The Pennsylvania State University

The Graduate School
of
Agricultural Sciences

EFFECT OF STORAGE CONDITIONS ON THE DRY MATTER, COMPOSITION, AND RESPIRATION CONCENTRATIONS OF WILLOW CHIPS

A Thesis in

Agricultural and Biological Engineering

by

Ricky R. Lewis

Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Master of Science

May 2014

The thesis of Ricky Lewis was reviewed and approved* by the following:

Tom L. Richard
Professor of Agricultural and Biological Engineering
Thesis Advisor

Evelyn Thomchick
Associate Professor of Supply Chain Management

Daniel Ciolkosz
Research Associate in Agricultural and Biological Engineering

Virenda Puri
Distinguished Professor of Agricultural and Biological Engineering
Graduate Program Coordinator

*Signatures are on file in the Graduate School

ABSTRACT

This research aimed to bring transparency and understanding to how willow, a 2nd generation feedstock, behaved in aerobic storage conditions. The hope was to investigate the performance of stored willow in ways that are relevant to a downstream biological conversion processes. From the analysis, it can be concluded that the interaction between time and temperature have no effect on dry mass loss. When the temperature variable was isolated, concentrations were significantly different at or around temperatures close to 19°C. And when the time variable was isolated, significant differences in rates of dry mass loss were observed during the storage duration from 0 to 60 days.

The interaction of time and temperature significantly impact the xylan, arabinan, mannan, and acetyl concentrations. Using a tukey's comparison evaluation, samples treated for 30 days in 19°C temperature had statistically different xylan concentration than those samples stored at either 90 day 27°C temperature or 30 day 40°C temperatures. Arabinan concentrations of treated samples were significantly different when stored for 60 days at 40°C than for those stored at 30 days at 27°C. Mannan concentrations found in the treated samples were found to be the most statistically different for samples stored for 60 days at 27°C, than for samples stored for 30 days at 19°C. Acetyl concentrations of treated samples were found to be statistically different when stored for 90 days at 27°C than for samples stored for 60 days at 19°C.

For respiration rates, interactions between temperature and time were statistically significant. Willow chips stored at lower temperatures respired at a lower rate than willow chips stored at higher temperatures. These results lead one to conclude that

biological activity did occur during this experiment, suggesting that spores and fungus formed over the storage period which may pose health issue for handlers of the raw material.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACKNOWLEDGEMENTS

I would first like to start off by thanking my Lord and Savior Jesus Christ, for without him none of this would be possible. Second I would like to thank my family for their encouragement and support over the years. Next I would like to give a special thanks to my advisor Dr. Tom Richard for all the ways he has challenged me to become a stronger person intellectually. I would like to thank my lab manager Kay DiMarco for all the discussion and mentorship she displayed over the years. I would also like to thank the professors in my department that have helped me through my classes and blessed me with life lessons that I shall never forget. I would like to thank the NEWBio consortium for allowing me to take part in their efforts to develop biomass supply chains in the northeast and the USDA and NIFA for funding the project. I would like to also give a special thanks to Tim Volk and the team at SUNY-ESF for making material available when I needed it. And lastly but certainly not least, I would like to thank the graduate students within my department for their support, motivation, and friendship.

Chapter 1

Introduction

Refined petroleum has many applications, but most Americans know it best as the primary ingredient used for gasoline production. Approximately 18.6 million barrels a day of petroleum products were consumed in the United States in 2012, of which 11 million barrels per day were imported (USDOE_EIA. 2013). Responding to concerns about international conflict, depleting resources, and various environmental concerns, the United States has recently increased domestic energy production of crude oil, natural gas, and renewable fuels to lower its dependence on foreign energy. Shale oil and gas production is increasing rapidly due to directional drilling and hydraulic fracturing ("fracking") technologies, but are still fossil fuels with the associated environmental impacts, including greenhouse gas emissions during production and use.

Renewable fuels can be defined as any fuel produced from a renewable or regenerative source, with the carbon coming from atmospheric CO_2 so that they complete the carbon cycle. While in theory such fuels could be produced by artificial photosynthesis using renewable electricity from sunlight or wind, at present renewable transportation fuels depend on natural photosynthesis that produces plant biomass.

To encourage renewable fuels, Congress passed the "Energy Independence and Security Act of 2007" (USA. 2007), which amended the "Energy Policy Act of 2005" by revising the Renewable Fuel Standard (RFS, now RFS2 after the 2007 amendments). This update mandated increased domestic production of clean energy from renewable

fuels, with major production from cellulosic feedstocks beginning in 2012. The volume of corn ethanol was projected to plateau at 15 billion gallons in the year of 2012, while cellulosic and other advanced biofuels were expected to grow to reach 36 billion gallons by the year of 2022. Of this total, nearly 16 billion gallons of renewable fuel would come from dedicated energy crops such as cellulosic biomass (U.S. Environmental Protection Agency. 2010). This aggressive plan was based on the supply of biomass feedstocks estimated to be possible to grow within the U.S. without negative impacts on food supplies, as well as continuing technological advancements within the clean energy sector. The RFS2 goals were intended to transition the production of renewable fuels from traditional or 1st generation crops such as corn, soybeans and sugar cane, to 2nd generation renewable woody and herbaceous materials. These 2nd generation biomass resources and have been classified into four major feedstock groups: dedicated energy crops, agricultural waste, forestry waste, and urban wood waste (USDOE_EIA. 2006).

The attention renewable fuels receive for their environmental impacts stems from the specific feedstocks' natural ability to lower the amount of the greenhouse gas and carbon dioxide emitted into the atmosphere. Through photosynthesis, feedstock sources convert sunlight, water, and carbon dioxide to glucose, providing the most common elements in plant cell walls (C, H, and O) as well as energy needed for the plants to grow. As plants grow and eventually die and decompose, some of this carbon absorbed from the atmosphere is trans-located into the soil. With annual crops, especially on fields that are regularly tilled, much of this soil carbon will be re-released to the atmosphere as CO_2.

But with perennial crops a greater share will remain in the soil for decades or even centuries, a process known as terrestrial carbon sequestration (Sartori et al. 2006).

First-generation biofuels derived from starch- and sugar-based crops such as corn, sugarcane, and oilseed, help reduce GHG emissions and also increase diversity amongst transportation energy resources (Gomez. 2008). However, first generation crops such as corn and sugarcane are perceived by the public to create a conflict over land for "food vs. fuel", which makes them appear unattractive as long term substitutes for petroleum based fuel. Second-generation feedstocks are viewed as being a better large scale strategy to ensure energy security for the United States because they are abundantly available and do not interfere with food supplies in the same way. Many of the 2nd generation biomass feedstocks are also perennials with extensive root systems that effectively sequester carbon in the soil, reducing the net CO_2 emissions even beyond the emissions avoided by substituting biofuels for fossil fuels.

Another environmental benefit of 2nd generation biofuel production is that it reduces the amount of fossil fuel used for biofuel production relative to first-generation feedstocks (Gomez. 2008). Many of these savings result from the reduced inputs needed for perennials – no annual tillage, less fertilizer and pesticides, and fewer farming operations (Camargo et al. 2013). Examples of second-generation biofuel feedstocks include materials comprised from non-edible portions of crops (i.e. corn stover), other cellulosic materials grown primarily for energy purposes (i.e. willow); and materials such as organic waste from municipal, industrial, and construction activities. These crops generally have high dry matter output per hectare and are considered dedicated energy

crops (Jessup, 2009). Favorable attributes of dedicated energy crops include flexible harvest times, high productivity in areas that are not suitable for food and feed crops, require minimal inputs, non-invasiveness, and the ability to produce considerable yields over their lifespan (Jessup, 2009).

Although legislation has created multiple incentives and requirements to drive the expansion of homegrown clean and renewable energy sources, the growth of commercial cellulosic and advanced biofuel capacity has lagged behind expectations, in large part because of economic and scale-up difficulties. Several third parties such as university researchers and consulting firms have evaluated 2nd generation renewable feedstocks to assess the economic challenges and potential of various scenarios. Several such techno-economic scenarios were analyzed by researchers at the Department of Science, Technology and Society at Copernicus Institute, Utrecht University in the Netherlands (Uslu et al. 2008). They evaluated a range of biomass to clean energy scenarios based on how well the pretreatment option (torrefaction, pyrolysis and pellitization) impacted storage, transportation, and conversion cost, and indicated that a combination of torrefaction and pellitization pretreatment options make the biomass to energy chain economically advantageous, especially for long-distance transport of feedstock to a biorefinery (Uslu et al. 2008). Ahumada and Villalobos (2009) also recommend that agricultural supply chains should emphasize the consumption and monetary value of the product at hand. Other researchers go as far as to map out specific logistical models to maximize economic potential (Carolan et al. 2007) and (Hess et al. 2009).

Satellite biomass processing and densification centers allow for the development of distributed biomass systems to feed centrally located biorefineries. Given the high costs of transporting low density cellulosic biomass, such “hub and spoke” systems allow economic supply chains to be more economically efficient. Not all are convinced of the economic benefits of the biomass to energy chain. Ravula (2008) suggests the expense of processing and transporting feedstocks alone in some supply chains constitute as much as 75% of supply chain costs. Youngs and Somerville (2012) document the technical feasibility of renewable fuels based on current research, but suggest that because of the high costs of logistics, renewable fuels produced from cellulosic feedstocks are too expensive to be cost-competitive with petroleum-based fuels at present.

Another market driver for dedicated biomass crops is consumer demand for biochemicals and biomaterials. Everyday consumers with a “green thumb” purchasing attitude naturally look for healthier products to purchase and use. Food industry giants like Coke and Pepsi utilize bioenergy crop derivatives to develop products such as bio-degradable plastic bottles, while others create biodegradable eating utensils, plates and cups. While these products are mostly made from corn starch today, the same technologies that produce cellulosic sugars for biofuels can be used for these products also. Other companies, such as auto manufacturers, have the potential to utilize lignocellulosic derivatives to develop renewable tires and/or car parts. However, the fact still remains that renewable biomass feedstock and fuel supply chains are still in their infancy. These systems will require greater efficiency and market stability to produce the

high volume outputs needed to substantially displace petroleum based additives with alternatives.

Due to the natural variation of climate and soil, there are regional differences among various biomass feedstocks with respect to their agronomic suitability and economic, environmental, and socio-cultural sustainability. As a result, many 2nd generation feedstocks have been identified as suitable for renewable fuel production. This diversity of options in turn requires extensive supply chain modeling and feedstock analysis on a regionally specific basis. Similarly, there are many cellulosic biomass conversion technologies but only heat, electricity and wood products have a substantial track record of high volume purchases at a commercial scale. This variability and uncertainty about costs, prices and demand in turn creates a weak market structure that impacts growers, suppliers, and buyers' decision making throughout the biomass supply chain. However, as government laboratories, universities, and the private sector continue develop optimized systems for the production and supply chain of renewable fuels, the economic uncertainty within the supply chain can be expected to lessen.

One specific uncertainty is the performance of renewable feedstocks throughout the supply chain and their ability to retain their original composition. Because feedstocks are subject to different storage and handling techniques, dry matter and mass composition may be affected. This research aims to bring transparency and understanding to how willow, a 2nd generation feedstock, behaves in aerobic storage conditions. The hope is to investigate the performance of stored willow in ways that are relevant to a downstream biological conversion process.

Chapter 2

Literature Review

2.1. Overview

If cellulosic biofuels are to be used as additives and in some cases alternatives to petroleum based products, the feedstock should have the following characteristics:

- Economically competitive
- Ecologically beneficial
- Abundantly available
- Compatible with food production systems

(Hill et al. 2006). These characteristics are not intrinsic to the feedstock material only, but must be examined within the content of the entire supply chain. Key supply chain parameters include: location, feedstock resource potential, infrastructure availability, and storage options. While all of these parameters are important, the one of particular interest in this study is feedstock storage.

Biorefineries and other capital intensive processing facilities are most cost effective when then operate year round. Because many biomass feedstocks are only harvested seasonally, storage becomes a necessary way to couple feedstock supply with biorefinery demand. Hess et al. (2007) analyzed the importance of intermediate short- and long-term storage for the typical short harvest window for biomass availability.

Before delving into the details of storage, it is important to note that there are alternatives to long-term storage for feedstocks that can be grown continuously in warmer

climates. For example, researchers from New Zealand and Italy designed an all-year-round harvesting model which cuts costs and dry matter losses associated with biomass storage by harvesting every eight to ten weeks, instead of once per year (Sims and Venturi. 2003). This strategy cut the costs of production, both because of the purchase of smaller, cheaper machinery for the smaller volumes harvested, and due to the evenly spaced labor cycle. More importantly this strategy cut the cost of storage by storing small amounts of feedstock in cycles. But this approach depends on mild climates and year-round production systems that are not possible where winters or dry seasons prevent year round growth.

The Feedstock Logistics Interagency Working Group (Group. FL. 2010) noted that the quality of feedstock changes during storage due to biological degradation. This oftentimes is a result of moisture in the biomass, enhanced by the availability of oxygen which is needed for lignin degradation. Microbial degradation can lead to continuous changes in the condition of the material and substantial dry matter losses. To investigate these impacts, Casal et al (2010) studied combustion characteristics using thermo gravimetric analysis to determine if outdoor-stored pine woodchips were subject to compositional losses over a 12 month storage period due to the natural surrounding environment. They concluded that the biomass experienced substantial degradation during the first three months, thereafter remaining stable for longer periods of storage.

The remaining sections of this literature review will focus on willow's significant biological properties that are subject to change while in storage and willow biomass supply chains.

2.2 Shrub Willow Properties

Shrub Willow (*Salix spp.*) is a short rotation perennial woody crop. Commercial varieties are often a hybrid of several species found primarily in the northern hemisphere growing upon moist soils of cold and temperate regions (Bassam. 2010). Willow can grow on a wide range of soils from light to loamy that contain soil pH ranges between 6.5 and 7.5. Willow has high water requirements and requires irrigation for rainfall less than 0.6 m yr^{-1}(Bassam. 2010). For biomass production, the common practice is to coppice willow, mowing after the first year's growth and then harvesting every 2 to 4 years. This practice allows for better shoot development because it removes dominance of the central stem, allowing other stems to develop, increasing crop yield (Karp and Shield. 2008). Willow has been studied extensively due to its rapid growth and establishment (Jessup. 2009). Noted yields of willow after irrigation and fertilization in three year rotations have exceeded 27 oven dried tons (ODT) per hectare on some North American soils and 30 ODT per hectare on some European soils each per year (Volk et al. 2006).

It is common practice to harvest willow in three year cycles and it may be commercially harvested up to eight cycles before replanting is necessary. Because willow is a C3 species, it can perform photosynthesis more efficiently at lower temperatures than most C4 species. C3 species generally operate optimally at temperatures between 15 and 20 degrees C and produce lower rates of CO_2 exchange. The optimal growing temperature for willow is between 15 and 26 degrees C (Bassam. 2010). Beneficial environmental properties of willow include its ability to accumulate heavy metals released from organic compounds found in soils (phytoremediation); willow's natural

ability to facilitate the breakdown of organics to non-toxic compounds; its natural ability to sequester carbon; and its ability to control water dynamics including runoff and infiltration *(*Volk et al. 2006).

2.2.1 Composition of harvested willow

Time, method of harvest, storage method, and environmental conditions can impact biomass composition (Lee et al. 2007). Compositional analysis is often reported, either as a proximate analysis determined by drying, extraction, or burning (typically ash, fixed carbons, and volatile matter content) or through an ultimate analysis which reports elemental compounds such as carbon, hydrogen, nitrogen, and sulfur. When measuring changes in composition during storage, it is important to distinguish concentration from total mass, as the fractional basis of composition, dry matter, is itself degrading during the course of the experiment. A recent study conducted by Singh et al (2011) discussed the nature of decomposed logging residues and how it influenced fuel properties. They concluded that for red maple and yellow poplar samples, environmental decomposition reduced acid detergent fiber (roughly equivalent to cellulose) and lignin, and resulted in substantial loss of potassium, calcium, and magnesium; however, on a concentration basis sodium and aluminum concentrations increased.

Keoleian and Volk (2007), reported on willow samples with the composition breakdown in Table 1.

Table 1: Composition of willow (Keoleian and Volk, 2007).

TABLE 1 Willow Biomass Characteristics	
Carbon	49.40%
Sulfur	0.05%
Oxygen	42.90%
Hydrogen	6.01%
Nitrogen	0.45%
Chlorine	265 ppm
Ash	1.24%
Moisture (at harvest)	~ 50%
Heating value	19.8 MJ -1 odkg

2.2.2 Cellulose

Cellulose, a glucan polymer composed of carbon, hydrogen, and oxygen, is the most abundant polymer available worldwide. It generally comprises 23-52% of lignocellulosic plants on a dry weight basis (Lui and Sun. 2010). Cellulose is the main structural constituent of the plant cell wall, where cellulose micro fibrils contribute significantly to the mechanical strength of the cell wall and act as the framework for the cell wall (Lui and Sun. 2010). Cellulose found in plants can be made more available to enzymatic hydrolysis via various pre-treatment options such as steam explosion, alkaline peroxide extraction, acid hydrolysis, and biological pretreatment. After hydrolysis the glucose can be biologically converted into ethanol or intermediate chemicals.

2.2.3 Hemicellulose

Hemicelluloses, also derived from carbon, hydrogen and oxygen, are roughly 20-40% of the total feedstock mass and are generally divided into four general groups of polysaccharides composed of 5- and 6-carbon sugars: xylans, mannans, xyloglucans, and mixed-linkage β-glucans (Lui and Sun. 2010). The primary monomers found in hemicelluloses are D-xylose, D-glucose, D-mannose, L-arabinose, and galactose. Hemicellulose forms covalent bonds with lignin, which restricts the liberation of hemicelluloses from the cell wall matrix (Karp and Shield. 2008). Ergo, like cellulose, hemicelluloses must undergo pretreatment to hydrolyze the polymers for further utilization as intermediate chemicals or for further conversion to fuel production.

2.2.4 Lignin

After cellulose, lignin is the second most abundant polymer on earth. Because it is polymerized in a semi-random process, there are never two identical lignin macromolecules with the same primary sequence of phenyl units (Rahman et al. 2012). Lignin is the most prevalent barrier for bioconversion as it bonds to hemicellulose and cellulose, is hydrophobic and resistant to degradation, thus restricting the sugar polymers from utilization. Pretreatment options for biological conversion such as hot water or acid separate this lignin from cellulose and hemicelluloses, allowing easier cellulose and hemicelluloses conversion into fuel and intermediates. In contrast to biochemical conversion, thermo chemical processes utilize this lignin by converting the whole

feedstock material into syngas, a mixture of CO, H_2, and CO_2, which can then be catalyzed into biofuel.

2.2.5 Ash and extractives

Ash is the mineral residual of biomass after thermo chemical oxidation of the carbon, hydrogen, oxygen and nitrogen, and is comprised of metal oxides and calcium carbonate (IATA. 2010). Extractives represent all of the compounds in a feedstock that are typically not essential in cellular structure and are co-products of biochemical conversion. Both ash content and extractive amounts will vary from feedstock to feedstock.

2.2.6 Moisture

Willow is often high in moisture, with values as high as 55% (wet basis) at harvest. Moisture content can have a significant impact on biomass conversion, and therefore must be accounted for at all times. Woody biomass can undergo continuous change in moisture during storage, and thus requires active management to control (Feedstock Logistics Interagency Working Group. 2010).

High moisture contents during storage can impact the structural integrity of the material and can potentially lead to biological degradation, and sometimes self-induced fires occur through spontaneous combustion. While conducting storage experiments

Casal et al (2010) concluded that increased moisture content impacts the feasibility of biomass to energy conversion.

2.2.7 Respiration

Respiration techniques have been used as markers for organic matters' decomposition in soil, water, and composts, and as an assay for compost stability (Sadaka et al. 2006). Microbial respiration occurs as microorganisms utilize aerobic processes to consume carbohydrates as a source of energy. As a waste product, carbon dioxide is produced and can be measured to identify the amount of activity that is occurring known as the biological oxygen demand (BOD).

2.3 Supply Chain Logistics

Supply chain logistics is the description of how goods are managed. In this case, willow is grown, harvested, chipped, and stored on location. Once needed, the willow is transported to a biorefinery for consumption in the form of fuel, heat, or electricity.

2.3.1 Harvesting

Key variables such as terrain and operation size should be considered before implementing a harvesting strategy involving the purchase or rent of equipment. Harvesting of willow is carried out when stems are bare of leaves, generally between the months of November and April (Kofman. 2012). There are three common methods for

harvest of short-rotation coppice: whole shoot harvesting, chip harvesting, and billet harvesting (Kofman. 2012). Chip harvesting equipment includes a harvester tractor that systematically collects and converts whole shoots of woody biomass into woodchips. The tractor then blows the chips into a trailer that can be either attached directly to, or towed alongside the harvester. Willow trials in Europe indicate that cut and chip harvesters that have both high throughput and power rates are successful systems (Volk et al. 2006).

2.3.2 Storage of collected biomass

For most biomass crops, storing biomass is essential to facilitate year round supply to a biorefinery. Low density materials often have high storage and transport costs, so for lignocellulosic biomass these are not trivial costs. Rentizelas et al. (2008) evaluated supply chain models and determined that it is common practice to select the cheapest storage solution, disregarding the advantages of a more sophisticated storage system. Storage can occur at the point of origin, at an intermediate facility, or based on the supply chain in use. However, lower cost storage options (i.e. windrows at the field), have the potential to limit the available land for production for some growers. Shastri et al 2011 and others have analyzed the feasibility of satellite storage facilities for storage and preprocessing as a method of improving supply chain effectiveness and reducing overall costs. However it is still a challenge to identify optimal storage processes because of varying geographic location and season of harvest.

Improper storage techniques can result in significant feedstock losses. Feedstock losses can occur as either dry matter mass loss or through degradation of high value constituents. Such losses occur naturally due to variables such as weather and moisture intrusion, as well as logistics challenges such as storage duration, harvesting, and transport/handling of the raw material (Mooney et al. 2010). These variables pose the most immediate threat to stored biomass prior to conversion, as spore and fungus formation may occur (Rentizelas et al. 2008). Hubbard et al 2007 cite two studies done in Sweden where green chips were stored in large piles for seven months losing 12% dry matter and bark stored in large piles for six months losing 26% of its dry matter. The bark piles studied had a 20% decrease in the energy content of the material (Hubbard et al. 2007). Therefore, due to the short harvesting season, biomass feedstock growers and buyers must note the importance of moisture content and storage duration when deciding which storage method to implement. Some storage examples include open air piles, silos, tanks, bunkers, and pallets. The appropriate storage technology depends on the storage amount, biomass format, and biorefinery demand and should account for shrinkage, soluble sugar capture, compositional and pretreatment impact.

Casal et al (2010) stored pine woodchips for 12 months in outdoor piles and concluded that, because of degradation related to weather conditions and the particle size of the woodchips, open-air storage was not an effective solution. Because storage conditions affect the quality of the material being stored, optimal storage temperatures and moisture levels should be identified to minimize the significant feedstock losses that can occur from microbial degradation.

2.3.3 Preprocessing of biomass materials

Preprocessing includes all of the physical, chemical, or biological processes necessary to turn feedstocks from one form to a more suitable state for transport from a storage location to the biorefinery for conversion to liquid fuels. Pre-processing includes torrefaction, densification/compression, pellitization, drying, and chemical treatment. Willow is usually chipped in this preprocessing step so that the material is more suitable for storage, conversion, handling, and transport. Though preprocessing techniques exist to mitigate transport costs and aid in conversion to fuel, the performance of willow in preprocessing, and the relevance of pre-processing for the willow supply chain have not been carefully studied.

2.3.4 Transportation

Transportation of feedstocks throughout the biomass logistics system occurs primarily when feedstocks are harvested and collected or when feedstocks travel downstream to intermediate processing or other users. Because common transportation systems such as rail, truck, barge, and even pipeline exist, it is common practice that one or a combination of these transports systems be utilized in a biomass-to-energy supply chain, with the optimal choice often a function of transport distances. Transport distance usually depends on a variety of factors including pretreatment process capacity, the biomass yield, and the percentage of land occupied with crops (Uslu. 2008). Current best practices in the biomass transport industry are to collect and transport low moisture

feedstock (typically less than 20% moisture) so it can be stored dry and hauled to a biorefinery when the time it is needed (Richard et al. 2012).

2.3.5 Conversion platforms

Woody plants produced on marginal lands can be converted into synfuel, hydrocarbons, or cellulosic ethanol (Hill et al. 2006). These conversions from whole material into alternative fuel or any assortment of intermediates, take place at bio-refineries. The platforms bio-refineries utilize for conversion are either bio-chemically or thermo-chemically based, and in specific instances both platforms are used to utilize all of the material available. Apart from their fundamental process differences of being thermal versus biological in nature, thermo chemical conversion platforms can convert cellulose, hemi-cellulose, and lignin during conversion while biochemical conversion as it is presently practiced only utilizes the cellulose and hemicellulose portions of a material.

2.3.5.1 Biochemical conversion

Biochemical conversion utilizes enzymes and yeast to break down and convert structural carbohydrates into sugars that can be further converted into fuels or other chemical molecules. Biochemical conversion generally involves a process as depicted in

chart 1 below;

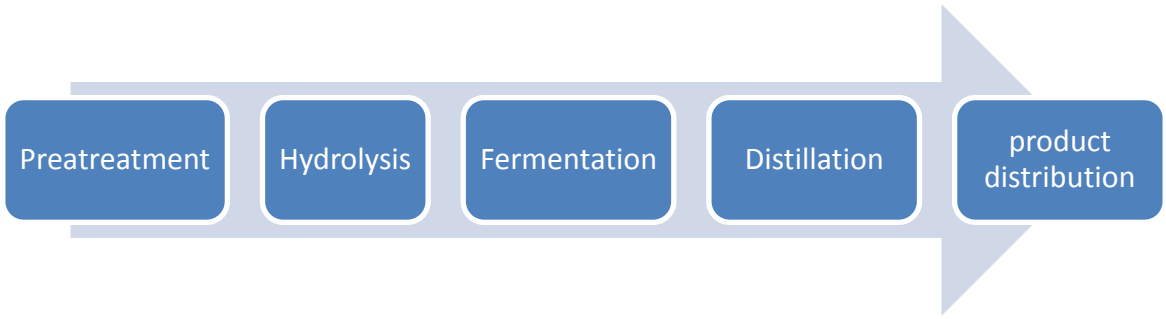

Figure 1: Bioconversion flow chart.

Pretreatment often refers to the separation of lignin from cellulose and hemicelluloses so that these carbohydrates become more accessible during enzymatic hydrolysis. Pretreatment options can include physical, chemical and biological processes that degrade lignin barriers within lignocellulosic feedstocks. Examples of well developed pretreatment technologies include liquid hot water, steam explosion, ammonium fiber expansion (AFEX), and acid pretreatment. Hydrolysis options include enzymatic or acid hydrolysis.

During enzymatic hydrolysis, enzymes further break cellulose and hemicelluloses polymer chains for conversion of cellulose and hemicellulose to sugars. This process usually takes several days and can be costly depending on the enzyme and company. In the next step fermentation, yeast such as *Saccharomyces cerevisae* (*S. Cerevsiae)* and *Zymomonas mobilis* (*Z. Mobilis)* are utilized during simultaneous saccharification and fermentation (SSF) to convert sugars into bio-ethanol. Distillation removes any impurities from the bio-ethanol, so the biofuel can then be distributed to downstream end-users. Processes have been developed to now co-ferment both pentose and hexose sugars (five and six carbon sugars respectively) in a process known as simultaneous

saccharification and co-fermentation. State of the art bioconversion processes mitigate time and cost by combining both hydrolysis and fermentation into one step known as consolidated bioprocessing. Acid hydrolysis was utilized in this experiment and will be explained further in the methodology section.

2.3.5.2 Thermochemical conversion

Thermochemical conversion of lignocellulosic materials utilizes heat and pressure to transform biomass into intermediate compounds that can then be converted into biofuel either by biochemical or thermochemical means. There are two common conversion processes, fast pyrolysis and gasification. They are used to produce bio-oil and syngas respectively. When biomass feedstocks undergo pyrolysis, the materials are placed in an oxygen starved atmosphere and broken down using heat creating a bio-oil that can be refined and used as a transportation fuel. Unlike fast pyrolysis, gasification converts lignocellulosic biomass into syngas; primarily H_2, and CO. Syngas produced via gasification can be refined using methods such as Fischer-Tropsch synthesis to produce a hydrocarbon product that can be used to produce chemical intermediates or cellulosic fuels.

2.4 State-of-the-art

Willow and other dedicated energy crops are being promoted as 2nd generation feedstocks due to their economic, environmental, and socio-economic sustainability

properties. Storage, a key component in biomass supply chains, will determine how much material is readily available year-round.

Biomass storage will typically occur immediately after harvest where lignocellulosic biomass could require long term storage (up to twelve months) for later utilization. However, storage options are subject to storage losses. Current storage practices often utilize the little to no cost strategy of storing materials outdoors in piles. However, this conventional approach subjects the material to feedstock losses due to degradation and dry matter loss. One way dry matter loss occurs is when wet material is not used immediately leaving it susceptible to colonization by fungi and mold (Hubbard et al. 2007). The metabolic activity of microorganisms creates heat, causing a reaction that accelerates oxidation, moisture adsorption, hydrolysis, pyrolysis, and other chemical processes that result in dry matter loss (Hubbard et al. 2007).

Compositional changes due to degradation in feedstocks impact conversion machinery and yields. However, little is known about how willow performs during storage with respect to the bioconversion yield downstream. This research aims to study the relationship between aerobic storage conditions and willow feedstock losses.

Chapter 3

Goals, Objective, and Hypothesis

3.1 Introduction

Late harvested willow was analyzed to determine how three storage temperatures and three storage durations affect composition, dry matter loss, and respiration of willow.

Factors:

1.) Time- 1 month, 2 month, 3 month (3 levels).

2.) Temperature- 19ºC, 27ºC, 40ºC (3 levels).

Response: The mass of dry matter, composition, and respiration rate due to the storage conditions stated above.

3.2 Goal

The goals of this research is to learn how storage conditions impact willow chips before they are converted into biofuel. Specifically, this research aims to identify changes in composition, mass, and respiration rate over 3 months of simulated aerobic storage duration for willow chips at varying temperatures.

3.3 Objectives

The objectives to accomplish this goal are to:

1. Measure mass loss amounts on a monthly basis during three months of storage.
2. Measure compositional changes on a monthly basis during three months of storage.
3. Measure the respiration rate (BOD) for willow during three months of storage.
4. Perform a statistical analysis on measured data to identify if the dry matter loss is significant (α=.05) within the first three months.
5. Perform a statistical analysis on measured data to identify if the compositional changes are significant within the first three months.

3.4 Hypothesis

The hypothesis for this project is that the conditions in which willow is stored will impact its mass, composition, and respiration rate concentrations.

For Time (days):

Null Hypothesis: The mean values of dry mass percentage loss amongst three times are equal.

Alternate Hypothesis: The mean values of dry mass percentage loss at three time intervals differ.

Null Hypothesis: The mean values for sugar and acid concentrations are equal.

Alternate Hypothesis: The mean values for sugar and acid concentrations differ.

Null Hypothesis: The mean values for respiration rates are equal.

Alternate Hypothesis: The mean values for respiration rates differ.

For Temperature (C^{o}):

Null Hypothesis: Mean values of dry mass percentage loss are equal.

Alternate Hypothesis: Mean values of dry mass percentage loss differ.

Null Hypothesis: The mean values for sugar and acid concentrations are equal.

Alternate Hypothesis: The mean values for sugar and acid concentrations differ.

Null Hypothesis: The mean values for respiration rates are equal.

Alternate Hypothesis: The mean values for respiration rates differ.

For interaction between time and temperature:

Null Hypothesis: There is no significant change in dry mass percentage loss due to interactions between time and temperature durations.

Alternate Hypothesis: There is a significant change in dry mass percentage loss due to interactions between time and temperature durations.

Null Hypothesis: There is no significant change in sugar and acid concentrations due to interactions between time and temperature durations.

Alternate Hypothesis: There is a significant change in sugar and acid concentrations due to interactions between time and temperature durations.

Null Hypothesis: There is no significant change in respiration rates due to the interactions between time and temperature durations.

Alternate Hypothesis: There is a significant change in respiration rates due to interactions between time and temperature durations.

The Level of Significance is set at 0.05.

Chapter 4

Methods and Materials

4.1 Introduction

This chapter will discuss the experimental design, laboratory methods, and equipment used to achieve the goals and objectives by testing the hypotheses of this research.

4.2 Overview of Methodology

The methodology for this project is divided into three phases: (1) experimental design, (2) experimental trial, and (3) statistical analysis. In the experimental design phase, the design was developed, measurement precision quantified, and preliminary trials were run. In the selected design, each experimental treatment starts with 118 grams of chipped biomass at the same initial moisture and exposed to storage temperatures of 18, 27, or 40 degrees C. During the storage trial in phase two of this experiment, compositional analysis, dry matter data (objectives 1 & 2) and respiration rates were measured. Dry matter data were collected by measuring out the mass of the jar filled with biomass before and after each time increment, drying a subsample in an oven at 45 degrees C and calculating the moisture content. Compositional analysis was carried out using an Accelerated Solvent Extractor (ASE) (Dionex, ASE 350 Sunnyvale, CA) for extractives and an Ion Chromatography System (ICS) (Dionex ICS 3000, Sunnyvale, CA) for mass fraction of carbohydrates found in the willow samples. Finally, respiration

rates were measured using the OxyTop system (WTW, OxyTop, College Station, TX). In phase 3, statistical analysis using Minitab v16 software was carried out to compare the results of the different storage conditions. The results were then analyzed to further test the hypotheses previously described.

4.3 Description of lab equipment

This experiment was conducted in the Biomass Conversion Laboratory, Room 113 Agricultural Engineering Building at Pennsylvania State University. The required equipment for this project which included incubators, jars, a laminar air flow hood, 600g scale (Ohaus, Scout Pro, Pleasant Prairie, WI), Spectrophotometer, Multivapor P-12 (New Castle, DE), furnace, an oven, and the previously mentioned Dionex ICS and ASE systems.

Figure 2: The Accelerated Solvent Extractor (ASE 350).

The Dionex ASE 350 Accelerated Solvent Extractor system (ASE 350), shown in Figure 2, was used for water and ethanol extraction. It is an automated extraction system

that uses elevated temperatures and pressures to extract constituents in very short period of time. Because of the elevated temperatures and pressures this machine is capable of extracting organic compounds from a variety of samples, and can also be used to pretreat biomass although in this study that was not done. The extraction programs are input in the front panel and can have temperatures up to 200°C and pressures up to 1700 psi. The cell tray can hold up to 24 sample cells. The collection tray holds the vials used to collect water and ethanol extract. The solvents used for extraction are stored atop the program panel and are used to extract any impurities that may hinder compositional analysis results.

Figure 3: Dionex ICS-3000 Ion Exchange Chromatography System.

The Dionex ICS-3000 Ion Exchange Chromatography System (Figure 3) is located in the biomass conversion lab at Pennsylvania State University as well. The device performs tasks such as purification, detection, and quantification of compounds. It contains two systems in which sugars, alcohols, and organic acids are detected. System 1 measures alcohol with an electrode detector and organic acids using a photodiode array

detector. System 2 measures monosaccharides using pulsed amperometry. The ICS-3000 was used in this research to determine sugar and organic acid levels of samples after their respective storage treatments.

Figure 4: OxyTop-C measuring systems.

The microbial activity, or respiration rate, of the woodchips was determined by filling 1 L bottles with 20 grams of woodchips sample. The bottles were then attached to a CO_2 trap system and were closed with biological oxygen demand (BOD) OxyTop-C measuring heads as shown in Figure 4 above. Measurements of the change in pressure were recorded every five to seven days for three months and theses data were used to calculate the respiration rates for woodchips at three soaking durations.

4.4 Methodology

4.4.1 Phase 1: Experimental design

Late harvested willow samples provided by The Department of Forest and Natural Resources Management at State University of New York College of Environmental Science and Forestry were utilized to determine how aerobic storage conditions impacted the sugar and acid concentration, biological oxygen demand, and the amount of mass remaining after storage. In phase 1, willow chips underwent laboratory simulated storage by being placed into twenty seven glass containers. Due to the physical limitations of the jars, each jar was filled with 118 grams (wet basis) of willow chips per container at ~55% moisture. The twenty seven sealed jars were then randomly distributed into three incubators set at three different temperatures 19, 27, and 40 (ºC). Once the treatment times were complete the three jars from each incubator were removed and weighed to measure the wet weight of the willow chips. The contents of the jar were then extracted to measure the moisture content as well as to be grounded for further compositional analysis.

To measure the respiration rate, willow chips soaked in nanopure water, (one overnight, the other for an hour) along un-soaked willow chips were placed separately into nine (three replicates of each) OxyTop vessels. They were then enclosed by the OxyTop-C measuring heads and placed into each respective incubator. The respiration rates were then recorded in 7 day increments for three months.

4.4.2 Phase 2: Experimental Trials

After each storage time increment, the replicates at each temperature were taken out in preparation for measuring the dependent variables.

4.4.2.1 Measurement of Mass Loss

The jars were weighed and then samples were collected for measuring moisture content relative to the mass loss calculation. Previous moisture tests showed that the moisture content of the willow chips is higher at the bottom of the jars, which skews the moisture calculations as the woodchip samples at the top of the jar are drier than the overall contents of the jar. Thirty day samples were collected from the tops of the jars and therefore were subject to analytical error and represented in separate tables. To prevent further errors of this type, sixty and 90 day samples were poured into a separate container and thoroughly mixed before sub-sampling for moisture. Three subsamples were collected and their moisture contents measured for the moisture content measurements of each of the jars. The final moisture content (wet basis) and dry mass for each of the samples was calculated from equations 4.4.1 and 4.4.2 below:

$$\textit{Moisture content} = \{(\textit{wet mass} - \textit{dry mass})/\textit{wet mass}\} * 100 \quad \text{(equation 4.4.1)}$$

$$\textit{Total dry mass} = \textit{Total wet mass} * (100 - \textit{moisture content})/100 \quad \text{(equation 4.4.2)}$$

4.4.2.2 Quantification of sugars and acids in treated willow chips

Untreated willow and the samples collected after treatment (0-30, 0-60, 0-90 days; 19, 27, 40 °C) were then left to air dry at room temperature for further processing using a Wiley mill (Wiley, model No. 4, Swedesboro, NJ) with a 2mm screen. The dried and ground willow was then stored in a tin container until compositional analysis could be carried out. The first steps in the compositional analysis determine the hemicellulose, cellulose, lignin, and extractives found in willow. The ASE 350 was used to remove any extractives that would alter true values of the analysis by water and ethanol extraction. The extraction conditions were as follows: Temperature = 100˚C, static time of 7 minutes, rinse volume of 150%, purge of 120 seconds, static cycles = 3, and solvent saver mode = OFF. Once the extraction process was complete, the ground willow samples were then left to air dry prior to quantitative saccharification using acid hydrolysis.

To investigate the impacts of compositional change during storage on downstream biochemical processing, acid hydrolysis was used to convert biomass to sugars. This method was adapted from the standard NREL protocol for biomass compositional analysis (Sluiter et al. 2008a and 2011b). The analysis started with an acid hydrolysis to remove the mass fractions from the binding lignin. This was performed by submerging ground samples of willow in 72% (w/w) sulfuric acid. They were then placed in a water bath set at 30˚ C for one hour with continuous stirring. Immediately following the concentrated sulfuric acid bath, the sample acid concentrations were then reduced to 4% (w/w) sulfuric acid by adding 84mL of water. These more dilute acid samples were then autoclaved for one hour at 250˚F and 20psi. Once the autoclaved samples cooled, they

were filtered for further sugar and organic acid analysis through a filtration process. The filtrated solids were then ashed in a muffle furnace with a program sequence that reached temperatures of 575˚C accounting for the acid insoluble lignin content.

The liquid samples from the acid hydrolysis were filtered for sugar and acid testing using a .2 micron PTFE syringe filter. To detect the sugar and organic acid amounts within the samples, the samples first needed to be diluted to a detectable range for the Dionex ICS-3000 system. Sugar recovery standards were run in conjunction with the treated samples to accurately quantify the sugars in the willow samples.

Acid levels were computed using the Dionex ICS-3000 system. The organic acids were detected by pulsed amperometry using (YSI model 2700 SELECT, Yellow Springs, Ohio). Both the sugar assay and the organic acid analyses were carried out in duplicate.

4.4.2.3 Quantification of respiration rates using the OxyTop system

The OxyTop vessels were removed from the incubator every five to seven days at which time the respiration rates were measured. First, the measuring heads were removed to replenish the oxygen within the vessels. Then the sodium hydroxide tablets, which are used to absorb CO_2 as it is produced by respiration, were replenished as needed. The microbial activity of the woodchips was derived based on the following principles. Microorganisms in the woodchips require oxygen to obtain energy, so the bacteria inhale the surrounding oxygen and exhale carbon dioxide into the measuring head compartment. The carbon dioxide released (and indirectly the oxygen consumed) is then measured as a change in pressure once it is absorbed by sodium hydroxide tablets. Absorption on the

base causes the carbon dioxide to be removed from the gas phase, resulting in a negative pressure which in turn influences the BOD value. BOD values were determined using equation 4.4.3 below:

$$BOD = \frac{M(O2)}{R * Tm} * \left\{ \frac{Vtot - Vl}{Vl} + \frac{Tm}{To} \right\} * p*(O_2)$$

(Equation 4.4.3)

M(O2) Molecular weight of oxygen (32000mg/mol)

R Gas constant (83,144 L*hPa/ (mol*K))

T_o Temperature (273.15 K)

T_m Measuring temperature (299.15) for BOD_5

V_{tot} Bottle volume [mL]

V_l Sample volume [mL]

α Bunsen absorption coefficient (0.03103)

Δp (O_2) Difference of the partial oxygen pressure [hPa]

4.4.4 Phase 3: Statistical analysis

Statistical analysis was conducted using Minitab 16 to apply the general linear model to the collected data.

Chapter 5

Results and Discussion

This chapter presents the results and a discussion of the dry matter loss of the samples associated with the various treatments. This is then followed by results and discussion of the composition analysis. Finally data and discussion of the respiration rates of willow chips is discussed.

5.1 Dry Matter Loss:

Dry mass loss of the samples shown in Table 2 ranged from 3% to 23%. To test the hypothesis for dry mass loss, the following model was used; mass loss was equal to the grand mean +time +temperature +time*temperature +error. The general linear model ANOVA was used to interpret the significance of the general model above. The dry mass was measured on days starting at 0 to 30, 60, and 90, and the dry mass loss was calculated by taking the difference between masses on specified days as a percentage of the original dry matter as shown below in Table 2. Zero to sixty day sample results were skewed due to the difficulty in calculating the moisture content before and after storage. Therefore, the percent of dry mass loss seem to be greater for samples stored from day zero to day sixty, than samples stored from day zero to day ninety.

Table 2: Percent Loss of Dry Mass During Storage.

Fraction loss in %		
Time (days)	Temperature (degrees Celsius)	percent change
0 to 30 days	19°C	-7%
	27°C	-3%
	40°C	-2%
0 to 60 days	19°C	-23%
	27°C	-14%
	40°C	-16%
0 to 90 days	19°C	-5%
	27°C	-5%
	40°C	-6%

Final dry matter was calculated by first recording the wet weight of the material after treatment, followed by drying the samples at 105 for 12 hours, then by weighing the material once more. Time and temperature significantly impacted the dry mass of stored willow (α =0.05) at P=0.025, however, the interaction between time and temperature was found to be insignificant, with a P value greater than 0.05 (thus failing to reject the possibility of that there is no significant change in dry matter percent loss due to time and temperature interactions).

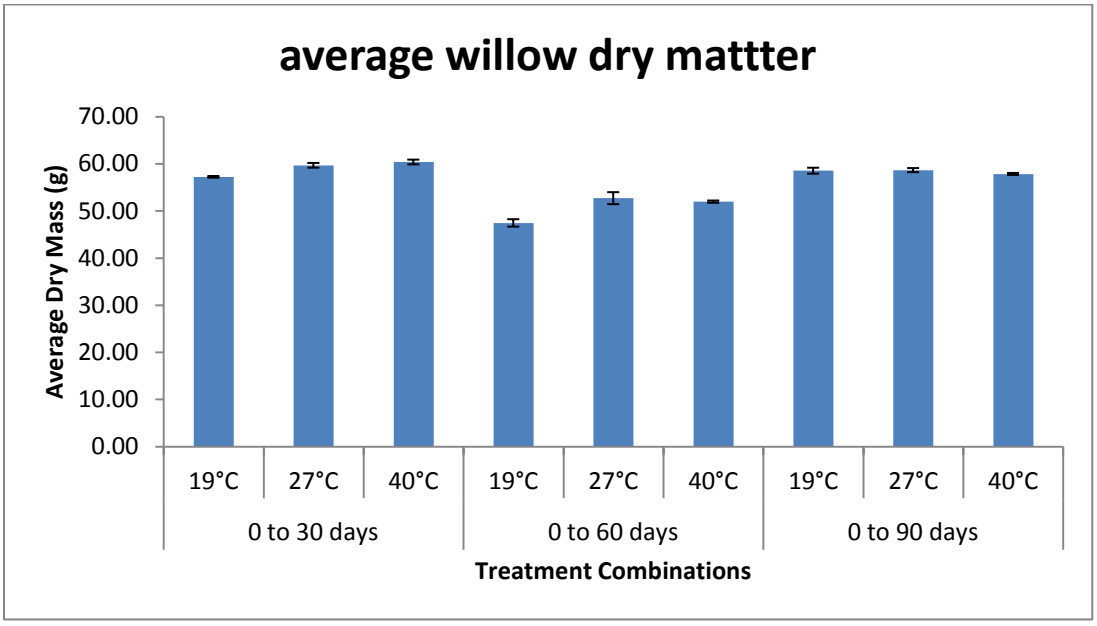

Figure 5: Dry mass percentage loss as a function of time and storage.

Figure 5 above depicts the dry mass percentage loss for each treatment stored from 0 to 30,60, and 90 days. Samples stored for 60 days had higher percentage losses due to the time spent in storage than those stored for the 30 or 90 day duration. While 60 and 90 day data were collected from samples representative of the whole jar, 30 day woodchip samples were extracted only from the top of the jar which due to respiration, were wetter samples from the jar. The way in which the samples at each time block were extracted may also may have distorted the actual dry mass loss result because some of the samples may not have been completely dry before measurement. It is imperative that the materials moisture content be controlled in a biorefinery setting. Also, transportation costs can be significantly impacted by moisture content (and hence mass) of the feedstock. Because of this, results indicated in Figure 6 above are important for supply chain design for advanced biorefineries.

5.2 Sugar and Acid Concentrations:

The mass compositions of the treated samples and the untreated sample are shown in Figure 6 and 7 below. When averaged, the total mass concentration percent equaled 99.74 % suggesting an accurate reporting of the concentration of the woodchips after treatment. However, total mass of individual treatments varied from sample to sample which may be indicative of variability in the analytical methods used. The treatment combination of time and temperature significantly impacted the mass concentrates percentages of xylan, arabinan, mannan, and acetyl acid with P values <0.05. Temperature as an isolated factor significantly impacted both glucan and galactan percent concentrations with a P value <0.05. Using a tukey's comparison evaluation, samples treated for 30 days in 19°C temperature had statistically different xylan concentration than those samples stored at either 90 day 27°C temperature or 30 day 40°C temperatures. Arabinan concentrations of treated samples were significantly different when stored for 60 days at 40°C than for those stored at 30 days at 27°C. Mannan concentrations found in the treated samples were found to be the most statistically different for samples stored for 60 days at 27°C, than for samples stored for 30 days at 19°C. Acetyl concentrations of treated samples were found to be statistically different when stored for 90 days at 27°C than for samples stored for 60 days at 19°C. Time as an isolated factor did not affect the percent concentrations of any of the components. These results lead one to conclude that biological activity did occur during this experiment, suggesting that spores and fungus formed over the storage period which may pose health issue for handlers of the raw material. These results indicate how important it is for a biorefinery to pay attention to how storage environments impact their downstream conversion process.

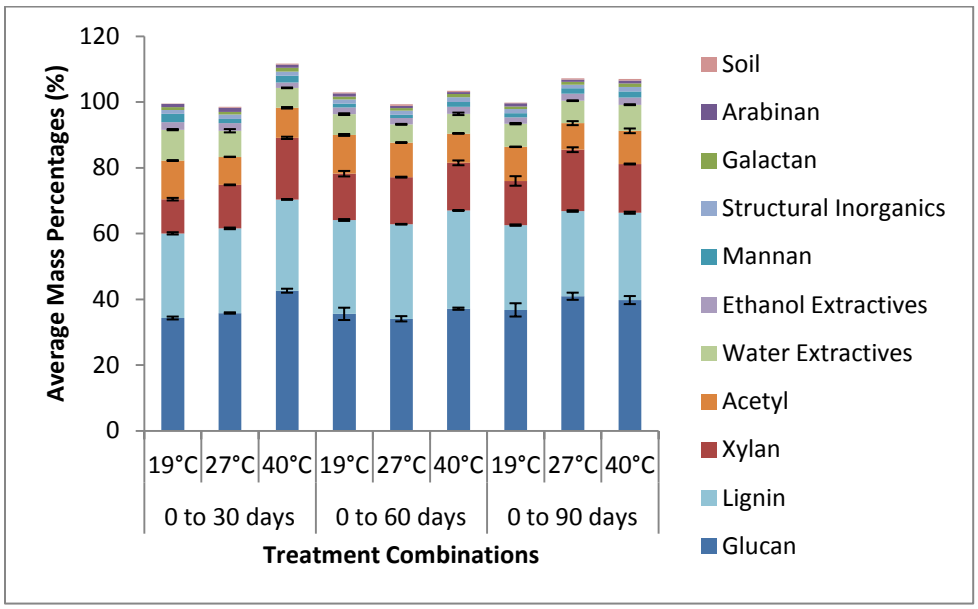

Figure 6: Compositional analysis concentrations as a function of time and storage temperature.

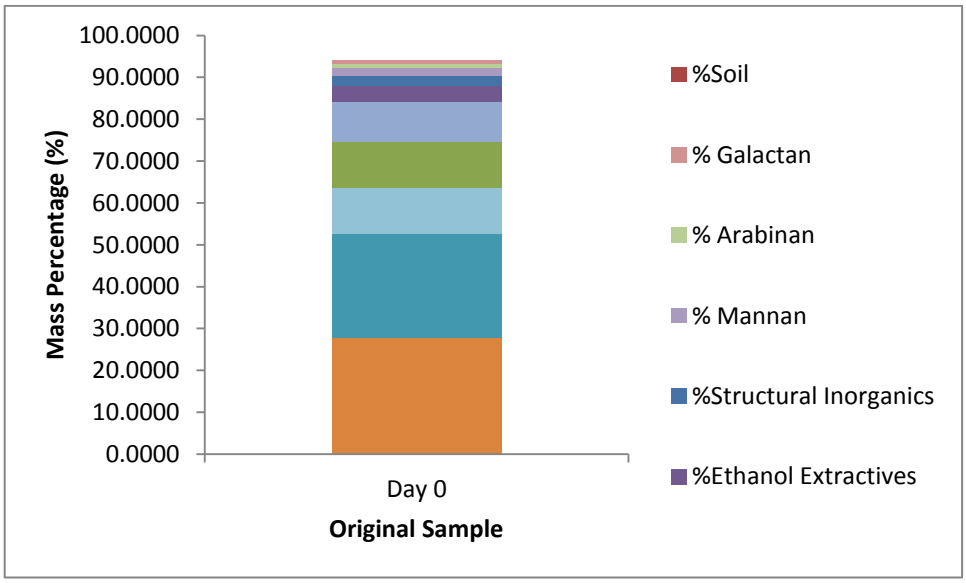

Figure 7: Untreated Willow.

5.3 Respiration Analysis Anova Model:

For analysis of respiration data; temperature and time factors were compared. Figure 8 shows an exponential relationship between respiration rate and time for the three treatment temperatures and as time increases samples placed under any temperature conditions trend towards the same respiration rate.

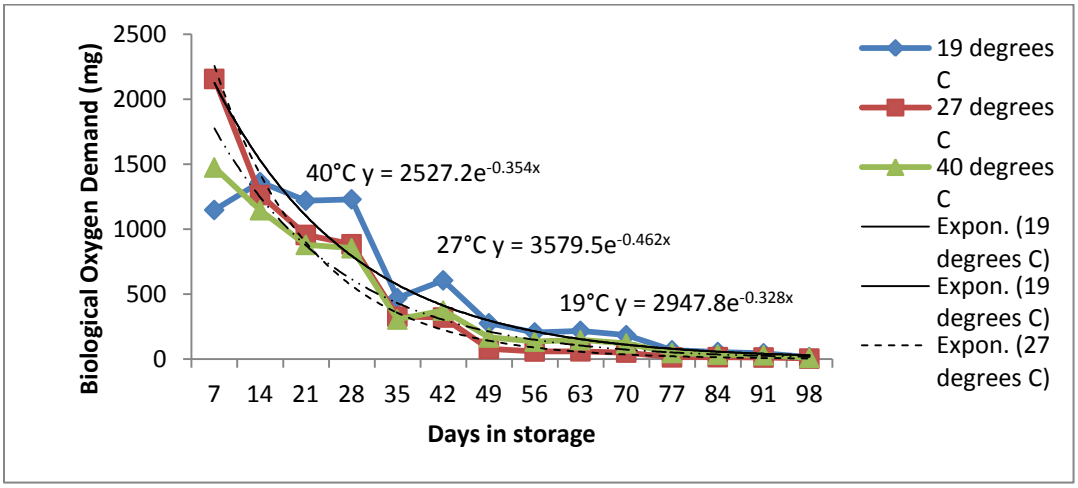

Figure 8: Biological oxygen demand as a function of time and temperature.

These trends show that the amount of biological activity slows dramatically over time resulting in a controlled respiration rate. These data support the idea that biological activity could be affecting the composition of willow material within the first 90 days of storage. It also suggests that the biological activity of willow stored at lower storage temperatures is less than at higher storage temperatures. The measured respiration responses seem to fit the exponential curve lines indicated in Figure 8. Because every moment of the experiment couldn't be controlled, it is expected of the curves to not fit perfectly. The differences could be a result of the OxyTops not having the exact amount of oxygen needed per cycle or other analytical error. Nearly 50% of the biological

activity at each temperature has occurred between days 21-35. About 75% of the biological activity has occurred between days 35 and 49. Roughly 90% of the biological activity has occurred by day 56 for all samples. These results indicate that biorefineries dealing with material stored for 0 to 35 will be subject to nearly 50% biological activity subjecting the material to compositional changes.

Chapter 6

Conclusions and Future Work

These willow biomass storage trials and reported analyses were carried out to provide a quantitative foundation for biomass supply chain model parameters under various storage conditions. From the analysis, it can be concluded that the interaction between time and temperature have no effect on dry mass loss. When the temperature variable was isolated, concentrations were significantly different at or around temperatures close to 19°C. And when the time variable was isolated, significant differences in rates of dry mass loss were observed from at 0 to 60 days.

The interaction of time and temperature significantly impact the xylan, arabinan, mannan, and acetyl concentrations. Using a tukey's comparison evaluation, samples treated for 30 days in 19°C temperature had statistically different xylan concentration than those samples stored at either 90 day 27°C temperature or 30 day 40°C temperatures. Arabinan concentrations of treated samples were significantly different when stored for 60 days at 40°C than for those stored at 30 days at 27°C. Mannan concentrations found in the treated samples were found to be the most statistically different for samples stored for 60 days at 27°C, than for samples stored for 30 days at 19°C. Acetyl concentrations of treated samples were found to be statistically different when stored for 90 days at 27°C than for samples stored for 60 days at 19°C.

For respiration rates, interactions between temperature and time were statistically significant. Willow chips stored at lower temperatures respired at a lower rate than willow chips stored at higher temperatures. These results lead one to conclude that

biological activity did occur during this experiment, suggesting that spores and fungus formed over the storage period which may pose health issue for handlers of the raw material.

Short term 19°C storage appears to have the fewest negative effects on willow biomass for downstream bioconversion processes. Storage facilities that maintain this storage condition will maximize the retention of mass within the material and will keep it as close as possible to its original form while it is in the storage phase of the supply chain. Further research should focus on understanding other elements that impact storage losses not only for willow but for other dedicated energy crops because these feedstocks may be stored for different durations and under conditions. Moisture content is another effect that should be analyzed and not controlled as in this experiment. Application of this experiment to other potential feedstocks such as switchgrass and miscanthus should also be carried out to determine how the material will perform throughout the storage period. Pretreating materials with processes such as torrefaction may also be an avenue for future research to learn about the performance of pretreated energy crops while in storage. Also, as larger amounts of material are to be handled, underlying health issues associated with spore and fungi growth during storage should be investigated for each feedstock material and storage condition.

References

Energy Information Administration. "Assumptions to the Annual Energy Outlook 2006- with Projections to 2030." 2006.

Bassam N. *Handbook of Bionenergy Crops*. London/Washington,DC: Earthscan, 2010.

Boyd J., Christersson L., and Dinkelbach L. *Energy From Willow*. Edinburgh EH9 3JG, UK: The Scottish Agricultural College (SAC) West Mains Road, December 2000.

Camargo G., Ryan M., and Richard T. "Energy Use and Greenhouse Gas Emissions from Crop Produciton Using the Farm Energy Analysis Tool." *BioScience* (April 2013): Vol. 63 No.4 Pages 263-273.

Carolan J., Joshi S., and Dale B. "Techincal and Financial Feasibility Analysis of Distributed Bioprocessing Using Regional Biomass Pre-processing Centers." *Journal of Agricultural and Food Industrial Organization Volume 5* (2007): Article 10.

Casal M. D., Gil M. V., Pevida C., Rubiera F., and Pis J.J. "Influence of storage time on the quality and combustion behavior of pine woodchips." *Energy 35* (2010): 3066-3071. document.

Energy Information Administration. *Energy in Brief*. 13 July 2013. 30 September 2012. <http://www.eia.gov/energy_in_brief/foreign_oil_dependence.cfm>.

Gomez J., and Ladislao B. "Second-generation biofuels and local bioenergy systems." *Biofuels Bioproducts and Biorefining* (2008): 2:455-469.

Group, Feedstock Logistics Interagency Working. "Biofuel Feedstock Logistics: Recommendations for research and commercialization." Interagency Report. 2010.

Hames B., Ruiz R., Scarlata C., Sluiter A., Sluiter J., and Templeton D. *Preparation of Samples for Compositional Analysis*. Technical. Golden, Colorado: National Renewable Energy Laboratory, 2008. document.

Hess J., Wright C., and Kenney K. "Cellulosic biomass feedstocks and logistics for ethanol production." *Biofuels, Bioproducts and Biorefining 1* (2007): 181-190.

Hill J., Nelson E., Tilman D., Polasky S., Tiffany D. "Environmental, economic, and energetic costs and benefits of biodiesel and ethanol biofuels." *PNAS Vol. 103 No.30* (2006): 11206-11210.

Hubbard, W., Biles, L., Mayfield c., and Ashton S. (Eds). *Sustainable Forestry for Bioenergy and Bio-based Products: Trainers Curriculum Notebook.* Athens, GA: Southern Forest Research Partnership Inc, 2007.

IATA, McGill University and. "2nd generation biomass conversion efficiency." Efficiency Study. 2010. document.

Jessup R. "Devopment and status of dedicated energy crops in the United States." *In Vitro Cell.Dev.Biol-plant (45)* (2009): 282-290.

Karp A., and Shield I. *Bioenergy from plants and the sustainable yield challenge*. Research. Hertfordshire, UK: Tansley reviews, 2008.

Keoleian G., A., and Volk T., A. "Renewable Energy from Willow Biomass Crops: Life Cycle Energy, Environmental and Economic Performance." *Critical Reviews in Plant Sciences Vol. 24* (2007): 385-406.

Kofman P. "Harvesting short rotation coppice willow." *Harvesting/ Transport No. 29* (2012): 1-4.

Lee D., Owens V.N., Boe A., Jeranyama P. *Composition of Herbaceous Biomass Feedstocks*. South Dakota: North Central Sun Graant Center, South Dakota State University, 2007. Document.

Lui C., and Sun R. "Cellulose." Sun R. *Cereal Straw as a Resource for Sustainable Biomaterials and Biofuels*. Guanghou: Elsevier, 2010. 131-167. Book chapter.

Mooney D., Larson J., English B., and Tyler D. "Effects of dry matter loss on profitablility of outdoor storage of switchgrass." *Biomass and Bioenergy 44* (2010): 33-42.

Rahman M. A., Santis D.D., Spagnoli G., Ramorino., Penco M., Phuong V.T., and Lazzeri A. "Biocomposites Based on Lignin and Plasticized Poly(L-lactic acid)." *Applied Polymer Science* (2012): 202-214. document.

Ravula P., Grisso, R., and Cundiff J. "Comparison between two policy strategies for scheduling trucks in a biomass logistic system." *Bioresource Technology* (2008): 5710-5721.

Rentizelas A. A., Tolis A. J., and Tatsiopoulos I. P. "Logistics issues of biomass: The storage problem and the multi-biomass supply chain." *Renewable and Sustainable Energy Reviews 13 2009* (2009): 887-894. document.

Richard T., Brownwell D., Ruamsook K., Lui J., and Thomchick E. "Biomass Harvest and Logistics." Kole C., Josh C., and Shonnard D. *Handbook of BIOENERGY CROP PLANTS*. CRC Press, 2012. 119-132.

Sadaka S.S., Richard T.L., Loecke T.D., and Liebman M. "Determination of Compost Respiration Rates Using Pressure Sensors Vol 14 No.2." *Compost Science & Utilization* (2006): 124-131.

Sartori F., Lal R., Ebinger M.H., and Parrish D.J. "Potential Soil Carbon Sequrstration and CO2 Offset by Dedicated Energy Crops in the USA." *Critical Reviews in Plant Sciences, 25:5* 2006: 441-472.

Shastri Y. N., Hanseen A. C., Rodriguez L.F., and Ting K.C. "Optimization of Miscanthus harvesting and handling as an energy crop ." *BioFeed model application. Biological Engineering 3* (2011): 37-69.

Sims R. E. H., & Venturi P. "All-year-round harvesting of short rotation coppice eucalyptus compared with the deliverd costs of biomass from more conventional short season, harvesting systems." *Biomass and Bioenergy 26 (2004)* (2004): 27-37.

Singh K., Zondlo J., Wang J., Sivanandan L., and Brar J. "Influence of Environmental Decomposition of Loggin Residues on Fuel Properties." Paper No. 1110572. 2011. Document.

Sluiter A., Hames B., Ruiz B., Scarlata C., Sluiter J.,Templeton D., and Crocker D. *Determination of Structural Carbohydrates and Lignin in Biomass*. Technical. Goldden, Colorado: National Renewable Energy Laboratory, 2011.

Sluiter A., Ruiz R., Scarlata C., Sluiter J., and Templeton D. *Determination of Extractives in Biomass*. Technical. Golden, Colorado: National Renewable Energy Laboratory, 2008.

U.S. Environmental Protection Agency. "Renewable Fuel Standard Program (RFS2) Regulatory Impact Analysis." 2010.

U.S. Senate and House of Representatives of the United States of America in Congress. *Energy Independance and Security Act of 2007*. Washington D.C.: U.S. Government, 2007.

Uslu A., Faaij A., and Bergman P. "Pre-treatment technologies, and their effect on international bioenergy supply chain logistics, Techo-economic evaluation of torrefaction, fast pyrolysis and pellitisation." *Energy 33* (2008): 1206-1223.

Volk T., Abrahamson L., Nowak C., Smart L., Tharakan P., and White E. "The development of short-rotation willow in the northeastern United States for bioenergy and bioproducts, agroforestry and phytoremediation." *Bioenergy and Bioenergy 30* (2006): 715-727.

Youngs H., and Somerville C. "Development of feedstocks for cellulosic biofuels." *F1000 Reports Biology* (2012).

Appendix

Sugar and acetyl concentrations

time	temperature	% Glucan	% Xylan	% Galactan	% Arabinan	% Mannan	% Acetyl
Day 0		27.9071	9.6035	0.8990	0.9165	2.0490	11.1574
0 to 60 days	19	36.6426	15.1999	0.8685	1.0005	1.2488	11.6999
	27	33.5454	14.6243	0.5919	0.6681	0.9306	10.4800
	40	38.2432	15.2724	0.9220	0.5762	1.5256	8.9288
	19	35.9212	14.2032	0.8976	0.9885	1.1552	12.0695
	27	34.7391	14.4028	0.8128	0.8527	0.9985	10.3720
	40	35.0227	13.3211	1.0036	0.5761	1.4810	8.2779
	19	34.0600	12.8521	0.7440	1.0124	1.2134	11.5683
	27	33.8597	13.9462	0.7457	0.7560	1.1496	10.7118
	40	38.0694	14.8721	0.9280	0.4687	1.5496	9.6377
0 to 90 days	19	30.2554	10.5392	0.6312	0.7922	1.0723	11.2730
	27	43.5366	18.3223	0.9066	0.8205	1.6736	7.8528
	40	39.8739	17.2695	1.1911	0.9892	2.2316	10.3668
	19	40.1158	14.7508	0.8641	1.1759	1.3622	10.3523
	27	38.8220	18.5051	0.7381	0.6650	1.5135	8.0589
	40	40.6575	13.1207	0.9634	0.7537	1.4903	10.0015
	19	39.8724	14.9754	0.8664	1.1396	1.5385	9.5463
	27	40.3412	19.1305	0.8511	0.7377	1.7472	8.3150
	40	38.6675	14.0561	0.9875	0.9187	1.6753	9.9042
0 to 30 days	19	36.8482	15.4125	0.9769	0.9521	3.0784	11.5531
	27	35.2114	12.7236	0.7681	1.1291	1.2871	7.7124
	40	38.9590	18.3959	0.9632	0.9547	1.6836	6.6580
	19	27.3657	8.0832	0.8653	1.3655	1.6956	11.9969
	27	32.8749	11.3411	0.8377	1.1439	1.1994	7.2293
	40	42.5046	19.2060	1.2017	0.9862	2.2992	10.4657
	19	38.6308	7.6868	0.9012	0.7253	2.5626	11.6953
	27	39.3229	15.6516	0.9435	1.3242	1.3298	10.5949
	40	46.2925	18.5971	1.2405	0.9626	2.1071	10.2915

Non-sugar or acetyl concentrations							
time	temperature	%Structural Inorganics	%Soil	%Water Extractable Others	%Ethanol Extractives	% Lignin	Total %
Day 0		2.2392	-0.0694	10.7670	3.9159	24.7041	94.0893
0 to 60 days	19	0.9526	0.5806	6.1818	2.0538	27.3503	103.7792
	27	1.0839	0.3457	6.7724	2.0703	28.1731	99.2857
	40	1.4220	0.2346	6.3097	1.9461	29.5162	104.8967
	19	1.4250	0.2303	5.8640	2.0761	28.9581	103.7887
	27	1.4653	0.4619	3.8826	1.7007	29.5689	99.2574
	40	1.5224	0.6327	5.8243	2.3506	30.2864	100.2988
	19	1.4525	0.1205	6.9285	2.0577	29.3203	101.3297
	27	1.2217	0.5607	5.9449	2.0658	28.4871	99.4492
	40	1.3780	0.4168	5.7274	2.1934	29.8033	95.0919
0 to 90 days	19	1.2210	0.0669	6.2949	1.9798	26.7181	90.8440
	27	1.1828	0.4024	6.5380	2.1326	26.2598	109.6279
	40	1.4095	0.3000	7.5931	2.2414	26.1573	83.4663
	19	1.1505	0.1833	7.8640	1.8468	25.5883	105.2538
	27	0.9962	0.4710	6.6269	2.0389	25.6116	104.0474
	40	1.4334	0.6858	7.0455	2.1363	26.8985	78.2880
	19	1.1465	0.1218	6.9378	2.0089	25.0499	103.2035
	27	1.1367	0.3292	7.3246	2.2649	25.8537	108.0318
	40	1.3636	0.4293	9.1988	2.3763	26.6288	79.5774
0 to 30 days	19	1.1417	0.0298	9.0095	2.3568	25.6476	107.0066
	27	1.2998	0.3656	8.3276	2.5120	25.2732	96.6097
	40	1.2556	0.4479	6.2963	1.8246	26.7136	104.1523
	19	1.2730	0.1092	10.1085	2.4377	26.4225	91.7230
	27	1.2942	0.4547	7.8036	2.2883	25.3687	91.8358
	40	1.2555	0.3089	5.5834	1.6588	28.5641	114.0341
	19	1.0858	0.0010	9.0744	2.2849	25.1503	99.7964
	27	1.2662	0.2708	7.6737	2.3914	26.5525	107.3215
	40	1.2424	0.2449	6.3077	1.5889	27.9679	116.8430

Dry mass before and after storage								
time	temperature	jar weight	total jar + willow before storage	willow before storage	willow dry matter before storage	total jar + willow after storage	willow after storage	willow after storage
days	degrees	(g)	(g) wet matter	(g) wet matter	(g) dry matter	(g) wet matter	(g) wet matter	(g) dry matter
0 to 60 days	19	257.11	375.63	118.52	61.84	348.33	91.22	44.73
	27	254.52	372.53	118.01	61.58	332.86	78.34	48.37
	40	256.86	375.36	118.50	61.83	320.74	63.88	51.35
	19	248.04	366.60	118.56	61.86	343.38	95.34	49.04
	27	256.62	374.52	117.90	61.52	335.45	78.83	55.51
	40	246.66	364.99	118.33	61.74	312.63	65.97	52.76
	19	244.81	363.09	118.28	61.72	339.19	94.38	48.60
	27	257.50	375.88	118.38	61.77	336.60	79.10	54.25
	40	254.99	373.39	118.40	61.78	319.16	64.17	51.81
0 to 90 days	19	257.17	375.63	118.46	61.81	317.65	60.48	57.86
	27	256.63	375.11	118.48	61.82	318.17	61.54	59.27
	40	256.84	374.99	118.15	61.65	316.69	59.85	57.46
	19	246.67	365.32	118.65	61.91	309.83	63.16	60.68
	27	244.44	362.84	118.40	61.78	306.75	62.31	59.54
	40	254.47	372.66	118.19	61.67	314.35	59.88	57.53
	19	255.10	373.38	118.28	61.72	314.67	59.57	57.09
	27	244.87	363.69	118.82	62.00	304.27	59.40	57.16
	40	256.59	374.93	118.34	61.75	317.59	61.00	58.55

5 day average for each oxy-top

Oxy-top 1	Oxy-top 2	Oxy-top 3	Oxy-top 4	Oxy-top 5	Oxy-top 6	Oxy-top 7	Oxy-top 8	Oxy-top 9
1136.861	864.2338	1442.052	2117.807	2906.922	1673.438	1109.466	1447.919	2566.589
1225.152	998.1801	1864.618	575.4842	1347.697	104.3083	516.5457	700.992	2577.02
1030.183	893.8006	1734.163	10.32244	1122.214	0	445.4368	439.9823	1898.479
1128.684	1057.266	1503.416	0	1148.685	0	930.3886	860.1706	1422.157
492.7784	401.8837	514.1745	0	469.0357	0	294.8648	350.0468	388.6022
697.2105	519.2105	603.2355	0	359.0161	0	283.5094	267.3596	79.94598
327.7105	267.1659	234.874	0	3.073961	0	116.5704	82.75706	18.50609
210.9161	230.1332	177.1992	0	1.357341	0	100.2404	69.53684	19.67978
213.3657	258.8385	182.7839	0	0	0	158.0584	7.630471	0
188.9947	212.3039	153.2501	0	0	0	56.95873	0	0
60.27784	101.9529	43.10166	0	0	0	195.9058	44.88504	27.23109
59.36898	58.69169	47.68255	0	0	0	59.93573	4.994183	3.668975
46.48643	50.9072	39.20083	0	0	0	14.7	0.325762	3.064266
16.02548	17.09501	14.2928	0	0	0	1.505263	0.18144	0.245429
original	1 hour	overnight	original	1 hour	overnight	original	1 hour	overnight
18			40			28		