanadi et al., 2012).

The specific energy cost (kWh/Mg pellets produced) is one of the more important measures since the electrical consumption costs of the pellet mill long-term will outweigh the investment cost (Thek and Obernberger, 2004). Furthermore, the pelletization process uses the most electricity in a pellet production facility with grinding consuming the second most electricity (Thek and Obernberger, 2004). Thus, the specific energy is often termed as pellet production efficiency. The production efficiency is largely based upon the throughput which is dependent upon the type of material, preconditioning characteristics, type of mill, and other factors.

2.8.2 Material Characteristics

Pelletization characteristics will be crop dependent and be influenced by the composition of the biomass: lignin, sugars, cellulose, amino acids and other components. Components such as lignin, starch, and protein can act as natural binders. Temperature, moisture content, and pressure allow for the binding of particles to be enabled (Kaliyan and Morey, 2010). Generally, the melting temperature for lignin is considered to be 140 °C (Mani, Tabil et al., 2006), however the glass transition temperature in wheat straw was found to occur at 53 °C - 63C (Stelte, Clemons et al., 2011) (Stelte, Clemons et al., 2012).

The moisture content of the biomass entering the pellet mill is a critical variable to the pelletization process and can manifest a varied effect on biomass as water can enhance binding and act as a lubricant (Kaliyan and Morey, 2009). Attractive forces such as the Van der Wall forces and hydrogen bonding are enhanced as water allows for more bonds to occur between particles which strengthens formation and durability. Furthermore, the moisture acts as a binder by allowing the glass transition temperature to be achieved at a lower level, which enhances solid-bridge formation. Moisture can be added directly during pelletization, mixed prior to the pelletization, or conditioned with steam. Of the moisture addition options, steam requires the most energy and is typically used in commercial applications. For pelletization with a ring roller die, the preconditioned moisture content has been observed to range from 8 to 15%. The addition of superfluous moisture can also deleteriously influence pellet production as die plugging or choking has been observed with ring roller dies above 10% for a smaller diameter die and 13 to 15% for larger diameter die.

While numerous factors can influence pellet quality, this study will seek to focus mainly upon process variables such as material moisture content which influence PDI, density, and pellet formation (Jiang, Pu et al., 2009) and the resulting energy

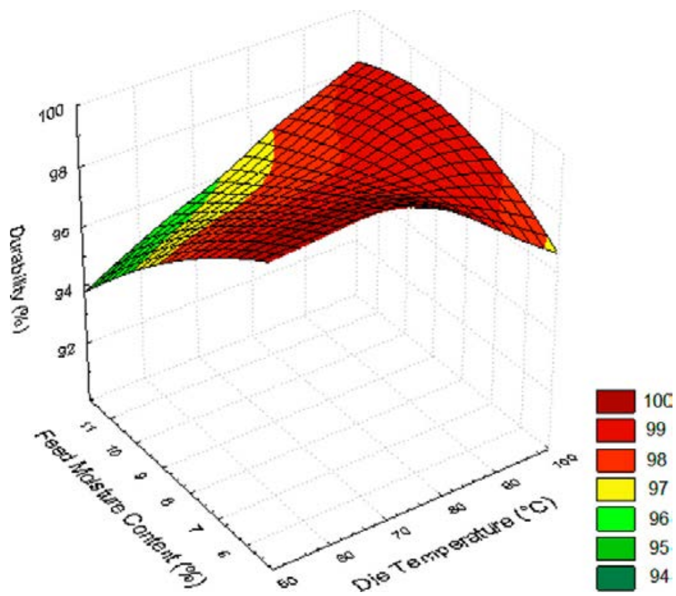


Figure 2-3. Relationship for durability, moisture content, and die temperature of a ring roller die for wheat DDGS (Jiang, Pu et al., 2009).

2.9 Production of Butanol

Another method available to increase the volumetric energy content of material is to convert the lignocellulosic material on-farm into liquid fuel. The majority of the biomass research efforts to date have focused on the conversion of lignocellulosics to ethanol. A model for the biomass crops associated with butanol production has yet to be developed (Jin, Yao et al., 2011). Butanol production could take place on-farm significantly altering the proposed biofuel production system. Ideally, the system would utilize a rotation of wheat straw, corn stover, and a dedicated biomass crop (i.e. switchgrass or miscanthus) with the goal being to produce fuel year round and minimize biomass storage. The production of butanol on-farm should hypothetically allow 175 tons of biomass to produce ~7,000 gallons of crude butanol (approximately 70% butanol, 25% ethanol, and 5% acetone). Converting baled biomass into an easy to pump and handle liquid product would significantly reduce costs and increase the energy density of the material transported.

CHAPTER 3: OBJECTIVE 1: DENSIFICAITON OF BIOMASS INTO PELLETED MATERIAL USING A PILOT SCALE MILL

3.1 Summary

The production characteristics of a pilot scale flat ring die pellet mill for use on-farm was evaluated for four different biomass materials (miscanthus, corn stover, switchgrass, and wheat straw) to determine the effect of different moisture preconditioning upon pelletization. The moisture content of the material entering the pellet mill was 10%, 15%, 20% and 25% for miscanthus, switchgrass, and wheat; while, only 15%, 20%, and 25% moisture content was evaluated for corn stover. For the flat ring die, moisture contents of 10% were not conducive to the formation of pellets from miscanthus, switchgrass, and wheat straw. Similarly, the material at a moisture content of 15% did not allow for pellet formation from switchgrass or wheat straw. For miscanthus, switchgrass, and wheat straw at the highest moisture content (25%), the pellet formation was readily achieved with the percent pellets produced being 92%, 92%, and 96%, respectively. For corn stover, 15% preconditioned moisture resulted in the highest rate of pellet formation, lowest specific energy requirement and similar durability to the other measured moisture contents. For the differing biomass materials, the specific energy requirements for the flat ring pellet mill was demonstrated to vary between 101 to 324 kWh/Mg. Across the different biomass types, energy input of pelletization was 2 to 7% of the final energy content of the pelletized product produced.

3.2 Introduction

The volumetric energy content for lignocellulosic material used for biofuels is lower than traditional fossil fuel sources (Brown, 2003) and this low energy density is largely the result of low bulk densities of biomass materials. Densifications of the biomass is essential to improved transportation, storage, and handling capabilities. Pelletization is one of the technologies that has been proposed to mechanically increase the bulk density of biomass. The advantages of pelletization go beyond increases in bulk density as the handling and storage of pelleted biofuel can be performed similar to grain (Mani, Sokhansanj et al., 2006). Biomass pellets can serve a variety of purposes with some being used on a smaller scale for residential heating or on a more industrial scale where they could be co-fired with coal at power plants (Holm, Henriksen et al., 2006). Worldwide the total production of pellets increased 10 fold from 2000 to 2010 with the US being one of the leaders in pellet production (Lamers, Junginger et al., 2012). The increased demand of pelleted fuel sources in Europe and domestically could allow for more biomass material resources to be used such as dedicated biomass crops or crop residues. The expansion of pellet production as a solid fuel source is expected to be essential to future biofuel uses.

From a transportation standpoint, the densification of biomass at localized satellite pelletization facilities or at larger on-farm facilities would allow for the greatest benefit in increased bulk density associated with transport to be realized. Pelletization has been performed using either a flat ring die or a ring roller die (Stelte, Sanadi et al., 2012). Advantages and disadvantages exist with each type of mill. For ring roller dies, pelletization properties have been assessed at many different moisture contents (Larsson and Rudolfsson, 2012). However, the flat ring die is suggested to have more robustness with input biomass material and the purchase price seems to be lower. The potential to use flat ring dies has yet to be fully assessed for the biomass industry. Flat ring die studies have been performed for poplar and other material (Mediavilla, Fernández et al., 2009, Mediavilla, Esteban et al., 2012) along with high (28% - 38%) moisture (Tumuluru, 2014) and pretreated corn stover (Hoover, Tumuluru et al., 2014). Nonetheless, the objective of this study was to characterize the sensitivity of the flat ring die to changes in the initial preconditioned moisture content for miscanthus, corn stover, switchgrass, and wheat straw. The most important variable in pellet production is moisture content as this property will ultimately determine the durability and density of pellet (Samson, Mani et al., 2005, Larsson and Rudolfsson, 2012). The quality of the pellets for a flat ring die will be evaluated by measuring the percentage of pellets produced, bulk density, and durability. Furthermore, data is not available characterizing the specific energy consumption of a flat ring die pelleting system given varied moisture contents.

3.3 Materials and Methods

Switchgrass (Alamo) and miscanthus (Miscanthus x giganteus) used in these studies were harvested at the University of Kentucky's North Farm, Lexington, KY. The sample material was harvested in late winter 2011, 2012 and 2013 using a disk mower and baled into small square bales. The bales were stored in a barn prior to transportation to campus. A No. 20 Hammer mill (C.S. Bell Co., Tiffin, OH) was used to grind the biomass and collected using a cyclone (Cincinnati Fan and Ventilation Inc., Mason, OH). Screen sizes of 3 mm, 5 mm, and 10 mm were used with the hammer mill.

3.3.1 Sample Conditioning

After grinding, samples were preconditioned in batches with 9 kg (20 lb) being rewetted within plastic storage containers. The moisture content of the ground material was approximately 8%. Material was rewetted and mixed to 10%, 15%, 20%, and 25% moisture contents (wet basis) using a pump sprayer. The moisture contents were randomly tested throughout the conditioning process and analyzed using an Ohaus moisture analyzer (Ohaus Corporation, Parsippany, NJ) with a 1 gram sample dried at 130°C. The measurement with the Ohaus were equivalent to that of the dried standard ANSI/ASAE (May2012) ($r^2 > 0.9$). Thus, the Ohaus was used since the determination of moisture content was conducted in minutes as opposed to days. The conditioned material was sealed inside the container and allowed to sit overnight. The material moisture content was retested the following morning and pelletized if the average was within 0.5% of the target value.

3.3.2 Pellet Mill

Material was fed into the pellet mill using a belt conveyor system with a paddle at the end to allow for uniform feeding. Pelletization was performed using a Model PM605 (Buskirk Engineering, Ossian, IN) pellet mill flat ring die with a 3.7 kW (5 horsepower) grease-packed gear motor that possessed the capacity to pelletize up to 90 kg/hour (200 lb/hour) according to manufacturer's specifications. The dimensions of the die used were 15.2 cm (6 in) diameter and 3.8 cm thick machined die plate. Typical pellets formed were approximately 6 mm in diameter and 18 mm in length. Prior to conducting each test, the die was preheated to 90 °C as this temperature is generally considered the minimum threshold for pelletization (Holm, Henriksen et al., 2006). Preheating of the die to 90 °C was conducted using distillers grain and was sequentially flushed with the lignocelluosic material that would follow. The die did not possess any form of heater, only the friction from the pellet formation increased the temperature. The die temperature was measured using a Fluke Hydra Series datalogger (Fluke Corporation, Everett, WA) with three type T thermocouples connected to side of the die as shown in Figure 3-2. The temperature was monitored during the test to ensure steady state operation and the temperature upon the completion of each pellization run was recorded.

3.3.3 Power Consumption

The pellet mill operated on a 230V three phase electrical system. Current within each line was measured with an AcuAMP current transducer (AutomationDirect, Cumming, GA, part number ACT050-10-S) which possessed a 1% accuracy. The voltage ouput from the current transducers was calibrated using an Extech Power Analyzer 380803 (Nashua, NH) with various sources providing the amperage source for calibration points. The current transducers were placed on the output side of the variable frequency drive (VFD) (Lenze Americas Corporation, Uxbridge, MA, USA) that drove the pellet mill. Current was logged using a Measurement Computing USB 1408FS analog to digital board (Norton, MA) and a program written using Visual Studio (Microsoft, Redmond, WA) to log the data onto a tablet. The software clock was used to achieve a sampling rate of 10 Hz. The voltage was measured on the output side of the VFD using a Fluke multimeter. The total power was calculated in terms of rms magnitude for a balanced wye load as shown in Equation 3-1 (Nilsson and Riedel, 2000).

$$P_T\ (kW) = \frac{\sqrt{3} \times V_L \times I_L \times Pf}{1000} \qquad \text{Equation 3-1}$$

P_T is power total (kW); V_L is the line voltage (V); I_L is the line current (A); and Pf is the power factor (dimensionless). The power factor for the inductive cyclo drive motor was not directly measured. However, the motor specification stated a power factor of 0.817 under full load (Sumitomo Drive Technologies). Power factor is known to change with load (Burt, Piao et al., 2008, Sharma, Khan et al., 2013), but for cyclo drives they can remain constant over a range of speeds (Shakweh, 2011). For the pellet mill used, all tests were performed at a constant speed of 1730 rpm. Furthermore, the feed rate of material into the pellet mill was manually controlled to allow for the VFD to consistently draw approximately 10 A or greater which would allow for the full-load amperage to approach 75% of full load (motor name plate specification for full load amperage was 13.1 A). Operation at 75% of full-load and greater, the power factor would be relatively constant (U.S. Department of Energy Motor Challenge, Natural Resources Canada, 2004, Burt, Piao et al., 2008). Thus, a constant power factor of 0.817 was assumed. The mass flow rate of the pellets was quantified by measuring the amount of pellets produced during a 120 second time span with the pellet mill operating at steady state conditions.

3.3.4 Pellet Durability Index (PDI)

Once the pellets had cooled to within ambient temperature, pellet durability was determined in accordance with the ASABE standard S269.4 to simulate the losses of pellets that would occur with handling, storage, and transport. The 5 mm diameter pellets were sieved on a 4.8 mm (12/64 in) screen. A 500 gram sample of the sieved pellets were rotated in a 300 mm (12 in) by 300 mm by 50 mm deep (2 in) box with a 290 mm (9 in) long baffle of 50 mm angle iron for 10 minutes as shown in Figure 3-3. The final pellet durability was determined using Equation 3-2.

$$Durability\ (\%) = \frac{mass\ of\ pellets\ after\ tumbling}{mass\ of\ pellets\ before\ tumbling} \times (100)$$

Equation 3-2

3.3.5 Bulk Density (wet)

The bulk density was performed according to USDA Grain Inspection, Packers and Stockyard (GIPS) adminstration Equipment Handbook Chapter 5 - Test Weight Per Bushel Apparatuses. Pellets were loaded into a funnel that was 50.8 mm (2 inches) above the top of a 1.102 liter (1 US dry quart) kettle. The bottom of the funnel was opened and pellets were loaded into the kettle. The excess pellets above the top rim of the kettle were removed by taking three strokes across the top of the kettle with a 4.76 mm (3/16 inch) rounded edge 305 mm by 44 mm by 10 mm (12 in by 1-3/4 in by 3/8 in) stick. With the tared kettle, the weight of pellets per volume were recorded and the bulk density calculated (wet).

3.3.6 Higher Heating Value (HHV)

Samples of each biomass crop were further ground to pass through a #60 mesh. The samples were processed by the Kentucky Center for Applied Energy Research to perform proximate analysis and heating value assessment. The higher heating value was measured using bomb calorimetry. The percent or fraction of energy used to make the pellets was measured according to Equation 3-3.

$$Percentage\ energy\ in\ pellets\ (\%) = \frac{P_T \times 60\ sec}{\left(\frac{kg\ pellets}{60\ sec}\right) \times HHV} \qquad \text{Equation 3-3}$$

Where:

PT = Total power (kw)

HHV = Higher Heating Value (MJ/kg)

3.3.7 Statistics

SAS (Statistical Analysis System, Cary, NC) v. 9.4 was used for the analysis. The Proc GLM procedure was used to perform the least significant differences (LSD) pairwise multiple comparison between the different moisture contents for each biomass crop.

3.4 Results and Discussion

Particle size had a major impact on pellet quality and throughput. Initial testing with the pellet mill demonstrated that material ground through the 10 mm screen demonstrated matting of the material as it entered the pellet mill and in front of the wheels. Consequently the 10 mm material would not pelletize. The 3 mm material would pelletize; however, with this grinding screen size the majority of the biomass was captured by the filter bag on the cyclone during grinding potentially skewing the sample quality. Consequentially only material that was ground through a 5 mm screen was used for pelletization.

3.4.1 Trends in Pellet Formation

For miscanthus, switchgrass, and wheat straw at a moisture content of 10%, no pellets were produced and only fines passed through the die (Figure 3-4, Figure 3-5, and Figure 3-6). Similar results were observed at a moisture content of 15%, although 60% of the material was pelleted with miscanthus. The viable production of miscanthus, switchgrass, and wheat straw pellets took place at moisture contents above 20% with the greatest percentage of pellets being produced at a moisture content of 25%. The numerically highest pellet production rate was also observed at the highest moisture content for these biomass materials. The improved formation of pelleted biomass as the moisture increased for these biomass types was indicative of the improved binding among the particles. The improved pellet production rate was also indicative of the lubricating aspects of water.

Corn stover exhibited a different trend than the other biomass materials (Figure 3-7). The percentage of pellets produced was equivalent at the 15 and 25% moisture level with the greatest percent of pellets being produced at 20%. For corn stover, the mass flow rate of pellets decreased 44% and 64% as the moisture increased from 15% to 20% and from 15 to 25%, respectively (Figure 3-8). With a flat ring die, (Tumuluru, 2014) achieved pelletization of corn stover at even higher moistures (28 - 38%) than conducted in this study but did not report the rate of production.

Unlike the ring roller die, the flat ring die demonstrated a greater capability of making pellets at a higher moisture content. When used to pelletize alfalfa, the ring roller die was shown to be able to handle moisture contents up to 9 - 12% before plugging of the die occurred (Groesbeck, McKinney et al., 2008). The lower moisture observed with alfalfa was likely due to differences in the composition between the biomass materials.

3.4.2 Effects of Moisture Content on Durability

Moisture content demonstrated a varied effect on pellet durability as well. For miscanthus, switchgrass, and wheat straw, the durability increased with increasing moisture content as shown in Figure 3-4, Figure 3-5, and Figure 3-6. Increasing the moisture content from 20 to 25% improved the pellet durability index by 23%, 17%, and 42% for miscanthus, switchgrass, and wheat straw, respectively. For corn stover pellets, the greatest durability was demonstrated at a 20% moisture content with the 15 and 25% moisture content demonstrating equivalent, but slightly lower PDI (Figure 3-7).

3.4.3 Pellet Mill Throughput

For miscanthus, switchgrass, and corn stover, the increased preconditioned moisture allowed for the improved formation of pellets and inherently augmenting the pellet throughput as shown in Figure 3-8. The increased moisture content allowed for more binding of material to form pellets and also acted as a lubricant with more pellets being produced (Kaliyan and Morey, 2009). For livestock pelletization with a ring roller die, a 5% increase in moisture allowed for the production rate to be increased by 31 to 50% (Moritz, Cramer et al., 2003). For corn stover, the increase binding of the material at 20% and 25% moisture inhibited the rate of pellet formation.

3.4.4 Bulk Density

The bulk density of 5mm loose (uncompressed) material at 10% moisture was 86, 95, 77, and 91 kg/m^3 for miscanthus, switchgrass, wheat straw, and corn stover, respectively. For miscanthus, the 15% and 20% moisture level resulted in comparable values, yet the 25% moisture level resulted in a value that was 27% and 38% higher than the 15% and 20% moisture content values (Figure 3-9). For switchgrass, the increase in moisture content from 20% to 25% elevated bulk density by 29%. For wheat straw, pellets formed at 25% precondition moisture resulted in a bulk density value that was 29% greater than that of pellets created at 20%. When compared to the 15% preconditioned moisture content, increasing the moisture to 20% and 25% for corn stover resulted in 16% and 15% increase in bulk density respectively. The Pellet Fuel Institute

(PFI) standard for bulk density is a minimum of 609 kg/m^3 and was achieved with only corn stover at 20% and 25%. The PFI premium standard of 641 kg/m^3 was not achieved by any of the pelleted material in this study. The lower than expected bulk densities of this study were surmised to be related to the differences in protocol for bulk density. PFI calculated the bulk density using the ASTM E 873 Standard -Test Method for Bulk Density of Densified Particulate Biomass Fuels which takes a 7.08 L (0.25 ft^3) container of densified materials and tapped the container on a solid surface 25 times from a height of 2.54 cm (1 in). The bulk density for corn stover at 25% in this study was 635 kg/m^3 that was comparable to the 618 kg/m^3 measured by (Tumuluru, 2014) with a 60 hz die speed, a die temperature of 110 °C, and a 28% moisture content.

3.4.5 Energy Consumption

The specific energy consumption (kWh/Mg pellets) is indicative of pellet production efficiency (Tabil and Sokhansanj, 1996, Groesbeck, McKinney et al., 2008). For the differing biomass crops in this study, the flat ring die demonstrated a varied energy consumption with corn stover at 15% moisture content demonstrating the lowest specific energy of 101 kWh/Mg, and the highest average of 324 kWh/Mg was recorded with the miscanthus at 15% (Figure 3-10). For miscanthus at 15% moisture content, increasing the moisture content to 20% and 25% resulted in the specific energy reductions of 24% and 42%, respectively. Similar to the response of miscanthus, switchgrass, and wheat straw, pelleted livestock feedstuffs demonstrated increased PDI and reduced specific energy consumption for increased preconditioned moisture contents (Moritz, Cramer et al., 2003). A 5% increase in moisture content resulted in 16 - 19% reduction in specific energy. Corn stover exhibited the opposite trend for moisture content and energy requirements. When compared to corn stover at 15%, increasing the moisture content of corn stover to 20% or 25% resulted in the specific energy consumption being increased by 80% and 168%, respectively.

When feedstuffs were processed, ring roller dies have exhibited production efficiencies of approximately 6 to 37.1 kWh/Mg (Young, Pfost et al., 1963, Skoch, Binder et al., 1983, Gilpin, Herrman et al., 2002, Groesbeck, McKinney et al., 2008). The pelletization of poultry by-product meal showed that increased moisture content resulted in increased operating costs due to higher specific energy requirements. The range for specific energy requirements for the ring roller was determined to be approximately 30 – 80 kWh/Mg for poultry by-product meal (Mohammad, Tawfik et al.).

For alfalfa pelletization, production efficiency was 26 to 33 kWh/Mg. Pellet production efficiency of biomass was stated as varying from 16 to 74 kWh/Mg (Stelte, Sanadi et al., 2012). For different studies, the flat ring die pelletization efficiency is stated to vary from 50 to 150 kWh/Mg for high moisture (28-38%) feedstocks (Tumuluru, Cafferty et al., 2014), 169 kWh/dry Mg for vine shoots (Mediavilla, Fernández et al., 2009), 121 kWh/dry Mg for industrial cork residue (Mediavilla, Fernández et al., 2009), and 166 kWh/dry Mg for pine sawdust (Mediavilla, Fernández et al., 2009). The flat ring die energy consumption increased to 138 – 408 kWh/dry Mg for poplar (Mediavilla, Esteban et al., 2012). Those authors also found that the addition of either lignosulfiante, corn starch, or both reduced the energy consumption to 95 – 123 kWh/dry Mg. The specific energy requirements from this study seemed to fit within the range that has been observed with other studies that had used flat ring die pellet mill, but also indicated that the flat ring die pellet mills may not be as efficient as those with ring roller dies. Stelte, Sanadi et al. (2012) stated that the production rate and energy use are strongly related which explains why the most desirable production efficiency was observed with the corn stover at 15% moisture content as this material possessed the highest pellet mass flow rate.

With ring roller die pellet mill, increases in the specific energy requirements resulted in an increased pellet durability (Tabil and Sokhansanj, 1996). Fahrenholz (2012) demonstrated that an uncertain relationship exists between the PDI and energy consumption as numerous variables could allow for the direct or indirect relationship to exist. Factors such as the addition of lignosulfinate or steam conditioning could increase both PDI and decrease energy consumption; while, adding oil or altering the composition could result in a decrease in both. The inconsistent relationship between the PDI and energy consumption seen by (Fahrenholz, 2012) was observed in this study. Bulk density and energy consumption have been surmised to be related. However, in this study, bulk density and pelletization efficiency were not related.

In relation to the final pelleted product, the fraction of energy that went into producing pellets was also shown to be dependent upon the biomass type and moisture content. Across the different biomass types, the percent of final pellet energy used to make pellets ranged between 2 to 7% which was generally higher than the 1-3% stated by Stelte, Sanadi et al. (2012). Again the higher energy consumption could be an inherent property of the flat ring die.

3.5 Conclusion

For a flat ring die, biomass moisture content was found to be influential in the formation and quality of pellets. For miscanthus, switchgrass, and wheat straw, preconditioned moisture contents less than 20% resulted in the poor (0 – 41%) formation of pellets. At moisture contents of 20% and 25%, the percentage of pellets formed increased to 73 - 96%, and the highest rate of pellet production was observed at the highest (25%) moisture content. Additionally the durability of miscanthus, switchgrass, and wheat straw pellets responded positively to the increasing moisture content with durabilities of 92%, 92% and 96% being observed for the 25% preconditioned moisture content. Corn stover demonstrated a different trend with the moisture content as the percentage of pellets formed (92% and 93%) was similar at the 15% and 25% moisture content level, with a moisture content level of 20 showing the highest percentage pellet formation (97%). Similarly, the PDI values for corn stover were also shown to be the greatest at the 20% precondition moisture content. Yet, the pellet production rate for corn stover decreased with increased moisture. When compared to 15% moisture content, corn stover pellet production rates for 20% and 25% moisture contents were reduced by 60% and 64%, respectively. For different biomass crops at the varied moisture contents, pellet production specific energy was found to range from 101 to 324 kWh/Mg for the flat ring die. The production efficiency of flat ring die formed pellets was surmised to limited by the pellet production rate. When compared to the uncompressed material, pelleted material increased the bulk density by 4.8 - 6.6, 4.5 - 5.8, 4.9 - 6.2, and 6.0 – 7.0 times that of uncompressed material for miscanthus, switchgrass, wheat, and corn stover, respectively.

Figure 3-1 Different Screen Sizes used in the Hammer Mill (from left to right 3 mm, 5mm, and 10 mm)

Figure 3-2 Location of thermocouples on die

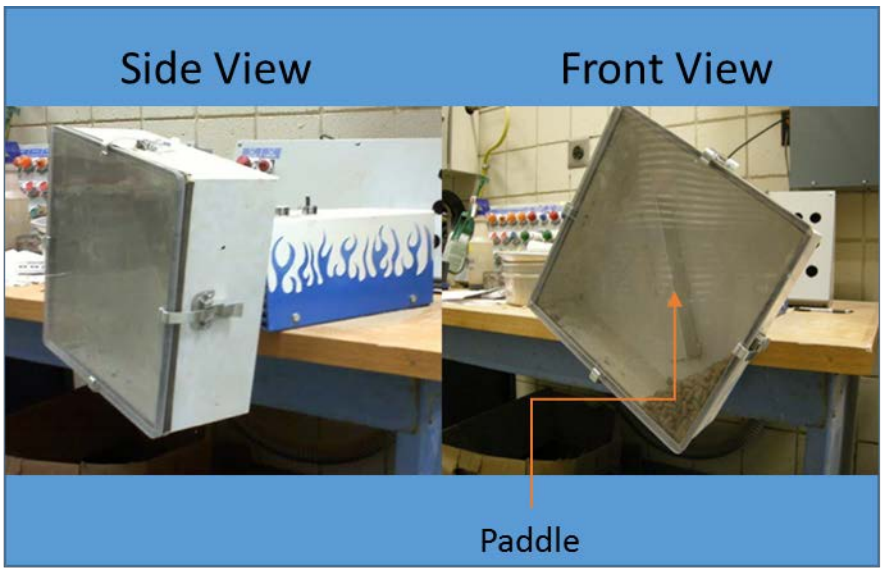


Figure 3-3 Pellet durability index apparatus built to ASAE standard S269.4

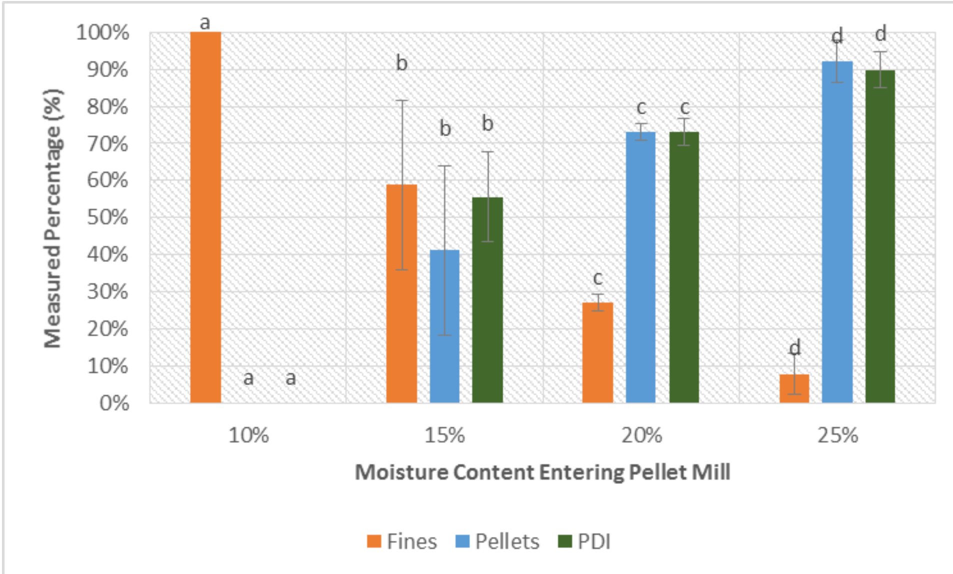


Figure 3-4 Percentage of fines, pellets, and pellet durability index for miscanthus at four moisture contents. [a,b,c,d] Means bearing differing superscripts within a group (Fines, Pellets, PDI) are significantly different ($p < 0.05$)

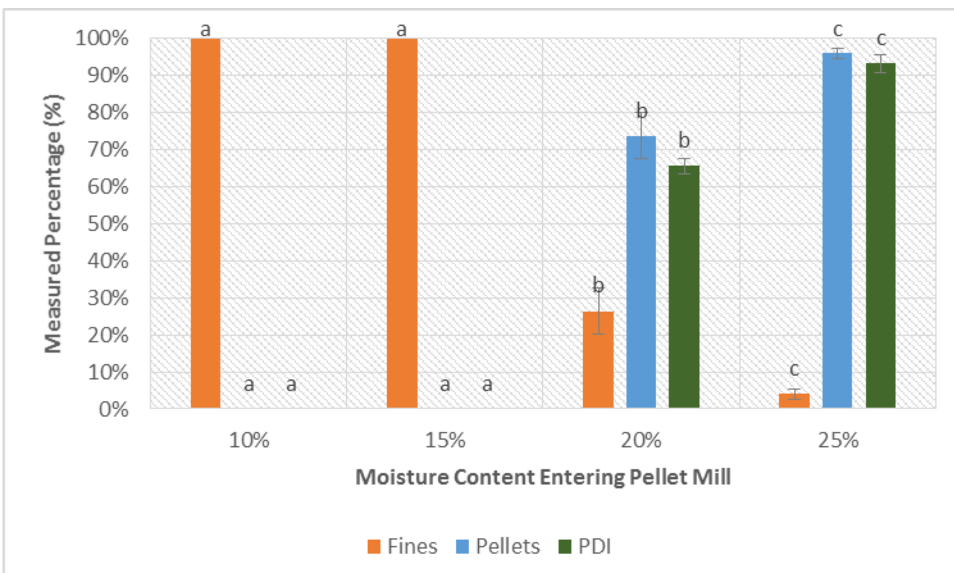


Figure 3-5 Percentage of fines, pellets, and pellet durability index for switchgrass at four moisture contents. Means bearing differing superscripts within a group (Fines, Pellets, PDI) are significantly different ($p < 0.05$)

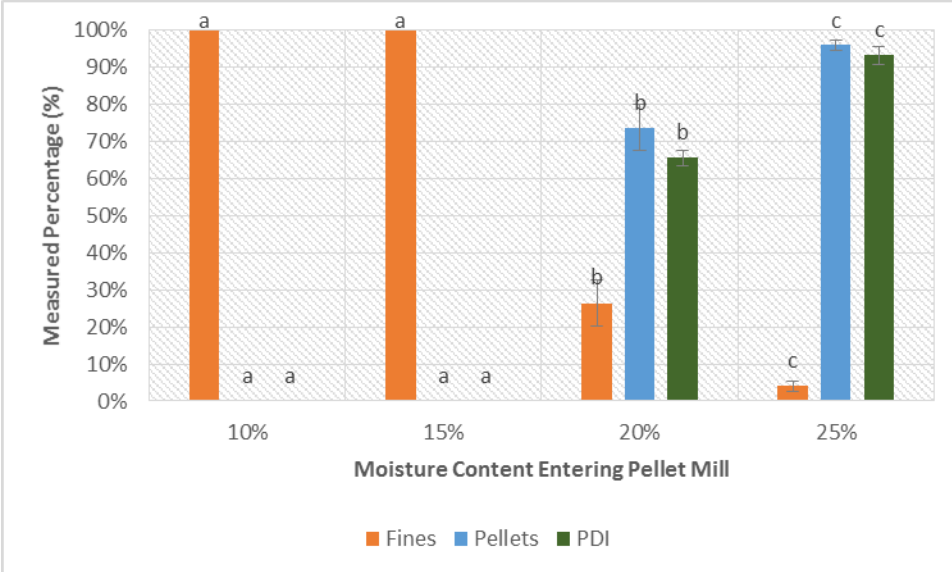


Figure 3-6 Percentage of fines, pellets, and pellet durability index for wheat straw at four moisture contents. [a,b,c,d] Means bearing differing superscripts within a group (Fines, Pellets, PDI) are significantly different ($p < 0.05$)

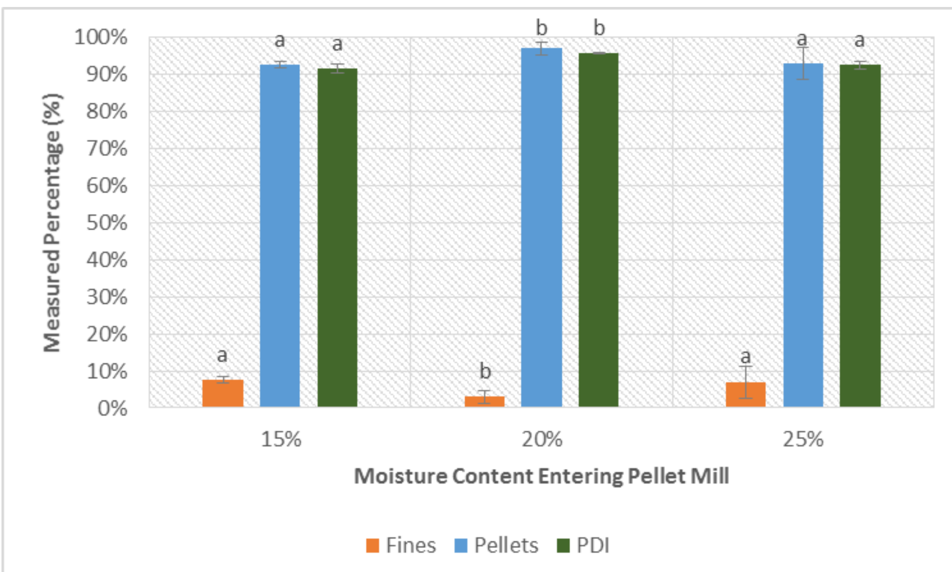


Figure 3-7 Percentage of fines, pellets, and pellet durability index for corn stover at four moisture contents. [a,b,c,d] Means bearing differing superscripts within a group (Fines, Pellets, PDI) are significantly different ($p < 0.05$)

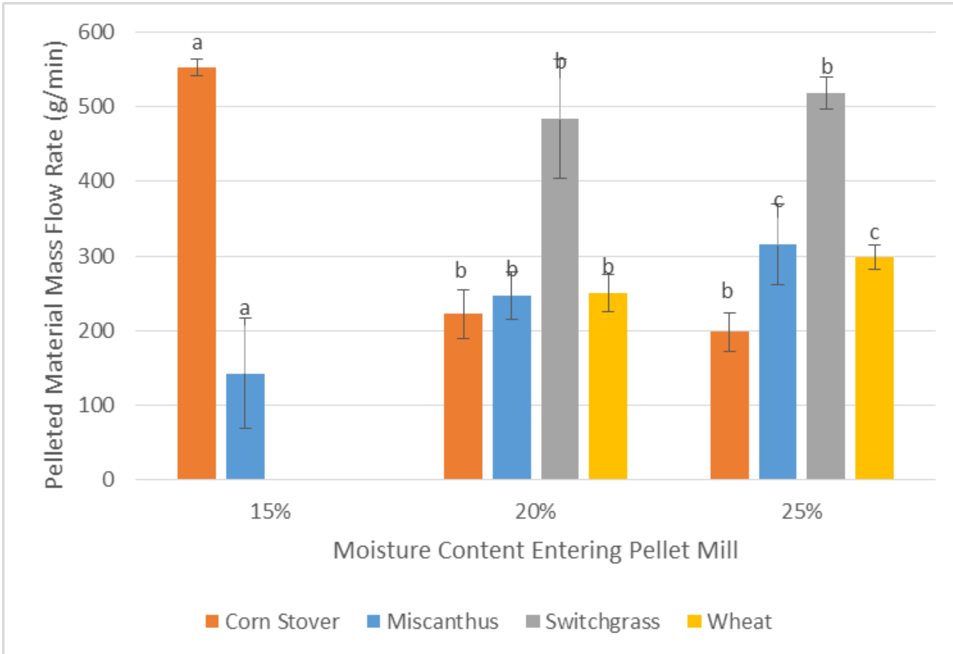


Figure 3-8 Production rate of pellets (g/min) at four moisture content levels for the four biomass feedstocks [a,b,c,] Means bearing differing superscripts within a feedstock are significantly different ($p < 0.05$)

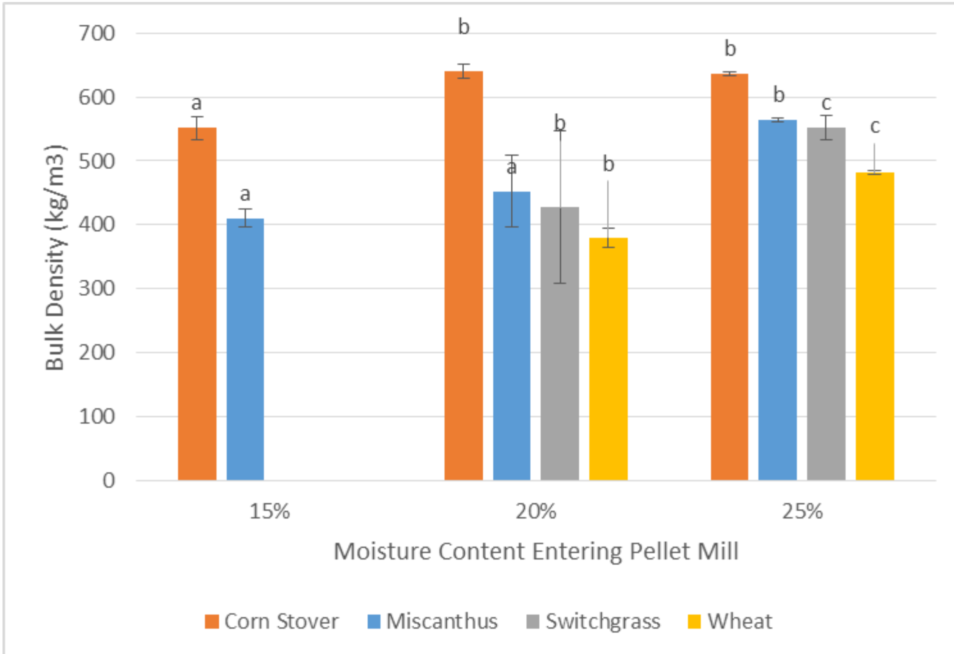


Figure 3-9 Bulk density of four feedstocks at three moisture content levels. [a,b,c,] Means bearing differing superscripts within a feedstock are significantly different ($p < 0.05$)

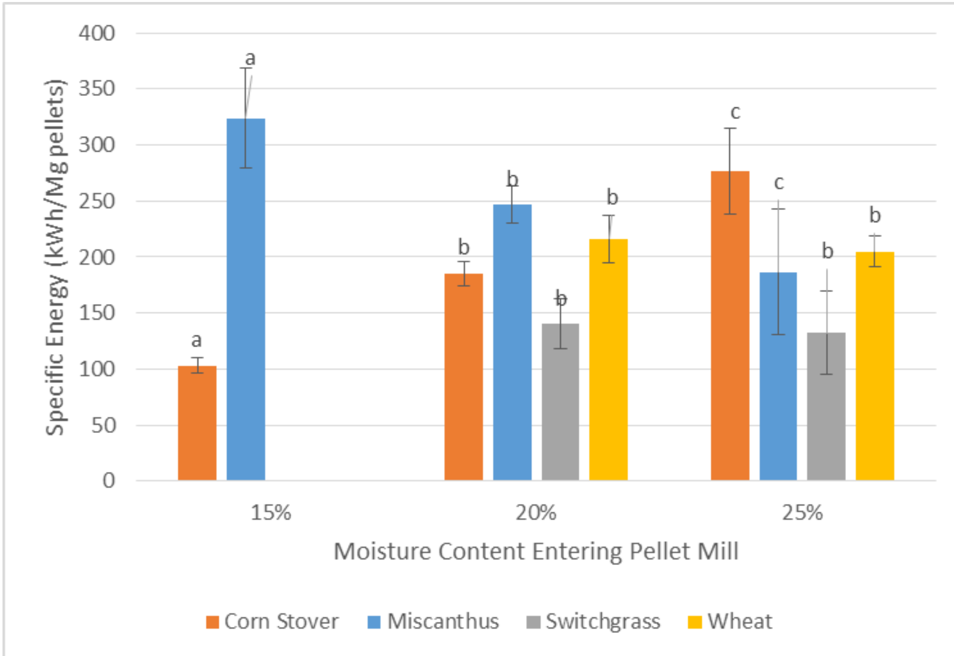


Figure 3-10 Pellet production efficiency measured in the specific energy consumption of the mill per Mg of pellets produced [a,b,c,] Means bearing differing superscripts within a feedstock are significantly different ($p < 0.05$)

CHAPTER 4: OBJECTIVE 2: THE EFFECT OF ALKALINE HYDROGEN PEROXIDE SPRAY PRETREATMENT ON LIGNOCELLULOSIC MATERIAL

4.1 Summary

On-farm biobutanol production would require pretreatment to improve the digestibility of biomass. Many differing types of pretreatment exist, but the goal of this research was to use one that could be easily, safely, and effectively utilized on-farm. Thus, oxidative delignification of wheat straw, corn stover, miscanthus, and switchgrass using alkaline hydrogen peroxide (AHP) spray was analyzed. AHP is a process that can be performed at ambient temperature and pressure making it attractive for potential on-farm use. For each biomass crop, 300 g of material ground through a 5 mm screen received no treatment (control), water, 5% NaOH, 5% NaOH with 2% H_2O_2, 5% NaOH with 5% H_2O_2, 10% NaOH, 10% NaOH with 2% H_2O_2, and 10% NaOH with 5% H_2O_2 The compositional changes were measured using both detergent fiber analysis for potential feed value and compositional analysis based on the National Renewable Energy Laboratory protocol.

The AHP mixture was prepared by grinding small square bales of miscanthus, switchgrass, corn stover, and wheat straw with a hammer mill through a 5 mm screen. Water, sodium hydroxide, and hydrogen peroxide were sprayed and mixed into the biomass sequentially to achieve a final product with a nominal dry matter content of 65% DM. Three levels of H_2O_2, two levels of NaOH, and a control were analyzed in this study. After mixing, the treated biomass (300 g) was placed in air tight containers for storage and subsequent sampling. the results demonstrated that AHP spray can be a beneficial and effective means of biomass pretreatment.

4.2 Introduction

As a potential renewable energy source, lignocellulosic material (consisting of either crop residues or dedicated biomass crops) is desirable since the material is widely available and manifests a limited impact upon the food supply. The transformation of this feedstock into a useable fuel for transportation involves the breakdown of the complex structures into monomers such as glucose and xylose using enzymatic hydrolysis. After the enzymatic hydrolysis, fermentation allows for the formation of biofuels such as ethanol and biobutanol. The formation of sugar for the fermentation step is limited by the hemicellulose and lignin that are naturally present within biomass. To reduce the deleterious effect that hemicellulose and lignin can have on sugar yield, biomass material is typically pretreated using either physical, chemical, physico-chemical, and/or biological means. With each methodology of pretreatment there are inherent tradeoffs that must be considered. The cost of the chemicals or machinery, potential byproducts formed that could inhibit downstream fermentation such as salts, energy intensiveness, and hazards associated with handling the product. One form of pretreatment that possesses many desirable qualities is oxidative delignification using alkaline hydrogen peroxide (AHP). AHP partially solubilizes hemicelluloses, lignin, and silica by using a combination of NaOH and H_2O_2 to improve subsequent enzymatic digestion. AHP has been conducted primarily using two different methodologies. One methodology developed by Gould (1984) uses a low solids loading (1 - 2% (w/v Distilled H_2O)) with high concentration biomass relatively high concentration H_2O_2 of 0.5 g H_2O_2/g biomass. While, the other methodology uses an AHP spray and mixing for a high solids (“dry”, ~65% DM) pretreatment with a low concentration of NaOH (5% w/w Dry Matter (Dm) biomass) and H_2O_2 (2% w/w DM biomass). The AHP spray pretreatment of the biomass material used in this study was based off of the large scale AHP spray treatment of wheat straw for use in livestock operations performed by Cameron, Fahey Jr et al. (1990) and Willms, Berger et al. (1991). The spray treatment requires less water for pretreatment than the typical method of soaking the biomass in AHP. The spray AHP pretreatment has been demonstrated to allow for low quality spray AHP forages to perform similar to higher quality forages with respect to animal performance characteristics (Cameron, 1990, Willms, Berger et al., 1991). The use of water is especially important when considering the final fuel produced. For fermentation, ethanol production uses 11.4 – 15.1 L water per L of ethanol produced (3 - 4 gallons water per gallon of ethanol) and biobutanol which forms acetone, butanol, and ethanol (ABE) would require substantially more water at an estimated 17 L of water per L of ABE (45.4 gallons per gallon ABE) (Xue, Zhao et al., 2014). The goal with this trial was to not only apply less water for the initial pretreatment step but also less NaOH. Washing will still be required and will likely be the largest user of water. This study will seek to analyze and compare the response of

AHP spray and alkaline spray for pretreatment and particle sizes of 2 and 5 mm for the enzymatic hydrolysis.

4.3 Materials and Methods

Samples of Alamo switchgrass (*Panicum virgatum*) and miscanthus (*Miscanthus giganteus*) were harvested and baled at the University of Kentucky North Farm in Lexington, Kentucky in March 2013. Corn stover and wheat straw samples were collected from the University of Kentucky C. Oran Little Research Unit, Versailles, Kentucky in June and September of 2013, respectively. A No. 20 Hammer mill (C.S. Bell Co., Tiffin, OH) was used to grind the biomass through a 5 mm screen and collected using a cyclone system (Cincinnati Fan and Ventilation Inc., Mason, OH).

4.3.1 AHP Pretreatment

Three hundred grams of the ground biomass were spray treated with their respective treatments as shown in Figure 4-1: control (no treatment or raw); water (treated with equivalent amount of water and washed); 5% NaOH (w/w dry matter (DM) biomass); 5% NaOH (w/w DM biomass) and 2% H_2O_2 (w/w DM biomass); 5% NaOH (w/w DM biomass) and 5% H_2O_2 (w/w DM biomass); 10% NaOH (w/w dry matter (DM) biomass); 10% NaOH (w/w DM biomass) and 2% H_2O_2 (w/w DM biomass); and 10% NaOH (w/w DM biomass) and 5% H_2O_2 (w/w DM biomass). The NaOH (Fisher Chemical, Bridgewater, NJ) for the required pretreatments was diluted in 75 ml of water and sprayed onto the biomass as it was being mixed with a plastic bottle sprayer. Immediately sequential to this the desired amount of 30% H_2O_2 (MacNan Enterprises, Birmingham, AL) was diluted with water until the final moisture content of each treatment was approximately 35% and sprayed on with a plastic bottle sprayer. The biomass materials were mixed for 5 minutes. Upon the completion of mixing, the treated biomass was placed into an air tight PVC pipe (0.1 m in diameter and 0.31 m in length) that was sealed at each end. The biomass material was allowed to react within the container for 7 days.

Following the pretreatment, the pH of the samples was measured according to Mishra, Chaturvedi et al. (2000) with 10 g of lignocellulosic material being added to 50 ml of water with manual mixing of the sample using a stir rod. After the pH measurement, the biomass was washed with 60 ml of DI water per gram of biomass through cheese cloth. The biomass was dried at 45 °C for 72 hours and placed into a storage container at room temperature until use.

4.3.2 Detergent Fiber Analysis

The detergent fiber analysis procedure was performed both prior and subsequent to washing for the different biomass types and pretreatments. The composition of the biomass was determined using the Ankom 200 (Ankom, Macedon, NY) Filter Bag Technique for Neutral Detergent Fiber (NDF), Acid Detergent Fiber (ADF), and Acid Detergent Lignin (ADL) in a daisy incubator. Before analysis, the biomass material was further ground to 1 mm using a Wiley knife mill (Thomas Scientific, Swedesboro, NJ). For this analysis, 0.5 g of each sample was loaded into pre-weighed filter bags. Measurements were serially taken as listed: NDF, ADF, and ADL following the Ankom procedure.

The NDF solution (18.61 g ethylenediaminetetraacetic disodium salt (dehydrate), 6.81 g sodium borate, 4.56 g sodium phosphate dibasic (anhydrous), and 10.0 ml triethylene glycol per one liter distilled water (DI) was combined with 4 ml of alpha-amylase and the filter bags containing 0.5 $\pm$ 0.05 g of biomass were agitated for 75 minutes at 100 ± 0.5 °C and a pressure of 69 - 172 kPa (10 - 25 psi). Sodium sulphite was added at a concentration of 1g/100ml NDF solution. The NDF solution was drained and 90 °C DI water and 4 ml of alpha-amylase was used to agitate the filter bags containing biomass for two 5 minute cycles. One final agitation was performed with only 90 °C DI water. The DI water was drained and superfluous water was removed from the bags by squeezing the bags. The bags were completely submerged in acetone for 3 - 5 minutes, placed upon a rack and air dried. Upon the complete evaporation of the acetone, the filter bags were placed into a 100 °C oven for 2 - 4 hours. The weight after drying was taken and used in Equation 4-1.

$$\%\,NDF = \frac{100\ x\ (w_3 - (w_1\ x\ c_1))}{w_2\ x\ DM} \qquad \text{Equation 4-1}$$

Where:

w_1 = Empty bag weight

w_2 = Sample weight
w_3 = Oven dried weight of bag and sample after NDF analysis
c_1 = Blank bag correction factor (Oven dried blank bag weight/original blank bag weight)

The ADF solution (20g cetyl trimethylammonium bromide (CTAB) per 1L 1N H_2SO_4) was agitated with the filter bags for 1 hour. After agitation the filter bags were rinsed with 70 - 90 °C DI water for a minimum of 3 rinse cycles with a duration of 5 minutes per cycle. Similar to the NDF procedure, the bags were completely submerged in acetone for 3 - 5 minutes, placed upon a rack and air dried. After complete evaporation of the acetone, the filter bags were placed into an oven at 100 °C for 2 - 4 hours. The weight after drying was taken and used in Equation 4-2 to calculate the percent ADF.

$$\% \, ADF = \frac{100 \; x \; (w_3 - (w_1 \; x \; c_1))}{w_2 \; x \; DM} \qquad \text{Equation 4-2}$$

Where:

w_1 = Empty bag weight
w_2 = Sample weight
w_3 = Oven dried weight of bag and sample after ADF analysis
c_1 = Blank bag correction factor (Oven dried blank bag weight after ADF/original blank bag weight)

After the completion of the ADF assay, the ADL assay was performed by placing the filter bags in 500 ml of 72% (w/w) H_2SO_4 for 3 hours and rinsed until the pH was neutral. Once again, the bags were soaked in acetone for 3 - 5 minutes, air dried, and then dried in an oven at 100 °C. The weight was taken after it had cooled to room temperature in a desiccator bag and the calculation is shown in Equation 4-3.

$$\% \, ADL = \frac{100 \; x \; (w_3 - (w_1 \; x \; c_1))}{w_2 \; x \; DM} \qquad \text{Equation 4-3}$$

Where:

w_1 = Empty bag weight
w_2 = Sample weight
w_3 = Oven dried weight of bag and sample after ADL analysis
c_1 = Blank bag correction factor (Oven dried blank bag weight after ADL/original blank bag weight)

The NDF, ADF, and ADL values obtained were used to predict hemicellulose and cellulose. Hemicellulose was calculated as the difference in NDF and ADF. Cellulose was calculated as ADF minus the ADL.

4.3.3 NREL National Renewable Energy Laboratory Compositional Analysis Procedure

Following washing, cellulose, hemicellulose, ash, and lignin were also determined using the National Renewable Energy Laboratory (NREL) procedure "Determination of Structural Carbohydrates and Lignin in Biomass" with the values for cellulose and hemicellulose being derived from glucose and xylose, respectively (Sluiter, Hames et al., 2004). Glucose and xylose were measured using an UltiMate 3000 Standard LC Systems (Dionex, Sunnyvale, CA) with a Bio-Rad Aminex HPX-87H column at 50 °C being used for the separation and a flow rate of 400 µl/min. The mobile phase was 5 mM H_2SO_4, and concentrations of the sugar monomers was determined using a Shodex RI-101 (Showa Denko America, Inc., New York, NY) refractive index detector with Chromeleon 7.1 software processed the chromatographs.

4.3.4 Cellulase Activity

The cellulase used in this study was generously provided by Alltech (Alltech, Nicholasville, KY). The NREL procedure LAP 006 "Measurement of Cellulase Activity" was used to determine the filter paper units (FPU) per ml of the enzyme (Adney and Baker, 1996). For this analysis, a 1 cm x 6 cm strip of number 2 filter paper was rolled up and loaded into a glass tube. Another set of tubes was prepared without the filter paper and was used for either enzyme blanks or for the glucose curve that had to be developed. Into each of the tubes 1 ml of sodium acetate was added. The 2.255 g lyophilized Alltech enzyme powder was added to 25 ml of 0.01 M Na-citrate buffer to create the stock solution for the enzyme analysis.

4.3.5 Enzyme Hydrolysis

Enzyme hydrolysis was conducted in 50 ml centrifuge tubes with 1 g DM of each pretreated biomass being loaded into each tube. The biomass solids loading was 2% in a 0.01 M Na-Citrate buffer (pH 4.8) at 50 °C. Two different enzyme concentrations were compared: 15 FPU/g solids and 60 FPU/g solid. Beta-glucosidase was added at a concentration of 2 cellobiase unit (CBU) per FPU. Samples were agitated at 190 rpm using an Innova 4200 Incubator Shaker (New Brunswick Scientific, Edison, NJ) for a total of 72 hours. Aliquots of 1 ml were taken at hour 6, 12, 24, 48, and 72 hours and loaded into 1.5 ml microcentrifuge tubes for sugar analysis. The microcentrifuge tube samples were placed into a 95 °C water bath for 5 minutes to stop enzyme activity. Afterwards, samples were vortexed and glucose concentration was immediately determined using the YSI 2900 Biochemical Analyzer (Xylem Inc. Rye Brook, NY) without being frozen or stored. Cellulose conversion % as a result of hydrolysis was defined as glucose

$$\text{Cellose conversion \%} = \frac{[glucose_{e+}] - [glucose_{e-}]\ x\ 0.9\ x\ 100)}{respective\ pretreatment\ NREL\ cellulose} \qquad \text{Equation 4-4}$$

Where:

$Glucose_{e+}$ = Hydrolysis performed with enzyme

$Glucose_{e-}$ = Hydrolysis conditions replicated but without enzyme

Respective pretreatment NREL cellulose = cellulose composition after washing of 5% NaOH, 5% NaOH with 2% H_2O_2, 5% NaOH with 5% H_2O_2, 10% NaOH, 10% NaOH with 2% H_2O_2, and 10% NaOH with 5% H_2O_2

4.3.6 Statistics

For this completely randomized experimental design, SAS (Statistical Analysis System, Cary, NC) v. 9.4 was used to ascertain the differences in cellulose, hemicellulose, lignin, and ash by utilizing PROC GLM. The control and wet were considered separately with a 2 (NaOH-5% and 10%) by 3 (H_2O_2-0%, 2%, and 5%) treatment structure. The correlation between the dietary fiber and detergent fiber analysis was conducted using PROC CORR and PROC REG.

4.4 Results

4.4.1 Effect of Pretreatment

The pH of the initially applied chemicals were all greater than 11.5. Upon removal from the limited air pretreatment chambers (PVC pipe with caps on the end).

The pH was also measured after seven days of pretreatment to ascertain the differences between the various treatment levels. Across the four biomass types: miscanthus (Figure 4-2), corn stover (Figure 4-3), switchgrass (Figure 4-4), and wheat straw (Figure 4-5), all but one of the treatments possessed a significantly different ($p < 0.0073$) pH from the positive control that received only water. The exception to this was corn stover with 5% NaOH and 5% H_2O_2 treatment which was not significantly different ($p = 0.0502$) from the positive control. Within the specific feedstocks, the pH of the biomass was largely influenced by the level of NaOH. As expected, the 10% NaOH pretreated biomass had a significantly higher pH for all biomass types then the 5% NaOH pretreated biomass.

Following washing, the dry matter content was determined in orderto quantify the dry matter lost due to pretreatment and washing (Figure 4-6). Across the biomass types, the dry matter losses were found to range from 7 to 31% with the lowest numerical losses occurring with water pretreated biomass. Additionally, the highest DM losses appeared to be associated with the highest concentration of NaOH and to a lesser extent higher concentrations of H_2O_2 for all the biomass materials.

4.4.2 Detergent Fiber Composition

The composition of the biomass materials was measured after pretreatment and after washing to characterize the effect of pretreatment and washing on the material. This also allowed for these data to be compared with prior trials that had been performed using detergent fiber analysis.

4.4.2.1 Miscanthus

Prior to washing, miscanthus pretreated with water was not significantly different from the control while all of the chemical pretreatments resulted in a 20-35% decline in NDF (Figure 4-7). For ADF, only the 5% NaOH with 2% H_2O_2 and 10% NaOH with 2% H_2O_2 resulted in a significant decrease (27%) relative to the control. The water pretreated material manifested a 49% increase for ADL; while, 5% NaOH with 2% H_2O_2 and all the pretreatments with 10% NaOH regardless of H_2O_2 resulted in 17 - 36% decrease in ADL when compared to the control. With respect to the control, all the chemical pretreatments exhibited a 30 - 57% decrease in hemicellulose. For cellulose, the control and water treatment were similar. None of the chemical treatments were different from the water pretreatment in terms of cellulose content.

After washing (Figure 4-11), the miscanthus demonstrated varied results. For the NDF, the water pretreated material demonstrated a 9% increase with respect to the control ($p < 0.05$). When compared to the control, the ADF for all the pretreatments including water was found to be significantly higher ($p < 0.05$) by 5-12%. The ADL values demonstrated that only 10% NaOH and 10% NaOH with 5% H_2O_2 treated materials were significantly decreased, by 34%, when compared to the control. Furthermore, hemicellulose was decreased by 31 - 52% ($p < 0.05$) for all the chemical pretreatments with 10% with 2% H_2O_2 and 10% with 5% H_2O_2 exhibiting the greatest decrease across the treatments. Similar to ADF, the cellulose values showed that all the pretreated material had a significantly higher cellulose content ($p < 0.05$) than the control, but not significantly different from each other.

4.4.2.2 Corn Stover

Prior to washing, corn stover pretreated with water manifested an elevated (13%, 125%, and 15%) value for ADF, ADL, and cellulose, respectively with a 12% decreased hemicellulose content compared to the control treatment (Figure 4-8). For the chemical pretreatments (NaOH and AHP), NDF declined 20 - 33% when compared to the control. ADL values for the chemical pretreatments were not significantly different from the control with the exception of the 10% NaOH and 10 NaOH with 2% H_2O_2 pretreatments which were increased by 23% and 63%. Hemicellulose decreased by 35 - 40% and 59 - 63% for the 5% NaOH across the differing H_2O_2 levels and 10% NaOH across the differing H_2O_2 levels. For cellulose only the 10% NaOH, 10% NaOH with 2% H_2O_2, and 10% NaOH with 5% H_2O_2 were decreased relative to the control by 4 - 8%.

After washing (Figure 4-12), the NDF for all the different pretreatment methods was determined to be equivalent to the control. For ADF, the control manifested the lowest value for ADF (46%) with the other pretreatments being 19 - 26% higher than the control. Concerning ADL, the washed sample was ($p < 0.05$) greater than the control by 76%; nonetheless, the chemical pretreatments were found to be equivalent to the values obtained for the control. Hemicellulose manifested similarities between the control, water, and 5% NaOH sample. The greatest decrease (51% and 47%) in hemicellulose was observed with the 10% NaOH with 2% H_2O_2 and 10% NaOH with 2% H_2O_2 and the remaining pretreatments decreased the hemicellulose by 30-34%. The water pretreated sample demonstrated a 10% increase in cellulose propotion when compared to the control. Samples treated with 5% alkaline pretreatments regardless of hydroxide treatment were found to be similar and increase the by 18 to 20% when compared to the control. Regardless of hydroxide addition levels, the 10% alkaline pretreatment also demonstrated a statistically equivalent 27 - 31% increase in cellulose when compared to the control.

4.4.2.3 Switchgrass

Prior to washing, the NDF for the control and water pretreatment were similar, but the chemical pretreatments had a significant decline of 11 – 38% when compared to the control (Figure 4-9). For ADF, a mixed result was observed with some chemical pretreatments similar to the control, some increased relative to the control, and the material treated with 10% NaOH significantly decreased from the control. ADL demonstrated that 5% NaOH with 5% H_2O_2 and 10% NaOH across all the level of H_2O_2 decreased relative to the control by 41 to 53%. When compared to the control, hemicellulose decreased for all the chemical pretreatments by 17 to 56%. Cellulose also exhibited a varied response to pretreatment as 5% NaOH increased (9%) while the 10% NaOH with all the H_2O_2 levels decreased.

After washing, the NDF for water pretreatment increased by 2% with respect to the control yet significantly decreased by 8 - 16% for the chemical pretreatments (Figure 4-13). ADF values demonstrated that the control and water pretreatment were equivalent, but the chemical pretreatments resulted in an increase (8 – 11%) in ADF when compared to the control. For ADL, the control, water, and 5% NaOH were demonstrated to not be significantly different. When compared to the control, the ADL values were shown to decrease by 15%, 16%, 27%, 36%, and 44% for 5% NaOH with 2% H_2O_2, 5% NaOH with 5% H_2O_2, 10% NaOH, 10% NaOH with 2% H_2O_2, and 10% NaOH with 5% H_2O_2 respectively. For hemicellulose, the water treatment increased ADL by 2% relative to the control. The chemical pretreatments resulted in decreased (23-49%) hemicellulose when compared to the control with the greatest decrease occurring with 10% NaOH with 2% H_2O_2 and 10% NaOH with 5% H_2O_2. Concerning cellulose, the control and washed sample were not significantly different. Regardless of hydrogen peroxide levels, the 5% alkaline treatment resulted in increased cellulose by 13 to 14 %. While, 10% NaOH, 10% NaOH with 2% H_2O_2, and 10% NaOH with 5% H_2O_2 resulted in elevated cellulose when compared to the control by 19%, 21%, and 21%

4.4.2.4 Wheat Straw

Prior to washing, the NDF for all the chemical pretreatments manifested a decreased (6 - 34%) composition relative to the control (Figure 4-10). Large decreases in NDF were observed for wheat straw pretreated with 10% NaOH at all H_2O_2 levels. ADF increased (5%) relative to the control for 5% NaOH and decreased (20 - 23%) for 10% NaOH across the different H_2O_2 concentrations. ADL was shown to increase only when pretreated with 5% NaOH. Hemicellulose decreased by 18 - 53% with the chemical pretreatments. Cellulose exhibited a 4% decrease for 5% NaOH with 2% H_2O_2 and 16 - 18% decrease for 10% NaOH across the different H_2O_2 concentrations.

Following washing (Figure 4-14), NDF was shown to be increase with water pretreatment compared to the control and decrease for all of the chemical pretreatments relative to the control. When compared to the control, the NDF values for the water pretreatment demonstrated a 4% increase while the other remaining pretreatments exhibited a decrease of 3-8%. The control and the water samples were not significantly different for ADF; nonetheless, the chemical pretreatments all resulted in values that were 8-12% higher than that of the control. ADL values demonstrated that the chemical pretreatments were not significantly different from the control with the exception of 10% NaOH with 2% H_2O_2 and 10% NaOH with 5% H_2O_2 which were decreased by 26 and 42%, respectively. For water, hemicellulose values were increased by 8% with respect to the control. For the chemical pretreatments the hemicellulose was decreased by 17 - 35% with the greatest decrease observed for 10% alkali pretreatment. Cellulose values were not significantly different for the control, water, and 5% NaOH. The remainder of pretreatments were increased by 12 – 21% with respect to the control.

4.4.3 NREL Composition

The composition of the biomass material was determined following the NREL procedure (4.3.3) after the material was pretreated and washed. In the case of the control, the material was washed as in the chemical pretreatments, but no water was added during the pretreatment.

4.4.3.1 Miscanthus

Acid insoluble lignin (AIL), acid soluble lignin (ASL), and cellulose demonstrated ($p > 0.05$) no significant differences due to pretreatment (Figure 4-15). For ash, 5% NaOH with 2% H_2O_2 demonstrated the lowest value when compared to all the other samples with the exception of 5% NaOH. For hemicellulose, no significant difference existed between the differing pretreatment methods and the control.

4.4.3.2 Corn Stover

For the various pretreatments, AIL, ASL, ash, and cellulose were all statistically similar (Figure 4-16). For hemicellulose the control and water were determined to be equivalent; nonetheless, 5% NaOH and 5% NaOH with H_2O_2 were shown to have increased hemicellulose by 33% when compared to the control.

4.4.3.3 Switchgrass

For AIL, ASL, ash, and cellulose, no significant difference existed among the pretreatments (Figure 4-17). Furthermore, hemicellulose values for the pretreatments were determined to not be significantly different from the control.

4.4.3.4 Wheat Straw

AIL, ASL, ash, and cellulose demonstrated no significant difference among the pretreatments (Figure 4-18). For hemicellulose, the control was also found to not be significantly different from the control but differences among pretreatments existed.

4.4.4 Comparison Between NREL and Detergent Fiber Composition

The correlation between NREL and the detergent fiber analysis was determined to ascertain how changes in each would be related. For cellulose, the correlation across the different biomass materials was $r = 0.459$ ($p = 0.081$) (Figure 4-19). For hemicellulose and lignin, the correlation across the differing biomass types between the two methods was $r = 0.0863$ ($p = 0.639$) and $r = 0.0734$ ($p < 0.0001$) respectively (Figure 4-20 and Figure 4-21). The regression data for cellulose, hemicellulose, lignin was characterized in Table 4-1.

4.4.5 *Enzyme Hydrolysis*

4.4.5.1 *Miscanthus*

Figure 4-22 summarizes the cellulose conversion from pretreated and washed miscanthus at two particle sizes (2 and 5 mm) and two enzyme loadings (15 and 60 FPU/g DM). Across the differing particle sizes, the 60 FPU/g substrate manifested a 14% higher ($p < 0.001$) glucose yield than that of the 15 FPU/g substrate. For the 2 mm material, cellulose conversion was increased by 17% with the higher enzyme concentration (60 FPU/g substrate); while, the 5 mm only saw a 10% increase due to the higher concentration of enzyme.

With regard to particle size, the 5 mm particles manifested a 6% lower cellulose conversion when compared to the 2 mm material. For the 15 FPU/g substrate enzyme loading, the 2 and 5 mm glucose yields were not significantly different yet the highest yield was exhibited by the 60 FPU/g substrate and smallest particle size (2 mm).

For the differing particle sizes and enzyme concentrations, the control and water pretreated samples demonstrated equivalent ($p \leq 0.05$) values. For the samples that had been treated with similar amount of NaOH, the addition of hydrogen peroxide was found to not significantly increase the conversion efficiency of miscanthus with the exception of 10% NaOH with 2% H_2O_2 with a 2 mm particle size and enzyme loading of 60 FPU/g which had the highest conversion efficiency for miscanthus. Although, the standard deviation of the results were also the highest.

4.4.5.2 *Corn Stover*

Across the particle sizes, 60 FPU/g allowed for 16% higher cellulose conversion than the 15 FPU/g (Figure 4-23). Within the 5 mm and 2 mm particle size, the higher enzyme concentration resulted in 18% and 15% more cellulose conversion. The influence of particle size on cellulose conversion showed that the 5 mm material allowed for 7% more conversion than the 2 mm material ($p < 0.05$).

Within the particle size and enzyme concentration, at a 5% NaOH pretreatment level, the addition of H_2O_2 did not significantly improve the cellulose conversion (Figure 4-23). A mixed effect was observed at the 10% NaOH with equivalent AHP pretreatment resulting in 9% increase (2% AHP with 15 FPU/g at 5 mm); decreased 13 to 15% (for all

5% AHP) and 4% (2% AHP with 60 FPU/g at 5 mm); and with the remainder of samples exhibiting no change.

4.4.5.3 Switchgrass

Across the different particle sizes, the 60 FPU/g substrate manifested a 17% higher cellulose conversion when compared to the 15 FPU/g substrate (

Figure 4-24). For the 2 mm material, the 60 FPU/g substrate resulted in a 13% higher conversion and 20% higher conversion for the 5 mm when compared to the 15 FPU/g substrate. When compared to the 2 mm, the 5 mm material displayed a 4% lower mean for cellulose conversion.

The control and water pretreated material manifested equivalent cellulose conversion, but the chemical pretreatment resulted in greater conversions as shown in

Figure 4-24. The numerically highest cellulose conversion occurred with the 2 mm material at 60 FPU/g substrate and 10% NaOH with 2% H_2O_2 pretreatment. At the highest NaOH loading level, the 5% addition of H_2O_2 demonstrated a decrease of 10%, 11%, and 11% for 2 mm with 15 FPU/g, 2 mm with 60 FPU/g, and 5 mm with 15 FPU/g, respectively. When compared to the 5% NaOH level, the 2% and 5% H_2O_2 additions resulted in a decrease of cellulose conversion by 12 to 23% within their respective enzyme and particle sizes.

4.4.5.4 Wheat Straw

Across the various particle sizes, the 60 FPU/g substrate demonstrated 20% more conversion than 15 FPU/g substrate (Figure 4-25). Within particle size, the 60 FPU/g was 18% and 22% greater than 15FPU/g for 2 mm and 5 mm material. Concerning the effect of particle size, the 5 mm material displayed 4% lower conversion than the 2 mm material.

When compared to the alkaline treatment only, the addition of hydrogen peroxide demonstrated a varied effect with increases, decreases, and no change being observed (Figure 4-25). When compared to the 5% NaOH pretreatment, the 5% NaOH with 2%H_2O_2 at 15 FPU/g substrate allowed for 10% and 15% increase in cellulose conversion for 2 mm and 5 mm material, respectively. When compared to the 10% NaOH pretreatment, the AHP pretreatments (2% and 5%) at 60 FPU/g demonstrated a 6 to 13%

decrease in conversion for the different particle sizes. Additionally, the 15 FPU/g resulted in a 12% decrease for the 2 mm 5% AHP pretreated material and a 7% decrease for the 5 mm 2% AHP pretreatment when compared to the respective 10% NaOH pretreatments.

4.5 Discussion

4.5.1 Effect of Pretreatment

Similar to the other trials that had used AHP spray pretreatment (Atwell, 1990, Cecava, Merchen et al., 1990, Cameron, Cameron et al., 1991, Willms, Berger et al., 1991, Chaudhry and Miller, 1996), this experiment did not adjust the pH during pretreatment. Without the corrections, the pH for AHP tends to drift downward with the formation of acetic acid by the biomass and hydrogen peroxide breakdown (Williams, 2014). Furthermore, pH corrections during pretreatment have been demonstrated to allow for greater enzyme hydrolysis yield, but this can be remediated by allowing the pretreatment reaction time to increase (Banerjee, Car et al., 2011). This study differs from most of the soaking AHP pretreatments in that instead of 24 - 48 hours being used for the reaction time, a 7 day pretreatment was used. When performed at farm scale, AHP pretreatment would not be adjusted for pH during pretreatment and long pretreatment times would be feasible.

Upon completion of the 7 day pretreatment, the addition of H_2O_2 was found to not significantly alter the pH when compared to the samples with similar alkaline loading with the exception of miscanthus at the 10% NaOH level. Gray (2013) used a hydrogen peroxide solution with a pH of 3.337, and the pH of the acetonitrile stabilized hydrogen peroxide used in this analysis was 2.204. Gray (2013) did not report the pH after pretreatment, but a much higher concentration of NaOH (40 g/g DM) and H_2O_2 (0.5 g/g DM) was used compared to this study with a NaOH loading of 0.05 g/gDM or 0.1g/g DM and 0 to 0.05g H_2O_2/g DM used in this study. The high NaOH loading in Gray’s study probably limited the decrease in pH due to the addition of H_2O_2 that was observed in this study with miscanthus with the increasing addition of H_2O_2.

For the differing biomass types, a similar trend with dry matter loss during pretreatment was observed. The increasing concentration of NaOH was generally shown to increase the amount of dry matter lost. To a lesser extent increasing concentrations of

H_2O_2 showed a slight trend in increased dry matter loss. These results are comparable to other studies (Chen, Chen et al., 2012) where dry matter losses of 27-35 % occurred during pretreatment of three biomass feedstocks (silvergrass, napiergrass, and rice straw) with 10% Ca(OH)2 or 3% NH_4OH. For corn stover, it has been proposed that NaOH loading over 8% may improve conversion, but this improvement is offset by the destruction of carbohydrates during pretreatment (Chen, Stevens et al., 2013).

4.5.2 Detergent Fiber Composition

Per the ANKOM protocol, sodium sulphite was added during the NDF analysis. The addition of sodium sulphite reduces the nitrogen contamination by removing proteinacous material from the fiber (Mertens, 2002, Udén, Robinson et al., 2005). For a number of years within the research community, concerns have existed with the use of sodium sulphite since measured ADL values were shown to be lower than ADL values for samples which had been analyzed without sodium sulphite. Research with forage legumes suggests that the difference in ADL values with and without sodium sulphite could be due to proanthocyanidins (Krueger, Albrecht et al., 1999). Nonetheless, the most recent recommendations still suggest using sodium sulfite (Mertens, 2002, Udén, Robinson et al., 2005) since it will remove any skewing from proteins. Although none of the biomass materials used in this study are considered to have high values for protein content, the use of sodium sulfite was considered acceptable with respect to the ADL determination.

Across the different biomass types, the composition after chemical pretreatment and prior to washing demonstrated a general decrease in the NDF and hemicellulose with the ADF, ADL, and cellulose demonstrating varied results relative to the control. After washing, the ADF and cellulose composition increased while hemicellulose decreased with respect to the control. Prior to washing, the NDF decrease relative to the control was presumed to be related to a rinsing effect during the NDF analysis. The NDF analysis dissolves all of the easily soluble sugars, pectin, and protein. Thus, it is not unconceivable this would also remove the chemicals that were applied during pretreatment. The NDF after washing resembled the value for the control more closely. The increased ADF after washing was reflective of hemicellulose being decreased. Decreases in hemicellulose have been observed with both alkaline and AHP pretreatments.

The addition of H_2O_2 was expected to decrease the lignin content, however a varied response was observed in these experiments. Based on the detergent fiber analysis, ADL was not strongly influenced by the addition of H_2O_2. In addition, the AIL was not influenced by the H_2O_2 levels applied based on the NREL protocols. Based on both measurement techniques, the addition of H_2O_2 would appear to have a minor impact on the lignin content of the four biomass feedstocks investigated under these pretreatment conditions.

The percentage point decrease in NDF and ADF of the 5% NaOH and 2% H_2O_2 treated wheat straw prior to washing was similar to results obtained by Cameron (1990). Wet AHP pretreated wheat straw demonstrated an approximately 13% decrease in hemicellulose (Lewis, Montgomery et al., 1988).

4.5.3 NREL Composition

Contrary to what Modenbach (2013) saw with corn stover, no significant increases in the proportion of cellulose were observed with the alkaline addition at 4 or 10%, nonetheless, numerical increases in the proportion of cellulose were observed for chemical pretreatment. For miscanthus, corn stover, switchgrass, and wheat straw, wet AHP resulted in increased cellulose and decreased hemicellulose and lignin contents (Gray, 2013); however, the concentration of NaOH and H_2O_2 was much higher than utilized in the current study. Furthermore, the current experiment used a greater volume of water for washing along with a longer duration of pretreatment. The altered hemicellulose of (Gray, 2013) could also be explained as Modenbach (2013) demonstrated with corn stover, that concentrations of NaOH over 20 g/g DM resulted in decreased hemicellulose. Across the measured biomass materials there was no clear and consistent alteration in the NREL composition yet enzymatic hydrolysis would indicate that a distinct difference existed between the controls and chemical pretreatments. Thus, perhaps the lignin and hemicellulose matrix was not solubilized but rather modified as with mild pretreatments such as hot water and dilute acid pretreatment (Selig, Viamajala et al., 2007, Donohoe, Decker et al., 2008).

4.5.4 NREL and Detergent Fiber Composition Comparison

The composition of the different biomass crops was determined using the detergent fiber analysis and NREL methodology with the goal being to see if one was more indicative of the potential benefits of pretreatment to enzyme hydrolysis. Detergent fiber analysis has been used for a number of years in forage studies and animal trials since its original conception in the early 1960s. Consequently, the detergent fiber analysis possesses a large data set of knowledge to provide comparable values. For the different biomass materials analyzed in this study, the detergent fiber analysis demonstrated a decreased hemicellulose content for the chemical pretreatments for both prior and subsequent to washing. In contrast, composition determined using the NREL protocols demonstrated an equivalent hemicellulose value after washing. This could explain why there was no correlation for hemicellulose.

As one of the primary barriers to digestion, lignin represents an important part of the plant structure and accurate lignin measurements are essential. The NREL method allows for the determination of both soluble and insoluble (Klason) lignin. Generally, ADL and Klason have been demonstrated to be an important indicator of subsequent digestion for lignocellulosic material with the exception of C4 (corn) crops (Jung, Mertens et al., 1997). Klason lignin will typically provide a higher (2 – 4 times) value for lignin than ADL as some of the lignin is lost during the ADF analysis with the low sulfuric acid conditions removing phenolic compounds. Jung, Mertens et al. (1997) stated that conceptually ADL and Klason lignin are inherently similar processes, but the order of reactions is different. For ADL, the low concentration of sulfuric acid is used before the high concentration; while, the opposite is true for the Klason lignin (acid insoluble lignin, AIL). The NREL procedure seems to provide more resolution for changes in the lignin composition relative to the ADL values. With the biomass materials analyzed this study, the R^2 value for AIL and ADL was highest when compared to the cellulose and hemicellulose methods.

4.5.5 Enzyme Hydrolysis

As predicted for all of the biomass crops, a higher concentration of enzymes demonstrated the greatest conversion efficiency. Reducing the particle size from 5 mm to

2 mm after pretreatment also demonstrated an improved conversion with all the crops except corn stover.

4.5.5.1 NaOH Loading

The enzyme hydrolysis demonstrated varied results for each of the biomass types, but an increasing concentration of NaOH was shown to increase the enzyme hydrolysis effectiveness for the different biomass types by almost doubling the conversion efficiency. For corn stover, other researchers have shown that increasing the concentration of NaOH loading from 4 to 10 g/g DM increased cellulose conversion by 35 to 215% (Chen, Stevens et al., 2013, Modenbach, 2013). This increase in enzymatic hydrolysis was likely the result of structural and morphological changes that can occur when alkali concentrations are greater than 6%. For NaOH, the concentration of NaOH (g/g DM) was found to more indicative of potential digestion than the solution concentration (g/ml of chemical solution). Another study with corn stover, found that increasing the NaOH concentration in mustard straw, the main effect of NaOH significantly increased cellulose regardless of hydrogen peroxide addition, yet the highest level IVODM was observed with the addition of H_2O_2 (Mishra, Chaturvedi et al., 2000).

4.5.5.2 H_2O_2 Loading

The addition of 2% hydrogen peroxide in this study was shown to have mixed results, either numerically decrease or increase the effectiveness of enzyme hydrolysis when compared to the respective alkaline treatment. Across biomass types, the 5% H_2O_2 was shown to reduce the glucose yields during hydrolysis. These results are contrary to the results seen in other studies which have specifically analyzed AHP as a means to improve the subsequent digestion over the sole addition of NaOH (Gould, 1984, Gould and Freer, 1984, Banerjee, Car et al., 2011, Li, Foster et al., 2012, Williams, 2014). The main explanation for this difference would be related to how the pretreatment was performed (time, temperature, NaOH loading, moisture content, etc.), sample storage, and further processing before enzyme hydrolysis.

A number of the studies (Gould, 1985, Banerjee, Car et al., 2011, Gray, 2013) used “wet AHP pretreatment” or “slurries” as a means for pretreating the material. The increased water content during pretreatment has been shown to increase the effectiveness for wheat straw pretreatment in some studies (Gould, 1985), yet (Chaudhry, 1998) demonstrated that biomass responded similarly at different moistures. For AHP pretreated corn stover slurry, increasing the solids loading from 12.7 to 29.3% (w/w) for pretreatment resulted in increased glucose yields yet further increasing the solids loading from 29.3 to 33.3% resulted in a decrease in glucose yield after 24 h of pretreatment (Williams, 2014). For the spray pretreatment, mixing of the material took place while the AHP spray was applied and after which no further agitation was performed during pretreatment. For the "wet or slurry" pretreatment, the samples are either agitated (gyro-shaker ~ 200 rpm) or mechanically mixed with a stir bar throughout the pretreatment process. Gould (1985) showed simply soaking the material caused no morphological changes yet there were benefits to mechanical agitation. Another important factor was the concentration of H_2O_2, used in wet pretreatment which was generally higher and used concentrations as high as 0.5 g/g DM.

Sample storage prior to hydrolysis involved drying which has been presumed to lead to the phenomenon of hornification (Minor, 1994, Diniz, Gil et al., 2004, Jeoh, Ishizawa et al., 2007, Luo and Zhu, 2011). Hornification, irreversible alterations of the physical/chemical characteristics of biomass due to drying, was surmised to limit the effectiveness of AHP when compared to similar NaOH pretreatments. Increased duration of drying and drying methodology (oven vs air) can enhance the severity of hornificaiton which in turn reduces the saccharification efficiency (Luo and Zhu, 2011). For AHP pretreated wheat straw, water absorption has been demonstrated to decrease by 17% due to drying at 110 °C for 24 hours (Gould, 1985). Wet (non-dried) pretreated wheat straw has been shown to have 12% higher enzymatic hydrolysis yields over the equivalent dried samples (Sun and Chen, 2008). For this study, drying at 45°C for 3 days would have reduced the internal surface area created by the chemical pretreatments that enhance enzyme saccharification. The further processing (grinding) that occurred in other studies prior to enzymatic hydrolysis could have been a key difference leading to the significant differences between tests (Lewis, Montgomery et al., 1988, Banerjee, Car et al., 2011, Li, Foster et al., 2012). (Minor, 1994, Diniz, Gil et al., 2004, Jeoh, Ishizawa et al., 2007, Luo and Zhu, 2011).

Changes in the enzymatic hydrolysis due to hornification could have skewed the results in this study. However, all samples were subjected to drying after pretreatment and it is believed that comparisons between treatments and feedstocks would be useful.

4.5.5.3 Corn Stover

Corn stover was the only one of the biomass feedstocks in this study in which the 5 mm material showed a 16% increase in cellulose conversion than material that was ground through a 2 mm screen. Generally, the surface area to volume increases with decreasing particle size, and this increase in the surface area allows for more potential locations for the enzyme complex to bind (Vidal Jr, Dien et al., 2011). Nonetheless, particle size reduction does not guarantee improved cellulose conversion characteristics. Ammonia fiber explosion (AFEX) pretreatment demonstrated paradoxical behavior for particle size with reduced glucose conversion for corn stover that had been ground to a smaller particle size (10 to 0.85 mm) (Chundawat, Venkatesh et al., 2007). The rationale for the decreased activity with smaller particle size in the AFEX study was surmised to be attributed to different composition of the smaller particle sizes. Reducing the particle size of dilute NaOH pretreated corn stover from 2 to 0.25 mm has been shown to increase the glucose yields by 42.5% (Li, Ruan et al., 2004). Nonetheless, this same study found that with homogenization combined with the NaOH pretreatment found that reduced particle size (2 mm to 0.25 mm) resulted in glucose yields that were not significantly different. For this study, the 2 mm material was ground directly from the 5 mm pretreated corn stover. Thus, the difference was surmised to be related to material lost during the grinding process.

Corn stover that had passed through a 0.25 - 0.5 mm screen prior to hydrolysis, neutralized with HCL (not washed), heated to 90 °C for 15 minutes, and lyophilized (Banerjee, Car et al., 2011) demonstrated increasing glucose yield (51 to 84%) with the increasing H_2O_2 concentration (0.125 $\rightarrow$ 50 g/g DM) with an enzyme loading of 45 FPU/g.

4.5.5.4 Switchgrass

For switchgrass, the AHP pretreatment showed either equivalent or reduced cellulose conversion values when compared to the equivalent pretreatments with only alkaline loading. Switchgrass pretreated as an AHP slurry material demonstrated increasing activity with increasing (0 – 0.25 g H_2O_2/g DM) H_2O_2 concentration (Williams, 2014).

4.5.5.5 Wheat Straw

The addition of hydrogen peroxide to wheat straw also resulted in mixed results with regard to cellulose converted. Lewis, Montgomery et al. (1988) used a soaking pretreatment with 10% H_2O_2, no washing, and further grinding after pretreatment (10 mm for pretreatment and ground further through a 425 µm screen after pretreatment) and found that H_2O_2 increased the in vitro dry matter degradation by 31% compared to NaOH alone. (Lewis, Holzgraefe et al., 1987) demonstrated that material ground to 10 mm and soaked in 10% AHP demonstrated equivalent dry matter disappearance in sacco for AHP and NaOH pretreated material with the straw in this study being kept wet before use. For an AHP slurry, increasing the level of H_2O_2 from 0 to 4.5% (v/v) resulted in greater sugar yields, up to H_2O_2 concentrations of 2.12% upon which further additions did allow for the for greater increases in sugar yields (Saha and Cotta, 2006).

4.6 Conclusion

Alkaline hydrogen peroxide spray pretreatment of corn stover, switchgrass, wheat straw, and miscanthus demonstrated mixed results. After pretreatment and washing, the cellulose content trended upward and the hemicellulose content trended downward based on the detergent fiber analysis. As expected, the cellulose content increased and the hemicellulose content decreased to a greater extent when pretreated with higher concentrations of NaOH. However, no clear trends were observed in cellulose and hemicellulose contents when higher concentrations of H_2O_2 were utilized.

Using the NREL composition procedure, minor changes in the composition were observed after washing between the various pretreatment methods. The concentration of NaOH was found to significantly influence the enzymatic hydrolysis of each biomass type. Although, the addition of H_2O_2 spray with the conditions analyzed in this study were found to not significantly enhance cellulose conversion. With respect to particle size, the reduction of particle size from 5 to 2 mm after pretreatment was found to be beneficial for all of the biomass material except corn stover. At the higher enzyme concentration, the biomass materials also demonstrated the greatest cellulose conversion. Drying after the pretreatment (hornificaiton) could have partially confounded the results for the chemical pretreatment.

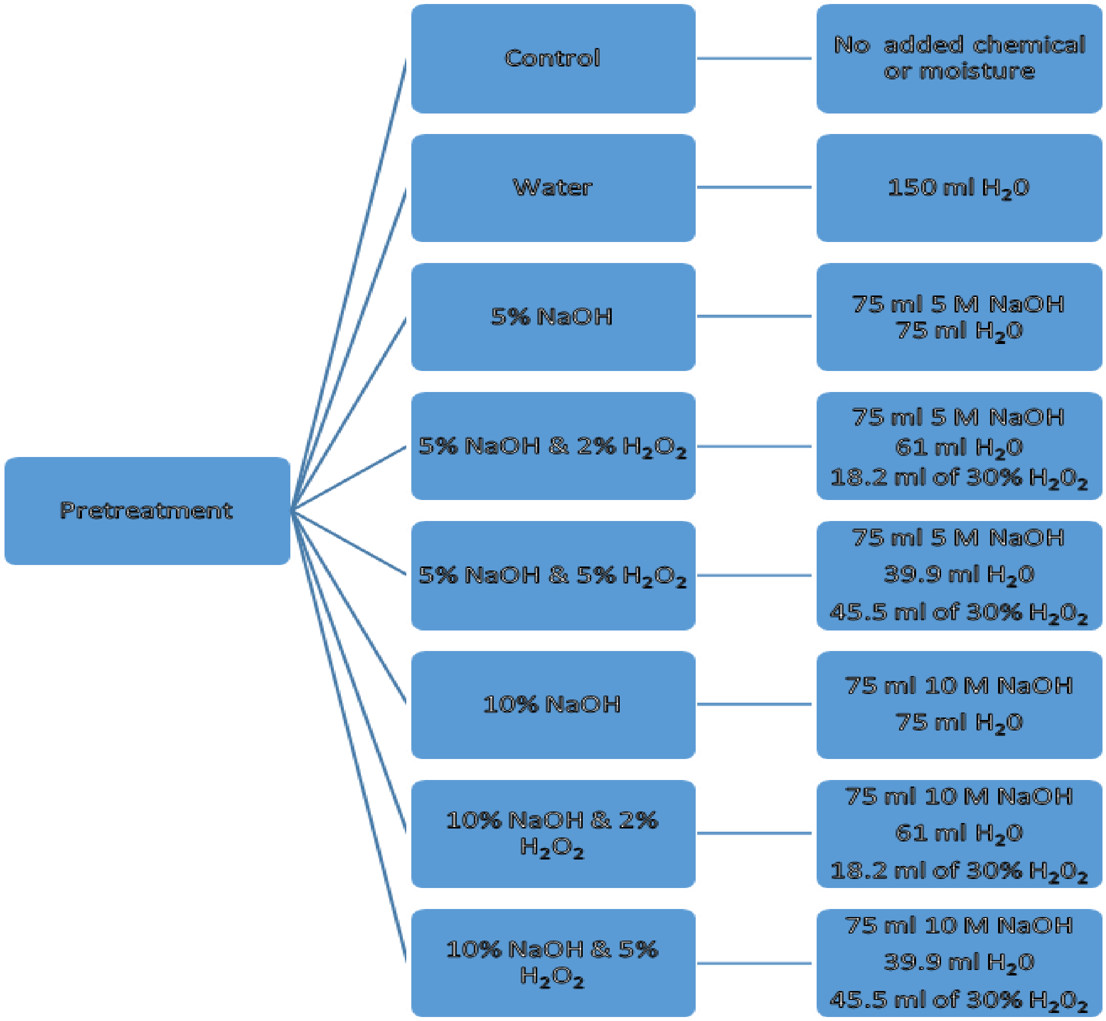


Figure 4-1 Pretreatments and conditions applied to 300 g (dry matter) of each biomass type

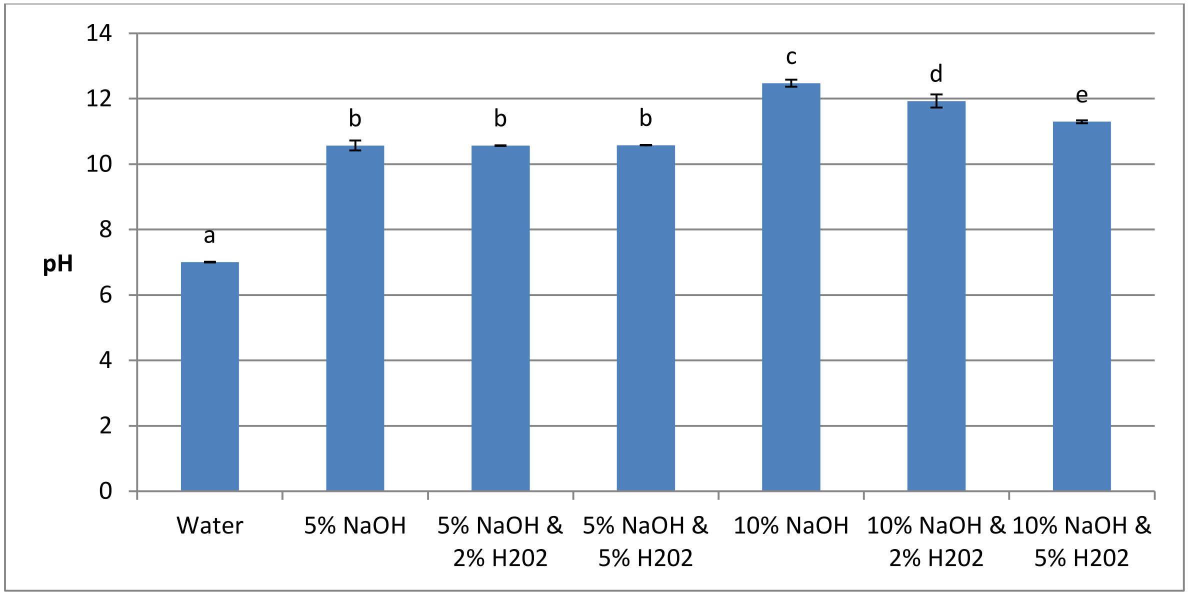


Figure 4-2 Miscanthus pH following 7 day pretreatment. Error bars represent the standard deviation from three replicates.

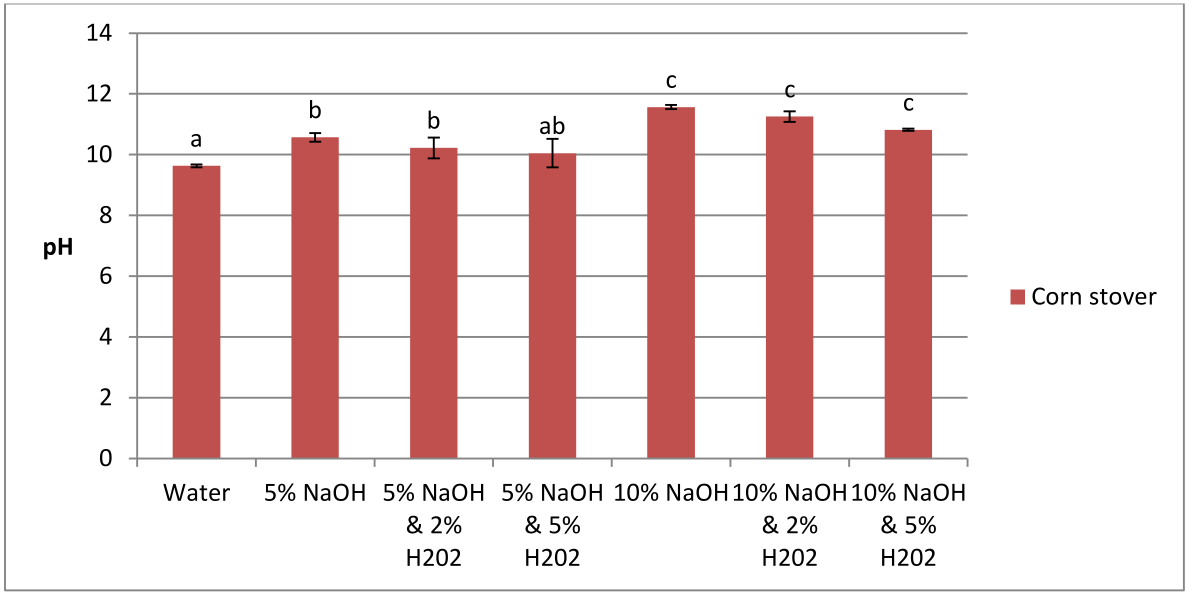


Figure 4-3 Corn stover pH following 7 day pretreatment. Error bars represent the standard deviation from three replicates.

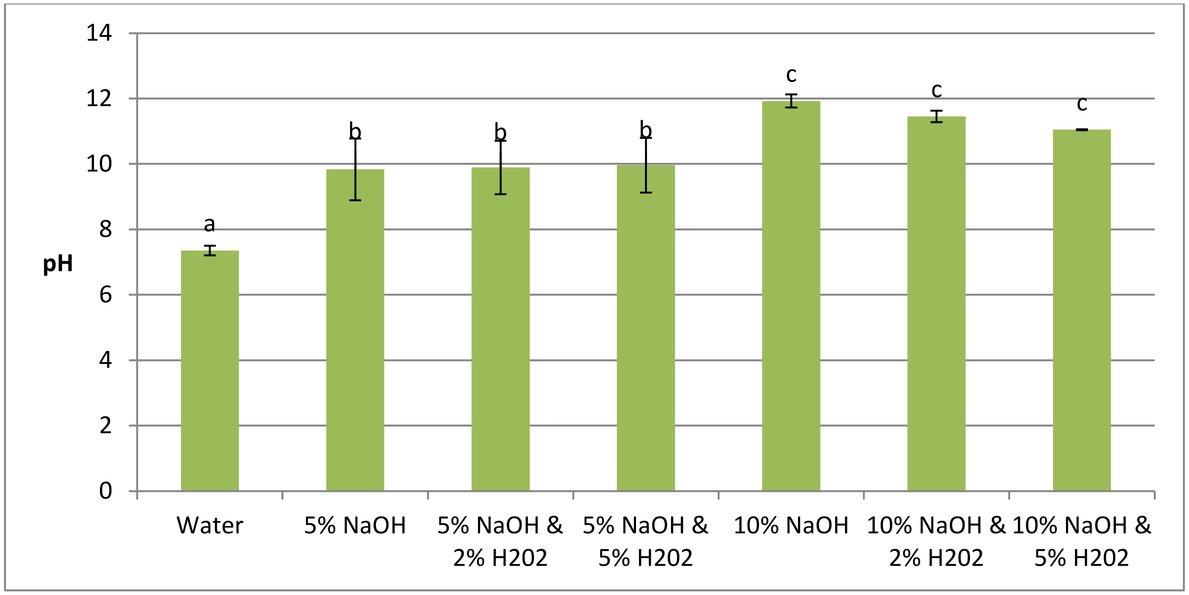


Figure 4-4. Switchgrass pH following 7 day pretreatment. Error bars represent the standard deviation from three replicates.

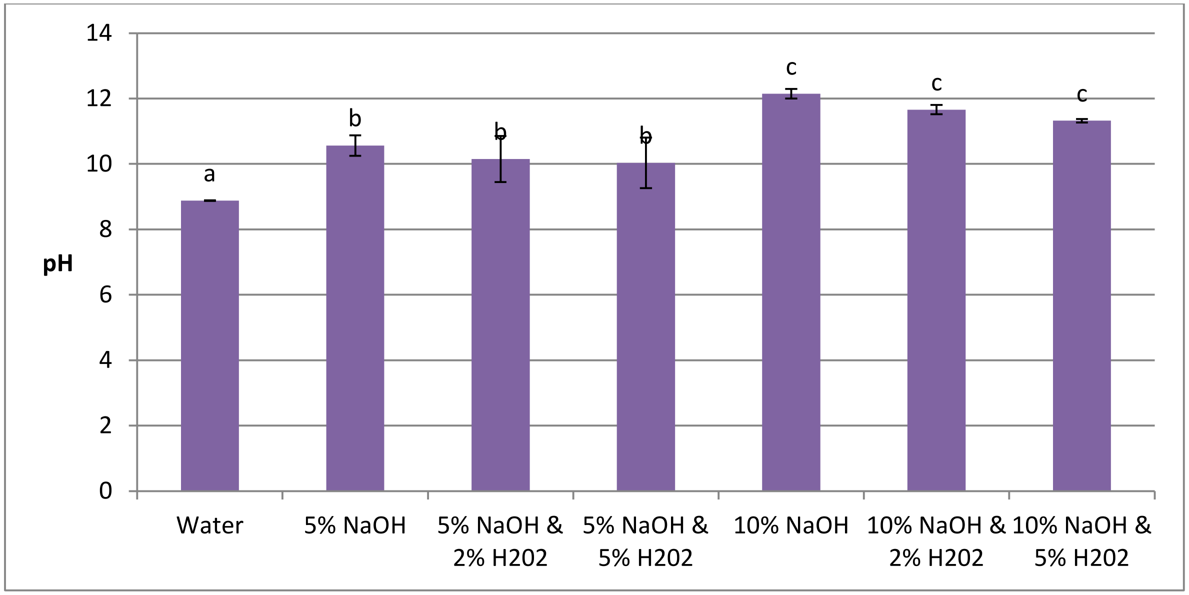


Figure 4-5 Wheat straw pH following 7 day pretreatment. Error bars represent the standard deviation from three replicates.

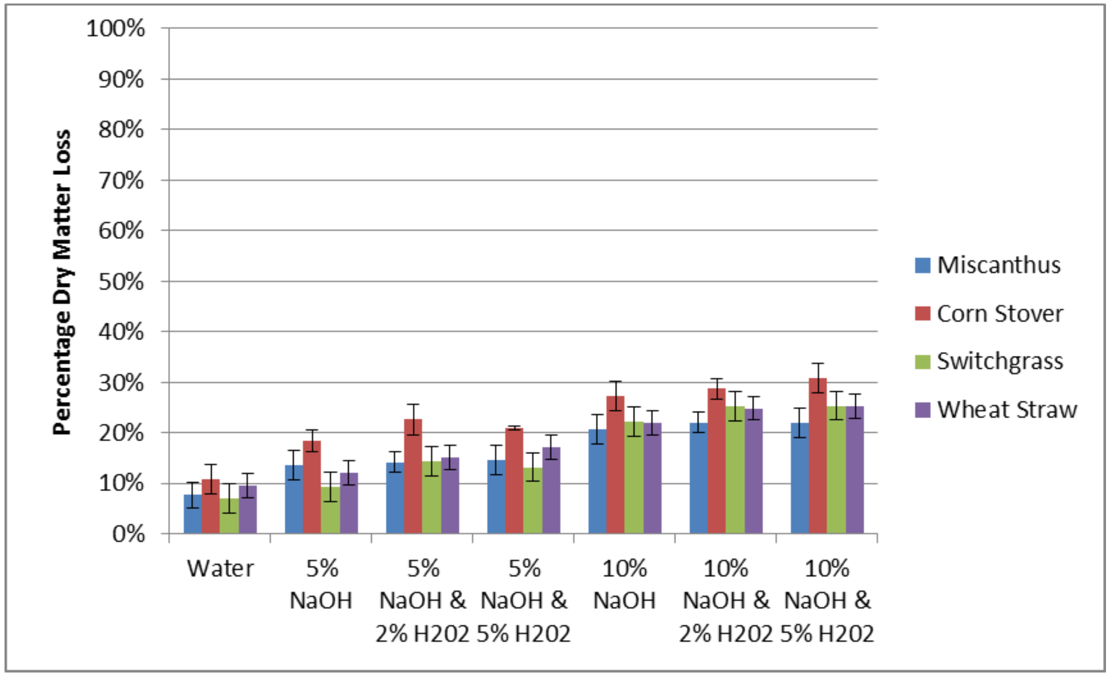


Figure 4-6 Dry matter loss after 7 day of pretreatment

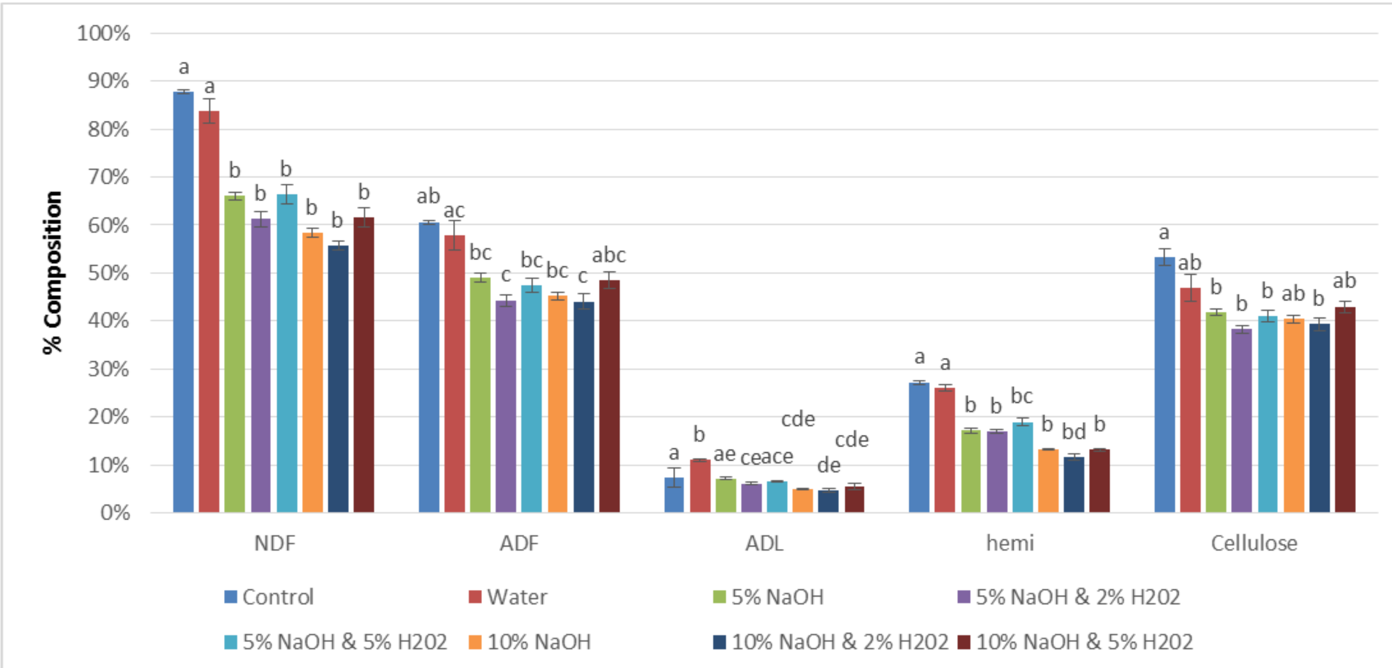


Figure 4-7 Miscanthus detergent fiber composition prior to washing

[1]Hemi= Hemicellulose (NDF – ADF)
[2]Cellulose = ADF – ADL
[a,b,c,d,e,f,g,]Means bearing differing superscript's within a group are significantly different ($p \leq 0.05$)

i

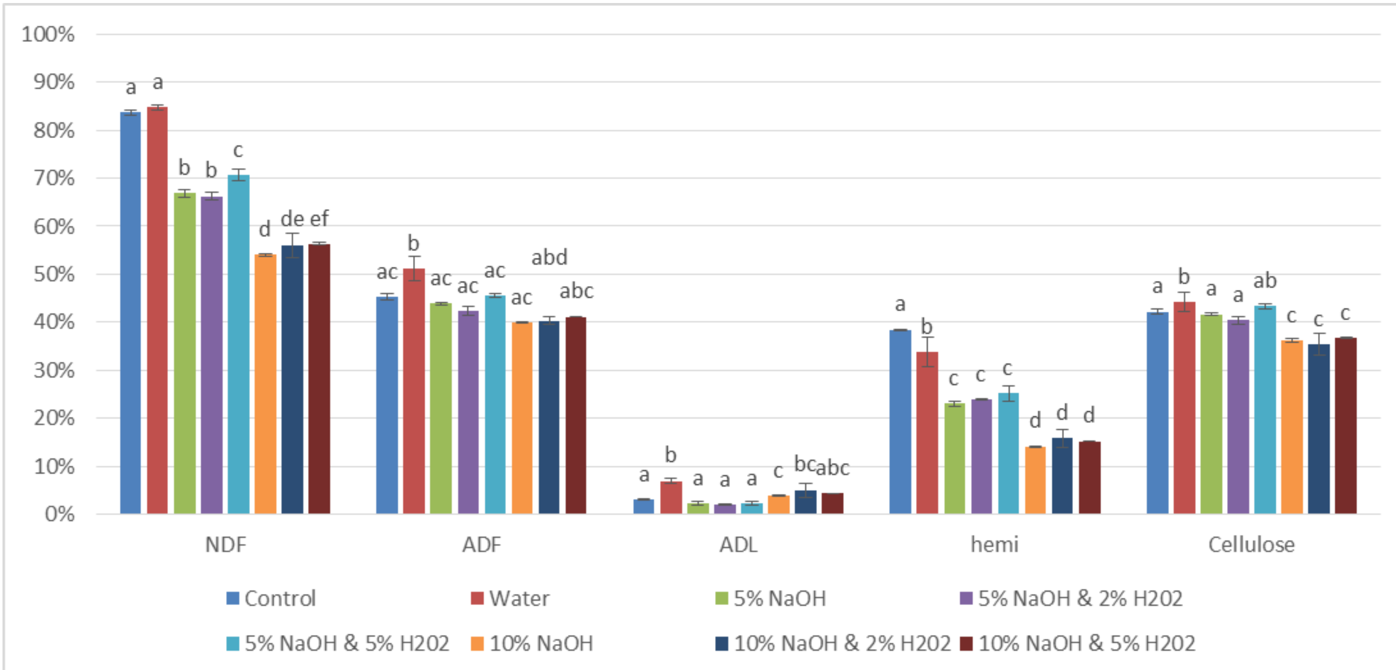


Figure 4-8 Corn stover detergent fiber composition prior to washing

[1]Hemi= Hemicellulose (NDF – ADF)
[2]Cellulose = ADF – ADL
[a,b,c,d,e,f,g,]Means bearing differing superscripts within a group are significantly different ($p \leq 0.05$)

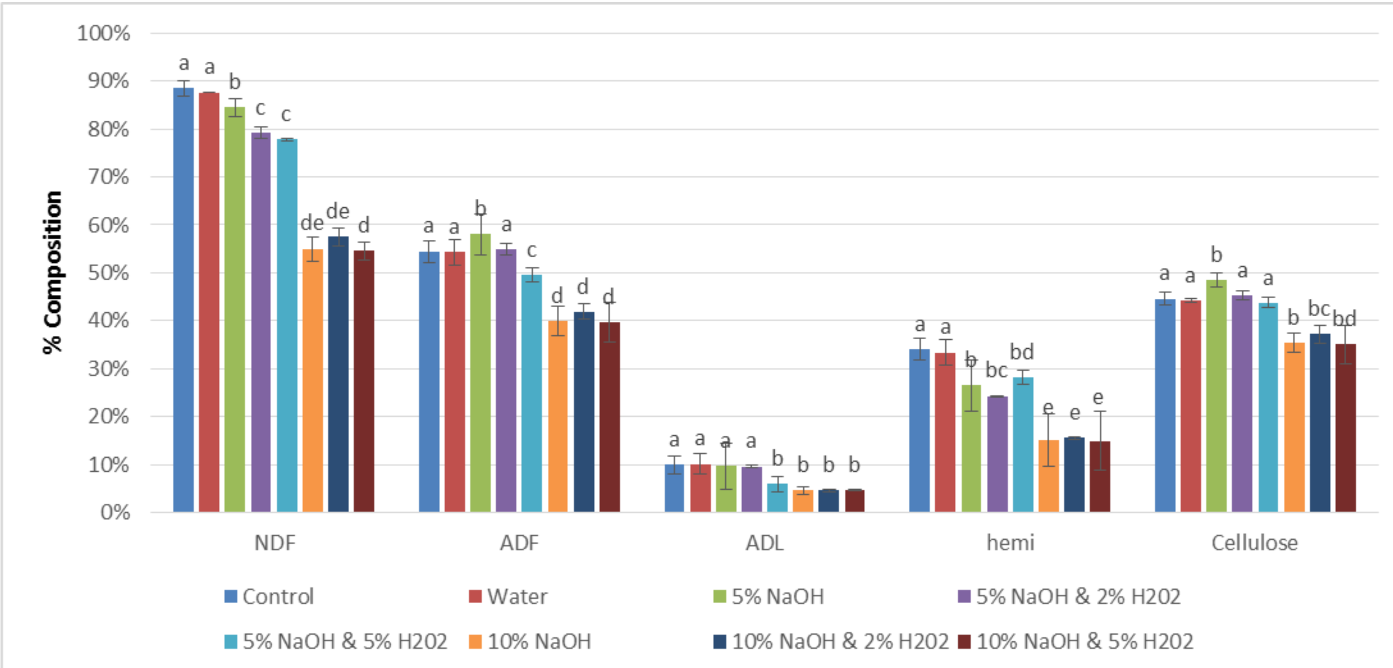


Figure 4-9 Switchgrass detergent fiber composition prior to washing

[1]Hemi= Hemicellulose (NDF – ADF)
[2]Cellulose = ADF – ADL
[a,b,c,d,e,f,g,]Means bearing differing superscripts within a group are significantly different ($p \leq 0.05$)

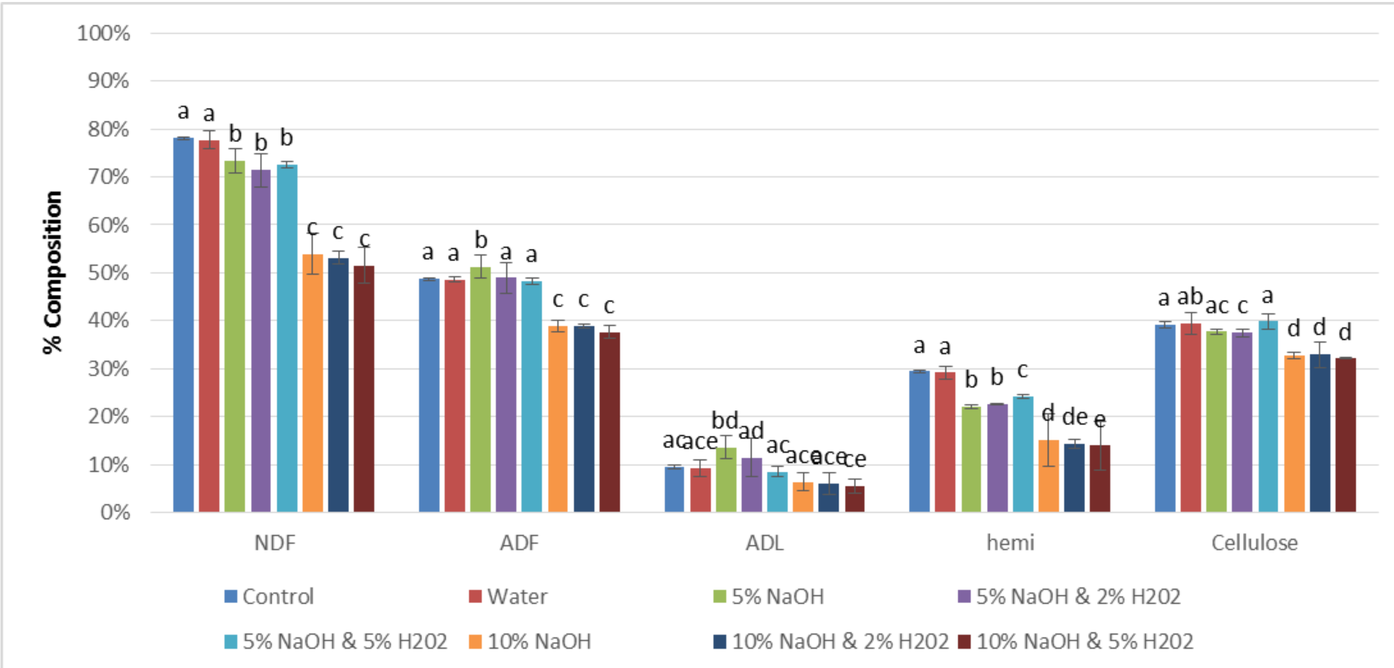


Figure 4-10 Wheat straw detergent fiber composition prior to washing

[1]Hemi= Hemicellulose (NDF – ADF)
[2]Cellulose = ADF – ADL
[a,b,c,d,e,f,g,]Means bearing differing superscripts within a group are significantly different ($p \leq 0.05$)

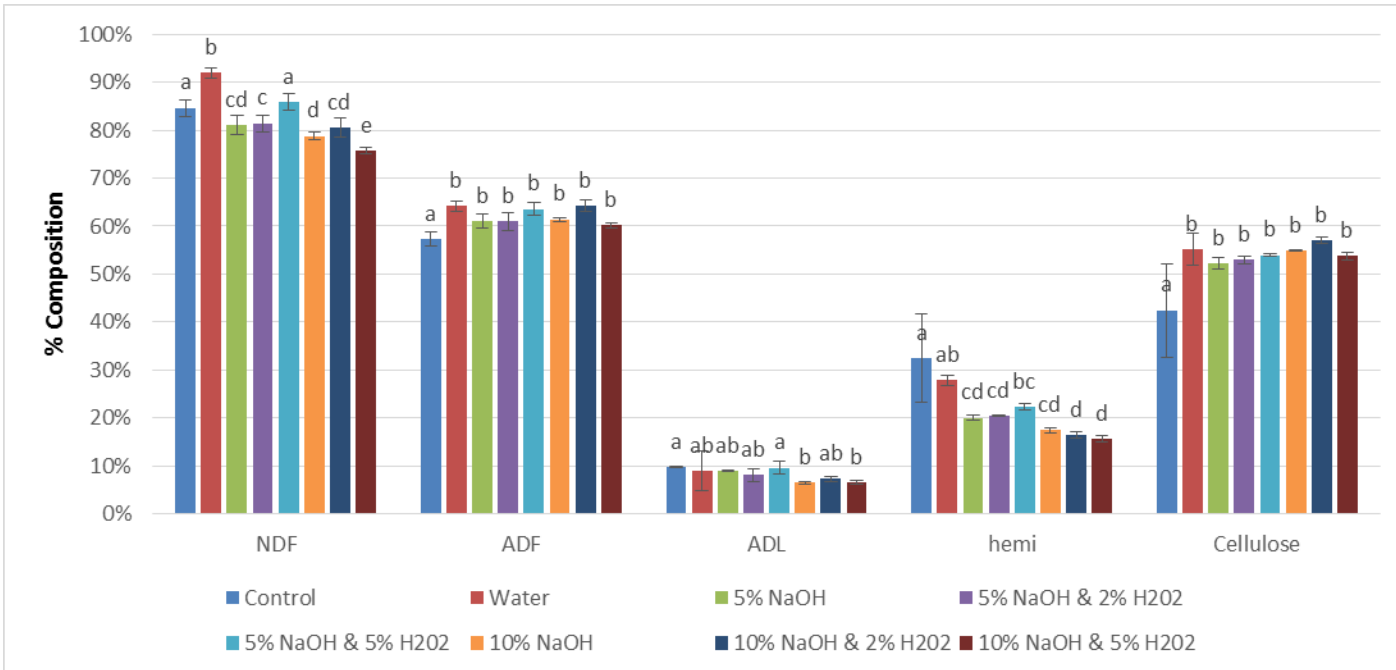


Figure 4-11 Miscanthus detergent fiber composition after washing

[1]Hemi= Hemicellulose (NDF – ADF)
[2]Cellulose = ADF – ADL
[a,b,c,d,e,f,g,]Means bearing differing superscripts within a group are significantly different ($p \leq 0.05$)

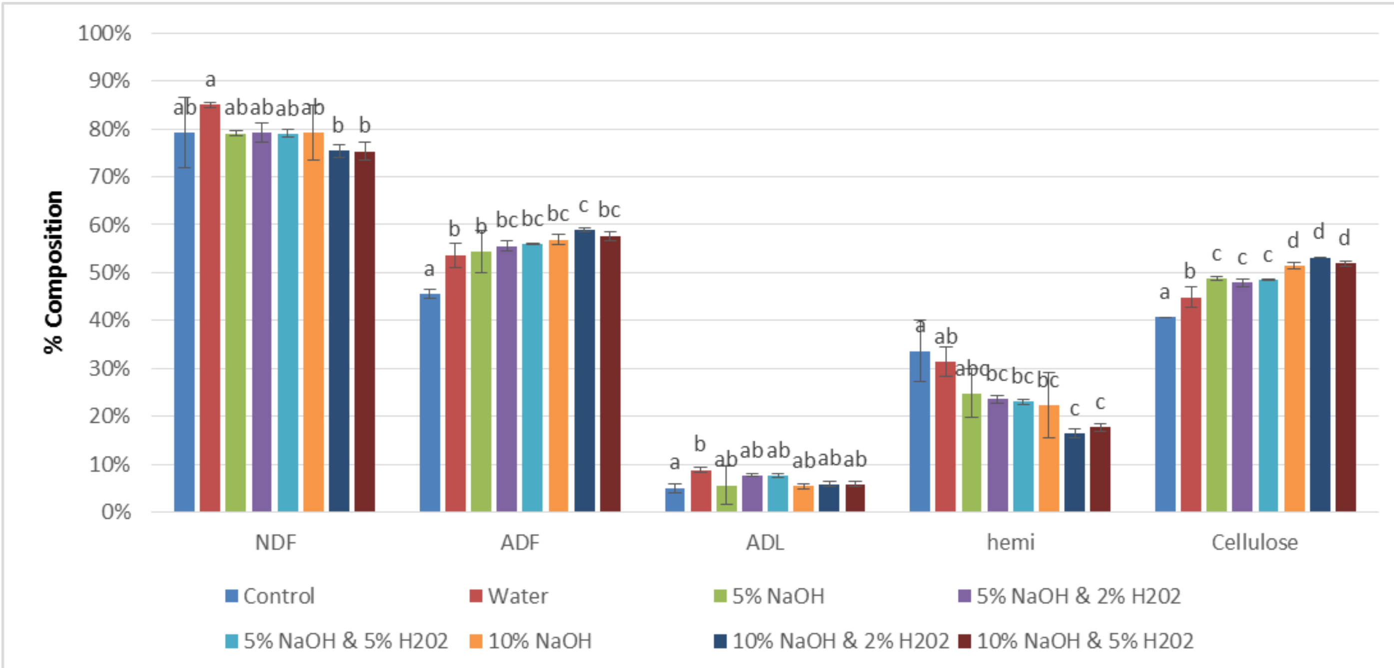


Figure 4-12 Corn stover detergent fiber composition after washing

[1]Hemi= Hemicellulose (NDF – ADF)

[2]Cellulose = ADF – ADL

[a,b,c,d,e,f,g,]Means bearing differing superscripts within a group are significantly different ($p \leq 0.05$)

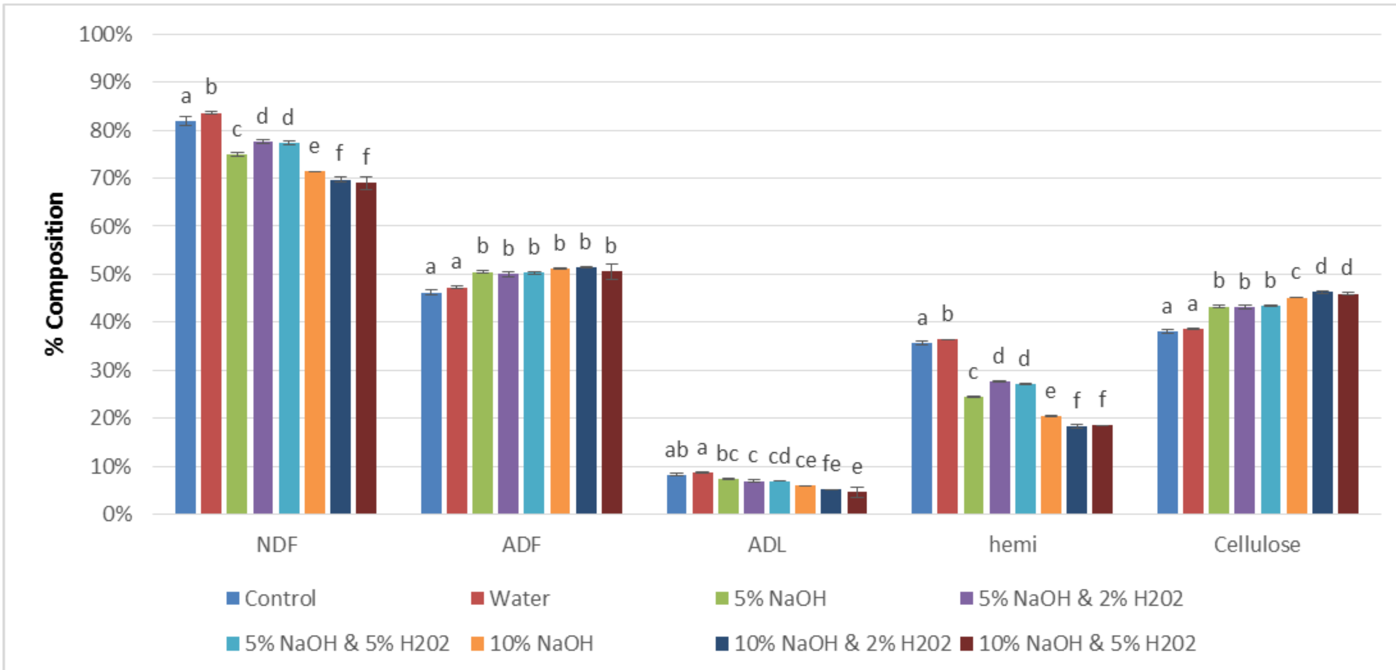


Figure 4-13 Switchgrass detergent fiber composition after washing

[1]Hemi= Hemicellulose (NDF – ADF)
[2]Cellulose = ADF – ADL
[a,b,c,d,e,f,g,]Means bearing differing superscripts within a group are significantly different ($p \leq 0.05$)

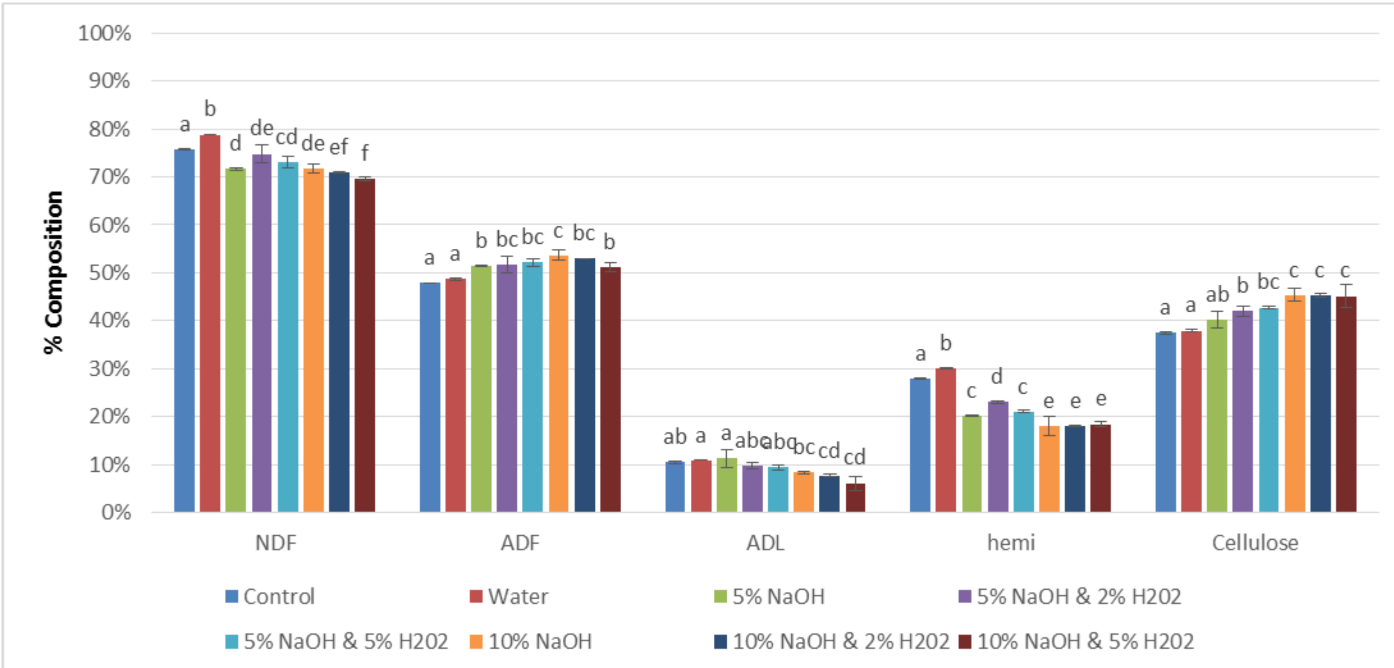


Figure 4-14 Wheat straw detergent fiber composition after washing

[1]hemi= Hemicellulose (NDF – ADF)

[2]Cellulose = ADF – ADL

[a,b,c,d,e,f,g,]Means bearing differing superscripts within a group are significantly different ($p \leq 0.05$)

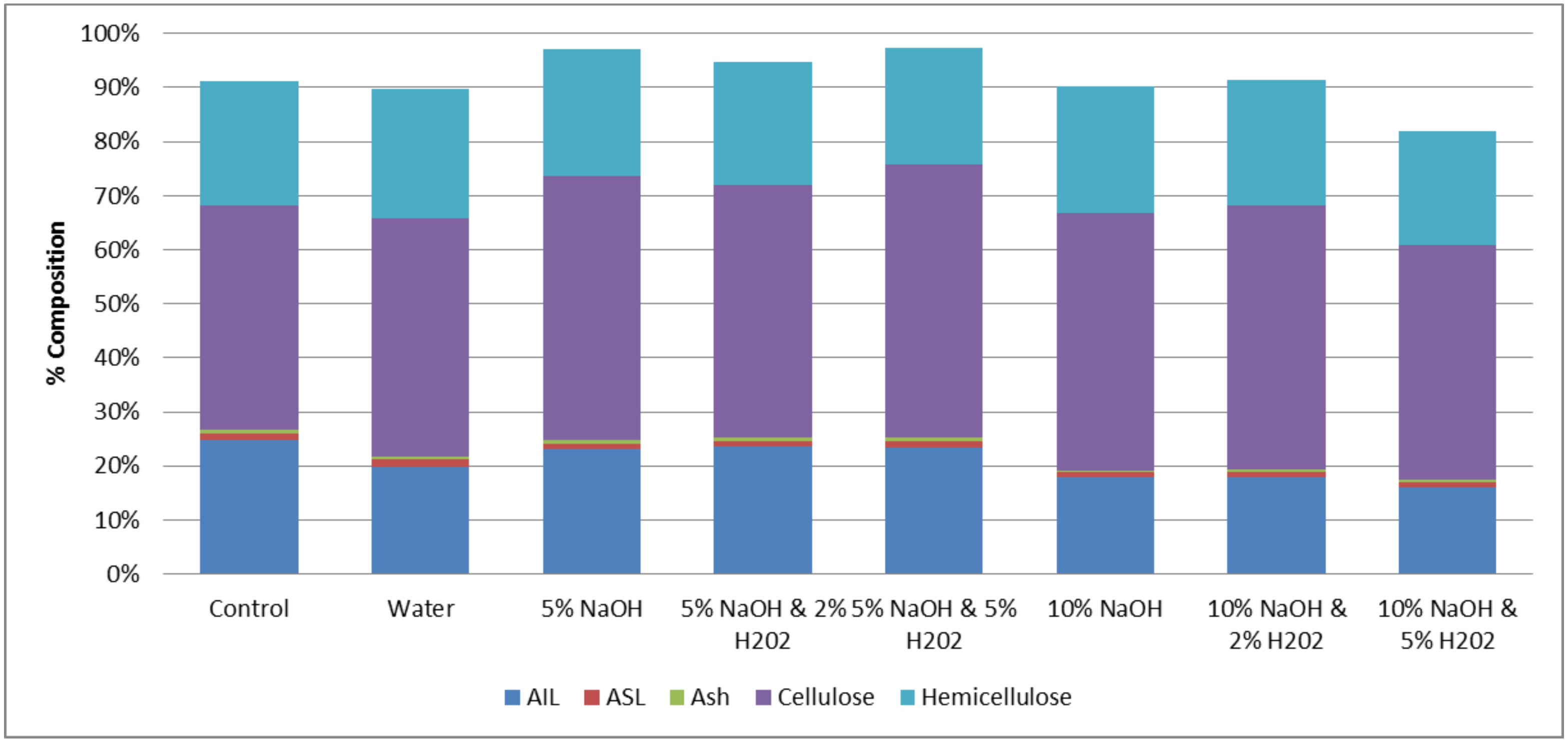


Figure 4-15 Miscanthus composition determined using NREL procedures after pretreatment and washing

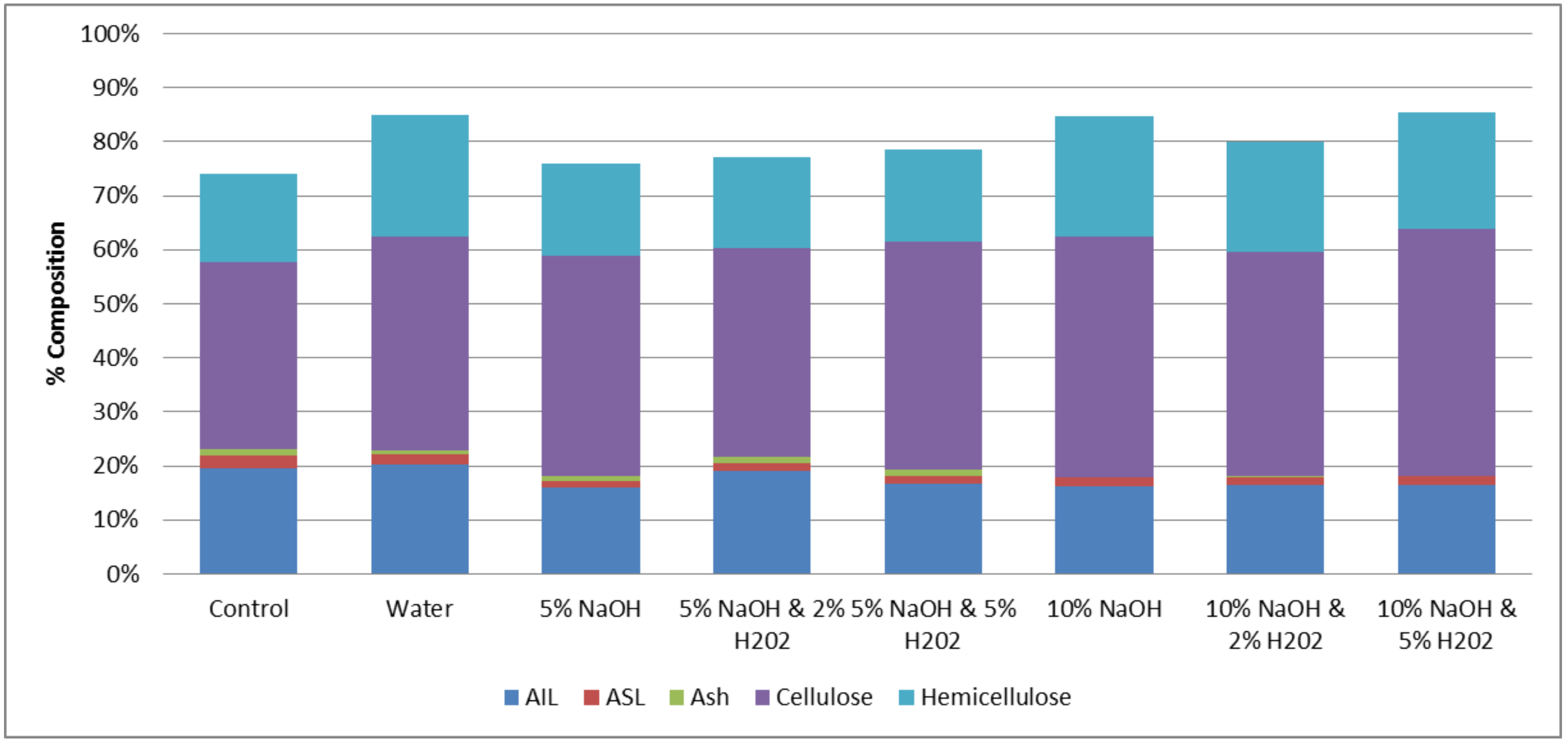


Figure 4-16 Corn Stover composition determined using NREL procedures after pretreatment and washing

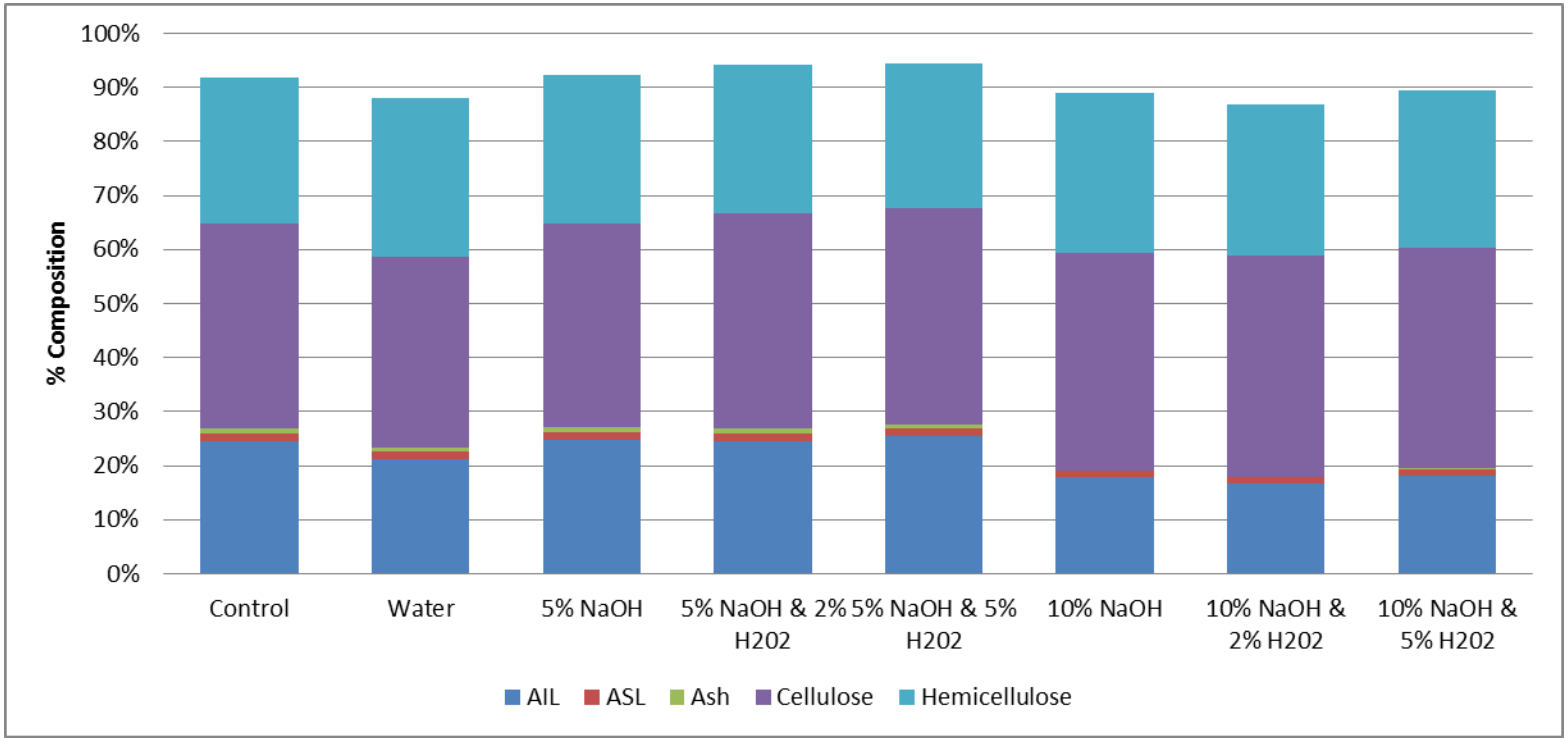


Figure 4-17 Switchgrass composition determined using NREL procedures after pretreatment and washing

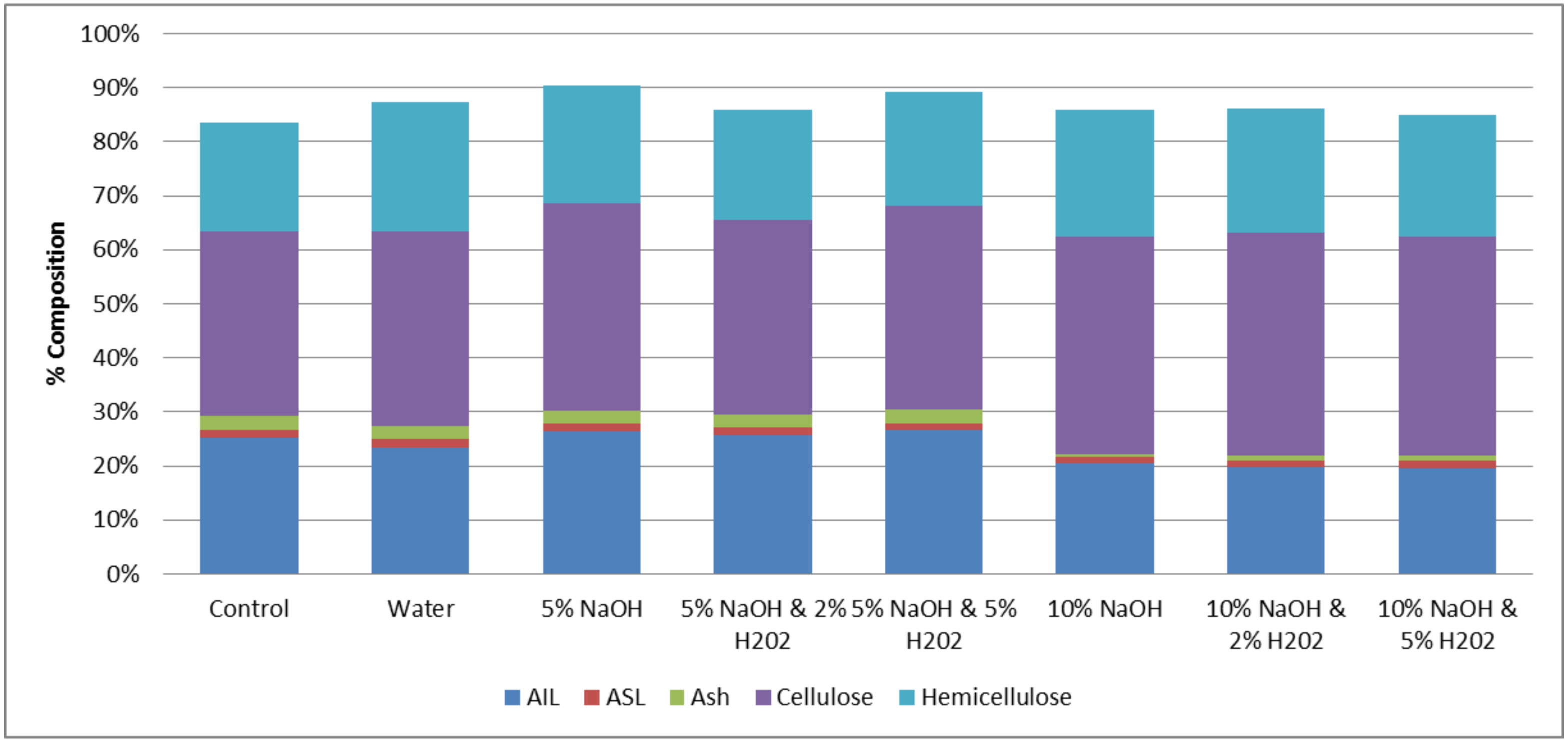


Figure 4-18 Wheat straw composition determined using NREL procedures after pretreatment and washing

Table 4-1 Regression characteristics for listed figures

Figure	Dependent Variable	Independent Variable	Slope	Intercept	R^2
Figure 4-19	NREL Glucose	Cellulose (ADF - ADL)	0.50 ± 0.18	0.23 ± 0.08	0.2113
Figure 4-20	NREL Xylose	Hemicellulose (NDF-ADF)	0.14 ± 0.30	0.20 ± 0.07	0.0074*
Figure 4-21	NREL Acid Insoluble Lignin	ADL	0.37 ± 0.06	-0.001 ± 0.0133	0.5382

± standard error
* correlation not significant

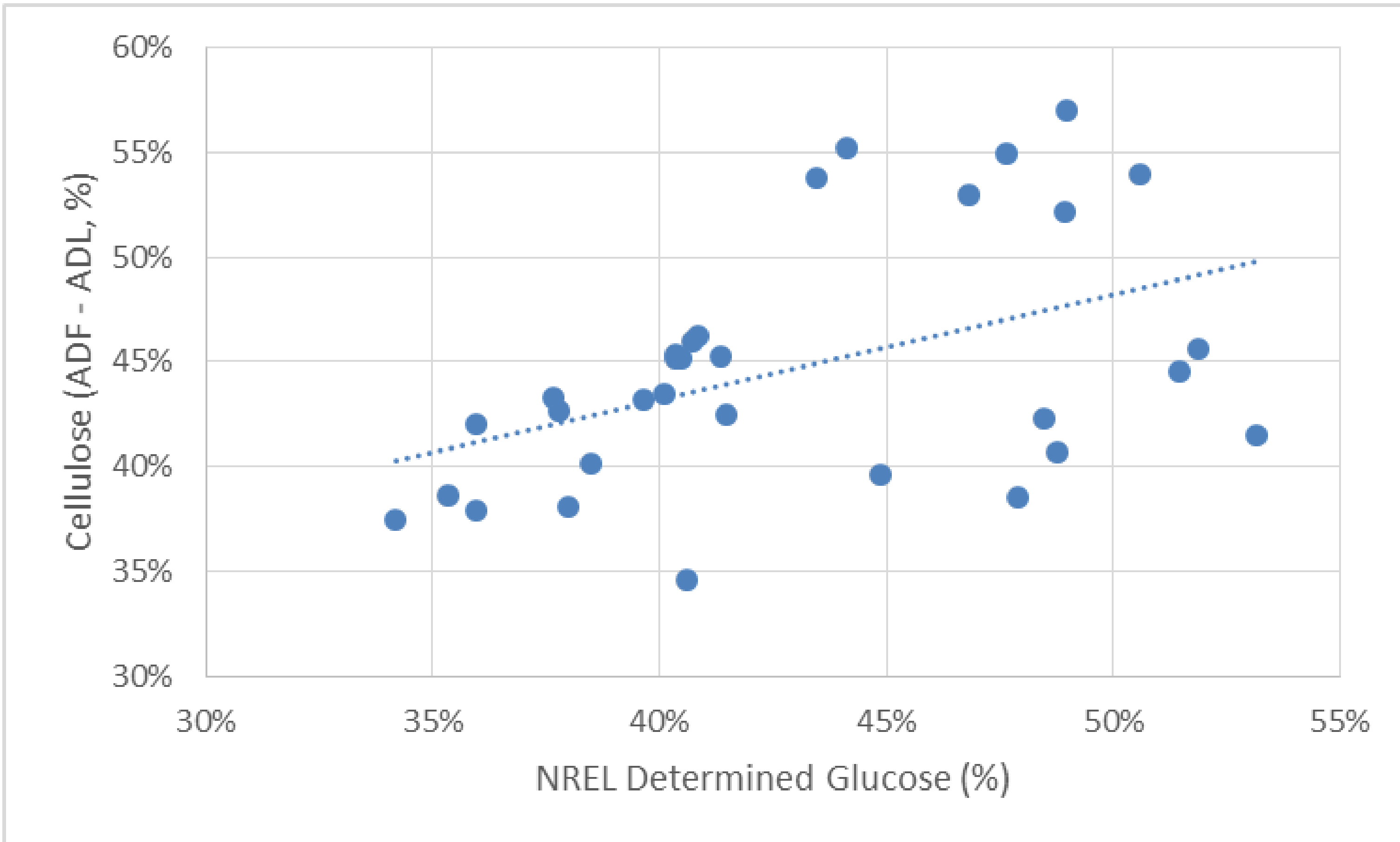


Figure 4-19 Average cellulose composition after washing determined using Ankom and NREL procedure for all crops studied

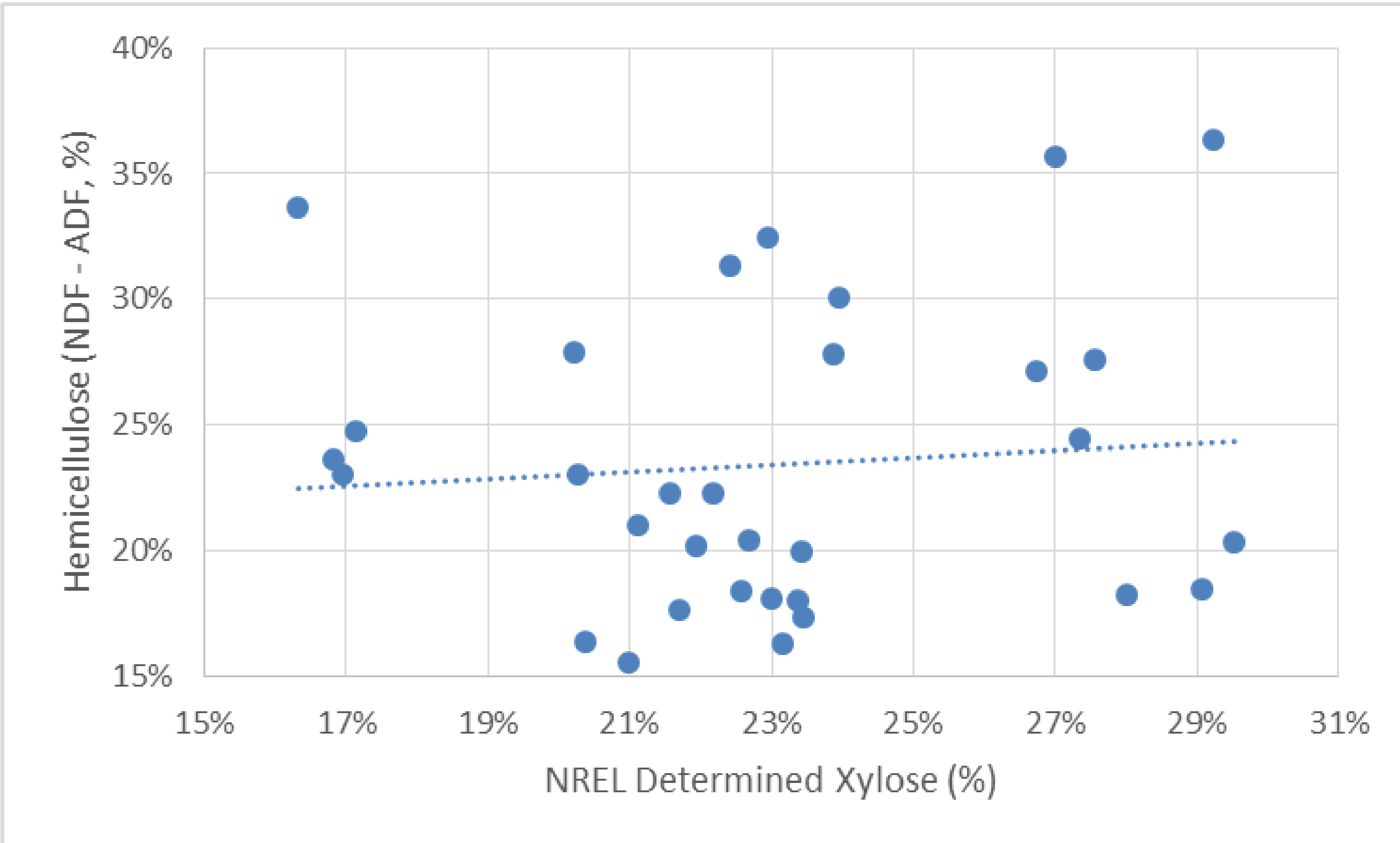


Figure 4-20 Average hemicellulose composition after washing determined using Ankom and NREL procedure for all crops studied

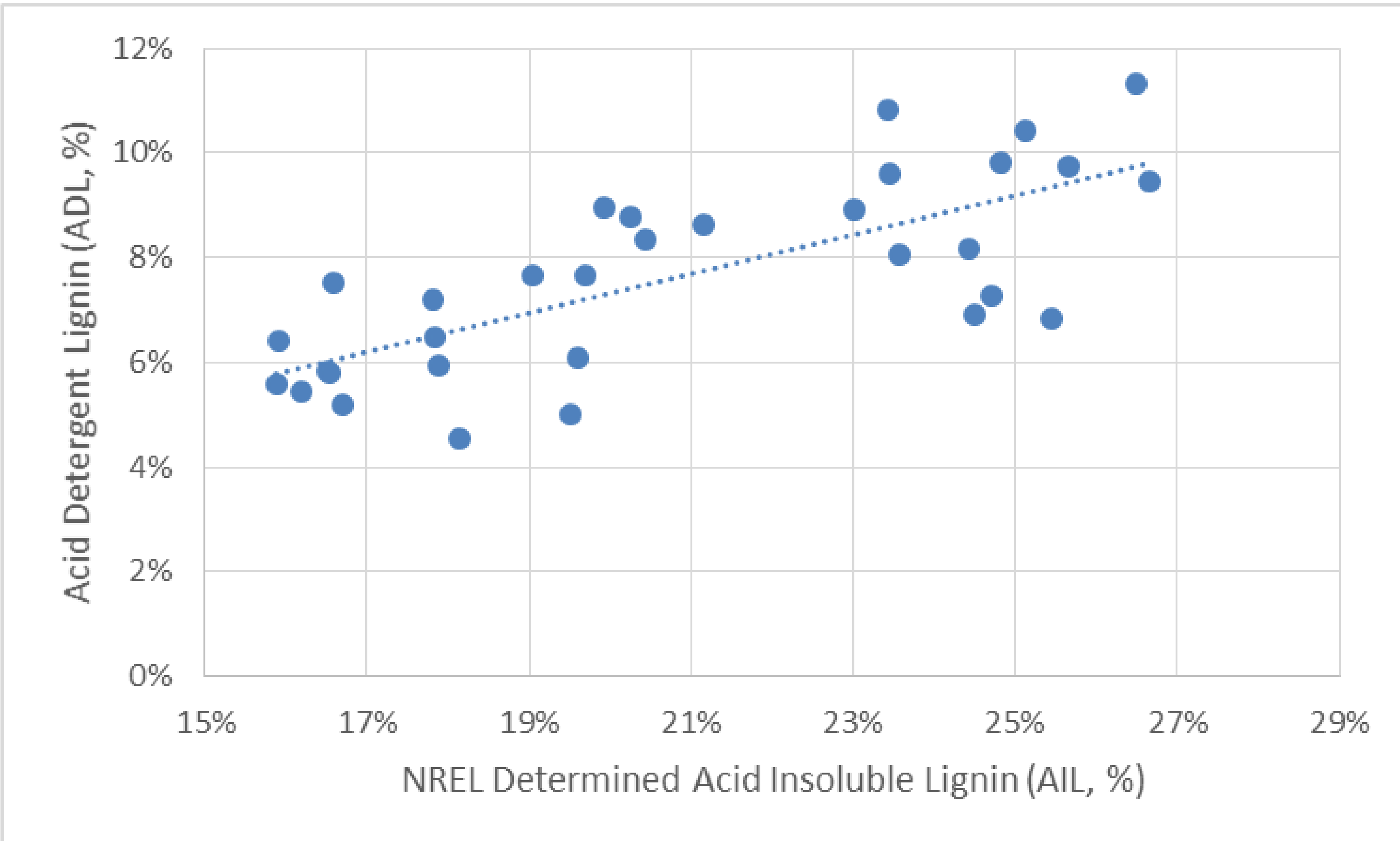


Figure 4-21 Average lignin composition after washing determined using Ankom (Acid Detergent Lignin, ADL) and NREL (Acid Insoluble Lignin, AIL) procedure for all crops studied

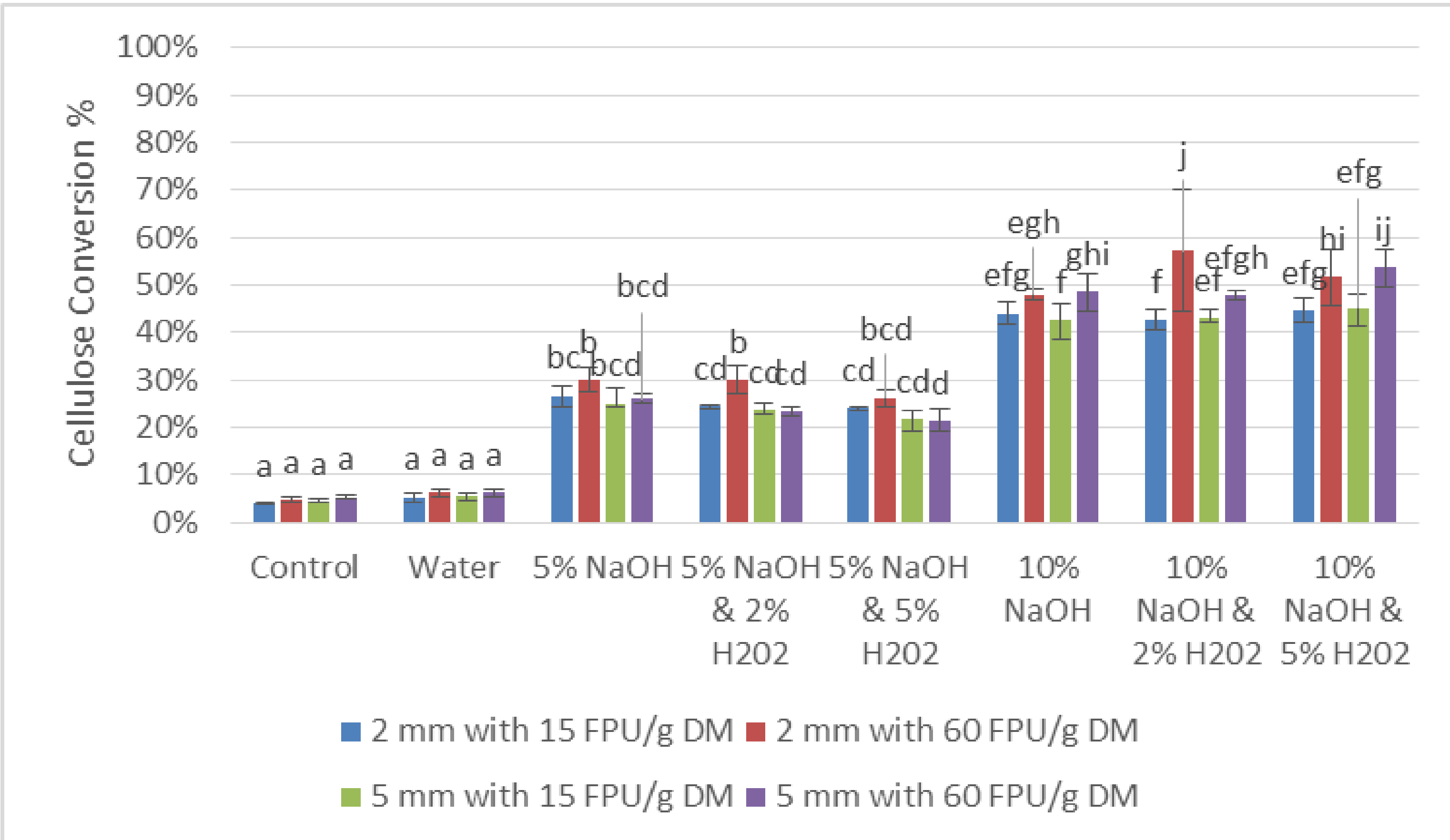


Figure 4-22 Cellulose conversion after enzymatic hydrolysis at 72 hours with a pH of 4.8 with a 2% solids loading at two enzyme concentrations (15 and 60 FPU/g DM) from pretreated and washed miscanthus ground through a 2 and 5 mm screen

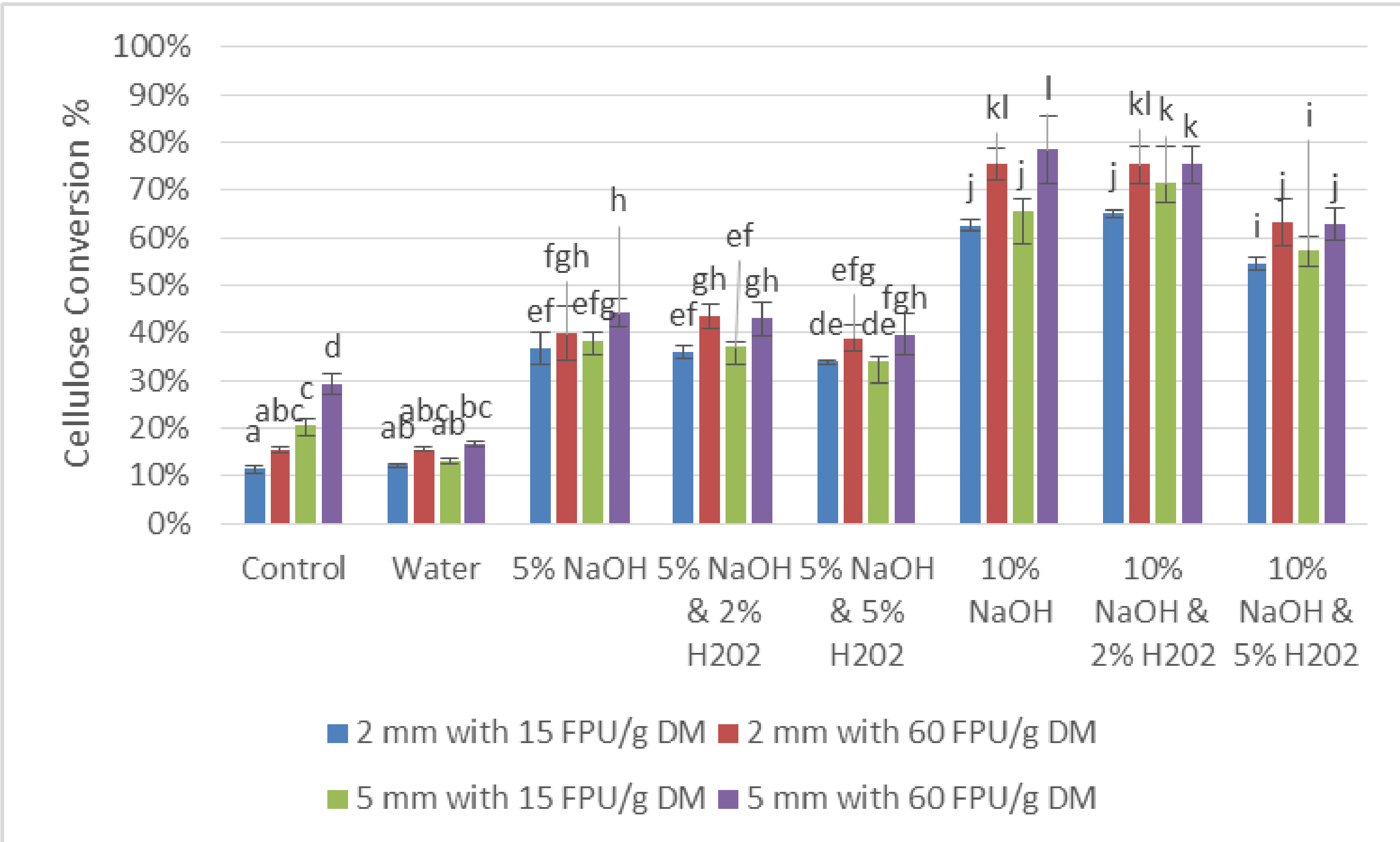


Figure 4-23 Cellulose conversion after enzymatic hydrolysis at 72 hours with a pH of 4.8 with a 2% solids loading at two enzyme concentrations (15 and 60 FPU/g DM) from pretreated and washed corn stover ground through a 2 and 5 mm screen

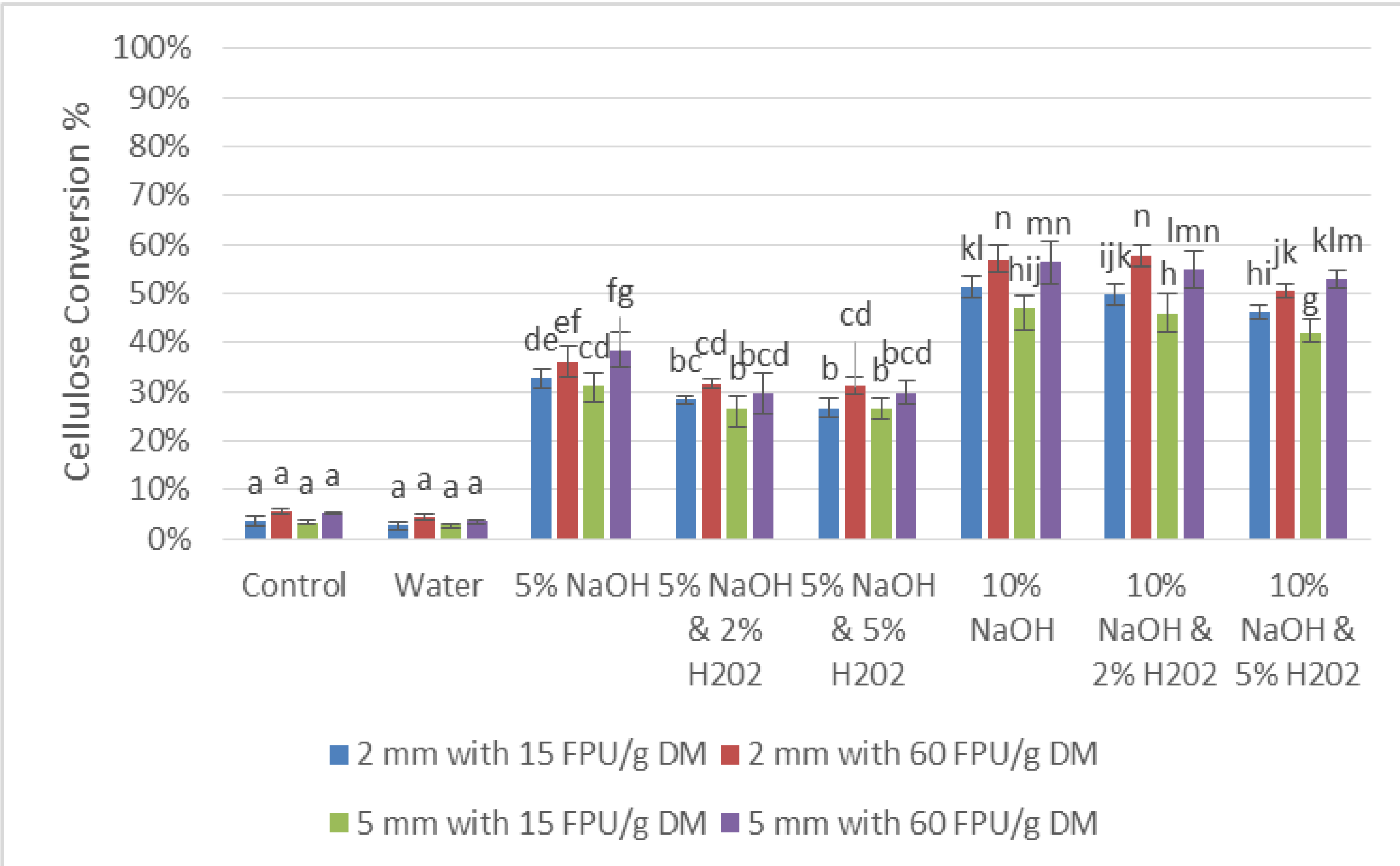


Figure 4-24 Cellulose conversion after enzymatic hydrolysis at 72 hours with a pH of 4.8 with a 2% solids loading at two enzyme concentrations (15 and 60 FPU/g DM) from pretreated and washed switchgrass ground through a 2 and 5 mm screen

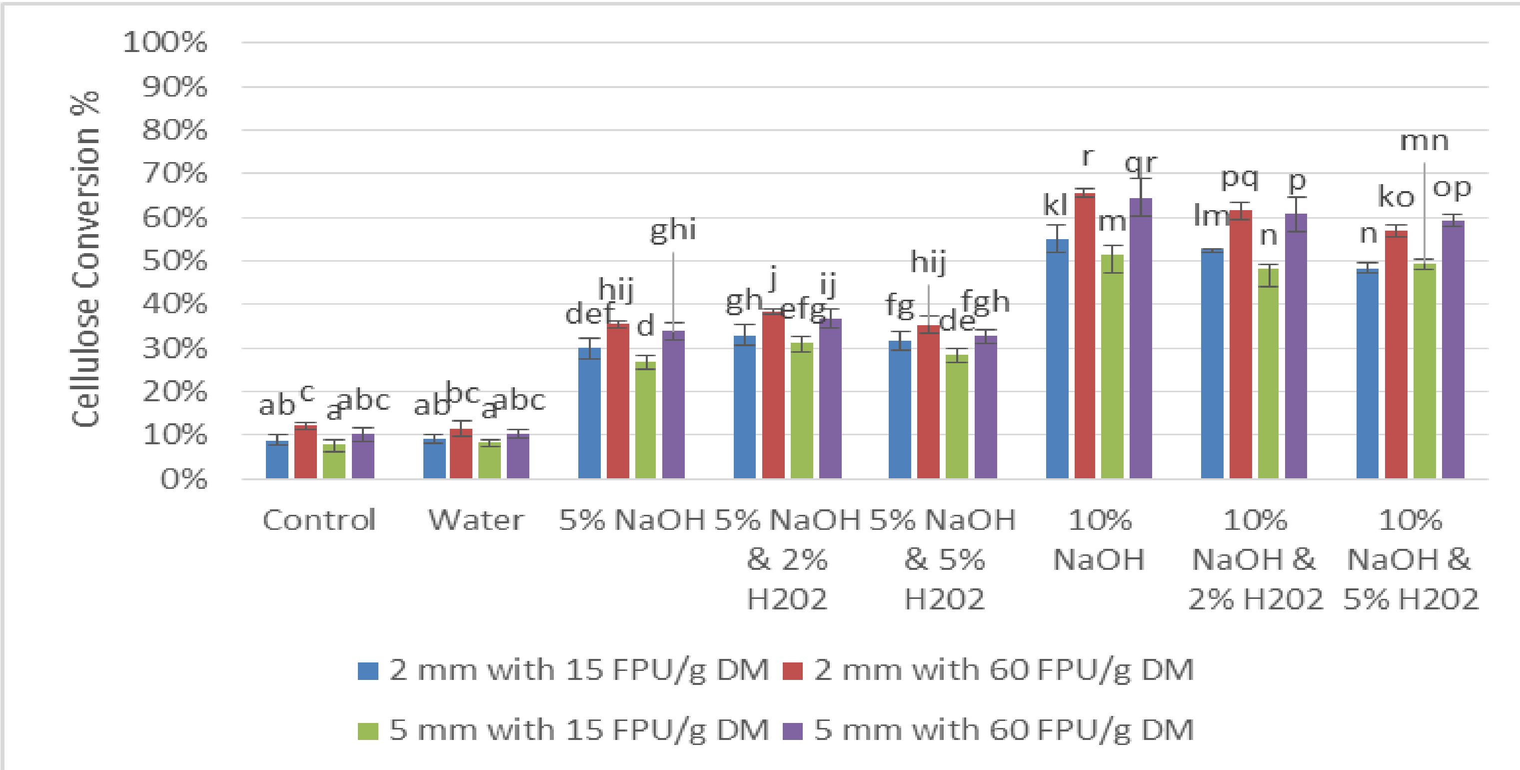


Figure 4-25 Cellulose conversion after enzymatic hydrolysis at 72 hours with a pH of 4.8 with a 2% solids loading at two enzyme concentrations (15 and 60 FPU/g DM) from pretreated and washed wheat straw ground through a 2 and 5 mm screen

CHAPTER 5:OBJECTIVE 3: GIS COMPARISION OF DISTRIBUTED NETWORK OF BIOBUTANOL PREPROCESSING FACILITIES

5.1 Summary

Traditional centralized processing facilities were compared to the proposed distributed preprocessing with centralized refining facilities in terms of transportation efficiencies. Centralized was defined as transport of corn stover in bales directly from the field to the refinery. Distributed preprocessing with centralized refining was specified as corn stover bales from the field to the biobutanol bunker and from the bunker to the centralized refinery with a dewatered crude biobutanol solution. Complete dewatering was assumed to be achieved at the distributed bunker facilities. For both transportation systems, the location of the corn fields and refinery were fixed. With the distributed system, the biobutanol bunker locations were variable and dependent upon differing maximum transportation (8 - 80 km) cutoffs for biomass transport from the field to biobutanol bunkers. With this case study, site specific transportation costs and biobutanol production capacities were developed for the differing transportation systems. The distributed designs produced a 38 - 59% reduction in total transportation cost when compared to the centralized system. Furthermore, the distributed design showed decreased (50 - 90%) fuel use and emissions when compared to the centralized system. The GIS transportation model demonstrated that "on-farm" biofuel production could be an effective means of producing biofuel and reducing the transportation costs.

5.2 Introduction

5.2.1 Butanol Rationale

The Renewable Fuel Standard Two (RFS2) mandated that 21 billion gallons of renewable fuel be produced from cellulosic biomass by 2022 (Urbanchuk and Association, 2009). One of the potential second generation biofuels to meet this demand is biobutanol. Biobutanol as a fuel source has many desirable qualities when compared to fuel ethanol. Biobutanol has a higher energy density (29 vs 19 MJ/L), is less miscible, can be combined at higher concentrations with gasoline without engine modification

(40% for butanol vs 10% for ethanol), and is less corrosive than ethanol (Bankar, Survase et al., 2013).

Despite these advantages, many challenges exist in the commercial viability of biobutanol or bioethanol. There is a direct relationship between the size of the bioprocessing facility and the distribution of biomass surrounding the plant, but diseconomies of scale are encountered as the size of the bioprocessing facility increase beyond a point due to transportation costs (Kumar and Sokhansanj, 2007). Biomass transportation costs for biomass ethanol processing facilities have been demonstrated to be 35 - 60% of the total cost depending on the conversion rate (Judd, Sarin et al., 2011). Transportation of bulk biomass (round baled, square baled, or ground) is constrained by volume rather than by weight because transportation vehicles will reach a maximum volume before the maximum weight is achieved due to the biomass density. The low bulk and energy density make the minimization of biomass transport costs imperative (Zewei, Shastri et al., 2011). Preprocessing biomass is one way to improve transport efficiency. Preprocessing for transport typically involves increasing the bulk and energy density of material through the formation of cubes, briquettes, and pellets (Morey, Kaliyan et al., 2010). However, the benefits of increased density are only realized when the preprocessing facility is located in close proximity to biomass production. Since the production of biomass (residue or dedicated biomass crops) is naturally distributed, consequently, the collection points for the preprocessing would also have to be distributed. From a logistics standpoint, satellite storage facilities (biomass collection points) with the ability to densify the material have been demonstrated to be effective means for reducing the delivered cost of corn stover (Judd, Sarin et al., 2012). The location and size of these preprocessing/processing facilities is primarily dependent upon the spatial availability of biomass and the distance along the road network to the preprocessing facility. The spatial availability of biomass and transportation network is reconciled with the use of suitability and optimization analysis. Suitability analysis allows for the potential bioenergy sites to either include or preclude potential locations based upon the positive or negative attributes of the surrounding area. Optimization of the system uses various methodologies, such as location-allocation to determine the most desirable locations for bioenergy facilities.

One of the proposed solutions to reduce biomass transportation costs is the localized or on-farm production of crude biobutanol using distributed on-farm (or cooperative operated) preprocessing facilities. The conversion of biomass to a crude dewatered, biobutanol stream will be accomplished on-farm utilizing a distributed farmer/cooperative operated processing facility. This is believed to result in a more energy dense product that can be more efficiently transported for further processing than hauling the raw, baled biomass. The crude, dewatered biobutanol stream is assumed to be acetone (5%), butanol (95%), and ethanol (<0.1%) (ABE) (Gunawardhana, 2014). From a volumetric energy content perspective, corn stover bales with an approximate density of 256 kg/m^3 (16 lb/ft^3) would possess 4.67 GJ/m^3 while completely dewatered crude biobutanol would possess an approximate energy density of 29.97 GJ/m^3. Furthermore, other studies with biodiesel have demonstrated that small-scale on-farm production of biodiesel to be energetically plausible and efficient methodology for biofuel production (Fore, Porter et al., 2011).

The assessment of localized biofuel production is dependent upon a number of geospatial data sources, such as mapsheet and plans, aerial/remote sensed images, surveys, and digital data products (Graham, English et al., 2000, Malczewski, 2004). The transformation of this geospatial data into useable data is aided by the use of Geographic Informational Software (GIS). The use of GIS to identify bioenergy crop yield dates back to studies performed by Ramsey and Cushman in the 1980’s and biomass facility location optimization back to 1996 with the Biomass Resource Assessment Version One (BRAVO) model (Noon and Daly, 1996).

Many different methodologies have been utilized to ascertain the acreage and yield of biomass through spatial analysis. The United States Department of Agriculture National Agricultural Statistics Service (NASS) provides annual data for crop production on a county and state level and has been used as a foundation in multiple studies to estimate the supply of biomass (Petrolia, 2008, Ekşioğlu, Acharya et al., 2009, Alex Marvin, Schmidt et al., 2012). For studies that use NASS or equivalent production statistics, the spatial variation of biomass has typically been assumed to be uniformly distributed across the study area (Voivontas, Assimacopoulos et al., 2001, Shastri, Hansen et al., 2011).

To identify specific areas of crop production within a study site at a more detailed scale than uniformly distributed NASS data, cropland data layers (CDL) have been used. CDL was developed by the USDA from satellite imagery and has been demonstrated to accurately identify 85% to 95% of the major crop ground (USDA, NASS et al., 2014). A constant yield (kg/ha) has generally been assumed in studies that utilize CDL or equivalent data layers (Perpina, Alfonso et al., 2009, Ha, Munster et al., 2014). To account for spatial variation in yield, soil type and other attributes can be combined with the CDL to more accurately quantify potential yields (Graham, English et al., 2000)

5.2.2 Candidate Site Selection for Biomass Fields and Processing Facilities

The selection of biomass facility locations using GIS has taken many formats and depends largely upon the scale in which the researchers have analyzed the area. For studies that focus on state, regional, or national models, a common assumption can be made that either the centroid of the county (Parker, Tittmann et al., 2010) or county seat is used as the primary collection point or location for the county. Grid design has also been used to predict biomass location (Wilson, 2009) with biomass origins and destinations being located at the center of these grids (Perpina, Alfonso et al., 2009). Grid designs lend themselves well to biomass analysis with the formation of rasters and the use of flow direction tools. The intersection of different transportation systems has also been used as potential candidate facility locations (Haddad and Anderson, 2008). Road intersections and junctions with other transportation networks have been demonstrated to be viable points for candidate facility site selections as these points are automatically created and represent the convergence point for differing transportation systems.

5.2.3 Transportation Network Analysis

Transportation network analysis can be used to exclusively analyze differing modes of transportation for biomass (road, rail, or barge), or combinations of transport systems can be examined in a multimodal analysis (Haddad and Anderson, 2008, Zhang, Johnson et al., 2011). The creation of transportation networks within GIS allows for the transportation costs to be more accurately represented and evaluated. Within the network analysis extension, ArcGIS possesses many different features for transportation analysis: routing, vehicle routing, service area, origin to destination (O-D) cost matrix, and location-allocation. Of these, location-allocation is the most versatile as this problem allow for the optimization of facility location to minimize travel distance required, number of facilities, time, or other factors.

Objective

The objective of this analysis was to evaluate the potential transportation benefits of distributed preprocessing of baled corn stover to produce a crude, dewatered biobutanol (butanol, ethanol, and acentone) stream versus transportation of baled corn stover to a centralized refinery (Figure 5-1). The two scenarios investigated were:

a. Transportation of baled corn stover to a centralized biorefining facility that performs all of the conversion and refining to a final product (referred to as centralized processing and abbreviated as CP);

b. Distributed processing at on-farm biobutanol facilities where the maximum one-way transportation distances for the baled corn stover from the field to the on-farm facility was 8, 16, 32, 48, 64, and 80 km. The crude biobutanol stream was dewatered and transported from individual on-farm facilities to a centralized refiner to produce the final products (referred to as distributed processing and abbreviated as DP).

The primary focus of the study was the costs associated with transportation. This model focuses on how transportation costs vary at differing transportation radii for intercounty scales and their application to the development of distributed on-farm biomass preprocessing facilities. Additionally, this study addressed how spatial variation in production influenced biomass availability with the inclusion of corn yield data for soil types across the state.

5.3 Materials and Methods

5.3.1 Geographic Information Systems (GIS)

ArcMap 10.2.1 (Environmental Systems Research Institute, Redlands, CA) was used to visualize and process data for this analysis with ModelBuilder being used to automate geoprocessing operations. Corn stover residue was considered to be the primary source of lignocellulosic material to narrow the scope. The collection of corn stover was assumed to be economically viable and an activity that all corn growers would engage in. The 2013 corn planted cropland data raster layer identified by CropScape was considered as the potential acreage for the collection of corn stover (NASS, 2013). GIS was utilized to combine this data with the line vector road network (Kentucky Transportation Cabinet), the line vector rail network (Kentucky Transportation Cabinet), area vector network for Kentucky counties (Network), and raster soil maps from the Soil Survey Geographic (SSURGO) database to predict grain yields and biomass availability that have been developed over the past century (Soil Survey Staff, 2014). Four different United States Department of Agriculture (USDA) agricultural regions within Kentucky were analyzed and are shown in Figure 5-2.

The network analysis extension of ArcMap was utilized to determine the optimum location of the on-farm biomass processing points. What made this trial unique was that the location-allocation tool was specifically used to minimize facilities for different maximum transportation distances within the agricultural regions across Kentucky.

5.3.2 Data Preparation/Geoprocessing

5.3.2.1 Soil Quality and Corn Stover Yield

The tabular data in Microsoft Access for the soil shapefiles were converted into Excel sheets. The SSURGO soil shapefiles (85 total for Kentucky) were added to the map and joined using the “mukey” field with the Excel tabular data containing crop yield in kg/hectare. The yield values were added to a new field within the soil data shapefile.

The CDL raster had to be transformed into a shapefile using the raster to polygon tool with the corn crop type being selected before the shapefile was converted for ease of representation and manipulation. The CDL polygons formed were not smoothed to allow for increased computational speed. This resulted in disjointed areas of production that did not represent actual fields. The aggregate polygon tool was used to combine polygon areas of corn production within a specified distance of 100 meters into fields and allow for only those greater than 2 hectares (5 acres) to be created. Furthermore, the aggregate polygon tool was used to fill holes in the CDL with 0.8 hectares (2 acres) representing the minimum size hole that was filed. The identified corn producing fields were split by using the road and rail network line shapefiles. Splitting increased the number of identified Kentucky corn fields to 43,132 from 16,788. Of this number, only 22,367 were selected again to be greater than 2 hectares. Before splitting, the largest corn field identified was 29,712 hectares (73,421 acres) and after splitting the largest field identified was 1,419 hectares (3,508 acres). The ability to split a polygon (identified corn fields) using lines (road and rail network) was not an option that was available within the standard GIS toolbox. Thus, splitting required the use of multiple GIS tools. The corn fields were transformed using the feature to lines tool and merged with the road and railroad lines. A temporary polygon shapefile was created from these merged lines using the feature to polygon tool. The geometric intersection of the overlapping portions from the corn field shapefile before splitting and the temporary polygon was conducted using the identify tool. The shapefile now possessed the split attributes.

After splitting, the identified corn field polygon was intersected with the SSURGO soil based grain yield data. For this analysis, the mass of stover available was surmised to be equal to the mass of grain (1:1 ratio of corn grain to stover) (Haddad and Anderson, 2008, Ekşioğlu, Acharya et al., 2009). An additional field was created in the intersected attribute table which would allow for the area of each individual soil type within the intersected polygon to be calculated. The area of each soil type and associated corn yields allowed for the overall estimation of stover yields. Intersected soils were dissolved based on the overall corn field identified and possessed accumulated corn stover yields. Subsequently, the feature to point tool could be used to transform the polygons to points which allowed for the spatial data for yields to be prepared for subsequent network analysis functions. These farm fields served as demand points for the on-farm biomass processing facilities.

County level corn production data was obtained from NASS to ensure that the results from this analysis did not deviate meaningfully from the predicted yields and hectares. A paired t-test was performed using SAS (Statistical Analysis System) v. 9.4 to compare the NASS and GIS calculated values.

5.3.2.2 Trucking Assumptions

Trucking was assumed to be performed using a class 8 vehicle with a loaded fuel consumption of 0.008941 L/Mg-km and unloaded fuel consumption of 0.025671 L/Mg-km (Davis, Diegel et al., 2014). The bales were assumed to weigh 714 kg (1575 lb) at a moisture content of 23% w.b. and would result in a payload of 23.6 Mg (52,000 lb). Payloads under 4.5 Mg (10,000 lb) were neglected. Diesel fuel was assumed to cost $1.06 L^{-1} ($4.00/gal) and labor costs were assumed to be $18 h^{-1}. Fixed loading and loading cost were assumed $5.29/Mg of corn stover. For both the trucking and loading contracting was assumed.

5.3.3 Location-Allocation

5.3.3.1 Corn Field to On-Farm Biomass Processing Facility

Location-allocation, within the network analyst function, was used in GIS to select the optimal locations for the on-farm processing facilities. The road shapefile was transformed into a road network in GIS and network junctions were automatically created at each intersection. The candidate facilities for on-farm processing facilities were located along these network junctions (at road intersections). The road data set was used to narrow the potential number of candidate facility locations by selecting against "CITY" type roads; this would prevent the location of an on-farm processing facility within city limits. The road shapefile was input into the feature vertices to points tool and created points that dangled (located at the end of the road-dead ends) from the network. The dangled points created were used in combination with select by location to remove these points from the analysis.

The demand points (fields over 2 ha where corn was grown) were loaded into the location-allocation model by region. Harvesting costs were neglected for this analysis and mid-size rectangular bales with dimensions of 0.9 x 1.2 x 2.4 m (3 x 4 x 8 ft) were assumed to be at the field edge. This analysis assumed only 25% of the total corn stover would be removed from the field for biobutanol to account for the residue that would be used by livestock, soil stability, and other purposes (Alex Marvin, Schmidt et al., 2012). The minimum bunker size was assumed to be 63.5 Mg (70 US tons) and each bunker would be able to complete four 80 day "treatment" cycles per bunker per year. Therefore, the minimum quantity of corn stover that could be delivered to a potential on-farm processing system was 254 Mg (280 tons) per year.

Loading the demand points into the location-allocation tool was not time intensive, yet loading was improved by creating a spatial index for the road network. The bales on the field edge were assumed to be located at a point that was closest to any road. The tolerable impedance (km from demand point to facility) was user defined and for this study was selected to be 8, 16, 32, 48, 64, and 80 km.

5.3.3.2 Minimize Facilities Problem

Every rural road intersection was a potential on-farm processing facility. The number of biobutanol bunker facilities within the areas of interest were minimized using the Minimize Facilities Problem Solver within the Location-allocation feature. The Minimize Facility Problem actually seeks to solve a Maximize Coverage problem with the impedance cutoff being specified as the maximum one-way travel distance with the number of facilities (P) being minimized by the solver (Church and Velle, 1974).

Maximize:

$$z = \sum_{i \in I} a_i y_i$$

Subject to the following constraints:

$$\sum_{j \in N_i} x_j \geq y_i; \; i \in I \tag{1}$$

$$\sum_{j \in J} x_j = P \tag{2}$$

$$x_j, y_i = (0,1); \; i \in I \; j \in J$$

$$N_i = \{ j \in J \big| d_{ij} \leq S \}$$

where i,I = index and set of demand points (fields) ; j,J = index and set of candidate facility locations (bunkers); S = cutoff distance (tolerable impedance); d_{ij} = shortest distance between demand point *i* and candidate facility site j; N_i = set of facilities eligible to cover point *i* within a distance less than or equal to S; a_i = population or resources to be served at demand point *i*; *P* = number of facilities to be located; x_j =1 if facility is chosen, = 0 otherwise, y_i = 1 if site is allocated to a facility, = 0 otherwise. Facilities within the specified cutoff distance must be greater than or equal to 1 for y_i to equal 1 as indicated by Constraint (1). Constraint (2) forces the number of facilities to be equal to *P*, and *P* was determined by the solver.

5.3.3.3 Bunker to Refinery

For the subsequent location-allocation analysis, the chosen biobutanol bunker facilities were designated as the demand points. The conversion efficiency for the bunker system was assumed to be 167 liters of ABE product per dry Mg of corn stover with only dewatering of fuel taking place at the biobutanol bunker. The dewatered ABE solution would be shipped by tanker truck to the refinery for separation. Four potential refineries within the state were located by an internet search and were geolocated so that a points shapefile. These were located near Ashland, Hopkinsville, Louisville, and Somerset, KY. For this analysis, all the refineries were assumed to have capabilities to process the biomass for the centralized design or the crude biobutanol for the distributed processing design. The transport of the crude butanol to and from the refinery was performed using a class eight vehicle with an approximately 26,500 liter (7,000 gallons) tanker trailer with a minimum load for transport being 2,650 liters. The minimum petroleum volumetric loading and unloading rate of 570 liters per minute (150 gallons per minute) was assumed along with an additional 20 minutes to connect and disconnect the associated equipment (Jones and Stan, 2006). The distribution of the fuel past the refinery was not considered in this analysis but the assumption was made that the refineries would use their existing distribution system for the fuel produced.

5.3.3.4 Transportation to the Refinery - P-median Problem

Transportation costs between the biobutanol bunker and the refinery, as well as the cost between the farm field and refinery was minimized using the P-Median Problem (PMP). The PMP seeks to minimize the impedance (distance traveled). For the PMP, the number of refineries was defined as four with no impedance being specified. The PMP seeks to solve the following (Longley and Batty, 1996, Church, 1999, Daskin, 2011):

Minimize:

$$Z = \sum_{i,j} a_i x_{ij} \, d_{ij}$$

Subject to the following constraints:

$$\sum_{j} x_{ij} = 1; i \in I \quad (3)$$

$$x_{ij} \leq y_i; \; i \in I \; j \in J$$

$$\sum_{j} y_j = p \quad (4)$$

$$x_{ij}, y_j \in \{0,1\} \; i \in I, j \in J$$

where i,I = index and set of demand points (bunkers or fields); j,J = index and set of candidate facility locations (refineries); d_{ij} = shortest distance between demand none i and candidate facility site j; a_i = amount of demand at node i; p = number of facilities to be located; x_{ij} = 1 if site i is allocated to a facility j, = 0 otherwise; and y_j =1 if facility is chosen, = 0 otherwise. Constraint (3) allow for demand points to be restricted to located facilities; while, constraint (4) fixes the number of facilities to be equal to P.

5.3.4 ModelBuilder

Within GIS, Modelbuilder was used to combine differing ArcGIS functions into specific tools and automate the workflow within the developed models. Modelbuilder has been used in other studies to create and execute tools associated with the conversion of cropland data layer (CDL) for service area calculations (Martinez and Maier) and for mobile pyrolysis units [12]. For this analysis, four separate tools were created to process the data. Joining cropland data to crop yields for the given soil type was one of the tools developed. Going from this CDL to the point shapefile with the total yield of corn stover was another. Evaluation of the transportation cost from the farm to the biobutanol facility was analyzed as another separate tool. Transportation from the biobutanol bunker to the refinery was the final model developed.

5.4 Carbon Dioxide Equivalents (CO_2-e)

The Alternative Fuel Life-Cycle Environmental and Economic Transportation (AFLEET) Tool (Laboratory, 2014) was used to determine the total GHG footprint for each region, cutoff distance, and transportation design. Default values were used with the exception of the following: Kentucky was selected as the state, combination long haul was selected as the vehicle type, 2000 was assumed for semi-truck model year. The GIS calculated distances traveled and fuel usage were inputs to determine the overall CO_2-e produced.

5.5 Results

5.5.1 Area and Yield Data

The total corn production and hectares predicted by the GIS model on a county basis were compared to the NASS reported values. For the 73 Kentucky counties with a reported corn harvest area in the 2013 NASS Survey, there was no significant difference ($p = 0.9866$) between CDL identified corn ground (greater than 2.02 hectares) and the NASS survey data. For the 74 counties with a 2013 NASS corn yield value, there was a significant difference ($p \leq 0.001$) between the NASS Survey results and the yield values calculated by the model. Using the soil attributes from the SSURGO model, an estimated average yield of 7,700 kg/ha (123 bu/acre) was calculated. The metadata indicated that the SSURGO yield values for corn were last updated in 2008 and the average corn yields have increased since that time. The previous 35 years of NASS yield data for Kentucky counties was fit to a linear regression line and predicted an average yield for 2013 of 8,980 kg/ha (143 bu/acre). A 17% adjustment factor was used to account for the lower values within the GIS calculation. The average yield for the CDL identified corn fields was 8368 kg/ha (133 bu/acre) and was increased by 17% to 9760 kg/ha 156 bu/acre). The comparison of the 2013 NASS and the adjusted GIS yield data demonstrated no significant difference.

5.5.2 Regional Location-Allocation

5.5.2.1 Potential Sites Within a Region

Based on the road networks, 20,529; 23,726; 19,837; and 16,723 potential bunker preprocessing sites were potentially available in the Bluegrass, Central, Midwestern, and Purchase regions respectively. These were locations where two or more rural roads had an intersection, that were not within city limits, and were not on a dead end road. Figure 5-3 demonstrates the selection of potential sites meeting the siting criteria.

5.5.2.2 Identified Bunker Sites Meeting Capacity Constraints

With the 8 km travel distance, in the Bluegrass and Central regions only 45% and 70% of potential facilities located at road intersections possessed enough corn stover to satisfy one biobutanol bunker, respectively. The Midwestern and Purchase Agricultural Regions demonstrated a higher concentration of potentially available corn stover at a maximum distance of 8 km, with 98% and 91% of the potential facilities identified satisfying the minimum biomass requirements, respectively. Within the Bluegrass and Central Regions, minimum biomass availability was still an issue at some potential facility locations with the 16 km maximum travel distance. With a maximum transportation distance 32 km or greater, achieving the minimum biomass supply at all bunkers was no longer an issue. The number of candidate facilities to be constructed in each region for the various transportation distances is shown in Figure 5-4.

5.5.2.3 Fuel Consumption

Across the regions, the sum of the fuel used going from the field to the bunker (F-B) increased with increasing maximum transportation distance (Figure 5-5). F-B transportation within the Bluegrass Region at the 80 km maximum one way transport distance resulted in a 9.6 fold increase in fuel consumed when compared to 8 km maximum distanced. Similarly, the Midwestern, Purchase, and Central Regions also showed 7.2, 8.0, and 9.5 fold fuel consumption increases, respectively for the 80 km maximum transport distance compared to the 8 km maximum.

For the differing transportation constraints from F-B, fuel use between the bunker and refinery (B-R) were found to be relatively similar within a region. Within the

Bluegrass Region, B-R fuel consumption increased by 20 percent with the increasing transportation cutoff from F-B. However in the other regions, the B-R fuel consumption decreased by up to 12% with the increasing F-B transportation constraint. For these regions the decreased number of facilities resulted in a reduced fuel usage. The breakdown of percentage of fuel across regions is shown in Figure 5-6. F-B fuel use was determined to be 28% at the 8 km transportation distance and increased to 79% at the 80 km transportation distance.

For the centralized analysis, going directly from the field to the refinery resulted in a greater overall fuel use than the distributed system with bunkers. The total fuel used for the four Regions is shown in Figure 5-5 comparing the distributed system with the centralized system. As expected, the fuel consumption increased as the on-farm bunker facilities drew a wider catchment area. Fuel required for the centralized method of transport resulted in over double the fuel use at 80 km in the Bluegrass Region. A similar trend is seen in the other regions as well with the centralized fuel use being 107%, 163%, and 108% higher for the Midwestern, Purchase and Central Regions, respectively.

5.5.2.4 Transportation Costs

The transportation costs followed a similar trend as the fuel usage. Across the regions, the average cost to get the material from the farm field to the bunker was $6.97/Mg for the 8 km maximum distance and $10.51/Mg for the 80 km transport distance with small differences seen between the regions, as shown in Figure 5-8. The cost to deliver corn stover to the bunker was largely dependent upon the cost to load and unload the truck with the shorter transportation distances to the bunker. Approximately 54 to 92% of the transportation cost at the shorter transportation distances was due to handling (both loading and unloading). Bunker to Refinery costs were similar within a region regardless of the maximum transportation distance from field to bunker. Across regions the unit transport cost ($/L) were similar, but the average amount of biomass processed at each bunker varied within each region. The production of corn stover by region showed the greatest production in the Midwestern Region followed by the Purchase, Central, and Bluegrass Regions (Figure 5-7).

Across the regions, distributed processing with bunkers resulted in lower (42-62%) total unit transport costs than the centralized design Figure 5-9. The lowest total transportation cost was found with the most distributed system processing system with a maximum transportation distance of 8 km for each region. Within the regions, the total unit cost of transport for the 80 km maximum impedance to the bunker was 45-56% greater than the 8 km maximum impedance distance.

5.5.2.5 Carbon Dioxide Emissions

Across all regions, the annual weight of CO_2 equivalents per Mg (kg CO_2e/Mg) of biomass produced as a direct result of truck transport increased (114 - 3090%) for the CP method than for the DP method as shown in Figure 5-10. For DP, the CO_2e/Mg for the Bluegrass Region was observed to be 3 – 232% higher than the other regions. For the CP transportation design, the Purchase Area demonstrated a 25-51% increase in the CO_2e/Mg when compared to the other regions.

5.6 Discussion

5.6.1 Area and Yields

The spatial variability of corn production, size, and location in Kentucky was resolved by utilizing ModelBuilder to combine the various forms of data and their attributes. Granted other biomass resources could be procured in a real world situation, yet corn stover was assumed to be the minimum baseline biomass supply for this analysis. The use of CDL allowed for corn production areas within Kentucky to be identified at a more detailed scale than NASS. CDL, developed by the USDA from satellite imagery, has been demonstrated to accurately identify 85 to 95% of the major crop production areas (USDA, NASS et al., 2014). The CDL harvest area was equivalent to that of the NASS survey data. However, the yield estimates had to be adjusted. A constant yield (kg/ha) has been assumed in studies that utilize CDL or equivalent data (Perpina, Alfonso et al., 2009, Ha, Munster et al., 2014). To better account for spatial variation in yield, soil type and other attributes have been combined with the CDL (Graham, English et al., 2000). Corn production was identified to take place upon some non-traditional soils and consequently yield data for these soils were lacking. Wilson

(2009) used the NASS county yields to create an adjustment factor for calculated crop yields to account for inconsistent data. Similarly, an adjustment factor of 17% was used in this trial to account for differences between the NASS and GIS calculated corn yields. Prior to the adjustment, the data "appeared" to consistently underestimate the total potential corn yields. The underestimation of the productivity (kg/hectares) could be attributed to the development of crop yield data based upon 2008 soil estimates (Metadata). In this trial, the soils with "no data" for the corn yields composed 4% of the acreage across the state and no adjustment or correction factor was used. As corn production averages increase across the state, a correction factor would have to be developed for future analysis to account for the future increases.

The automated geoprocessing of crop production data using ModelBuilder was surmised to be easier than manual identification. Faulkner (2012) visually identified corn and wheat production areas for the Purchase Region using Google Maps and calculated transportation costs to potential biorefineries using Google Maps. This methodology lacked repeatability and was labor intensive; while, GIS manifested less human induced error and reduced processing time (Martinez and Maier, 2011). Taking into account the spatial and yield variation in field level production area allowed for the interpretations to be more representative of actual transport costs than assuming uniformity of yield and distribution (Jenkins, Arthur et al., 1983).

5.6.2 Location-Allocation

Noon Noon, Zhan et al. (2002) stated that the capital and operational cost are largely equivalent, but the cost associated with biomass procurement can have a great influence upon economic viability of biofuel processors. The location-allocation tool allowed for the site specific transportation costs to be developed as well as site specific corn stover availability given the varied distance constraints. The suitability aspects of this analysis were primarily reliant upon the distributed nature of the biomass and the exclusion of points within 305 m (1000 ft) of "CITY" roads along with dead end points in the network being removed from the Region analysis. Removing the candidate bunker facilities from the "CITY" and dead ends makes the location-allocation analysis more computationally feasible [13] and allows the bunker site selection to be focused upon rural areas. Factors other than “CITY” roads could have been used in regards to the suitability analysis.

Road intersections and junctions with other transportation networks have been demonstrated to be viable points for candidate facility site selections as these points are automatically created and represent the convergence point for differing roads. From a practical standpoint, this is a reasonable constraint and most producers would locate bunker facilities at road intersections.

The minimize facilities tool within ArcMap was used to locate the biobutanol bunkers while most other studies have used PMP as the primary location-allocation tool for biofuel facilities (Möller, 2003, Dong, 2008, Sultana and Kumar, 2012). The objectives of PMP and minimize facilities are different. With PMP, the number of facilities and the maximum impedance can be modified to achieve the minimized weighted or unweighted transportation cost in distance or time. In the case of centralized processing, PMP was used because four potential refining locations were identified within the state. Minimize facilities seeks to maximize the coverage of all the demand points within the given impedance. In the case of on-farm facilities, the locations were determined and in this case the minimum number of bunker facilities for each transportation distance were desired and the minimize facilities tool was most appropriate. With equivalent impedance and facilities parameters, the location of fire stations in Kuwait demonstrated no difference between the use of PMP and minimize facilities, but the researchers surmised this could have been partially due to the reduced spatial variation in demand points (Algharib, 2011). PMP was used to analyze transport from the biobutanol bunker to the refinery as minimizing the transport cost where locating the number and location of the centralized refineries was not the overall goal. A weighted factor consisting of fuel consumption was used for location-allocation analysis transport to the bunker and refinery.

5.6.3 Regional Variations

The prevailing thought was that there would be a greater spatial distribution of biomass within the Bluegrass Region as compared to the other regions and would manifest a higher cost of transport from the farm to the bunker. Nonetheless, costs per

Mg were demonstrated to be relatively equivalent for each region. This was largely due to the high cost associated with bale loading and unloading relative to transporting corn stover over a short distance. From an overall transportation perspective, the use of distributed preprocessing of corn stover into a dewatered, crude biobutanol solution resulted in a greater cost saving than the exclusive use of centralized refineries. The greatest saving from a transportation standpoint was demonstrated with a maximum distance of 8 km from the field to the bunker. The capital and operational costs associated with the bunkers would be similar with the exception of the heat and processing units. However, these capital and operational costs were excluded from the current analysis as some have yet to be finalized. The inclusion of these costs would be utilized to ultimately determine the optimal travel distance to the bunker. With a 18,225 km^2 area and greater, You and Wang (2011) demonstrated that distributed ethanol processing resulted in the minimized overall (capital, production, and transportation) cost and minimized unit cost when compared to a centralized design. The transportation costs of the biobutanol bunker system seem promising, but the capital and processing cost would ultimately determine the viability of ABE production.

Within this study, the transportation related carbon dioxide equivalents were found to be higher for the centralized transport as compared to the distributed centralized transport. You and Wang (2011) had demonstrated that from a transportation standpoint the distributed-centralized approach resulted in more total transport greenhouse gas (GHG) emissions. The difference between the two studies could be related to the use of actual road networks in this study. Across all DP transportation distances, the greatest amount of CO_2-e/Mg baled corn stover was found in the Bluegrass Region. The elevated GHG emissions per bale would be indicative of the more disperse nature of production taking place in that region. For the centralized design, the Purchase Area exhibited the greatest CO_2-e/Mg baled and this was surmised to be related to more biomass being transported from the lower edge of the state and the road network in the far western corner of the state. For travel distances ranging from 32 km to 160 km, the integrated biomass supply analysis and logistics (IBSAL) model found GHG emissions for trucking to be higher at 49.875 CO_2-e/Mg (Sokhansanj, Kumar et al., 2006).

This analysis assumed corn stover was delivered and processed as large square bales. Differences in the type of bale (round versus square) was ignored for this analysis. Bale type would only change the analysis if the load/unloading characteristics and overall mass loaded onto a truck were different. Transportation of bales was assumed to be conducted only with class eight vehicles that are the largest trucks available for moving biomass.

5.6.4 Limitations

Models are only as resilient as the data that was obtained, and this is one of the main limitations of the GIS approach (Panichelli and Gnansounou, 2008). Yearly variability in the biomass supply would only account for changes in acreage planted and not with other intrinsic factors such as rainfall, growing degree days, dates planted, or harvest time that would determine the amount of corn stover available. Differing weather patterns could be used to adjust the overall yield and equipment required on the farm (Shastri, Hansen et al., 2011). Harvested dates can affect the total ratio of corn grain:stover ratio but would vary depending upon a number of factors. Furthermore the model only considered corn stover. The use of other crop residues or dedicated biomass crops would alter the location of potential facilities. Nonetheless, the methodology developed here for corn stover could be used for the other biomass resources.

Differing unit costs and energy usage exist for the differing baling (square vs round) schemes in switchgrass (Kumar and Sokhansanj, 2007) and distinct advantages and disadvantages exist with the differing baling methods (Larson, Mooney et al., 2010). The conversion of biomass into crude biobutanol uses a bunker system designed for the use of square bales.

From a completeness of data standpoint, the road shapefile (AllRds) lacked speed limits. The average speed of transportation vehicles for biomass has been defined by whether the vehicle is loaded or unloaded [30], by type of road [27], and by the specified road statute within GIS shapefiles [15]. The use of speed limits would have enhanced the analysis, but the assumed speed was in line with average speed used in equivalent studies (Noon, Zhan et al., 2002).

The most time consuming portion of this analysis was the location-allocation minimize facilities tool. The processing time for minimized facilities was an average of 20 minutes for an 8 km maximum distance and over an hour for the 50 km distance. In order to improve processing time, the number of candidate sites for on-farm conversion facilities would need to be reduced with further selection criteria for the suitability analysis. The farms themselves could be used at the potential candidate facility sites as the results of the transportation analysis indicated that the 8 km travel distance would be preferable.

Economies of scale for the on-farm processing versus the centralized processing facilities could have impacts far greater than the transportation. The proposed on-farm biomass processing scheme should have minimal capital costs, but would still be sensitive to economies of scale. To date, no concrete numbers are available to estimate the costs associated with the on-farm processing system. It was assumed that the crude ABE solution was fully dewatered. On-farm dewatering research is still on-going, but the investments (in terms of energy and capital) to dewater the crude biobutanol solution could have a major impact.

5.7 Conclusion

Within GIS, the use of the actual road network and calculated corn yields based on soil type resulted in a more representative measurement of transportation costs. Site specific transportation costs were developed for corn stover and crude biobutanol. Across the regions, the total unit cost ($/L) was found to be similar within the differing transportation cutoff to the biobutanol bunker. The number and capacity of biobutanol bunker facilities was characterized by the differences in region and cutoff distance to the bunker. This GIS based model provides a good tool for the development of an overall comparison between the distributed-centralized and centralized production of biobutanol. Across the regions, distributed-centralized production exhibited a lower total transportation cost than the centralized design.

The use of ModelBuilder for this analysis allowed for automated workflow and could be performed with differing biomass types, transportation costs, and areas. In this analysis, the minimize facility tool demonstrated effectiveness to locate biobutanol facilities.

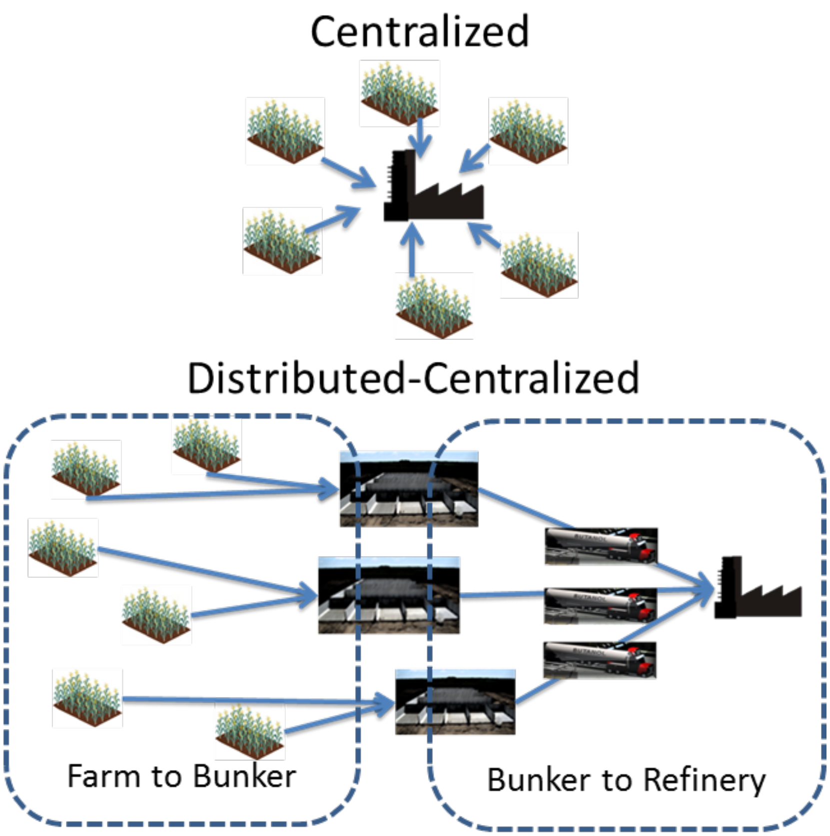


Figure 5-1 Illustrative example of transportation designs analyzed. The location of the farm field and refinery was fixed. The location of the bunker was minimized with respect to maximum transportation distance and location of corn fields

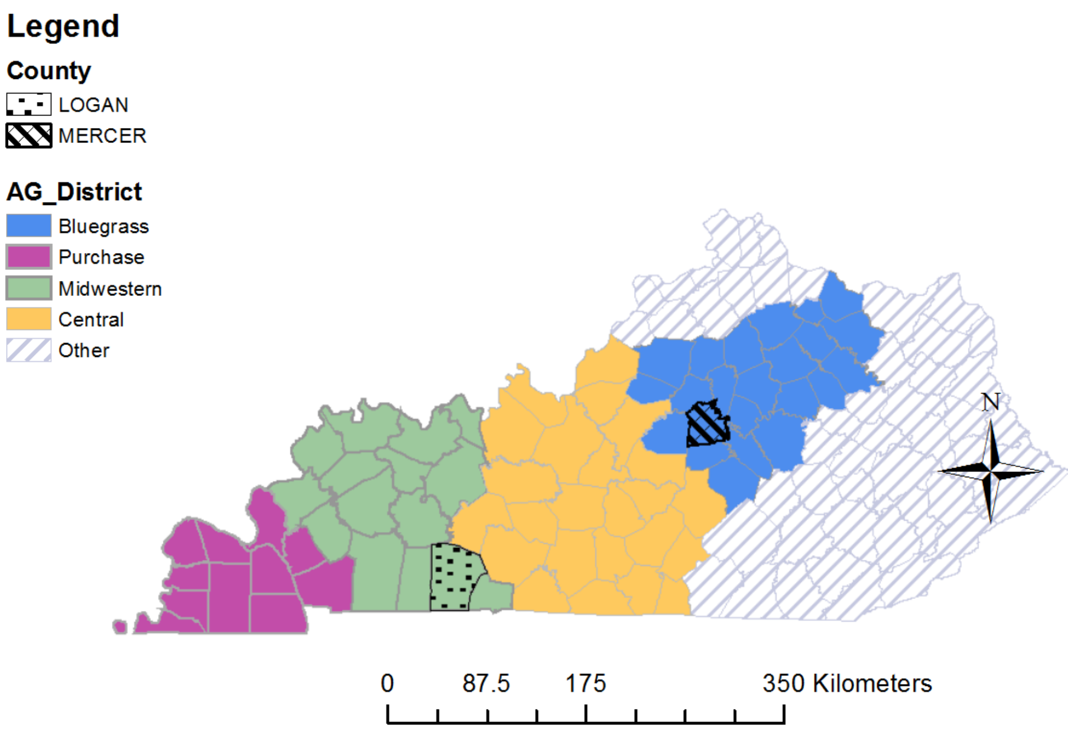


Figure 5-2 Agricultural district where corn production was prevalent in the state [Bluegrass Region (15,319 km^2), Purchase Area (9,357 km^2), Midwestern Region (16,422 km^2), Central (23,792 km^2)] and counties that were randomly selected [Logan (1,443 km^2) and Mercer (655 km^2)] for individual analysis

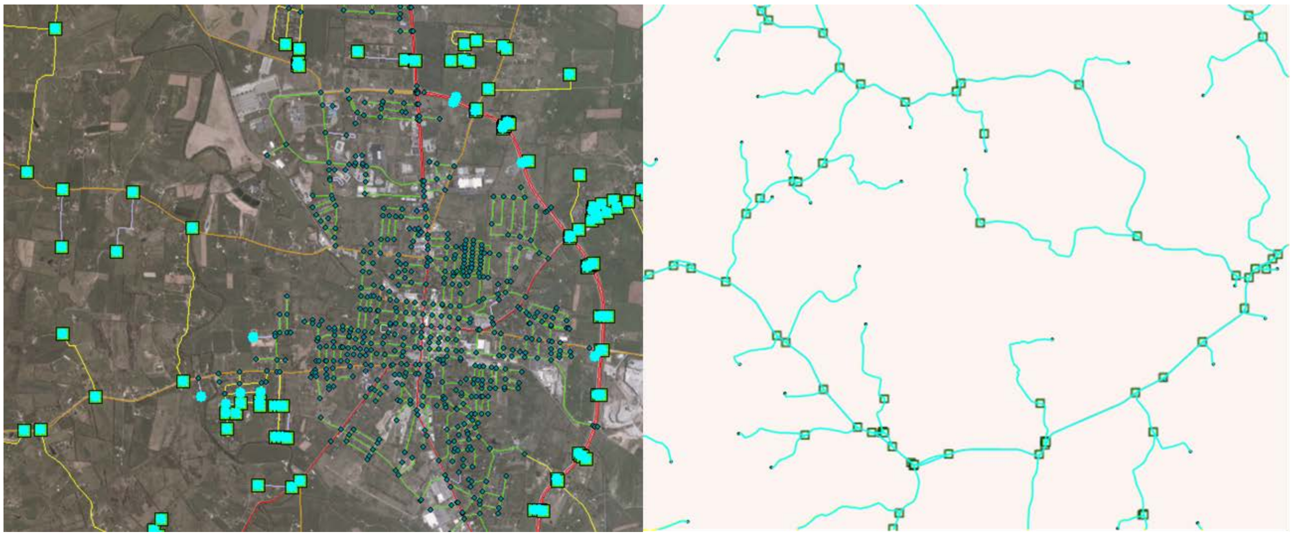


Figure 5-3 (a) Highlighted squares are network junctions that were selected as potential candidate sites for biobutanol bunker facilities while points located along “city” roads were excluded from the analysis. (b) Highlighted squares are network junctions that were selected as potential candidate sites for biobutanol bunker facilities and example of dangle points (dead end of roads) that were removed from consideration.

Table 5-1 Assumptions used to select bunker sites in GIS analysis

Parameter	Value	Reference
Crude BioButanol Transport (BioButanol Bunker to Refinery)		
Class 8 Truck Max. Payload	23.6 Mg (52,000 lb)	
Max. Volume	26,498 L (7,000 gal)	
ABE Conversion	151 L ton^{-1} (40 gal/dry ton)	
Trucking Costs		
Diesel Fuel Costs	\$1.06 L^{-1}	
Other Variable Costs(non-fuel)	\$0.339/km	(Trego and Murray, 2010)
Labor Cost	\$18 $hour^{-1}$	Trego and Murray (2010)
Transport speed	72.4 km h^{-1}	
Loading/Unloading	\$5.29/Mg	

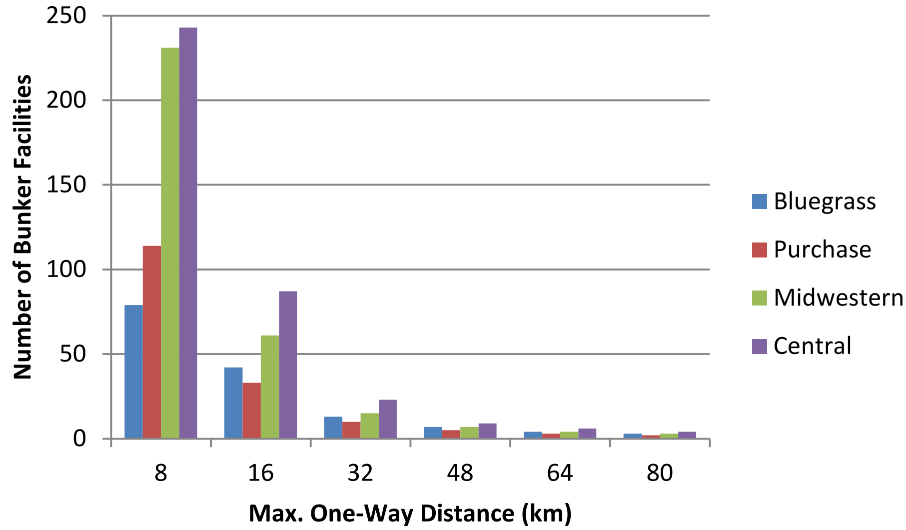


Figure 5-4 Number of identified bunker sites by region (Only facilities with more than 254 Mg of available biomass were considered)

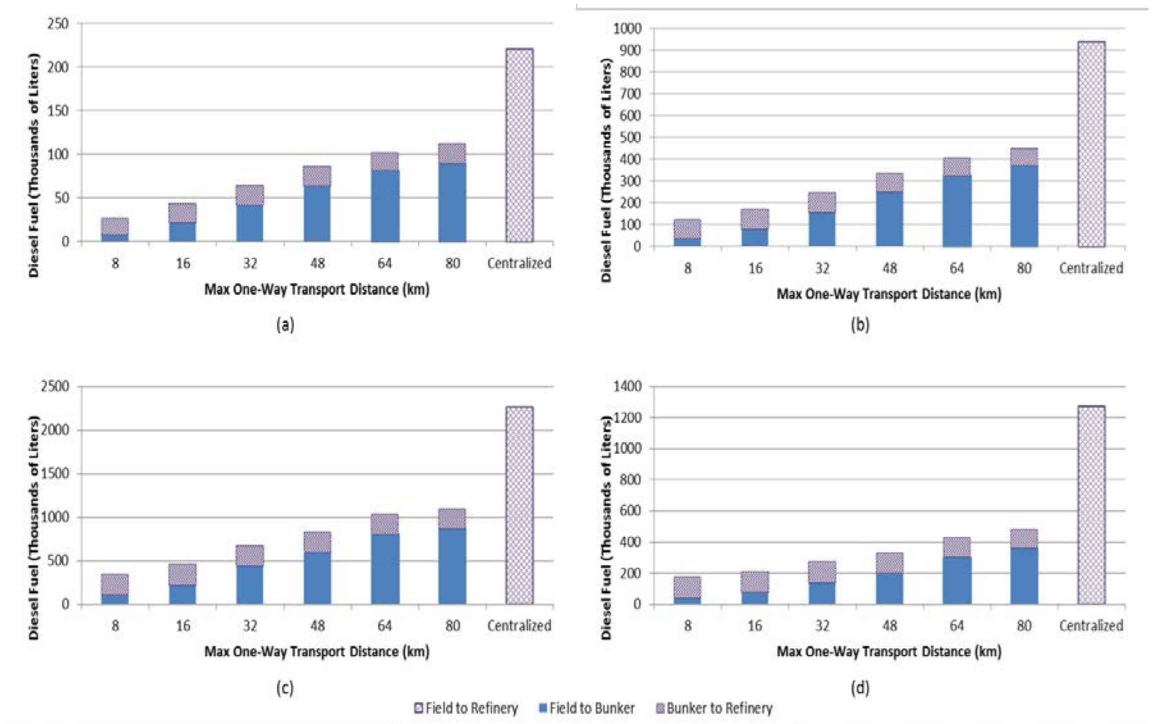


Figure 5-5 Total diesel fuel use for transport (a) Bluegrass Region, (b) Purchase Region, (c) Midwestern Region, and (d) Central Region

Figure 5-6 Percentage of fuel use across regions for distributed preprocessing

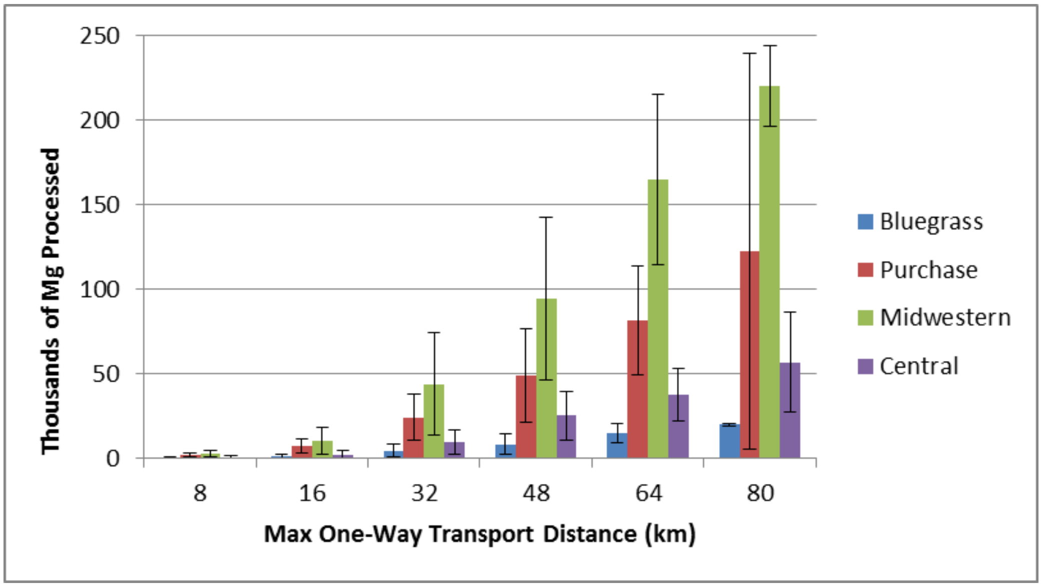


Figure 5-7 Average annual corn stover processed at on-farm facilities with one standard deviation.

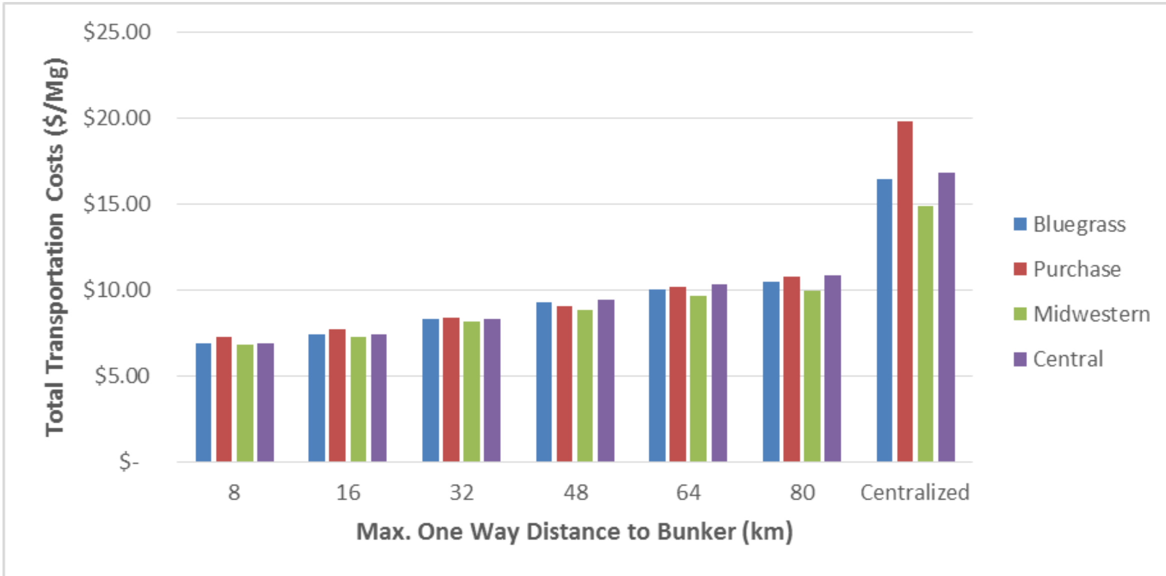


Figure 5-8 Total transportation and handling costs for distributed processing and centralized processing by region in terms of dollars per Mg

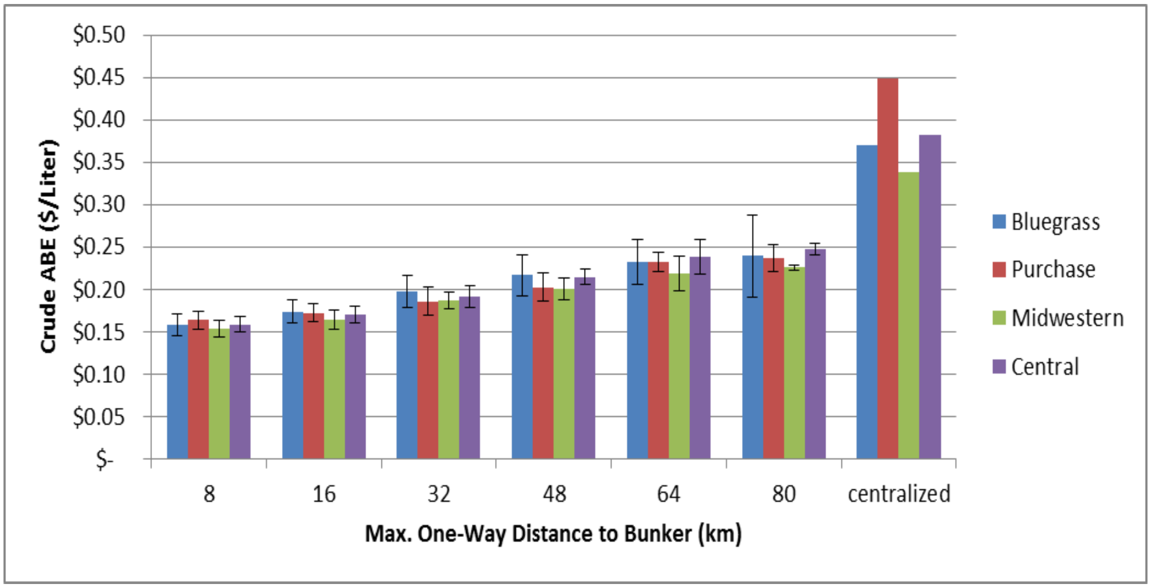


Figure 5-9 Total transport cost for distributed processing and centralized processing by region in terms of dollars per liter of dewatered ABE solution with one standard deviation

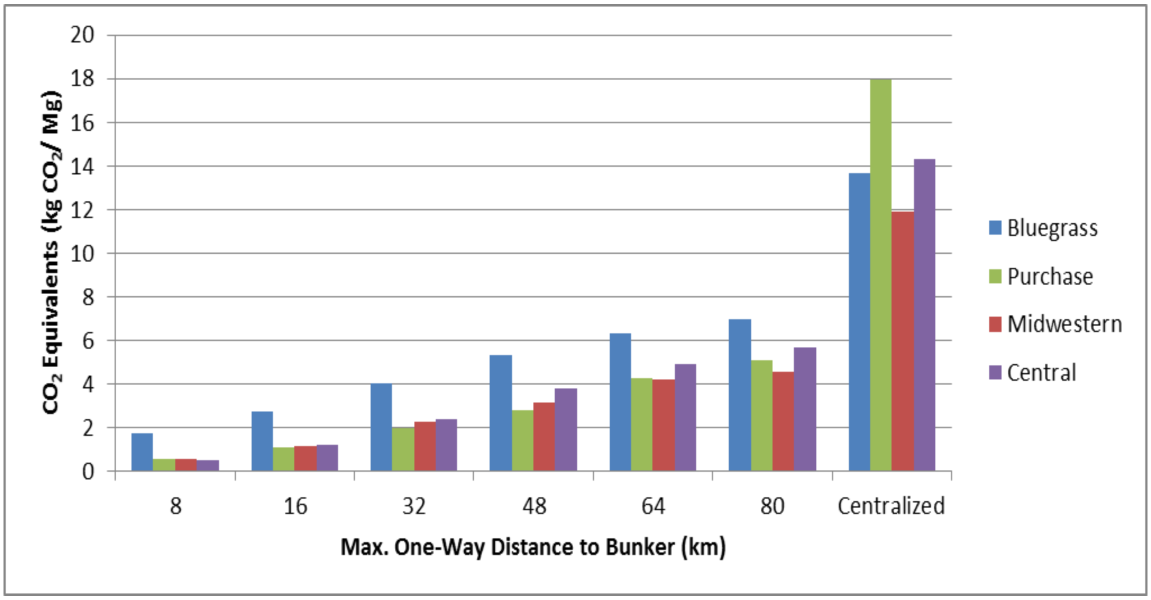


Figure 5-10. Annual truck transportation GHG emissions totals per Mg of baled material moved

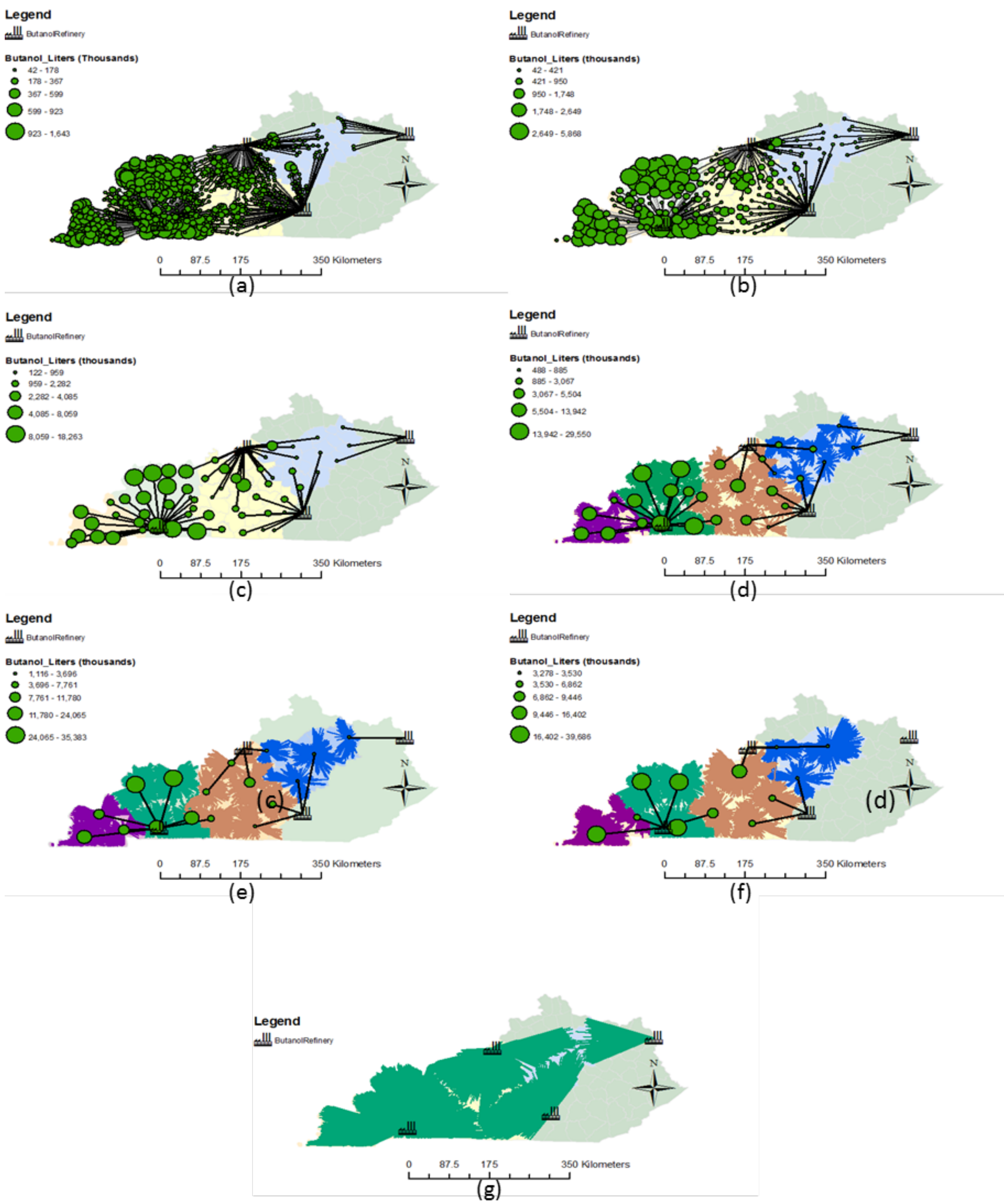


Figure 5-11. Liters of Crude biobutanol produced at each Bunker Facility (a) 8 km maximum impedance cutoff (b) 16 km maximum (c) 32 km maximum impedance cutoff (d) 48 maximum impedance cutoff (e) 64 maximum impedance cutoff (f) 80 maximum impedance cutoff (g) centralized

CHAPTER 6: SUMMARY AND CONCLUSIONS

The primary goal of this dissertation was to ascertain the viability of on-farm preprocessing methodologies to convert biomass to either liquid or solid biofuels. For the solid biofuel, the influence of moisture content upon the mechanical densification of biomass into pelleted material by a flat ring die was assessed and determined to have a dynamic response that depended upon the biomass. For miscanthus, switchgrass, and wheat straw, preconditioned moisture contents above 20% resulted in consistent pellet formation, and a moisture content of 25% produced the most durable pellets of 92%, 92% and 96%. Corn stover produced pellets at the measured 15%, 20% and 25% moisture contents with the greatest rate of pellet production at 15%. The pellet production efficiency, or specific energy consumption, of the biomass used in this study was found to vary from 101 kWh/Mg to 324 kWh/Mg and depended upon the biomass and moisture content. For miscanthus, the pellet throughput increased with moisture content which led to improved pellet production efficiency for biomass. Unlike the other biomass material in this study, corn stover displayed the best efficiency of 101 kWh/Mg at a 15% moisture content.

With regard to the conversion of material to liquid fuel such as biobutanol, the pretreatment of miscanthus, corn stover, switchgrass, and wheat with alkaline hydrogen peroxide was evaluated at different enzyme concentrations and grind sizes. Grind size was found to improve the efficiency of hydrolysis with all the biomass material except corn stover. The higher concentration of enzyme (60 FPU/g DM) was found to increase the conversion efficiency for all the biomass crops. For the alkaline and AHP pretreatments, hornification was surmised to have partially limited the response. Nonetheless for the different biomass materials, AHP was generally shown to not significantly enhance the cellulose conversion efficiency when compared to alkaline pretreatments.

From a transportation standpoint, the use of distributed preprocessing into liquid fuel was determined to be more cost effective and produce less CO_2 equivalents than a the transportation of biomass to centralized refineries. Kentucky was chosen as the study area with the four different Agricultural Regions being analyzed. For this case study, ArcMap was used to assess the different variables associated with this analysis as both tabular and spatial data can be effectively combined. For this analysis to accurately assess the difference between the distributed-centralized and centralized design, a number of factor had to be assessed such as crop, location, and yields of biomass had to be defined. The 2013 cropland data layers were used to ascertain the location of corn production. The CDL were aggregated together to remove holes in the data, and for a more practical representation of field size CDL were split using roads and railroads. The variable rate of collection of corn stover was based upon the soil characteristics and adjusted for 2013 NASS yields. Candidate locations for biomass production was defined as using junction points (intersections) of the transportation network. The analysis was more computationally feasible with network junctions along the city road and the end point (dead end of roads) being removed as potential candidate facilities. Within the Network Analysis, Location-allocation with minimize facilities was performed to calculate the impact that varying the distance to the bunker facility (8 km, 16 km, 32 km, 48 km, 64km and 80 km could have on overall transportation costs. The cost of transport from the edge of the field to the distributed preprocessing facilities increased with increasing transportation distance to the bunker with a 51% increase in the cost per Mg being observed as the distance increased from 8 km to 80 km. Nonetheless, the conversion of fuel at distributed preprocessing location reduced the total cost/Mg by 38 -59 % when compared to the centralized transport of corn stover directly to the refinery. Furthermore, the CO_2 equivalent produced and fuel use were reduced by at least 50% for the distributed design when compared to the centralized design.

CHAPTER 7: FUTURE WORK

The distributed preprocessing of biomass into a liquid fuel with complete dewatered crude ABE was shown to be viable from a transportation standpoint. The degree to which separation would influence subsequent transportation costs warrant evaluation. The total cost savings associated with levels of separation would help ascertain how much to invest in separation technologies. With many small to medium sized farming operations within the state, the direct transport of crude biobutanol from the preprocessing facility to the refinery could be enhanced by the use of milk-run logistics. The cost and potential saving associated with this has yet to be directly studied.

The flat ring die pelletization characteristics for biomass at varied moisture was determined, and the characteristics for different types of woody biomass would need to be evaluated as there exists considerable forest residue available within the eastern region of the state. Furthermore, pelleted material could be handled and stored similar to corn; thus, mechanical properties associated with handling and storage would need to be studied. The influence of scale and diameter of the die would need to be assessed as a larger diameter flat ring die with more rollers may result in greater, equivalent, or lower pellet production efficiency.

With respect to the AHP and NaOH pretreatment, hornification is known to impair conversion efficiency. Consequently, the quantifiable impact of hornification upon chemical pretreatments requires further studies.

APPENDICES

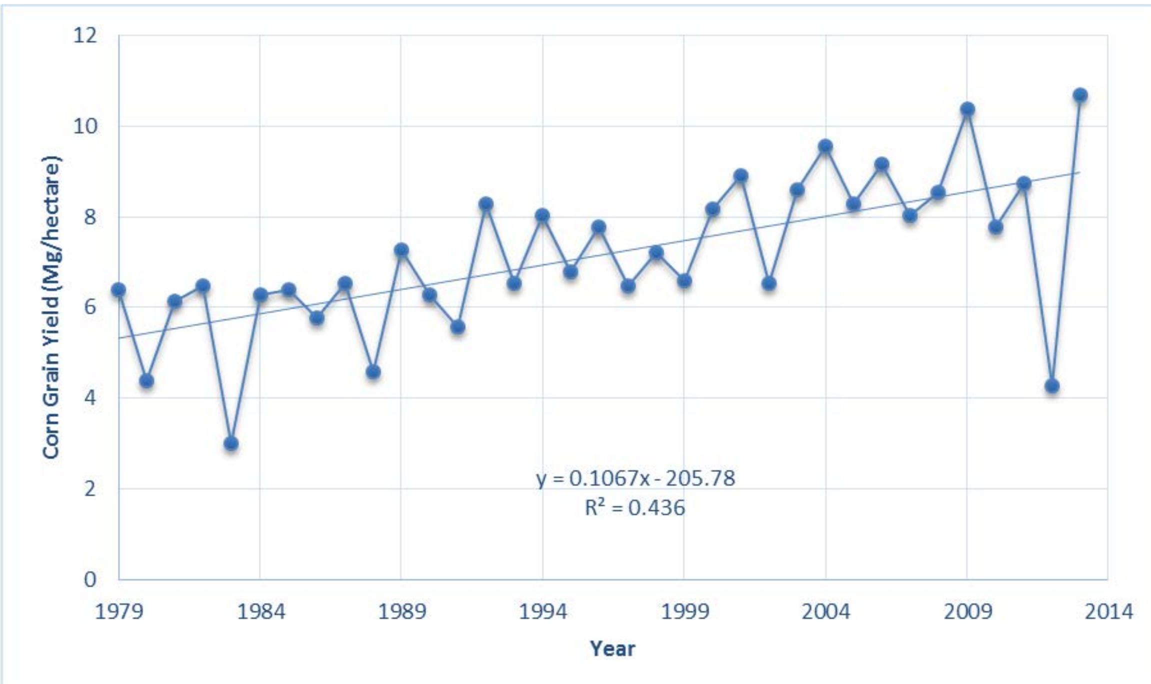
Appendix A. **Pelleting Data**

Appendix Table 1 Proximate Analysis for Biomass Crops

Biomass Material	HHV (MJ/kg) (Dry)	Proximate Analysis (Dry)[1]		
		% Volatile Matter	% Ash	% Fixed Carbon
Miscanthus	18.09	82.98%	2.53%	14.49%
Corn stover	17.86	80.24%	3.93%	15.82%
Switchgrass	18.61	83.65%	2.99%	13.37%
Wheat straw	18.30	78.61%	5.49%	15.89%

[1]Analysis conducted by Kentucky Center for Applied Energy Research

Appendix B. **USDA NASS Kentucky Average Corn Yield**



Appendix C. ABE Yield Assumptions for GIS Analysis

$$Cs \times Dm \times P_{C\&M} \times C_{eff} \times B_{Con/Sep} \qquad \text{Appendix Eqn. 1}$$

Where:

Cs = Corn stover (as is)

Dm = Dry matter content (0.77)

$P_{C\&M}$ = Percent cellulose and hemicellulose (0.6)

Ceff = Conversion Efficiency of cellulose and hemicellulose to sugar monomers (0.7)

$B_{Con/Sep}$ = Conversion efficiency of sugars monomers into ABE products (0.42)

Appendix D. Cost of Tractor for Loading/Unloading Bales on the Class 8 Semi-Truck and Trailer (American Society of Agricultural and Biological Engineers., 2011)

$$C_O = \left[\frac{1 - S_v}{L} + \frac{1 + S_v}{2} I + K_2\right] \times 100 \qquad \text{Appendix Eqn. 2}$$

Where:

C_O = Annual cost of ownership (%)

S_v = Salvage value factor (0.3)

L = Machine life (12 years)

I = Interest rate (0.08)

K_2 = Ownership factor (taxes, housing, and insurance) (0.02)

$$A_{OC} = \frac{P_P \times C_O}{H} \qquad \text{Appendix Eqn. 3}$$

Where:

A_{OC} = Annul Ownership Cost per hour ($/hr)

P_P = Purchasing Price ($60,000)

C_O = Annual cost of ownership (0.13)

H = Annual operating hours (225 hours)

$$Q_{avg} = 0.305 \times 0.73 \, x \, P_{pto} \, (SI)$$ Appendix Eqn. 4

$$Q_{avg} = 0.06 \times 0.73 \, x \, P_{pto} (English)$$

Where:

Q_{avg} = Average hourly fuel consumption

P_{pto} = Maximum PTO (power take off) power (~78 kW, 105 hp)

Appendix E. Fixed Cost of Transport of Baled Biomass

Appendix Table 1 Fixed Cost of Transport ($/Mg)

Operation	**Time (min)**	**Labor Cost ($)**	**Fuel Cost ($)**	**Ownership Cost ($)**	**Total Cost ($)**
Loading	45	$13.50	$13.86	$26.07	$53.43
Unloading	45	$13.50	$13.86	$26.07	$53.43
Wait	60	$18.00			$18.00
Overall Cost per truckload ($)					**$124.85**
Total Cost per Mg ($/23.6 Mg)					**$5.29**

$60,000 loader tractor with ~78 kW (105 pto hp)

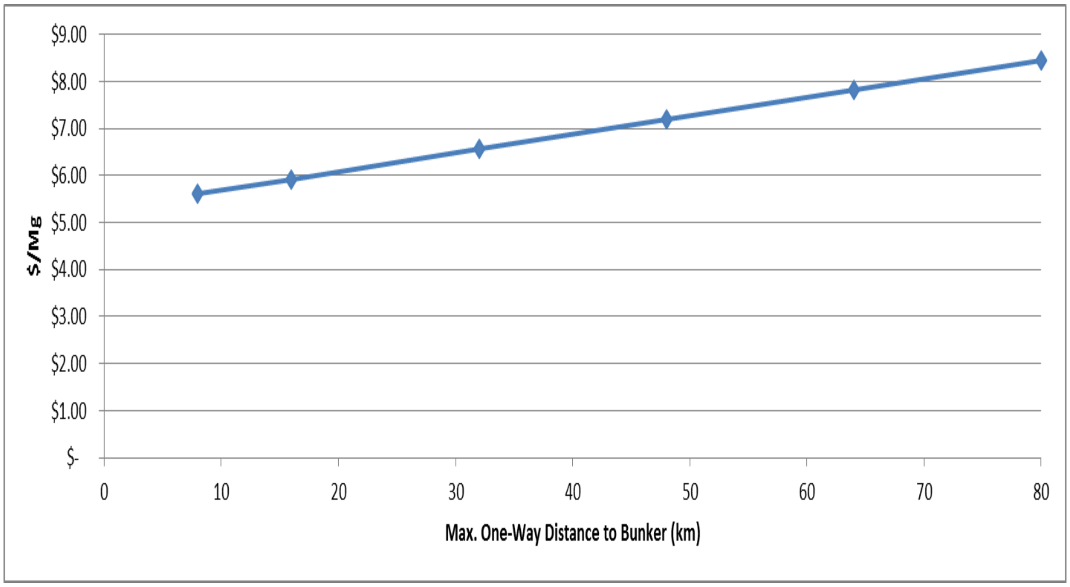
Appendix F. Variable Cost of Transport

Appendix Table 3 Variable Cost of Transport Based upon Distance

	Costs per mile		Cost per km	
Vehicle Based Costs	**Trego and Murray, (2010)**	**Adjusted for 2008-2014 Inflation[1]**	**Tredo and Murray, (2010)**	**Adjusted for 2008-2014 Inflation[1]**
Truck/Trailer Lease or Payment	$0.21	$0.23	$0.13	$0.14
Repair and Maintenance	$0.09	$0.10	$0.06	$0.06
Fuel Taxes	$0.06	$0.07	$0.04	$0.04
Truck Insurance Premiums	$0.06	$0.07	$0.04	$0.04
Tires	$0.03	$0.03	$0.02	$0.02
Licensing and Overweight-Oversized Permits	$0.02	$0.03	$0.01	$0.02
Tolls	$0.02	$0.02	$0.01	$0.01
Total	**$0.49**	**$0.55**	**$0.31**	**$0.34**

[1] Inflation calculated using http://www.usinflationcalculator.com/

Appendix G. **Total Transportation Cost**



Appendix H. SAS Results for Original Yield data

The SAS System

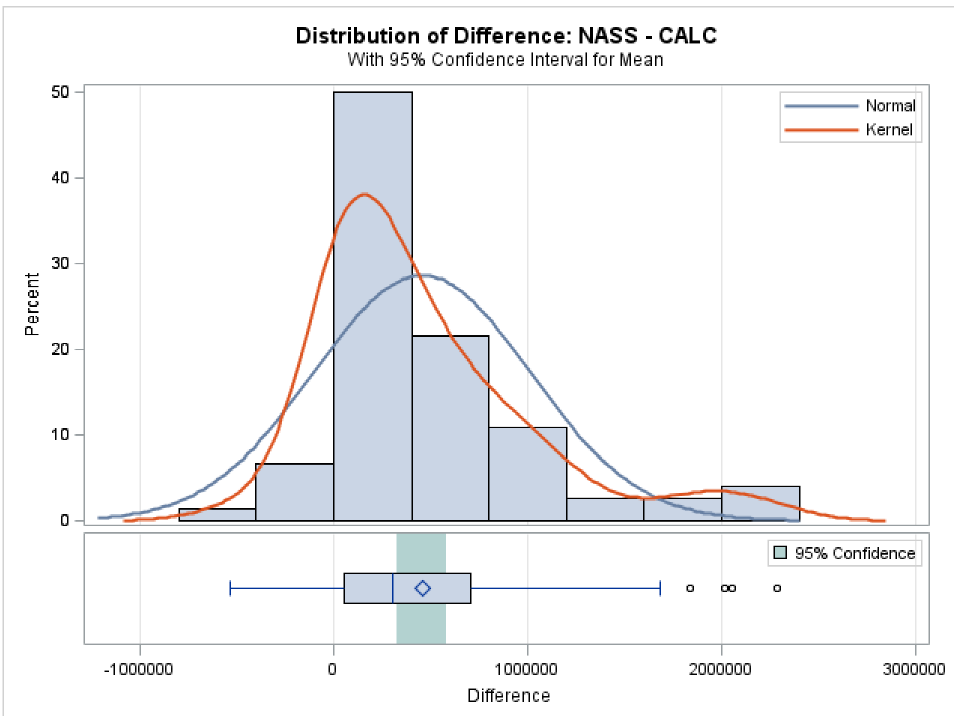
The TTEST Procedure

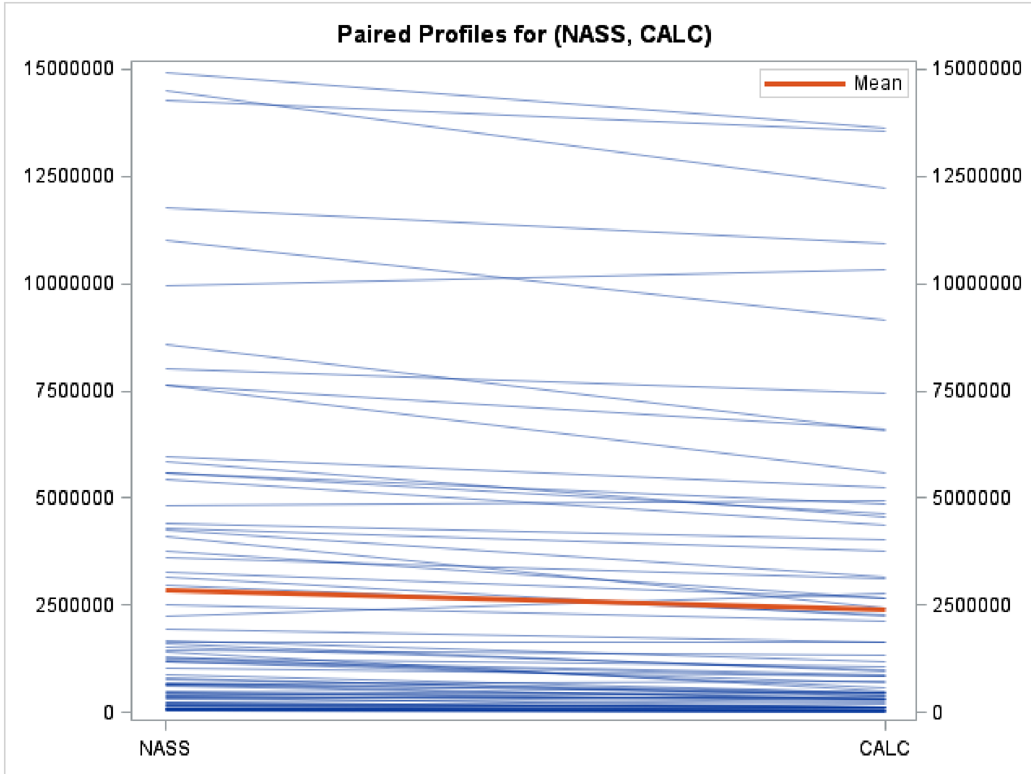
Difference: NASS - CALC

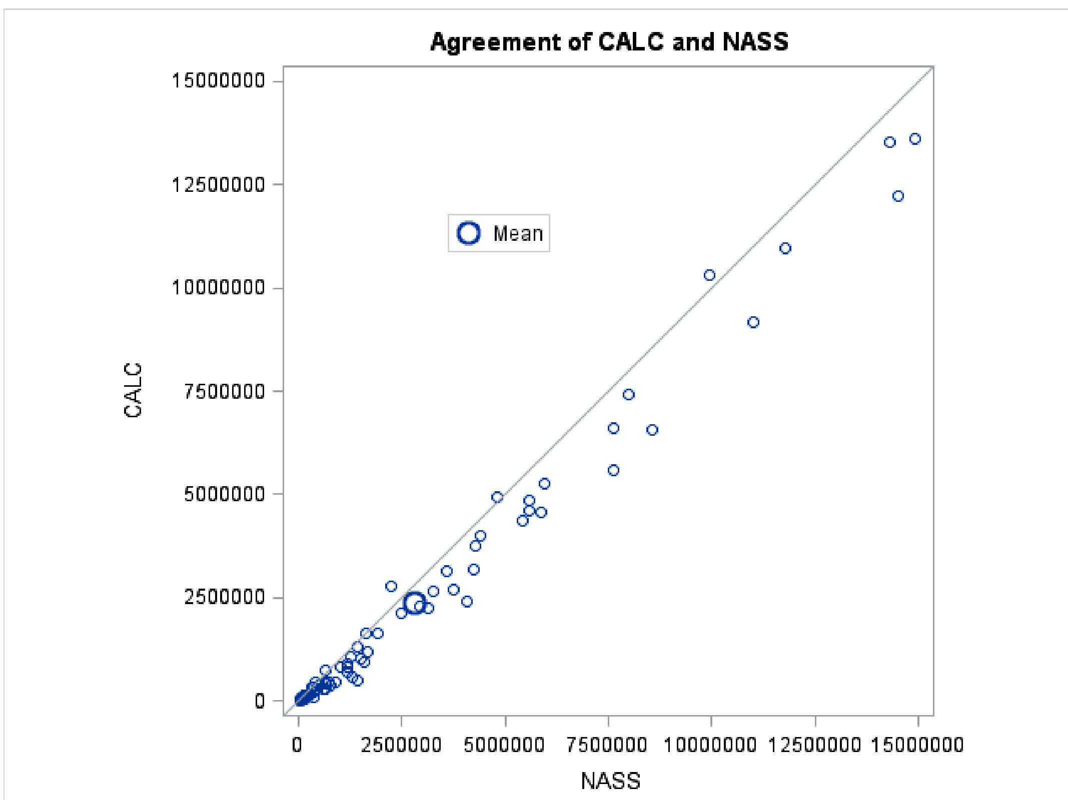
N	Mean	Std Dev	Std Err	Minimum	Maximum
74	454196	557463	64803.8	-532963	2290044

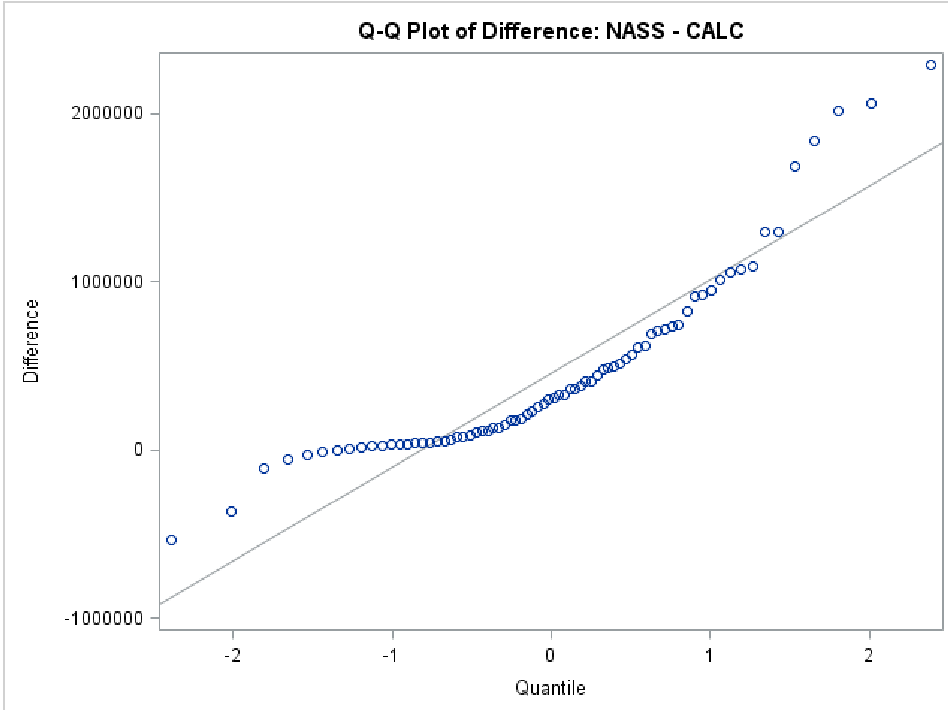
Mean	95% CL Mean		Std Dev	95% CL Std Dev	
454196	325042	583350	557463	479870	665224

F	t Value	Pr > |t|
3	7.01	<.0001




Paired Profiles for (NASS, CALC)
Mean
15000000
12500000
10000000
7500000
5000000
2500000
0
NASS
CALC


Agreement of CALC and NASS
Mean
CALC
NASS
15000000
12500000
10000000
7500000
5000000
2500000
0



Appendix I. **SAS Results for Adjusted Yield data**

The SAS System

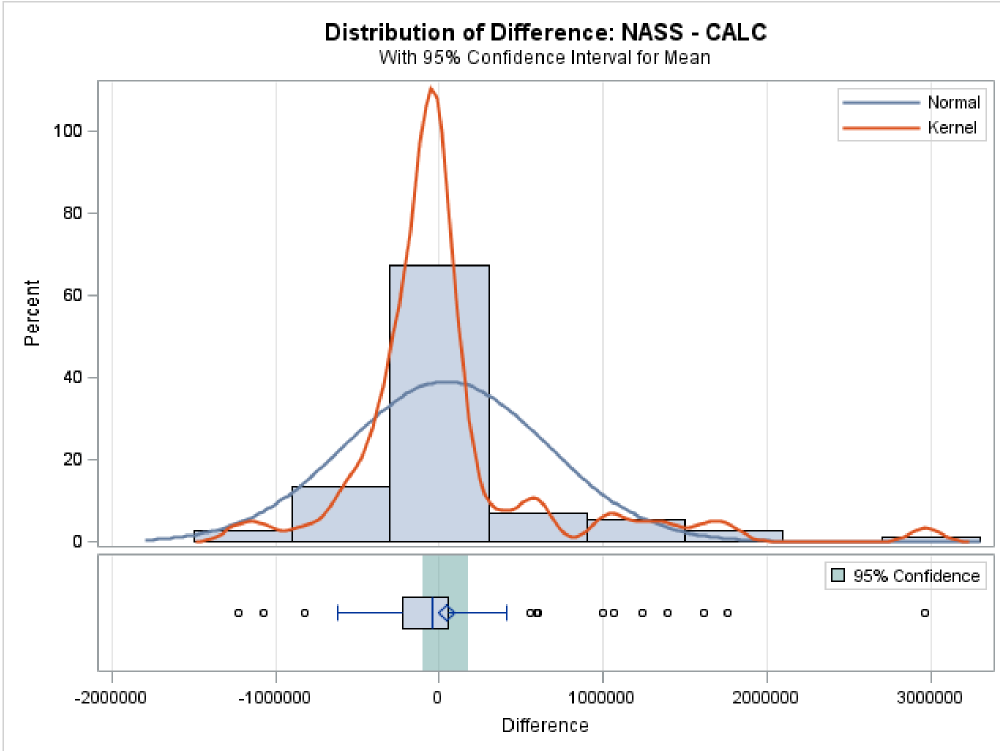
The TTEST Procedure

Difference: NASS - CALC

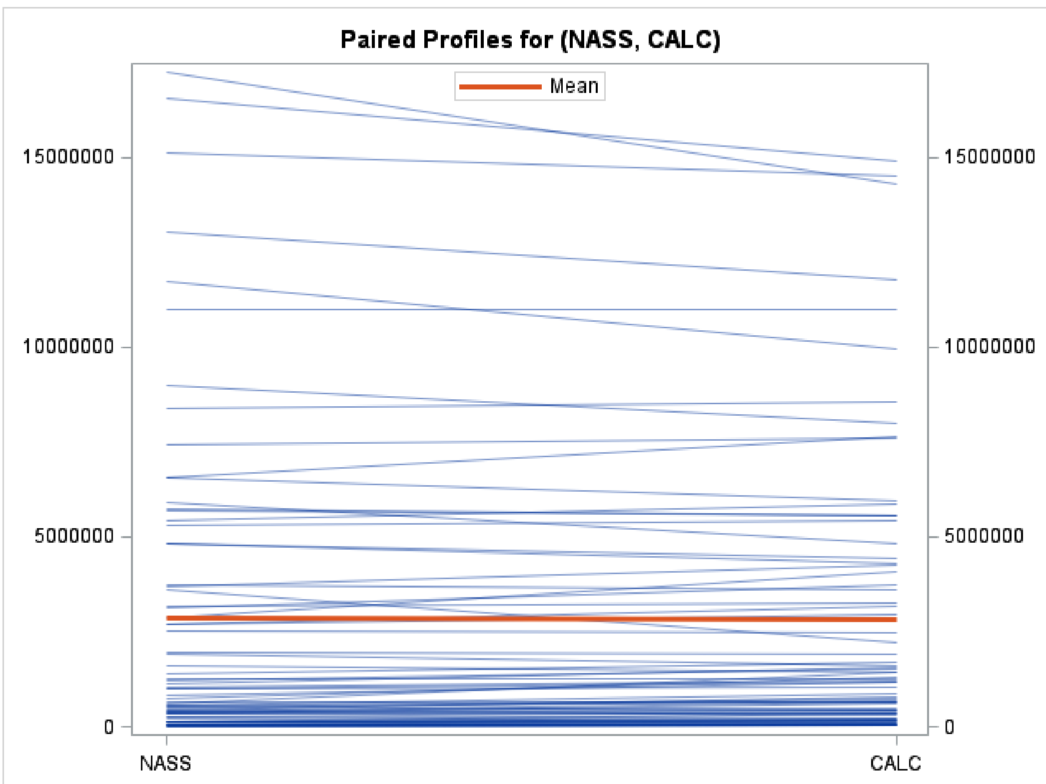
N	Mean	Std Dev	Std Err	Minimum	Maximum
74	40561.0	613323	71297.3	-1230800	2966541

Mean	95% CL Mean		Std Dev	95% CL Std Dev	
40561.0	-101534	182656	613323	527955	731882

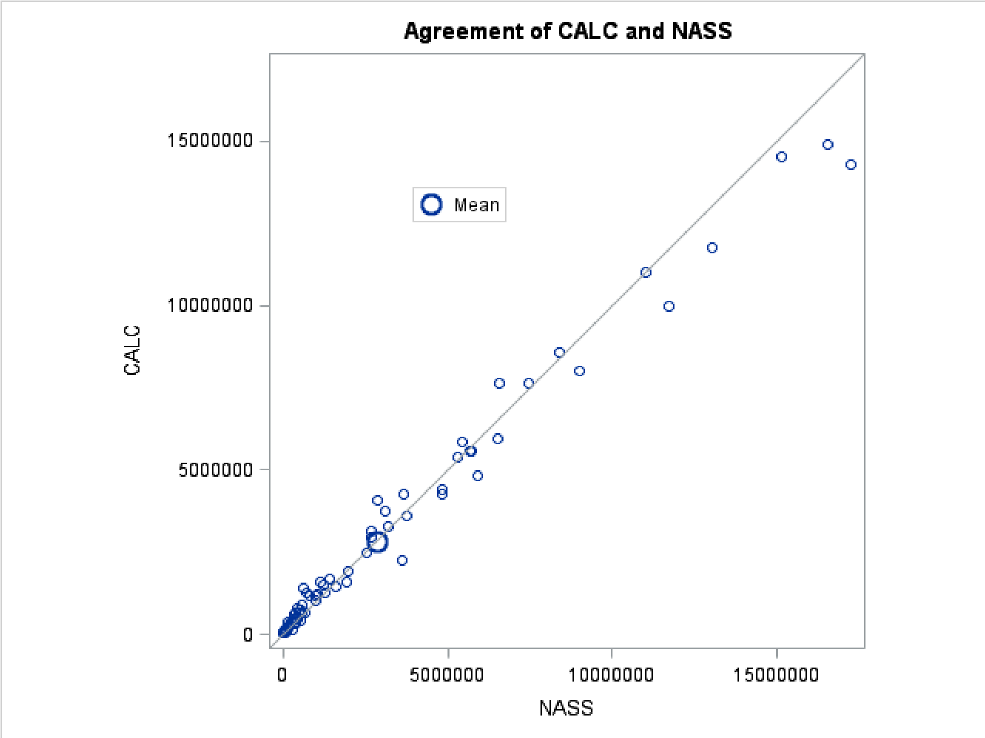
DF	t Value	Pr > |t|
73	0.57	0.5712



Distribution of Difference: NASS - CALC
With 95% Confidence Interval for Mean
Normal
Kernel
Percent
100
80
60
40
20
0
95% Confidence
-2000000
-1000000
0
1000000
2000000
3000000
Difference



Paired Profiles for (NASS, CALC)
Mean
15000000
10000000
5000000
0
NASS
CALC


Agreement of CALC and NASS
15000000
10000000
5000000
0
CALC
Mean
0
5000000
10000000
15000000
NASS

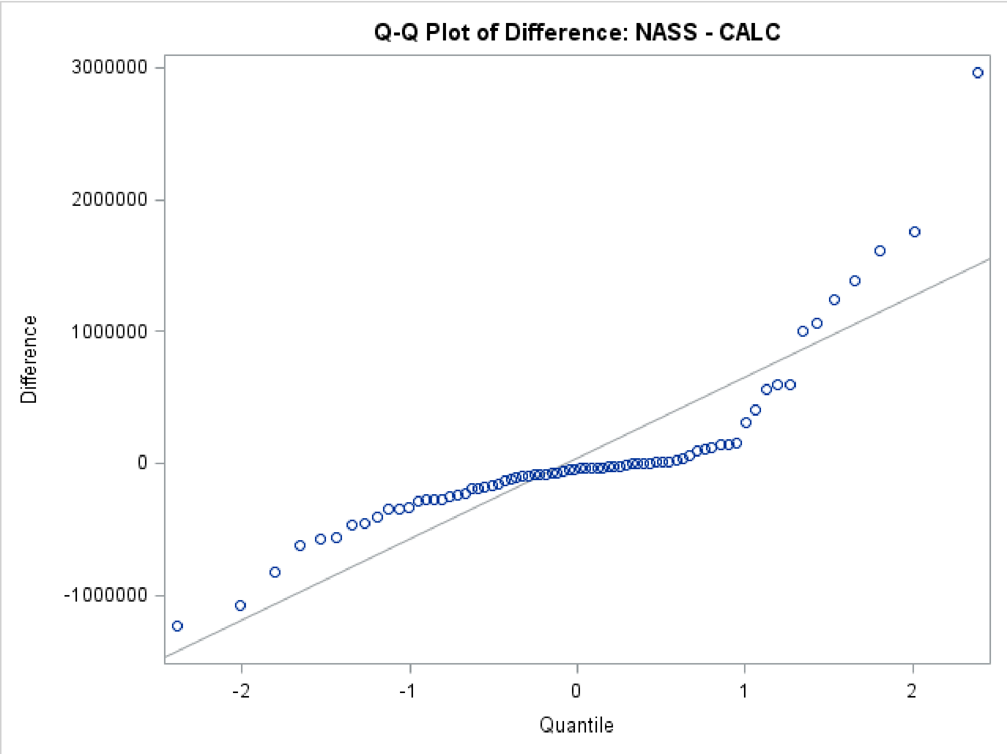

Q-Q Plot of Difference: NASS - CALC
3000000
2000000
1000000
0
-1000000
Difference
-2
-1
0
1
2
Quantile

Table 4 County Stover Yields for GIS Calculated Values Based upon 2008 SSURGO Data, 17% Adjusted Value, and 2013 NASS Data

County Name	2008 Yield Values (Mg)	Adjusted Yield Values for 2013 (Mg)	2013 NASS Values (Mg)
Morgan	254	278	922
Whitley	911	1063	1146
Grant	348	381	1257
Kenton	319	374	1562
Laurel	689	787	1580
Clay	616	713	1616
Knox	938	1093	1913
Campbell	912	1058	1981
Carter	2031	2309	2050
Jessamine	2342	2915	3023
Greenup	2788	3248	3658
Owen	1414	1671	3963
Rowan	2527	7083	4090
Pendleton	2612	3540	4572
Garrard	2938	3426	4902
Estill	3235	3773	5512
Lewis	3184	3647	5995
Rockcastle	4482	5292	7316
Woodford	8494	10264	8840
Montgomery	2705	3462	9144
Bullitt	8056	9360	9424
Boone	5483	6416	9881
Russell	11287	13515	11024
Bath	7715	9734	11456
Oldham	7173	8442	11532
Scott	9298	11365	12574
Fleming	7404	8579	15571
Clark	7452	9530	16536
Spencer	11194	14719	16892
Edmonson	18419	16872	16917
Fayette	10314	12611	17247
Boyle	11196	13050	19102
Harrison	9444	11106	19838

Bourbon	11525	14210	22683
Hart	20828	25563	26163
Wayne	17802	20959	29923
Casey	20957	25245	30075
Mercer	22408	26645	30735
Adair	27354	32186	31955
Henry	14587	18471	32869
Mason	12703	15252	36146
Hancock	33608	40760	36984
Green	25578	31157	38559
Lincoln	24426	28524	40235
Marshall	41918	48958	41150
Pulaski	30139	35636	42699
Marion	41522	49701	49024
Muhlenberg	70310	92030	56772
Mccracken	53686	64260	63376
Crittenden	57565	68508	75035
Meade	57301	68637	80369
Butler	67884	80775	83265
Barren	79300	95358	91622
Breckinridge	67938	79301	95204
Shelby	61486	72932	104196
Carlisle	80443	93629	108209
Trigg	95100	122929	108768
Ballard	101958	122543	112222
Hopkins	125509	149696	122637
Caldwell	110880	134806	137547
Hardin	117545	144295	141612
Calloway	123134	145200	141739
Warren	115884	138275	148749
Ohio	133140	166169	151086
Simpson	167823	189251	193557
Hickman	141655	166548	193887
Todd	188865	228498	203159
Mclean	166557	212770	217815
Logan	262412	297774	253072
Graves	232680	279588	279413
Daviess	278162	330551	299124
Henderson	344032	438159	362805
Christian	310681	384142	368850
Union	346156	420035	379036

American Society of Agricultural and Biological Engineers. (2011). ASAE EP496.3 Agricultural Machinery Management. ASABE Standards 2011. St. Joseph, MI, American Society of Agricultural and Biological Engineers**:** v.

BIBLIOGRAPHY

Adney, B. and J. Baker (1996). "Measurement of cellulase activities. LAP-006 NREL Analytical Procedure." National Renewable Energy Laboratory, Golden, CO

Alex Marvin, W., L. D. Schmidt, S. Benjaafar, D. G. Tiffany and P. Daoutidis (2012). "Economic optimization of a lignocellulosic biomass-to-ethanol supply chain." Chemical Engineering Science **67**(1): 68-79.

Algharib, S. M. (2011). Distance and Coverage: An Assessment of Location-allocation Models for Fire Stations in Kuwait City, Kuwait. Ph.D. Dissertation, Kent State University.

American Society of Agricultural and Biological Engineers. (2011). ASAE EP496.3 Agricultural Machinery Management. ASABE Standards 2011. St. Joseph, MI, American Society of Agricultural and Biological Engineers**:** v.

Amit, K., J. Carol and S. Bhavna (2010). Characteristics and Compositional Variation in Round and Square Switchgrass Bales Under Different Storage conditions. ASABE Annual International Meeting. Pittsburgh, Pennsylvania.

ANSI/ASAE (May2012). Moisture Measurement - Forages. **S358.3**.

Atwell, D. G. (1990). Utilization of alkaline hydrogen peroxide-treated wheat straw-alfalfa combinations by ruminants. Ph.D. Dissertation 9026128, University of Illinois at Urbana-Champaign.

Atwell, D. G., N. R. Merchen, E. H. Jaster, G. C. Fahey and L. L. Berger (1991). "Site and extent of nutrient digestion by sheep fed alkaline hydrogen peroxide-treated wheat straw-alfalfa hay combinations at restricted intakes." Journal of Animal Science **69**(4): 1697-1706.

Ayoub, N., R. Martins, K. Wang, H. Seki and Y. Naka (2007). "Two levels decision system for efficient planning and implementation of bioenergy production." Energy Conversion and Management **48**(3): 709-723.

Bals, B., H. Murnen, M. Allen and B. Dale (2010). "Ammonia fiber expansion (AFEX) treatment of eleven different forages: Improvements to fiber digestibility in vitro." Animal Feed Science and Technology **155**(2-4): 147-155.

Banerjee, G., S. Car, T. Liu, D. L. Williams, S. L. Meza, J. D. Walton and D. B. Hodge (2012). "Scale-up and integration of alkaline hydrogen peroxide pretreatment, enzymatic hydrolysis, and ethanolic fermentation." Biotechnology and Bioengineering **109**(4): 922-931.

Banerjee, G., S. Car, J. Scott-Craig, D. Hodge and J. Walton (2011). "Alkaline peroxide pretreatment of corn stover: effects of biomass, peroxide, and enzyme loading and composition on yields of glucose and xylose." Biotechnology for Biofuels **4**(1): 16.

Bankar, S. B., S. A. Survase, H. Ojamo and T. Granstrom (2013). "Biobutanol: the outlook of an academic and industrialist." Royal Society of Chemistry Advances **3**(47): 24734-24757.

Bowling, I. M., J. M. a. Ponce-Ortega and M. M. El-Halwagi (2011). "Facility Location and Supply Chain Optimization for a Biorefinery." Industrial & Engineering Chemistry Research **50**(10): 6276-6286.

Brodeur, G., E. Yau, K. Badal, J. Collier, K. B. Ramachandran and S. Ramakrishnan (2011). "Chemical and physicochemical pretreatment of lignocellulosic biomass: A Review." Enzyme Research **2011**.

Brosse, N., A. Dufour, X. Z. Meng, Q. N. Sun and A. Ragauskas (2012). "Miscanthus: a fast-growing crop for biofuels and chemicals production." Biofuels Bioproducts & Biorefining **6**(5): 580-598.

Brown, R. C. (2003). Biorenewable resources : engineering new products from agriculture. Ames, Iowa, Iowa State Press.

Bunselmeyer, H. A. and J. G. Lauer (2015). "Using Corn and Soybean Yield History to Predict Subfield Yield Response." Agronomy Journal **107**(2): 558-562.

Burt, C. M., X. Piao, F. Gaudi, B. Busch and N. Taufik (2008). "Electric motor efficiency under variable frequencies and loads." Journal of Irrigation and Drainage Engineering **134**(2): 129-136.

Cameron, M. G. (1990). Effects of treating lignocellulosics with alkaline hydrogen peroxide on feed intake and digestion by dairy cattle. Ph.D. Dissertation 9114187, University of Illinois at Urbana-Champaign.

Cameron, M. G., M. R. Cameron, G. C. Fahey, J. H. Clark, L. L. Berger and N. R. Merchen (1991). "Effects of Treating Oat Hulls with Alkaline Hydrogen-Peroxide on Intake and Digestion by Midlactation Dairy-Cows." Journal of Dairy Science **74**(1): 177-189.

Cameron, M. G., G. C. Fahey Jr, J. H. Clark, N. R. Merchen and L. L. Berger (1990). "Effects of Feeding Alkaline Hydrogen Peroxide-Treated Wheat Straw-Based Diets on Digestion and Production by Dairy Cows." Journal of Dairy Science **73**(12): 3544-3554.

Cattafi, M., M. Gavanelli, M. Milano and P. Cagnoli (2011). "Sustainable biomass power plant location in the Italian Emilia-Romagna region." Association for Computers and Machinery Transactions on Intelligent Systems and Technology **2**(4): 1-19.

Cavalli, R. and S. Grigolato (2010). "Influence of characteristics and extension of a forest road network on the supply cost of forest woodchips." Journal of Forest Research **15**(3): 202-209.

Cecava, M. J., N. R. Merchen, L. L. Berger and G. C. Fahey (1990). "Intestinal Supply of Amino-Acids in Sheep Fed Alkaline Hydrogen Peroxide-Treated Wheat Straw-Based Diets Supplemented with Soybean-Meal or Combinations of Corn Gluten Meal and Blood Meal." Journal of Animal Science **68**(2): 467-477.

Chaudhry, A. S. (1998). "In vitro and in sacco digestibility of wheat straw treated with calcium oxide and sodium hydroxide alone or with hydrogen peroxide." Animal Feed Science and Technology **74**(4): 301-313.

Chaudhry, A. S. and E. L. Miller (1996). "The effect of sodium hydroxide and alkaline hydrogen peroxide on chemical composition of wheat straw and voluntary intake, growth and digesta kinetics in store lambs." Animal Feed Science and Technology **60**(1–2): 69-86.

Chen, B.-Y., S.-W. Chen and H.-T. Wang (2012). "Use of different alkaline pretreatments and enzyme models to improve low-cost cellulosic biomass conversion." Biomass and Bioenergy **39**: 182-191.

Chen, Y., M. A. Stevens, Y. Zhu, J. Holmes and H. Xu (2013). "Understanding of alkaline pretreatment parameters for corn stover enzymatic saccharification." Biotechnol Biofuels **6**(8): 1-10.

Chiueh, P.-T., K.-C. Lee, F.-S. Syu and S.-L. Lo (2012). "Implications of biomass pretreatment to cost and carbon emissions: Case study of rice straw and Pennisetum in Taiwan." Bioresource Technology **108**(0): 285-294.

Chundawat, S. P., B. Venkatesh and B. E. Dale (2007). "Effect of particle size based separation of milled corn stover on AFEX pretreatment and enzymatic digestibility." Biotechnology and Bioengineering **96**(2): 219-231.

Church, R. and C. R. Velle (1974). "The maximal covering location problem." Papers in Regional Science **32**(1): 101-118.

Church, R. L. (1999). "Location modelling and GIS." Geographical Information Systems **1**: 293-303.

Curtin, K. M. (2007). "Network analysis in geographic information science: Review, assessment, and projections." Cartography and Geographic Information Science **34**(2): 103-111.

Daskin, M. S. (2011). Network and Discrete Location: Models, Algorithms, and Applications, John Wiley & Sons.

Davis, S. C., S. W. Diegel, R. G. Boundy and S. A. Moore (2014). 2013 Vehicle Technologies Market Report**:** Medium: ED.

De, S. and M. Assadi (2009). "Impact of cofiring biomass with coal in power plants–A techno-economic assessment." Biomass and Bioenergy **33**(2): 283-293.

Dean, D. J. (1997). "Finding optimal routes for networks of harvest site access roads using GIS-based techniques." Canadian Journal of Forest Research **27**(1): 11-22.

Dijkstra, E. W. (1959). "A note on two problems in connexion with graphs." Numerische mathematik **1**(1): 269-271.

Diniz, J. F., M. Gil and J. Castro (2004). "Hornification—its origin and interpretation in wood pulps." Wood Science and Technology **37**(6): 489-494.

Dong, J. (2008). "GIS and location theory based bioenergy systems planning."

Donohoe, B. S., S. R. Decker, M. P. Tucker, M. E. Himmel and T. B. Vinzant (2008). "Visualizing lignin coalescence and migration through maize cell walls following thermochemical pretreatment." Biotechnology and Bioengineering **101**(5): 913-925.

Doraiswamy, P. C., J. L. Hatfield, T. J. Jackson, B. Akhmedov, J. Prueger and A. Stern (2004). "Crop condition and yield simulations using Landsat and MODIS." Remote Sensing of Environment **92**(4): 548-559.

Ekşioğlu, S. D., A. Acharya, L. E. Leightley and S. Arora (2009). "Analyzing the design and management of biomass-to-biorefinery supply chain." Computers & Industrial Engineering **57**(4): 1342-1352.

Environmental Systems Research Institute (ESRI). "Algorithms used by Network Analyst." Retrieved 6/5/15, from http://help.arcgis.com/en/arcgisdesktop/10.0/help/index.html#//004700000053000000.

Fahrenholz, A. C. (2012). Evaluating factors affecting pellet durability and energy consumption in a pilot feed mill and comparing methods for evaluating pellet durability. Ph.D. Dissertation, Kansas State University.

Faulkner, W. H. (2012). Economic modeling & optimization of a region specific multi-feedstock biorefinery supply chain. Masters Thesis, University of Kentucky.
Fike, J. H., D. J. Parrish, D. D. Wolf, J. A. Balasko, J. T. Green Jr, M. Rasnake and J. H. Reynolds (2006). "Switchgrass production for the upper southeastern USA: influence of cultivar and cutting frequency on biomass yields." Biomass and Bioenergy **30**(3): 207-213.
Fore, S. R., P. Porter and W. Lazarus (2011). "Net energy balance of small-scale on-farm biodiesel production from canola and soybean." Biomass & Bioenergy **35**(5): 2234-2244.
Forsberg, G. (2000). "Biomass energy transport: Analysis of bioenergy transport chains using life cycle inventory method." Biomass and Bioenergy **19**(1): 17-30.
Galbe, M. and G. Zacchi (2012). "Pretreatment: The key to efficient utilization of lignocellulosic materials." Biomass and Bioenergy **46**: 70-78.
Garcia-Maraver, A. and M. Carpio (2015). Biomass Pelletization Process. Biomass Pelletization: Standards and Production. A. Garcia-Maraver and J. A. Pérez-Jiménez. Southampton, Boston, WIT Press**:** 53-66.
Gilpin, A. S., T. J. Herrman, K. C. Behnke and F. J. Fairchild (2002). "Feed moisture, retention time, and steam as quality and energy utilization determinants in the pelleting process." Applied Engineering in Agriculture **18**(3): 331-338.
Gould, J. M. (1984). "Alkaline peroxide delignification of agricultural residues to enhance enzymatic saccharification." Biotechnology and Bioengineering **26**(1): 46-52.
Gould, J. M. (1985). "Studies on the mechanism of alkaline peroxide delignification of agricultural residues." Biotechnology and Bioengineering **27**(3): 225-231.
Gould, J. M. and S. N. Freer (1984). "High-efficiency ethanol production from lignocellulosic residues pretreated with alkaline H_2O_2." Biotechnology and Bioengineering **26**(6): 628-631.
Grabber, J., S. Quideau and J. Ralph (1996). "p-coumaroylated syringyl units in maize lignin: Implications for beta-ether cleavage by thioacidolysis." Phytochemistry **43**: 1189 - 1194.
Graham, R. L., B. C. English and C. E. Noon (2000). "A Geographic Information System-based modeling system for evaluating the cost of delivered energy crop feedstock." Biomass and Bioenergy **18**(4): 309-329.
Gray, M. K. (2013). Alkaline hydrogen peroxide pretreatment for its use in an on-farm bioprocessing facility. Master's Thesis, University of Kentucky.
Groesbeck, C. N., L. J. McKinney, J. M. DeRouchey, M. D. Tokach, R. D. Goodband, S. S. Dritz, J. L. Nelssen, A. W. Duttlinger, A. C. Fahrenholz and K. C. Behnke (2008). "Effect of crude glycerol on pellet mill production and nursery pig growth performance." Journal of Animal Science **86**(9): 2228-2236.
Gunawardhana, T. L. (2014). Environmental and economic feasibility of on- farm processing of corn stover to mixed alcohols. Master's Thesis, University Of Wisconsin – Madison.
Ha, M., C. Munster and T. Provin (2014). "A geographic information systems program to optimize feedstock logistics for bioenergy production for mobile pyrolysis units." Transactions of the ASABE **57**(1): 249-257.

Ha, M., C. L. Munster, S. Capareda, D. Vietor, T. Provin and M. Palma (2011). GIS program to optimize feedstock utilization for mobile pyrolysis units. ASABE Annual International Meeting. Lexington, Kentucky.
Haddad, M. A. and P. F. Anderson (2008). "A GIS methodology to identify potential corn stover collection locations." Biomass and Bioenergy **32**(12): 1097-1108.
Hart, P. W. and A. Rudie (2007). Hydrogen peroxide : An environmentally friendly but dangerous bleaching chemical. TAPPI engineering, pulping and environmental conference, Jacksonville, FL, TAPPI Press.
Hatakka, A. (1983). "Pretreatment of wheat straw by white-rot fungi for enzymic saccharification of cellulose." European journal of applied microbiology and biotechnology **18**(6): 350-357.
Heaton, E. A., F. G. Dohleman and S. P. Long (2008). "Meeting US biofuel goals with less land: the potential of Miscanthus." Global Change Biology **14**(9): 2000-2014.
Hess, J. R., C. T. Wright and K. L. Kenney (2007). "Cellulosic biomass feedstocks and logistics for ethanol production." Biofuels, Bioproducts and Biorefining **1**(3): 181-190.
Holm, J. K., U. B. Henriksen, J. E. Hustad and L. H. Sorensen (2006). "Toward an understanding of controlling parameters in softwood and hardwood pellets production." Energy & Fuels **20**(6): 2686-2694.
Hoover, A. N., J. S. Tumuluru, F. Teymouri, J. Moore and G. Gresham (2014). "Effect of pelleting process variables on physical properties and sugar yields of ammonia fiber expansion pretreated corn stover." Bioresource Technology **164**: 128-135.
Jack, M. W. (2009). "Scaling laws and technology development strategies for biorefineries and bioenergy plants." Bioresource Technology **100**(24): 6324-6330.
Jackson, M. G. (1977). "Review article: The alkali treatment of straws." Animal Feed Science and Technology **2**(2): 105-130.
Jenkins, B., J. Arthur and P. Eibeck (1983). "Selecting optimum biomass utilization sites." Transactions of the ASAE **26**(5): 1551-&.
Jeoh, T., C. I. Ishizawa, M. F. Davis, M. E. Himmel, W. S. Adney and D. K. Johnson (2007). "Cellulase digestibility of pretreated biomass is limited by cellulose accessibility." Biotechnology and Bioengineering **98**(1): 112-122.
Jiang, N., Y. Pu, R. Samuel and A. Ragauskas (2009). "Perdeuterated pyridinium molten salt (ionic liquid) for direct dissolution and NMR analysis of plant cell walls." Green Chem **11**: 1762 - 1766.
Jin, C., M. Yao, H. Liu, C.-f. F. Lee and J. Ji (2011). "Progress in the production and application of n-butanol as a biofuel." Renewable and Sustainable Energy Reviews **15**(8): 4080-4106.
Jones, D. and S. J. Stan (2006). Support systems common to most refineries. Handbook of Petroleum Processing. D. J. S. Jones and P. Pujadó, Springer Netherlands**:** 521-610.
Judd, J., S. C. Sarin and J. S. Cundiff (2011). Cost analysis of a biomass based logistics system. ASABE Annual International Meeting. Louisville, Kentucky.
Judd, J. D., S. C. Sarin and J. S. Cundiff (2012). "Design, modeling, and analysis of a feedstock logistics system." Bioresource Technology **103**(1): 209-218.

Jung, H., D. Mertens and A. Payne (1997). "Correlation of acid detergent lignin and Klason lignin with digestibility of forage dry matter and neutral detergent fiber." Journal of Dairy Science **80**(8): 1622-1628.

Jung, H. G., F. R. Valdez, A. R. Abad, R. A. Blanchette and R. D. Hatfield (1992). "Effect of white rot basidiomycetes on chemical composition and in vitro digestibility of oat straw and alfalfa stems." Journal of Animal Science **70**(6): 1928-1935.

Kaar, W. E. and M. T. Holtzapple (2000). "Using lime pretreatment to facilitate the enzymic hydrolysis of corn stover." Biomass and Bioenergy **18**(3): 189-199.

Kaliyan, N. and R. V. Morey (2009). "Factors affecting strength and durability of densified biomass products." Biomass & Bioenergy **33**(3): 337-359.

Kaliyan, N. and R. V. Morey (2010). "Natural binders and solid bridge type binding mechanisms in briquettes and pellets made from corn stover and switchgrass." Bioresource Technology **101**(3): 1082-1090.

Kato, K. L. and R. E. Cameron (1999). "A review of the relationship between thermally-accelerated ageing of paper and hornification." Cellulose **6**(1): 23-40.

Keith, E. A. and L. B. Daniels (1976). "Acid or alkali-treated hardwood sawdust as a feed for cattle." Journal of Animal Science **42**(4): 888-892.

Kentucky Transportation Cabinet. "Active Rail KYTC.zip."   Retrieved 6/22/2014, from ftp://ftp.kymartian.ky.gov/trans/statewide/shape/Active_Rail_KYTC.zip.

Kentucky Transportation Cabinet. "All Roads."   Retrieved 6/22/2014, from ftp://ftp.kymartian.ky.gov/trans/statewide/shape/AllRds.zip.

Kerley, M. S., G. C. Fahey, L. L. Berger, J. M. Gould and F. Lee Baker (1985). "Alkaline Hydrogen Peroxide Treatment Unlocks Energy in Agricultural By-Products." Science **230**(4727): 820-822.

Kerley, M. S., G. C. Fahey, L. L. Berger, N. R. Merchen and J. M. Gould (1986). "Effects of alkaline hydrogen-peroxide treatment of wheat straw on site and extent of digestion in sheep." Journal of Animal Science **63**(3): 868-878.

Kim, T. and Y. Y. Lee (2007). "Pretreatment of corn stover by soaking in aqueous ammonia at moderate temperatures." Applied Biochemistry and Biotechnology **137-140**(1-12): 81-92.

Kim, T. H., J. S. Kim, C. Sunwoo and Y. Y. Lee (2003). "Pretreatment of corn stover by aqueous ammonia." Bioresource Technology **90**(1): 39-47.

Klopfenstein, T. (1978). "Chemical treatment of crop residues." Journal of Animal Science **46**(3): 841-848.

Kravchenko, A. N. and D. G. Bullock (2000). "Correlation of corn and soybean grain yield with topography and soil properties." Agronomy Journal **92**(1): 75-83.

Krueger, C. G., K. A. Albrecht, J. D. Reed, E. J. Bures and V. N. Owens (1999). "Sodium sulphite effects on recovery and composition of detergent fibre and lignin from forage legumes varying in levels of proanthocyanidins." Journal of the Science of Food and Agriculture **79**(11): 1351-1356.

Kumar, A. and S. Sokhansanj (2007). "Switchgrass (< i> panicum vigratum</i>, L.) delivery to a biorefinery using integrated biomass supply analysis and logistics (IBSAL) model." Bioresource Technology **98**(5): 1033-1044.

Kumar, A. and S. Sokhansanj (2007). "Switchgrass (Panicum vigratum, L.) delivery to a biorefinery using integrated biomass supply analysis and logistics (IBSAL) model." Bioresource Technology **98**(5): 1033-1044.

Kumar, P., D. M. Barrett, M. J. Delwiche and P. Stroeve (2009). "Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production." Industrial & Engineering Chemistry Research **48**(8): 3713-3729.

Laboratory, A. N. (2014). Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) Model 2014.

Lamers, P., M. Junginger, C. Hamelinck and A. Faaij (2012). "Developments in international solid biofuel trade—An analysis of volumes, policies, and market factors." Renewable and Sustainable Energy Reviews **16**(5): 3176-3199.

Larson, J. A., D. F. Mooney, B. C. English and D. D. Tyler (2010). Cost analysis of alternative harvest and storage methods for switchgrass in the Southeastern U.S. Southern Agricultural Economics Association.

Larson, J. A., T.-H. Yu, B. C. English, D. F. Mooney and C. Wang (2010). "Cost evaluation of alternative switchgrass producing, harvesting, storing, and transporting systems and their logistics in the Southeastern USA." Agricultural Finance Review **70**(2): 184-200.

Larsson, S. H. and M. Rudolfsson (2012). "Temperature control in energy grass pellet production - Effects on process stability and pellet quality." Applied Energy **97**: 24-29.

Lewandowski, I., J. C. Clifton-Brown, J. M. O. Scurlock and W. Huisman (2000). "Miscanthus: European experience with a novel energy crop." Biomass and Bioenergy **19**(4): 209-227.

Lewis, S. M., D. P. Holzgraefe, L. L. Berger, G. C. Fahey, J. M. Gould and G. F. Fanta (1987). "Alkaline hydrogen-peroxide treatments of crop residues to increase ruminal dry-matter disappearance in sacco." Animal Feed Science and Technology **17**(3): 179-199.

Lewis, S. M., L. Montgomery, K. A. Garleb, L. L. Berger and G. C. Fahey (1988). "Effects of alkaline hydrogen peroxide treatment on in vitro degradation of cellulosic substrates by mixed ruminal microorganisms and Bacteroides succinogenes-S85." Applied and Environmental Microbiology **54**(5): 1163-1169.

Li, M., C. Foster, S. Kelkar, Y. Pu, D. Holmes, A. Ragauskas, C. Saffron and D. Hodge (2012). "Structural characterization of alkaline hydrogen peroxide pretreated grasses exhibiting diverse lignin phenotypes." Biotechnology for Biofuels **5**(1): 38.

Li, Y., R. Ruan, P. L. Chen, Z. Liu, X. Pan, X. Lin, Y. Liu, C. Mok and T. Yang (2004). "Enzymatic hydrolysis of corn stover pretreated by combined dilute alkaline treatment and homogenization." Transactions of the ASABE **47**(3): 821-826.

Lobell, D. B., K. G. Cassman and C. B. Field (2009). "Crop yield gaps: their importance, magnitudes, and causes." Annual Review of Environment and Resources **34**(1): 179-204.

Longley, P. A. and M. Batty (1996). Spatial analysis: modelling in a GIS environment, John Wiley & Sons.

Luo, L., E. van der Voet and G. Huppes (2009). "Life cycle assessment and life cycle costing of bioethanol from sugarcane in Brazil." Renewable and Sustainable Energy Reviews **13**(6–7): 1613-1619.

Luo, L., E. van der Voet, G. Huppes and H. Udo de Haes (2009). "Allocation issues in LCA methodology: a case study of corn stover-based fuel ethanol." The International Journal of Life Cycle Assessment **14**(6): 529-539.

Luo, X. and J. Zhu (2011). "Effects of drying-induced fiber hornification on enzymatic saccharification of lignocelluloses." Enzyme and microbial technology **48**(1): 92-99.

Mahmudi, H. and P. C. Flynn (2006). "Rail vs truck transport of biomass." Applied Biochemistry and Biotechnology **129**(1-3): 88-103.

Malczewski, J. (2004). "GIS-based land-use suitability analysis: a critical overview." Progress in Planning **62**: 3-65.

Mani, S., S. Sokhansanj, X. Bi and A. Turhollow (2006). "Economics of producing fuel pellets from biomass." Applied Engineering in Agriculture **22**(3): 421.

Mani, S., L. G. Tabil and S. Sokhansanj (2006). "Effects of compressive force, particle size and moisture content on mechanical properties of biomass pellets from grasses." Biomass & Bioenergy **30**(7): 648-654.

Martinez, A. and D. E. Maier (2011). "Quantifying feedstock availability using a Geographical Information System." Biological Engineering **4**(3): 133-146.

Mediavilla, I., L. S. Esteban and M. J. Fernández (2012). "Optimisation of pelletisation conditions for poplar energy crop." Fuel Processing Technology **104**(0): 7-15.

Mediavilla, I., M. J. Fernández and L. S. Esteban (2009). "Optimization of pelletisation and combustion in a boiler of 17.5 kWth for vine shoots and industrial cork residue." Fuel Processing Technology **90**(4): 621-628.

Mertens, D. R. (2002). "Gravimetric determination of amylase-treated neutral detergent fiber in feeds with refluxing in beakers or crucibles: collaborative study." Journal of AOAC International **85**(6): 1217-1240.

Minor, J. L. (1994). "Hornification-its origin and meaning." Series: Journal Articles.

Mishra, A. S., O. H. Chaturvedi, A. Khali, R. Prasad, A. Santra, A. K. Misra, S. Parthasarathy and R. C. Jakhmola (2000). "Effect of sodium hydroxide and alkaline hydrogen peroxide treatment on physical and chemical characteristics and IVOMD of mustard straw." Animal Feed Science and Technology **84**(3–4): 257-264.

Modenbach, A. (2013). Sodium hydroxide pretreatment of corn stover and subsequent enzymatic hydrolysis: An investigation of yields, kinetic modeling and glucose recovery. Ph.D. Dissertation, University of Kentucky.

Mohammad, H., M. Tawfik and A. El Shal "Effect of using poultry by-product meal on aquatic pellets quality and fish growth using ring-die pelleting machine." Misr Agricultural Engineering Journal **27**(2): 501 - 520.

Möller, B. (2003). "Least-cost allocation strategies for wood fuel supply for distributed generation in Denmark – a geographical study." International Journal of Sustainable Energy **23**(4): 187-197.

Morey, R. V., N. Kaliyan, D. G. Tiffany and D. R. Schmidt (2010). "A Corn Stover Supply Logistics System." Applied Engineering in Agriculture **26**(3): 455-461.

Moritz, J., K. Cramer, K. Wilson and R. Beyer (2003). "Feed manufacture and feeding of rations with graded levels of added moisture formulated to different energy densities." The Journal of Applied Poultry Research **12**(3): 371-381.
Mueller, R. and M. Harris (2013). Reported uses of CropScape and the national cropland data layer program. Sixth International Conference on Agricultural Statistics. Rio de Janeiro, Brazil.
Mulkey, V. R., V. N. Owens and D. K. Lee (2006). "Management of switchgrass-dominated conservation reserve program lands for biomass production in south dakota " Crop Science **46**(2): 712-720.
Naidu, S. L., S. P. Moose, A. K. Al-Shoaibi, C. A. Raines and S. P. Long (2003). "Cold tolerance of C_4 photosynthesis in Miscanthus× giganteus: adaptation in amounts and sequence of C_4 photosynthetic enzymes." Plant Physiology **132**(3): 1688-1697.
NASS (2013). "CropScape-cropland data layer." US Department of Agriculture, National Agricultural Statistics Service, Washington, http://nassgeodata. gmu. edu/CropScape.
Natural Resources Canada (2004). Office of Energy Efficiency technical fact sheet—Premium-efficiency motor. Ottawa, Canada, Office of Energy Efficiency. Energy Innovators Initiative,.
Network, K. G. "County_Poly1z.zip."   Retrieved 1/27/15, from ftp://ftp.kymartian.ky.gov/county/.
Nilsson, J. W. and S. A. Riedel (2000). Electric circuits. Upper Saddle River, N.J., Prentice Hall.
Nokes, S. E., B. C. Lynn, S. Rankin, B. Knutson, M. D. Montross and M. Flythe (2013). On-farm integrated high-solids processing system for biomass, Google Patents.
Nolan, A., K. M. Donnell, G. J. Devlin, J. P. Carroll and J. Finnan (2010). "Potential availability of non-woddy biomass feedstock for pellet production within the Republic of Ireland." International Journal of Agricultural and Biological Engineers **3**(1): 63-73.
Noon, C., F. B. Zhan and R. Graham (2002). "GIS-based analysis of marginal price variation with an application in the identification of candidate ethanol conversion plant locations." Networks and Spatial Economics **2**(1): 79-93.
Noon, C. E. and M. J. Daly (1996). "GIS-based Biomass Resource Assessment with BRAVO." Biomass & Bioenergy **10**(2-3): 101-109.
Overend, R. (1982). "The average haul distance and transportation work factors for biomass delivered to a central plant." Biomass **2**(1): 75-79.
Panichelli, L. and E. Gnansounou (2008). "GIS-based approach for defining bioenergy facilities location: A case study in Northern Spain based on marginal delivery costs and resources competition between facilities." Biomass & Bioenergy **32**(4): 289-300.
Parker, N., P. Tittmann, Q. Hart, R. Nelson, K. Skog, A. Schmidt, E. Gray and B. Jenkins (2010). "Development of a biorefinery optimized biofuel supply curve for the Western United States." Biomass and Bioenergy **34**(11): 1597-1607.
Pavlostathis, S. G. and J. M. Gossett (1985). "Alkaline treatment of wheat straw for increasing anaerobic biodegradability." Biotechnology and Bioengineering **27**(3): 334-344.

Perpina, C., D. Alfonso, A. Perez-Navarro, E. Penalvo, C. Vargas and R. Cardenas (2009). "Methodology based on Geographic Information Systems for biomass logistics and transport optimisation." Renewable Energy **34**(3): 555-565.

Petrolia, D. R. (2008). "The economics of harvesting and transporting corn stover for conversion to fuel ethanol: A case study for Minnesota." Biomass & Bioenergy **32**(7): 603-612.

Qi, B. K., X. R. Chen, F. Shen, Y. Su and Y. H. Wan (2009). "Optimization of enzymatic hydrolysis of wheat straw pretreated by alkaline peroxide using response surface methodology." Industrial & Engineering Chemistry Research **48**(15): 7346-7353.

Qureshi, N., B. C. Saha, R. E. Hector and M. A. Cotta (2008). "Removal of fermentation inhibitors from alkaline peroxide pretreated and enzymatically hydrolyzed wheat straw: Production of butanol from hydrolysate using Clostridium beijerinckii in batch reactors." Biomass & Bioenergy **32**(12): 1353-1358.

Rentizelas, A. A., I. P. Tatsiopoulos and A. Tolis (2009). "An optimization model for multi-biomass tri-generation energy supply." Biomass & Bioenergy **33**(2): 223-233.

Saha, B. C. and M. A. Cotta (2006). "Ethanol production from alkaline peroxide pretreated enzymatically saccharified wheat straw." Biotechnology Progress **22**(2): 449-453.

Samson, R., S. Mani, R. Boddey, S. Sokhansanj, D. Quesada, S. Urquiaga, V. Reis and C. H. Lem (2005). "The potential of C_4 perennial grasses for developing global BIOHEAT industry." Critical Reviews in Plant Sciences **24**(5-6): 461-495.

Selig, M. J., S. Viamajala, S. R. Decker, M. P. Tucker, M. E. Himmel and T. B. Vinzant (2007). "Deposition of lignin droplets produced during dilute acid pretreatment of maize stems retards enzymatic hydrolysis of cellulose." Biotechnology progress **23**(6): 1333-1339.

Sewell, J. R., L. L. Berger, T. G. Nash, M. J. Cecava, P. H. Doane, J. L. Dunn, M. K. Dyer and N. A. Pyatt (2009). "Nutrient digestion and performance by lambs and steers fed thermochemically treated crop residues." Journal of Animal Science **87**(3): 1024-1033.

Shakweh, Y. (2011). 33 - Drives Types and Specifications. Power Electronics Handbook (Third Edition). M. H. Rashid. Boston, Butterworth-Heinemann**:** 881-913.

Sharma, A., S. Khan, S. Sharma and P. Lehana (2013). "Effect of impedance load on the power factor of microcontroller based power system." International Journal of Engineering and Advanced Technology (IJEAT) **2**(5): 419 - 422.

Shastri, Y., A. Hansen, L. Rodriguez and K. C. Ting (2011). "Development and application of BioFeed model for optimization of herbaceous biomass feedstock production." Biomass & Bioenergy **35**(7): 2961-2974.

Shastri, Y., A. Hansen, L. Rodriguez and K. C. Ting (2011). Impact of weather on biomass feedstock harvest system operations and cost. ASABE Annual International Meeting. Louisville, Kentucky.

Shi, X., A. Elmore, X. Li, N. J. Gorence, H. M. Jin, X. H. Zhang and F. Wang (2008). "Using spatial information technologies to select sites for biomass power plants: A case study in Guangdong Province, China." Biomass & Bioenergy **32**(1): 35-43.

Shinners, K. J., G. C. Boettcher, R. E. Muck, P. J. Weimer and M. D. Casler (2010). "Harvest and storage of two perennial grasses as biomass feedstocks." Transactions of the ASABE **53**(2): 359-370.
Shrivastava, B., S. Thakur, Y. Khasa, A. Gupte, A. Puniya and R. Kuhad (2011). "White-rot fungal conversion of wheat straw to energy rich cattle feed." Biodegradation **22**(4): 823-831.
Silva, G. G. D., M. Couturier, J.-G. Berrin, A. Buléon and X. Rouau (2012). "Effects of grinding processes on enzymatic degradation of wheat straw." Bioresource Technology **103**(1): 192-200.
Simpson, S. L., M. Hamann, C. Parnell, S. Emsoff, S. Capareda and B. Shaw (2007). Engineering of Seed Cotton Transport Alternatives. Beltwide Cotton Conference.
Skoch, E., S. Binder, C. Deyoe, G. Allee and K. Behnke (1983). "Effects of pelleting conditions on performance of pigs fed a corn-soybean meal diet." Journal of Animal Science **57**(4): 922-928.
Sluiter, A., B. Hames, R. Ruiz, C. Scarlata, J. Sluiter and D. Templeton (2004). NREL Analytical Procedure National Renewable Energy Laboratory, Golden, CO.
Soil Survey Staff, N. R. C. S., United States Department of Agriculture (2014). Web Soil Survey.
Sokhansanj, S., A. Kumar and A. F. Turhollow (2006). "Development and implementation of integrated biomass supply analysis and logistics model (IBSAL)." Biomass & Bioenergy **30**(10): 838-847.
Sokhansanj, S., S. Mani, A. Turhollow, A. Kumar, D. Bransby, L. Lynd and M. Laser (2009). "Large-scale production, harvest and logistics of switchgrass (Panicum virgatum L.) - current technology and envisioning a mature technology." Biofuels Bioproducts & Biorefining-Biofpr **3**(2): 124-141.
Steffe, J. F. (1996). Rheological methods in food process engineering, Freeman press.
Stelte, W., C. Clemons, J. K. Holm, J. Ahrenfeldt, U. B. Henriksen and A. R. Sanadi (2011). "Thermal transitions of the amorphous polymers in wheat straw." Industrial Crops and Products **34**(1): 1053-1056.
Stelte, W., C. Clemons, J. K. Holm, J. Ahrenfeldt, U. B. Henriksen and A. R. Sanadi (2012). "Fuel Pellets from Wheat Straw: The Effect of Lignin Glass Transition and Surface Waxes on Pelletizing Properties." Bioenergy Research **5**(2): 450-458.
Stelte, W., A. R. Sanadi, L. Shang, J. K. Holm, J. Ahrenfeldt and U. B. Henriksen (2012). "Recent developments in biomass pelletization – A review." BioResources **7**(3).
Stephen, J. D., S. Sokhansanj, X. Bi, T. Sowlati, T. Kloeck, L. Townley-Smith and M. A. Stumborg (2010). "Analysis of biomass feedstock availability and variability for the Peace River region of Alberta, Canada." Biosystems Engineering **105**(1): 103-111.
Streeter, C. L., K. E. Conway, G. W. Horn and T. L. Mader (1982). "Nutritional-evaluation of wheat straw incubated with the edible mushroom, pleurotus-ostreatus." J Anim Sci **54**(1): 183-188.
Sultana, A. and A. Kumar (2012). "Optimal siting and size of bioenergy facilities using geographic information system." Applied Energy **94**: 192-201.
Sultana, A. and A. Kumar (2014). "Development of tortuosity factor for assessment of lignocellulosic biomass delivery cost to a biorefinery." Applied Energy **119**(0): 288-295.

Sumitomo Drive Technologies Technical Information for a Cyclo 6000 gearmotor.
Sun, F. and H. Chen (2008). "Enhanced enzymatic hydrolysis of wheat straw by aqueous glycerol pretreatment." Bioresource Technology **99**(14): 6156-6161.
Tabil, L. J. and S. Sokhansanj (1996). "Process conditions affecting the physical quality of alfalfa pellets." Applied Engineering in Agriculture **12**(3): 345-350.
Thek, G. and I. Obernberger (2004). "Wood pellet production costs under Austrian and in comparison to Swedish framework conditions." Biomass & Bioenergy **27**(6): 671-693.
Thomason, W., W. Raun, G. Johnson, C. Taliaferro, K. Freeman, K. Wynn and R. Mullen (2005). "Switchgrass response to harvest frequency and time and rate of applied nitrogen." Journal of Plant Nutrition **27**(7): 1199-1226.
Trego, T. and D. Murray (2010). An analysis of the operational costs of trucking. Transportation Research Board 2010 Annual Meetings CD-ROM. Washington, DC.
Tumuluru, J. S. (2014). "Effect of process variables on the density and durability of the pellets made from high moisture corn stover." Biosystems Engineering **119**(0): 44-57.
Tumuluru, J. S., K. G. Cafferty and K. L. Kenney (2014). Techno-economic Analysis of Conventional, High Moisture Pelletization and Briquetting Process 2014 ASABE Annual International Meeting. Montreal, Quebeck Canada.
Turner, A. P. (2014). Laboratory scale concept validation and evaluation of compromising plant nodal integrity as a means to increase bale density. Master's Thesis, University of Kentucky.
U.S. Department of Energy (2011). U.S. billion-ton update: Biomass supply for a bioenergy and bioproducts industry. R. D. Perlack and B. J. Stokes. Oak Ridge National Laboratory, Oak Ridge, TN.**:** 227p.
U.S. Department of Energy Motor Challenge. "Determining electric motor load and efficiency." from https://www1.eere.energy.gov/manufacturing/tech_assistance/pdfs/10097517.pdf.
Udén, P., P. Robinson and J. Wiseman (2005). "Use of detergent system terminology and criteria for submission of manuscripts on new, or revised, analytical methods as well as descriptive information on feed analysis and/or variability." Animal Feed Science and Technology **118**(3): 181-186.
Urbanchuk, J. M. and R. F. Association (2009). Contribution of the Ethanol Industry to the Economy of the United States, LECG LLC.
USDA, NASS, RDD, GIB and SARS. (2014). "USDA, National Agricultural Statistics Service, 2013 Kentucky Cropland Data Layer." 2013. Retrieved 10/9/2014, from http://www.nass.usda.gov/research/Cropland/metadata/metadata_ky13.htm.
Velazquez-Marti, B. and E. Annevelink (2009). "GIS application to define biomass collection points as sources for linear programming of delivery networks." Transactions of the ASABE **52**(4): 1069-1078.
Vidal Jr, B. C., B. S. Dien, K. Ting and V. Singh (2011). "Influence of feedstock particle size on lignocellulose conversion—a review." Applied biochemistry and biotechnology **164**(8): 1405-1421.

Voivontas, D., D. Assimacopoulos and E. G. Koukios (2001). "Assessment of biomass potential for power production: a GIS based method." Biomass & Bioenergy **20**(2): 101-112.

Williams, D. (2014). Impact of alkaline hydrogen peroxide pretreatment on cell wall properties that contribute to improved enzymatic digestibility of structural carbohydrates to be utilized for biofuel production. Ph.D. Dissertation, Michigan State University.

Willms, C. L., L. L. Berger, N. R. Merchen and G. C. Fahey (1991). "Utilization of alkaline hydrogen peroxide-treated wheat straw in cattle growing and finishing diets." Journal of Animal Science **69**(10): 3917-3924.

Wilson, B. S. (2009). Modeling Cellulosic Ethanol Plant Location Using GIS. Master's Thesis, University of Tennessee.

Xie, Y., K. Zhao and S. Hemingway (2009). Optimally locating biorefineries: A GIS-based mixed integer linear programming approach. 51st Transportation Research Forum.

Xue, C., J.-B. Zhao, L.-J. Chen, F.-W. Bai, S.-T. Yang and J.-X. Sun (2014). "Integrated butanol recovery for an advanced biofuel: current state and prospects." Applied Microbiology and Biotechnology **98**(8): 3463-3474.

You, F., L. Tao, D. J. Graziano and S. W. Snyder (2012). "Optimal design of sustainable cellulosic biofuel supply chains: Multiobjective optimization coupled with life cycle assessment and input–output analysis." American Institute of Chemical Engineers Journal **58**(4): 1157-1180.

You, F. and B. Wang (2011). "Life Cycle Optimization of Biomass-to-Liquid Supply Chains with Distributed-Centralized Processing Networks." Industrial & Engineering Chemistry Research **50**(17): 10102-10127.

You, F. Q., L. Tao, D. J. Graziano and S. W. Snyder (2012). "Optimal design of sustainable cellulosic biofuel supply chains: Multiobjective optimization coupled with life cycle assessment and input-output analysis." Aiche Journal **58**(4): 1157-1180.

Young, L. R., H. B. Pfost and A. M. Feyerherm (1963). "Mechanical Durability of Feed Pellets." Transactions of the ASABE **6**(2).

Yu, H. D., Q. H. Wang, K. E. Ileleji, C. J. Yu, Z. Y. Luo, K. F. Cen and J. Gore (2012). "Design and analysis of geographic distribution of biomass power plant and satellite storages in China. Part 1: Straight-line delivery." Biomass & Bioenergy **46**: 773-784.

Zadrazil, F., D. Kamra, O. Isikhuemhen, F. Schuchardt and G. Flachowsky (1996). "Bioconversion of lignocellulose into ruminant feed with white rot fungi—Review of work done at the FAL, Braunschweig." Journal of Applied Animal Research **10**(2): 105-124.

Zewei, M., Y. Shastri, T. E. Grift, A. C. Hansen and K. C. Ting (2011). Lignocellulosic Biomass Feedstock Supply Logistic Analysis. ASABE Annual International Meeting. Louisville, Kentucky.

Zhang, F. L., D. M. Johnson and J. W. Sutherland (2011). "A GIS-based method for identifying the optimal location for a facility to convert forest biomass to biofuel." Biomass & Bioenergy **35**(9): 3951-3961.

VITA

Joshua James Jackson

EDUCATION

- M.S. in Animal Science. University of Kentucky, Lexington, KY. Completion Date: December 2011. Thesis Topic: Duration of Grazing High Versus Low Endophyte (Neotyphodium coenophialum)-Infected Tall Fescue by Growing Steers Differentially Affects Blood Concentrations of Prolactin, Enzymes, and Metabolites.
- B.S. in Animal Science. University of Kentucky, Lexington, KY. Completion Date: May 2007.

NON-REFEREED CONFERENCE PAPERS, PRESENTATIONS, AND ABSTRACTS

- **Jackson, J.J.**, W. Adams, M.D. Montross, J.M. Phillips. 2011. The Effect of Moisture Content and Binders on the Pelleting of Switchgrass and Miscanthus. ASABE International Meeting, Louisville, KY August 7-10.
- Adams W.C., M.D. Montross, **J.J. Jackson**, S. DeBolt. 2011. Biomass Pellet Gasification Characteristics. ASABE International Meeting, Louisville, KY August 7-10.
- **Jackson, J.J.**, S.G. McNeill, M.D. Montross. 2012. Designing a Feedlot Operation Using ArcGIS and AutoCAD-An Extension Method. ASABE International Meeting, Dallas, TX July 29-August 1.
- Adams, W.C., M.D. Montross, A. Turner, **J.J. Jackson**, L. Mathis, W. Hammond, N. Bush, M. Fogle. 2012. Evaluation of Current Technology for the Determination of Representative Bale Moisture Content ASABE International Meeting, Dallas, TX July 29-August 1.
- **Jackson, J.J.**, M. Montross. 2013. Pretreatment of Biomass Using an Alkaline Hydrogen Peroxide Spray. ASABE International Meeting, Kansas City, KS July 21-24
- Turner, A.P., C. Rodrigues, D. Schiavone, **J.J. Jackson**, M.D. Montross, S.G. McNeill, J.M. Boac, R. Bhadra, S. Thompson, M.E. Casada, R. Maghirang. 2013. Field Measurement of Packing in Stored Grain. ASABE International Meeting, Kansas City, KS July 21-24

- Gray, K., S. Nokes, M.D. Montross, A. Modenbach, **J.J. Jackson**. 2013. Investigation of Alkaline Hydrogen Peroxide Pretreatment for its Use in an On-Farm Butanol Bioprocessing Facility ASABE International Meeting, Kansas City, KS July 21-24
- Adams, W.C., M. Montross, A. Turner, **J.J. Jackson**. 2013. Using Neutron Thermalization to Determine the Dry Matter Content of Baled Biomass. ASABE International Meeting, Kansas City, KS July 21-24.

REFEREED PAPERS,

- Turner, A.P., M.D. Montross, **J.J. Jackson**, N.K. Koeninger, S.G. McNeill, M.E. Casada, J.M. Boac, R. Bhadra, R.G. Maghirang, S.A. Thompson. 2015. Error Analysis in the Measurement of Stored Grain Volume. Transactions of ASABE (Under Review).
- **Jackson, J. J**., M. D. Lindemann, J. A. Boling, and J. C. Matthews. 2015 Blood clinical and biochemical analytes of growing beef steers are affected by duration of grazing high versus low endophyte (Neotyphodium coenophialum)-infected tall fescue, (Ready for Submission to JAS)

TEACHING EXPERIENCE

- BAE 103. Energy in Biological Systems. Spring 2011. University of Kentucky.

COMPETITIVE GRANTS (NOT FUNDED)

J.J. Jackson. Forage and Resource Management Tool for Beef Producers Implementing Rotational Grazing. USDA-AFRI Post Doctoral Fellowships $149,952.00. Mentors: M.D. Montross and J. Lehmkuhler

Montross, M.D., W. Burris, R. Smith, and T. Mark (Morehead State University). Feasibility of Alkaline Hydrogen Peroxide Treated Switchgrass as a Feedstock in Growing Cattle Diets. USDA-AFRI $500,000-Developed idea, contacted researchers to ascertain interest in this research project, and worked on writing the grant.

M.D. Montross. Determining Baled Biomass Dry-Matter Content Using Neutron Thermalization USDA-AFRI $500,000 –writing, editing, and literature review.

OUTREACH

- UK E-Day (Displayed BioButanol display 2014)
- National Farm Machinery Show (Helped manage the UK booth and explain current research projects 2012-2013)
- Morehead Event (Displayed Mobile pelleting unit and BioButanol display 2012)
- Quicksand Field Day (Displayed Mobile pelleting unit and BioButanol display 2012)
- Bracken County Field Day (Displayed Mobile pelleting unit and BioButanol display 2012)
- GIS assistance for disease outbreak prevention and response (Helping improve, update, and modify maps for KY Poultry Federation 2012-Present)
- Farm visits for improving beef operations (2012-2013)

PROFESSIONAL ORGANIZATIONS

- American Society of Agricultural and Biological Engineers (2006-Present)
- American Society of Animal Scientist (2009)