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Pretreatment optimization methods for increased sugar yields from biomass pyrolysis

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Pretreatment optimization methods for increased sugar yields from biomass pyrolysis

by

Kayla E. Johnson

A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Major: Mechanical Engineering

Program of Study Committee:
Robert C. Brown, Major Professor
Mark Mba Wright
Ted Heindel

Iowa State University

Ames, Iowa

2017

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DEDICATION

To my parents, for all of their love and support.

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ABSTRACT

In the search for a renewable energy source that could replace petroleum and other nonrenewable energy sources, pyrolysis of biomass is a hopeful alternative and pretreatment could further improve its potential. There are several possible routes for pretreating lignocellulosic biomass, but many need further refining before becoming economical. The main obstacle for the conversion of biomass to high quality products is the presence of alkali and alkaline earth metals (AAEMs) that are known to impair cellulose decomposition to levoglucosan and promote char, water, and light oxygenate formation. One pretreatment option is to remove the AAEMs from the biomass by washing. Another efficient process of converting biomass into high quality bio-oil is a dilute acid pretreatment that passivates AAEMs in biomass, leading to decreased cellulose monomer fragmentation and thus increasing sugar yields. In this study the effectiveness of a washing method--involving a recycled carboxylic acid rich, aqueous fraction of bio-oil--is looked at for red oak. This study also presents an optimization of three important variables in the dilute acid pretreatment process of the agricultural byproduct, cornstover, to increase the value of the bio-oil produced.

In the preliminary study, red oak was washed with an aqueous fraction of bio-oil to remove the AAEMs. While effective at removing AAEMs, the levoglucosan yield did not improve, unless a water rinse was incorporated--increasing levoglucosan yields from 3.3 to 13.3 wt%. Passivating the remaining AAEMs in the washed samples with sulfuric acid was less effective but increased levoglucosan yields from 3.3 wt% to 9.8 wt%. These processes were compared to samples that were only passivated with sulfuric acid, which led to levoglucosan yields of 20.8 wt%.

In the pretreatment optimization study for cornstover, the variables considered were the particle size upon acid infusion, the biomass to water ratio, and the diffusion time. Pretreatment of 400 g batches of cornstover was carried out in a paddle mixer equipped with a pump and sprayer. From these batches 250 μg samples were pyrolyzed to examine their effect on product yields, mainly levoglucosan. Levoglucosan yields increased more than 2,000%, reaching yields as high as 17 wt% on a dry biomass basis. With process optimization the amount of water necessary for acid passivation can be reduced significantly. Reducing the amount of water in the pretreatment process led to increased levoglucosan yields; a 2:1 biomass to water ratio was found to be more effective than a 1:1 ratio at increasing yields. The particle size also played an important role. 3.17 mm particles resulted in the highest levoglucosan yields. Diffusion time was not an important factor in the acid infusion process. Overall, optimal levoglucosan yields were achieved with 3.17 mm cornstover particles, a 2:1 biomass to water ratio, over any length of diffusion time.

CHAPTER I

INTRODUCTION

An Alternative to Fossil Fuels: Renewable Energy

In the 1950s, petroleum became the world's leading source of energy due in a large amount to the proliferation of the automobile [1]. Today in the United States transportation sector, 92% of fuel comes from petroleum [1]. The burning of fossil fuels has serious negative environmental consequences and accounts for two-thirds of global carbon dioxide emissions [2]. Despite these environmental impacts, petroleum remains a major energy source across various energy sectors due to its accessibility and efficiency, but leaves the United States heavily reliant on foreign countries' oil reserves.

The oil crisis in the 1970s sparked interest in the further development of renewable energy sources such as solar, wind, geothermal, and biomass, but the effort soon slowed down when oil prices decreased. In recent years the desire to lower greenhouse gas emissions, decrease dependence on foreign oil, and mitigate the other effects of fossil fuels has again caused a resurgence in the effort in finding a renewable fuel source capable of competing with petroleum and other non-renewable energy sources. Every day the U.S. and other countries are depleting the earth's resources, which take thousands of years to replenish. Thus, the need for sources which can be replenished within decades is becoming increasingly inevitable.

In the past few decades alone society and research have tried to move towards a more sustainable economy. Wind turbines are scattered across the vast lands in the Midwest and offshore, incentives are offered for installing solar panels, household objects are made from recycled plastics, and ethanol fuel is made using corn. While there are methods of producing

sustainable energy capable of providing electricity, an efficient, sustainable process for making liquid transportation fuel is lacking. Thus, in recent years the conversion of biomass to fuels and other products has been investigated due to its many advantages over fossil fuels. Bio-oil derived from biomass fast pyrolysis offers decreased dependence on foreign oil, an offset of carbon dioxide emissions through plant growth, zero SO_x emissions, 50% lower NO_x emissions than diesel in a gas turbine, as well as other advantages [2]. The U.S.'s energy sources are beginning to transform and the thermochemical conversion of lignocellulosic biomass shows promise for helping to meet these renewable energy needs. Lignocellulosic biomass is ideal for conversion to high value bio-oil.

Lignocellulosic biomass

Lignocellulosic biomass has great potential to provide a sustainable liquid transportation fuel. The composition of biomass is very different than fossil fuels. Biomass from hardwoods, softwoods, and herbaceous plants have three major components: cellulose, hemicellulose, and lignin. Together they form the structural material and energy storage of plants known as lignocellulose. The relative weight percentages of these three components vary from one material to another and are shown for a few different feedstocks in Table 1.

Table 1: Composition of various lignocellulosic biomass (adapted from [3])

	Cellulose (wt%)	Hemicellulose (wt%)	Lignin (wt%)
Corn stover	53	15	16
Wheat straw	38	36	16
Bagasse	35	25	20
Waste paper	76	13	11

Cellulose is the major constituent of most biomass and a linear polymer built on chains of glucose as seen in Figure 1. During the pyrolysis of pure cellulose, depolymerization to levoglucosan (1,6-anhydro- β -D-glucopyranose) occurs, with yields as high as 59 wt% [4]. Levoglucosan is a highly desired product in bio-oil, but the presence of alkali and alkaline earth metals (AAEMs) in biomass hinder its formation. The AAEMs are believed to catalyze pyranose ring fragmentation leading to increased yields of char and light oxygenates as opposed to levoglucosan and other anhydrosugars [5-7].

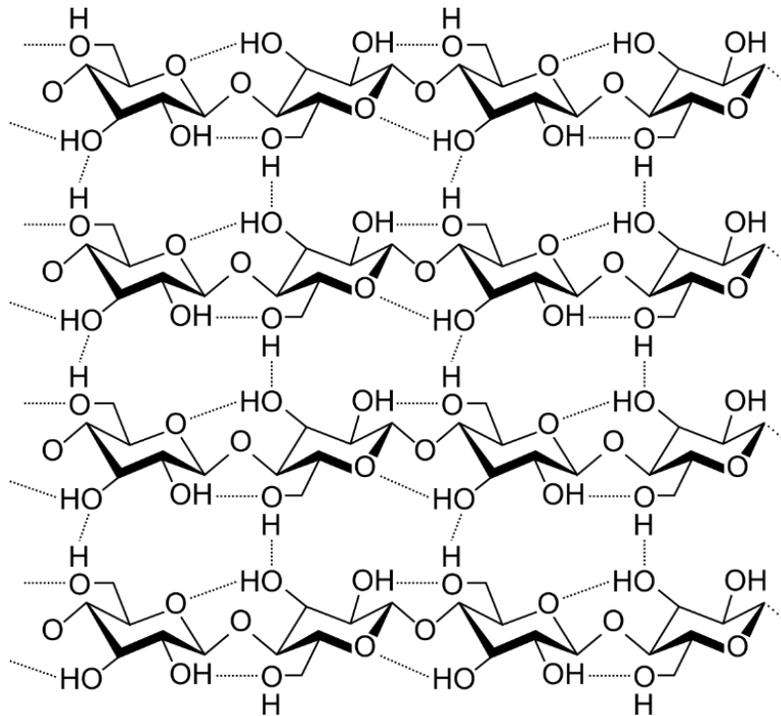


Figure 1: Structure of Cellulose [8]

Hemicellulose also comprises a large portion of biomass. While cellulose is only composed of glucose, hemicellulose is a heteropolysaccharide. Some of its polymerized monosaccharides are glucose, mannose, galactose, xylose, and arabinose. Hemicellulose is more

susceptible to depolymerization than cellulose due to its non-crystalline structure. Most plants have hemicellulosic structures with a xylopyranose backbone. There are a multitude of side chains from the backbone whose linkages vary depending on the plant type. An example of the hemicellulose structure can be seen in Figure 2.

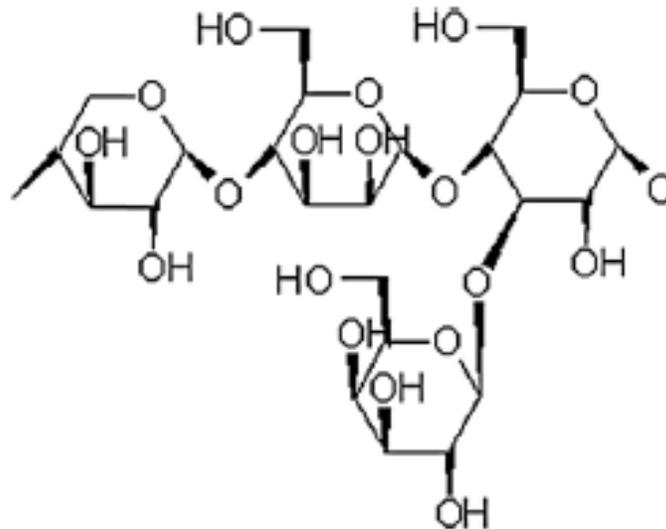


Figure 2: Sample Structure of Hemicellulose [9]

Along with the hemicellulose, lignin surrounds the cellulose in biomass as seen in Figure 3. Lignin, as shown in Figure 4, is an amorphous polymer composed of three monomers: paracoumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. Lignin protects the plant from pests and fungal destruction, but it can also be difficult to extract. Pyrolysis has the advantage of being able to convert the lignin in biomass to more valuable products. Up to 20 wt% of lignin can be converted to phenolic monomers and 40 wt% to char [10]. Phenolic monomers have the potential to be upgraded to fuels and char can be used as a soil amendment.

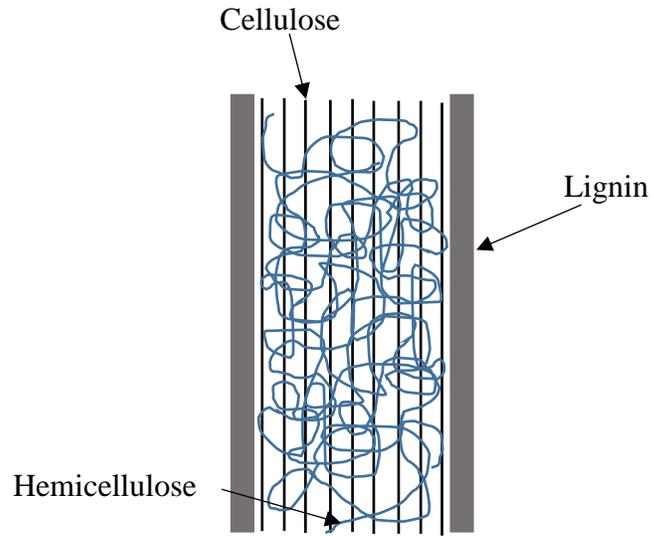


Figure 3: Diagram of Lignocellulose

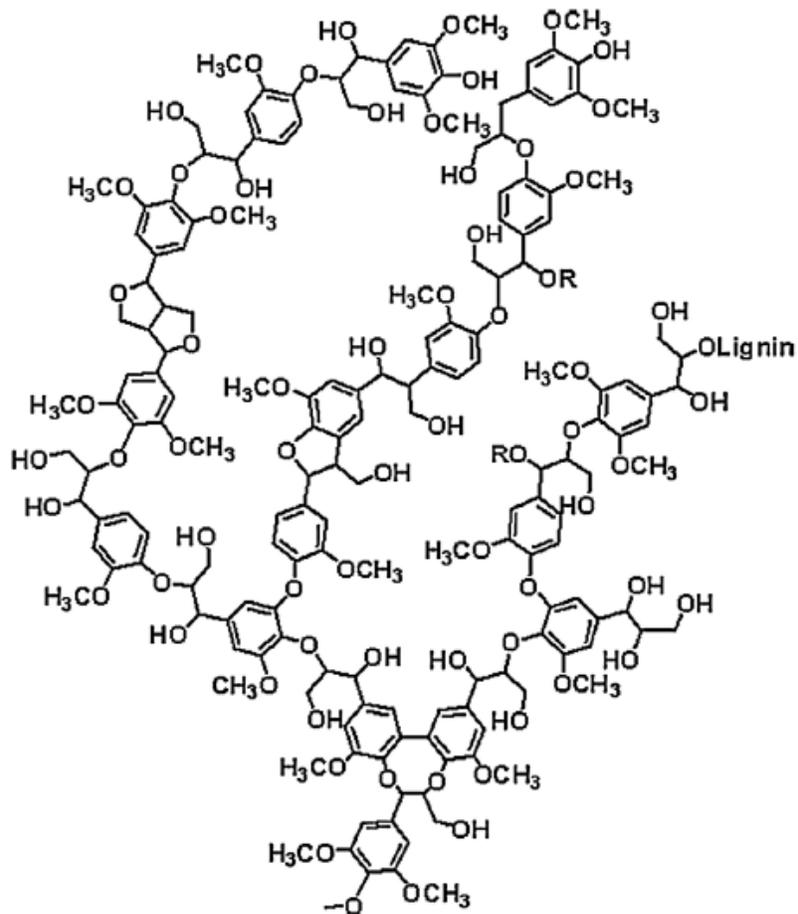


Figure 4: Sample Lignin Structure [9]

Increasing the yields of the more desirable products in bio-oil is essential to the successful conversion of biomass and thus an energy source capable of competing with petroleum. The high concentrations of cellulose in biomass signal its high potential. Although, due to various obstacles, the potential levoglucosan yields from cellulose are not currently being attained. As stated previously the main hindrance is the presence of AAEMs. Several pretreatment processes aiming to decrease their damaging effect seem promising, but require further optimization to increase desirable product yields and decrease energy and chemical inputs. The following review will cover various pretreatment methods previously studied and then present a study comparing different pretreatment options using red oak as a feedstock, along with a study on the optimization of a dilute acid pretreatment for the agricultural residue cornstover.

CHAPTER II

LITERATURE REVIEW

Introduction

The energy needs of the U.S. fall into two main categories: electricity and transportation. Many renewable energy sources such as solar, wind, geothermal, and hydroelectric are available and show promise for current and future electricity production. On the other hand, alternative energy sources for transportation are less prevalent. Biomass is currently the only renewable energy source capable of meeting the United States demands for a liquid transportation fuel [11]. “Waste” materials such as agricultural residues, food processing waste, and manure, are particularly promising sources for conversion to bio-oil for upgrading to transportation fuels or chemicals. These “waste” products are just as propitious as dedicated energy crops because they will always be readily available, cheap, and offer no competition with food sources.

Feasibility of Biomass Conversion

According to the *Billion Ton Study* by the U.S. Department of Energy in 2016, the United States are capable of producing enough biomass feedstock for biofuel, biopower, and bioproducts, to displace at least 30 percent of the 2005 petroleum consumption by 2030, without negatively affecting the production of food or other agricultural products [12]. This would require one billion dry tons of biomass from forestlands (logging and removal residues, thinnings, etc.), agricultural lands (grain and oil crops, perennial grasses, agricultural crop residues, woody crops), and secondary residue and waste resources (pulping liquors, mill residues, animal manure, waste oil and greases) [12]. Thus, with successful conversion to bio-oil

and other products, biomass may be capable of competing with petroleum in the future. The conversion from biomass to products varies depending on the feedstock and what the desired product is: chemicals, transportation fuel, or other products. There are two main routes for conversion: thermochemical and biochemical. Thermochemical conversion is broken down into four main processes: combustion, gasification, solvolysis, and pyrolysis. Combustion involves the rapid oxidation of biomass to yield flue gas for thermal energy, where temperatures can exceed 1650 °C. Gasification uses oxygen starved conditions and temperatures around 750-1500 °C to primarily convert biomass to a flammable gas. Solvolysis involves the thermal decomposition of biomass in a solvent to produce chemical products. Pyrolysis is the thermal decomposition of biomass in the absence of oxygen at temperatures ranging from 300°C to 700 °C, yielding bio-oil, char, and light oxygenates. There are different rates of pyrolysis, with fast pyrolysis being the most attractive due to liquid being the primary product. Fast pyrolysis involves rapid heating of biomass at temperatures between 300°C and 500°C, followed by rapid cooling of products. This review will focus on fast pyrolysis, specifically the methods to increase yields of the products desirable for upgrading to fuels and conversion to products.

Problematic Behavior of Alkali and Alkaline Earth Metals

In the search for the fast pyrolysis conditions optimal for high quality bio-oil, process variables have been studied extensively. While these conditions are significant, the importance of the composition of the feedstock is a parameter that is sometimes overlooked. AAEM content varies from one feedstock to another, but the main elements present in the biomass included in this study are sodium, potassium, calcium, magnesium, and chlorine. It is critical to understand

how these minerals affect the product distribution of cellulose, and thus biomass, in order to obtain high quality products.

The presence of small amounts of AAEMs in biomass can greatly alter the product yields from fast pyrolysis. Many studies have shown that AAEMs lead to decreased levoglucosan yields, as well as increased char, water, and light oxygenate yields [6, 13-16]. Upon studying the effect of demineralizing 13 different types of biomass, Raveendran et al. [17] determined that sodium, potassium, calcium, magnesium, iron, phosphorous, aluminum, and silicon are the major elements found in most biomass. They found that the liquid yields increased and the gas yields decreased for all samples when ash was removed prior to pyrolysis. They developed a correlation, concluding that the pyrolysis product distribution and properties are strongly influenced by the mineral matter in biomass.

Gray et al. [13] found that, in the presence of ash, yields of small aqueous products always increased while bio-oil always decreased. Upon pyrolyzing untreated and deashed wood at 460 °C, they found the deashed wood increased bio-oil yields by 92% and decreased the light aqueous compounds and gaseous yields by 34% and 33% respectively. These high quantities of bio-oil from deashed wood are important, but the quality of the bio-oil is also central to efficient conversion of biomass to fuels.

Pan and Richards [14] demonstrated that adding 0.01% NaCl to pure cellulose reduced levoglucosan yields by as much as half. Pan and Richards went a step further and examined which minerals most strongly affected the yields of carbon dioxide, carbon monoxide, acetic acid, formic acid, and methanol. They removed inorganic salts as well as added potassium and calcium ions by ion exchange and concluded that potassium acted as a catalyst resulting in an increase of the aforementioned products, but calcium did not.

Kuzhiyil et al. [15] found that when doping pure cellulose with potassium acetate (similar to naturally occurring AAEMs in biomass), levoglucosan yields from pyrolysis were as low as 3.5 wt%. This is dramatically lower than the typical expected yield of approximately 60 wt% from pure cellulose. The authors also propose that depending on the nature of the AAEMs in biomass, the AAEMs have varying degrees of catalytic activity during pyrolysis. If AAEMs can be converted to thermally stable salts their catalytic activity may be greatly decreased. In the study, pure cellulose was also doped with various potassium salts and pyrolyzed at 500 °C. The yield of levoglucosan was lower (than that of pure cellulose) with each salt, but to different degrees. Of the 10 salts, potassium acetate lowered levoglucosan yields the most, to only ~3.5 wt%, while potassium bisulfate had the least effect, yielding ~29 wt%. Thus, they deduce that the composition of AAEMs in the biomass can also alter levoglucosan yields.

Kawamoto et al. [16] also observed reduced levoglucosan yields from pyrolyzed samples impregnated with salts. In the presence of lithium chloride, sodium chloride, potassium chloride, magnesium chloride, and calcium chloride there was an increase in primary char, but secondary char formation decreased along with levoglucosan yields. They attribute the lower secondary char yields to the reduced formation of volatile levoglucosan as shown in Figure 5.

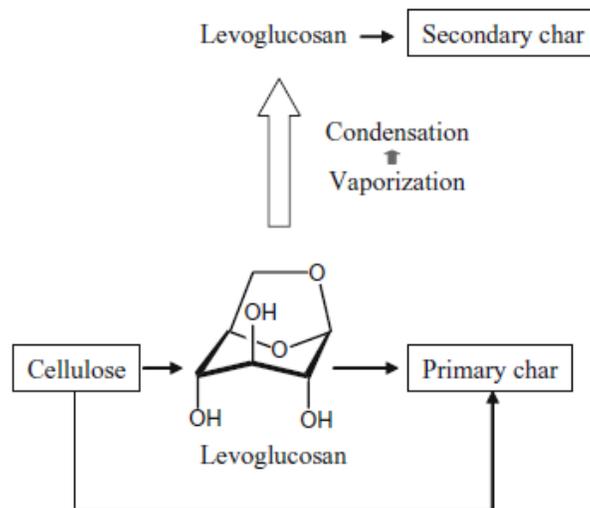


Figure 5: Levoglucosan as a secondary char formation intermediate [16].

Piskorz et al. [5] argues that AAEMs offer the most insight for determining the mode of thermal decomposition of cellulose. They propose two fast pyrolysis reaction pathways: fragmentation, leading to increased yields of char and light oxygenates, and depolymerization, resulting in higher yields of levoglucosan. They also conclude that the anions present influence the reaction, noting that levoglucosan yields were much less for sodium chloride (with the chloride ion) than for sodium sulfate (with the sulfate ion) determined in a study by Golova [18].

Patwardhan et al. [6] postulated a mechanism for cellulose pyrolysis reactions involving these two pathways as seen in Figure 6. The dominate mechanism for pure cellulose leads to the formation of levoglucosan. Pyranose rings join together to form cellulose chains when glycosidic bond cleavage occurs from fast pyrolysis of cellulose. The other pathway for cellulose decomposition is through fragmentation of pyranose rings which produces light oxygenates. It has been hypothesized that levoglucosan yields are significantly lower when AAEMs are present because they catalyze the pyranose ring fragmentation reactions.

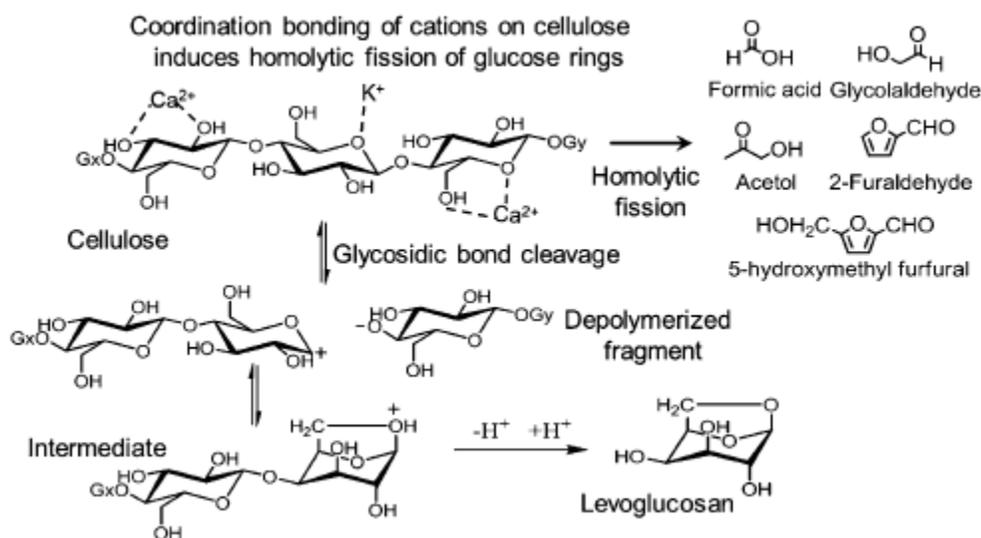


Figure 6: Mechanism for cellulose pyrolysis with AAEM catalyzed ring fragmentation [15].

Patwardhan et al. [6] also studied the degree of catalytic effect of various AAEMs on cellulose pyrolysis. Inorganic salts that can be found in biomass were added to cellulose to determine their influence on the pyrolysis products. From strongest to least influence on levoglucosan yields they found the order to be K^+ , Na^+ , Ca^{2+} , Mg^{2+} . Pyrolysis yields were dramatically altered even for inorganic salt concentrations as low as 0.005 mmol/g of cellulose. Chloride was the anion found to have the most negative effect on levoglucosan yields. They conclude that careful control of the mineral content can alter the composition of the bio-oil produced.

These studies and others depict the importance of the mineral content in biomass. Deciphering how AAEMs alter the mechanism of cellulose conversion to levoglucosan and other products is crucial to determining methods to reduce their effect. Removing the metals or altering how they react within the biomass during pyrolysis can be achieved through careful pretreatment of biomass.

Pretreatment Methods

Various pretreatment methods for decreasing the effect of AAEMs have been studied. Most methods include various forms of washing biomass to remove metals, circumventing their effect. This can include washing with water, mineral or carboxylic acids, or a combination to pull the cations out of the biomass. Others propose eliminating their catalytic effect through passivation. The process of passivation of metals reduces their harmful catalytic effect while not requiring their removal from the biomass. Some methods have looked at adding small amounts mineral or carboxylic acids, with water as the transport mechanism, into biomass or using steam explosion to distribute acid into biomass particles.

Mourant et al. [19] studied different pretreatments methods for mallee wood samples in order to better understand which AAEM species most affected the products and determine which method was most effective. A water wash was carried out at room temperature for 2, 24, or 48 hours, with 10 mL of liquid per gram of biomass. A dilute acid wash, with 0.1 wt% nitric acid was also performed with the same conditions, but only for 2 hours. The samples were then rinsed with water, filtered, and dried. They found that removing the AAEMs had no significant effect on the yields of bio-oil or char, but the bio-oil properties were affected. The sodium, potassium, magnesium, and calcium content was reduced 50 to almost 100% for the water washes, with calcium and magnesium being more recalcitrant. The calcium could not be completely removed with the water wash, but with the acid wash only 4% remained in the biomass. Figure 7 from Mourant et al. [19] shows the effectiveness of each wash at removing the AAEMs. Although the water wash removed most of the water-soluble AAEMs and resulted in a large decrease in the total AAEM content, there was only a very small increase in sugar yields. On the other hand, the acid wash removed the water-insoluble AAEMs leading to almost double the sugar yields of untreated biomass. The trend for levoglucosan yields as a function of AAEM content are in Figure 8. The authors conclude that the removal of water-soluble AAEM species is not as important as the removal of the water-insoluble, acid-soluble AAEMs, thus leading to the belief that the acid-soluble AAEMs are closely linked with the organic matter in the biomass, and hence more involved in the pyrolysis reactions.

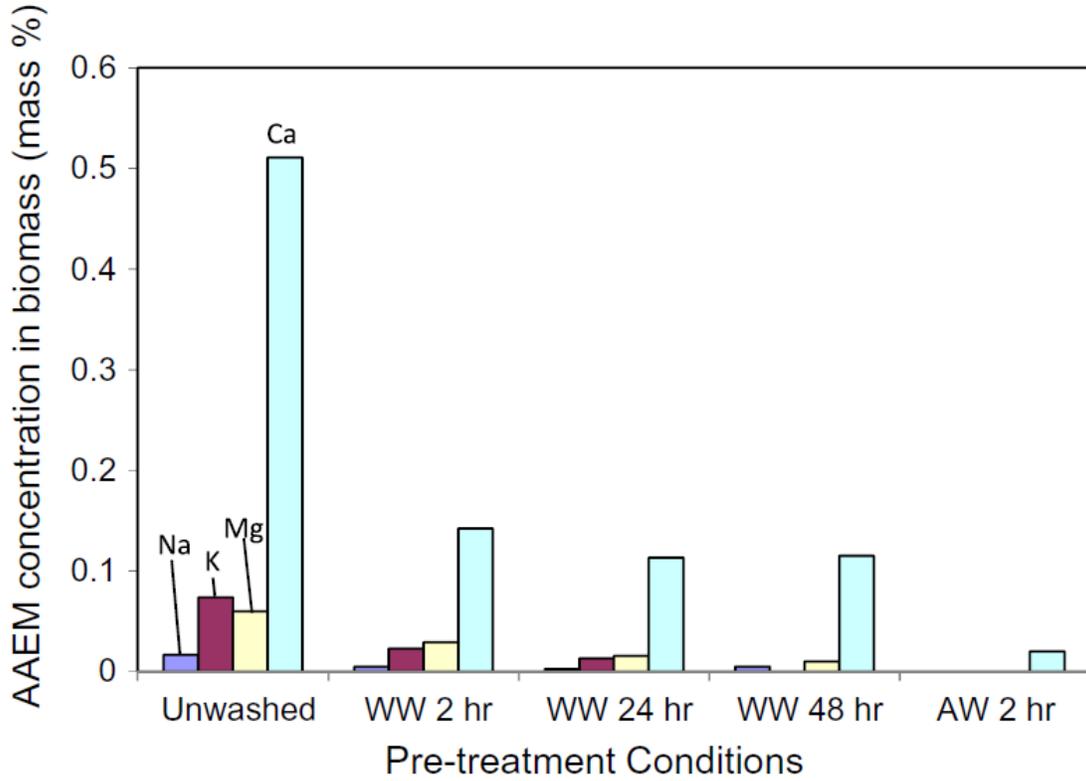


Figure 7: AAEM concentrations remaining in the biomass (WW = Water Washed, AW = Acid Washed) [19].

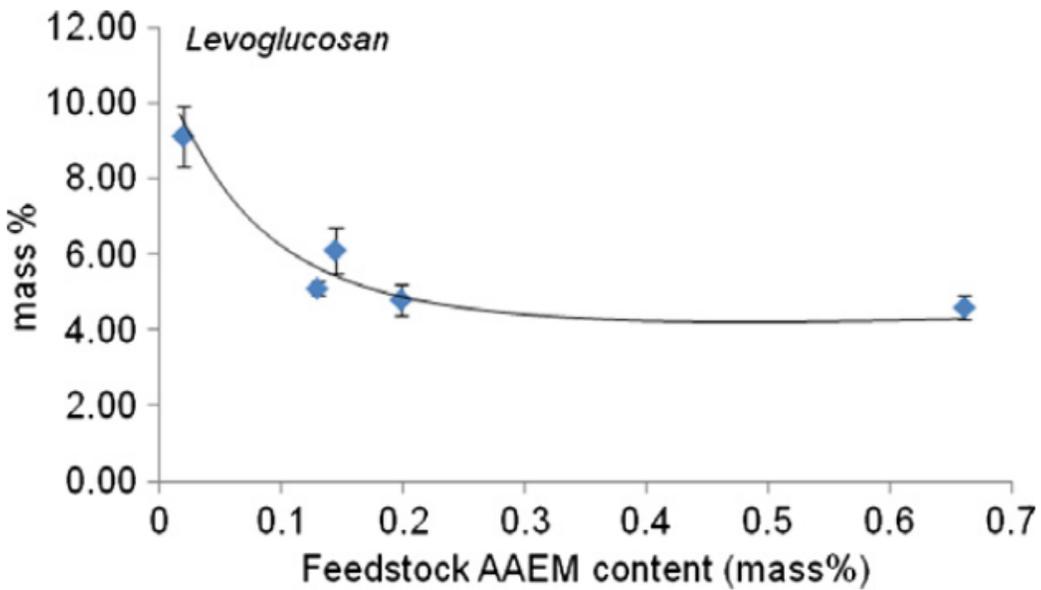


Figure 8: Levoglucosan mass percent of bio-oil as a function AAEM content [19].

Piskorz et al. [5] also incorporated elevated temperatures into the pretreatment of biomass. A mild acid hydrolysis of poplar wood and various cellulose samples was performed at 100 °C for 2 hours. This hydrolysis was followed by a wash with distilled water then drying. As a result of pretreatment, levoglucosan yields increased from 3.04 to 30.42 wt%, the pyrolytic oil yield rose from 65.8 to 79.6 wt%, and the gas, char, and water yields were all reduced. About 90% of the ash was removed from the wood with the acid pretreatment. Overall, the percentage of the cellulose that could potentially be converted to hydrolysable sugars increased from around 20.4% to 83.4%.

In 2003 Dobele et al. [20] studied the effect of phosphoric acid concentration, the sorption capacity of feedstocks, as well as drying temperature on levoglucosan and levoglucosenone yields. The pretreatment process involved heating samples for 1 hour at 100 °C in water or an aqueous solution of phosphoric acid (0.05-3.0%). This was done at a sample to solution weight ratio of 1:100, followed by filtering and drying of the samples. They observed that cellulose impregnated with 0.05% phosphoric acid increased the levoglucosan yield by 300% to that of untreated cellulose. For wood impregnated at this same concentration, levoglucosan yield increases were much smaller but grew from 3.6-3.8% to 14-15% when impregnated with the 0.5 and 1% acid solutions. After varying the concentration of the impregnation solution for cellulose, newsprint paper, recycled kraft pulp, and birch wood they concluded that different feedstocks will require different impregnation parameters based on their porosity and hydrophilicity thus the solution concentration should be determined by the sorption capacity of the feedstock. The highest levoglucosan yield from wood (0.5% phosphoric acid solution) was 15%, which was approximately 30% of the potential levoglucosan yield from the cellulose contained in the biomass, based on the experimental yield from cellulose pyrolysis.

While levoglucosan yields increased with acid concentrations as low as 0.5%, the sample to solution weight ratio was 1:100, thus requiring filtering and large amounts of water in the pretreatment process.

In an attempt to reduce water and acid consumption in the pretreatment process Oudenhoven et al. [21] developed a pretreatment method involving an organic acid wash, with the acids produced from the same pyrolysis process. The produced wash was mainly composed of acetic acid, acetol, propionic acid, and guaiacol, as well as 60.5 wt% water. Pinewood was loaded into a mixing apparatus filled with the solution, with a 10:1 solution to biomass ratio, and washed at 90 °C for 2 hours. AAEMs were effectively removed prior to pyrolysis, but several water rinses were required after washing. Upon washing the biomass with a synthetic condenser liquid, composed of acetic acid, ethanol, acetone, propionic acid, guaiacol, and 79.5 wt% water, 92-96 wt% of the ash was removed when a water rinse was incorporated. This resulted in a 10 percentage point increase in bio-oil yield, slightly decreased char yields, and a levoglucosan yield of 17.6 wt% (3.4 wt% untreated). It was concluded that washing the biomass with a recycled acetic aqueous solution removed most AAEMs and increased bio-oil and levoglucosan yields, but was most effective when a water rinse followed the washing process.

Kuzhiyil et al. [15] also proposes that reducing the catalytic activity of the AAEMs may not only be a factor of removing them from the biomass, and the acid pretreatment is not necessarily determined by the sorption capacity of the feedstock. They hypothesize that passivation can be achieved by converting the cations into thermally stable salts, thus reducing ring fragmentation and allowing cellulose to depolymerize to levoglucosan. Biomass was infused with various acids at five different loadings. The low water to biomass ratio, 3:1, resulted in damp biomass that needed to be dried, but not filtered. Based on the pyrolysis of

these samples a correlation was developed relating the potassium, sodium, calcium, magnesium, and chlorine present in the biomass, to the optimal amount of mineral acid necessary to convert the metals into thermally stable salts. The AAEM valency is calculated as: $K + Na + 2Ca + 2Mg - Cl$. They demonstrated that an infusion of a small amount of mineral acid into biomass greatly increased the levoglucosan yields from micropyrolysis of various feedstocks. The optimal amount of acid ranged from 0.4 to 4.1 wt% (dry feedstock) depending on the composition of the biomass and the acid incorporated. Figure 9 displays the experimental impact of varying the amount of acid infused into cornstover on the levoglucosan yields.

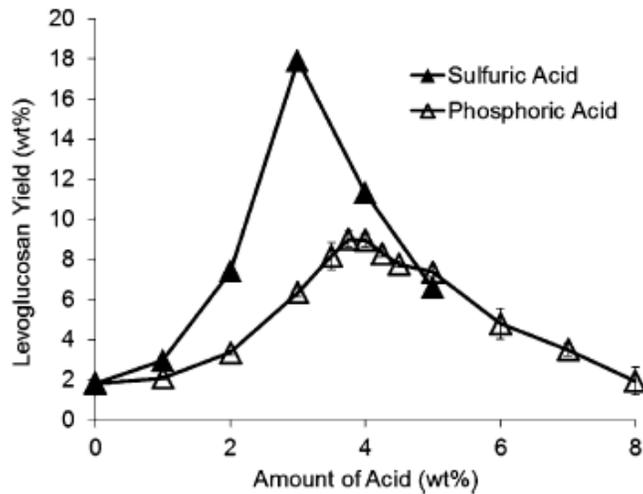


Figure 9: Levoglucosan yields from pyrolysis of acid infused cornstover [15].

The study by Kuzhiyil et al. [15] also found that the effectiveness of the infused mineral acids in decreasing order was: sulfuric acid, phosphoric acid, hydrochloric acid, nitric acid. For switchgrass, cornstover, red oak, and loblolly pine, 83.4 to 99.7% of the potential levoglucosan was obtained following pyrolysis of sulfuric acid infused biomass. It was concluded that the passivation contributed to 80% of the enhanced levoglucosan yield and a buffering of pH levels favoring glycosidic bond breakage accounted for the remaining 20% of yield increase.

Recently, Dalluge et al. [22] has also demonstrated acid passivation of the AAEMs in biomass, using the correlation determined by Kuzhiyil et al. [15], on a kilogram scale using a continuous flow reactor. Enhanced production of sugars was achieved by passivating red oak and switchgrass with 0.4 and 2.0 wt% sulfuric acid, respectively. The biomass to water ratios were 1:1 for red oak and 1:2 for switchgrass. The acid solution was mixed thoroughly into the biomass by hand and then dried in an oven. Pyrolysis sugars from red oak were increased from 7.8 wt% to 15.9 wt%, and from 4.5 wt% to 16.2 wt% for switchgrass as a result of the pretreatment process. Light oxygenates and non-condensable gases were decreased, but char yields increased by 65% and 30% for red oak and switchgrass respectively. Such small amounts of acid, resulting in dramatic increases in levoglucosan yields, make dilute acid infusion a promising pretreatment method. With optimization, the inputs, such as the water to biomass ratios, drying time, and energy expended on particle size reduction, may be decreased to render the process even more efficient. The following study compares various washing and acid infusion methods for red oak and another study presents an optimization of multiple variables for the passivation of cornstover, a promising feedstock in itself as an agricultural residue.

CHAPTER III

MATERIALS & METHODS

Recycled Bio-oil Fraction Wash

Feedstock

This study used red oak with a particle size around 3.17 mm when received. A Retsch® knife mill was used to reduce the feedstock to under 250µm. After pretreatment, further size reduction was performed in a Retsch® ball mill to obtain a fine powder and help ensure homogeneous feedstock on the microgram scale. The feedstock moisture content before and after pretreatment was around 8 wt%.

Pretreatment solutions

Aqueous, carboxylic acid wash

The washing solution consisted of the last two stage fractions (5 and 6) of bio-oil produced from a fast pyrolysis process. The fractions consist of formic, acetic, and propionic acids, between 9 and 12 wt% total acid content. The percent of each fraction in the prepared washing solution was proportional to the quantity of each produced from the initial pyrolysis process. 27.7 wt% of the whole bio-oil was stage fraction 5 (SF5) and 2.5 wt% was stage fraction 6 (SF6). Thus, 91.7 wt% of the washing solution was SF5 and the remaining portion was SF6.

Initially, approximately 15 g of untreated red oak was treated with the carboxylic acid rich solution in a 1:1 ratio. The biomass was placed on a filter in a funnel and the washing solution was slowly poured over it. After excess solution had drained, the biomass was spread

evenly over the filter paper and dried at 60 °C for 2-5 hours, until the moisture content was around 8 wt%. Half of the washed biomass was reserved and a water rinse was also incorporated. Deionized water (18.2 MΩ) was slowly poured over the wet biomass until the pH of the solution was neutral, removing the acidic washing solution. The sample was also dried at 60 °C for 2-5 hours. The AAEM was also determined after the acid wash in order to calculate the amount of additional acid necessary to passivate the remaining AAEMs.

Sulfuric acid passivation

For the passivation process, a dilute sulfuric acid solution was prepared using the correlation, $K + Na + 2Ca + 2Mg - Cl$, developed by Kuzhiyil et al. [15]. The correlation calculates the mass ratio of sulfuric acid needed to passivate all of the AAEMs in the biomass. The AAEM content was determined for the untreated red oak and the corresponding amount of required acid was calculated. 96.6 wt % purity sulfuric acid obtained from Fisher Scientific® was added to the amount of water for a 1:1 biomass to infusion solution ratio. The appropriate volume of solution was slowly poured onto approximately 5 g of biomass in a 250 mL beaker and stirred thoroughly. The samples were dried at 40°C in a vacuum oven for 10-12 hours. The same process was followed to passivate the aqueous, carboxylic acid washed samples with the calculated amount of sulfuric acid.

Pyrolysis

The pyrolysis of 250 µg samples was carried out in a Frontier single-shot 2020iS® micropyrolyzer. Samples were tested in triplicate. To analyze the volatile products, a Bruker 430-Gas Chromatograph® (GC) with a flame ionization detector (FID) was used. The interface (the lowest heated area) was held at 320 °C and the main furnace was maintained at 500 °C. The

capillary column used for volatile compound separation was a 60 m by 0.25 mm Zebron ZB-1701 by Phenomenex. The GC method used set the injector temperature to 280 °C and had a split ratio of 1:100. The temperature of the oven, which was initially at 35 °C, was held constant for 3 minutes, then increased at 5 °C/minute to 280 °C. This temperature was then held for 4 minutes, for a total time of 56 minutes. Helium makeup flow was 28 mL/min through the FID which was at 280 °C. The air flow was 300 mL/min and hydrogen flow was 30 mL/min.

Calibration of levoglucosan, the compound of primary importance, was performed using liquid standards. Levoglucosan was dissolved in 18.2 MΩ deionized water and the calibration levels were set based on the range of expected yield from pyrolysis of red oak samples. The calibration curve had a total of 8 different points to account for the wide range of the expected yields with and without pretreatment. Three injections were performed at each level and the coefficient of determination of each of the linear calibrations produced were at least 0.99.

Experimental design

Two separate routes for the pretreatment of red oak were considered in this study. The effectiveness of a wash involving a carboxylic acid rich, aqueous fraction of bio-oil produced from a fast pyrolysis process was compared to a sulfuric acid passivation pretreatment. The aim of the carboxylic acid wash was to decrease the amount of sulfuric acid necessary to passivate the remaining AAEMs in the biomass by removing them from the biomass. Four separate processes were considered: an aqueous carboxylic acid wash (SF5/6 wash), SF5/6 wash with a water rinse, SF5/6 wash followed by passivation with sulfuric acid, and passivation with sulfuric acid. The effectiveness of the different pretreatments were determined based on which methods increased levoglucosan yields the most.

Analytical methods

Inductively Coupled Plasma Mass Spectrometry and X-Ray Fluorescence Spectroscopy

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was used to determine the sodium, magnesium, potassium, and calcium, content of the red oak samples. The standard acid digestion method ASTM D6349 was used to digest these samples prior to ICP-MS analysis with an ISTU-4 standard. Untreated red oak and carboxylic acid washed samples were also sent in to Test America to be tested for chlorine, sodium, magnesium, potassium, and calcium by X-Ray Fluorescence spectroscopy (XRF).

Thermogravimetric Analysis (TGA)

A Mettler Toledo Thermogravimetric Analyzer (TGA) was used to determine the moisture, volatiles, ash, and fixed carbon content of the feedstock. 50-100 mg samples were placed in a nitrogen atmosphere at 25 °C and heated to 105 °C at 10 °C/min. The sample was then held at 105 °C for 40 minutes, the temperature was then heated again at 10 °C/min to 900 °C where it was held for 50 minutes (the last 30 minutes of which the sample was purged with air at 100 mL/min). Each sample was tested in triplicate.

Optimization of Cornstover Passivation

Feedstock

The multipass cornstover used in this study was obtained from the BioCentury Research Farm in Boone, Iowa. The particle size of the cornstover was 12.7 mm and 3.17 mm when received. Experiments were carried out with the received 3.17 mm particles as well as 6.35 mm and 1.59 mm cornstover. A Retsch® knife mill was used to reduce the feedstock to the desired size. After pretreatment, further size reduction, solely to prepare samples for micropyrolysis,

was performed in a Retsch® ball mill to obtain a fine powder. This helped ensure consistent results on the microgram scale. The feedstock moisture content before pretreatment was around 8 wt%.

Acid pretreatment solution

The parameter that was held constant throughout the pretreatment process was the mass of sulfuric acid infused into equal masses of cornstover. The dilute sulfuric acid solution was prepared using the correlation, $K + Na + 2Ca + 2Mg - Cl$, developed by Kuzhiyil et al. [15]. The correlation calculates the mass ratio of sulfuric acid needed to passivate all of the AAEMs in the biomass. In this study 3.3 wt% (biomass basis) sulfuric acid was added to the appropriate amount of water, depending on the desired biomass to water ratio. Each trial consisted of approximately 400 g of cornstover. Thus, 13.2 g of 96.6 wt % purity sulfuric acid from Fisher Scientific® was added to 200, 300, or 400 g of 18.2 MΩ-cm ultrapure deionized water to treat the biomass.

Pretreatment mixer

A 14,200 cc Erweka Paddle Mixer was acquired from the Food Science Department at Iowa State University and is shown in Figure 10. The mixer was affixed with a pump and nozzle to evenly distribute the dilute acid onto the biomass. Two separate nozzles, a PJ6 and a PJ10, were used to allow for two different flow rates, 30 and 200 mL/min respectively. Once the biomass was loaded into the hopper, the lid, affixed with the nozzle, was secured and the paddles were set to rotate in reverse rotation at a speed of 20 Hz. The mixing began, followed by the spraying of the acid solution, when the diffusion time started. The device was continuously

mixed until all of the acid solution was sprayed on. Varying amounts of the acid and water solution were incorporated in the study, thus there were multiple flow rates and a range of times over which the solution was sprayed on. Once all of the acid was sprayed onto the biomass, it was left to sit for varying time intervals to allow uniform acid diffusion into the particles. Next the biomass was loaded into an oven at 105 °C and left for 10-12 hours (with stirring every 2-4 hours) until dried uniformly to 8-10% moisture. This biomass was then stored in sealed plastic buckets. 10 random samples of around 3 g were taken from the batch and reserved in sealed plastic bags. The samples were later combined and placed into the ball mill for size reduction. From the resulting powder 250 µg samples were taken for micropyrolysis trials.

Pyrolysis

Pyrolysis conditions were the same as the method described for the pretreatment of red oak. At least 10 replicates of pyrolysis experiments were performed by equipping the micropyrolyzer with an AS-1020E® autosampler.



Figure 10: 14,200 cc paddle mixer for biomass acid infusion.

Experimental design

When large particle size biomass is received at any moisture level there are three main processes that need to be completed before it is ready for pyrolysis. Biomass needs to undergo varying amounts of drying and size reduction, but more importantly the feedstock will be passivated with acid prior to pyrolysis. The parameters involved and the point at which the acid is infused are critical to making this process as effective and efficient as possible. Illustrated in

Figure 11 are four main routes for obtaining acid infused biomass ready for thermochemical conversion to high quality bio-oil via fast pyrolysis. The first two methods require the biomass to undergo drying prior to acid infusion in addition to drying following infusion. Two periods of drying would increase the energy inputs into the process, so in this study the third and fourth routes were tested using the as received biomass moisture content. In these two processes the biomass could be first reduced to sizes appropriate for pyrolysis, or infused with acid and then undergo particle size reduction. Consequently, the first variable introduced is the size of the biomass particles upon acid infusion. The second variable is the quantity of water used to infuse the acid into the biomass, potentially leading to varying degrees of drying following infusion. It is important to have sufficient water available to distribute the acid to all of the particles, while reducing any excess water. The final variable is the length of time that the acid is allowed to diffuse into the biomass. This variable helps determine whether the infusion process can be effective by simply coating the particles or if it needs time to diffuse all the way to the center of the particles.

A Response Surface Methodology (RSM) was created in JMP to test the influence of the three variables in the pretreatment process, the particle size of the biomass, the biomass to water ratio, and the total diffusion time. The particle sizes incorporated were 6.35 mm, 3.17 mm, and 1.59 mm. If cornstover under 6.35 mm is recovered from the field, size reduction would only occur once, after infusion. The two smaller sizes were chosen since they are common to use for pyrolysis in larger reactors (kg scale), thus when using a large reactor, size reduction would only be required prior to infusion. The three biomass to water ratios were based around the difference between the saturation point and the initial moisture content of the received feedstock. In other words, the amount of additional water that the particles could take on was used as a midpoint for

the amount of water needed in the pretreatment process. The saturation point of the biomass was determined by soaking the particles in deionized water for varying time intervals, throughout which the moisture content was measured until its perceived maximum was reached (no change in mass occurred). With a saturation point of approximately 83 wt% and an initial moisture content of about 8 wt%, the biomass to water ratios were chosen to be 2 to 1, 4 to 3, and 1 to 1 for cornstover. The diffusion times were chosen to be 2 minutes, 30 minutes, and 60 minutes. This range of times allowed for the acid to be able to just coat the biomass, and a longer amount of time for the acid to infuse into the whole particle. The maximum diffusion time of 60 minutes was based on the length of time the smallest particles required to reach their saturation point. The diffusion time began when the spraying commenced and ended when drying started. The complete RSM for the design of experiments is on Table 2.

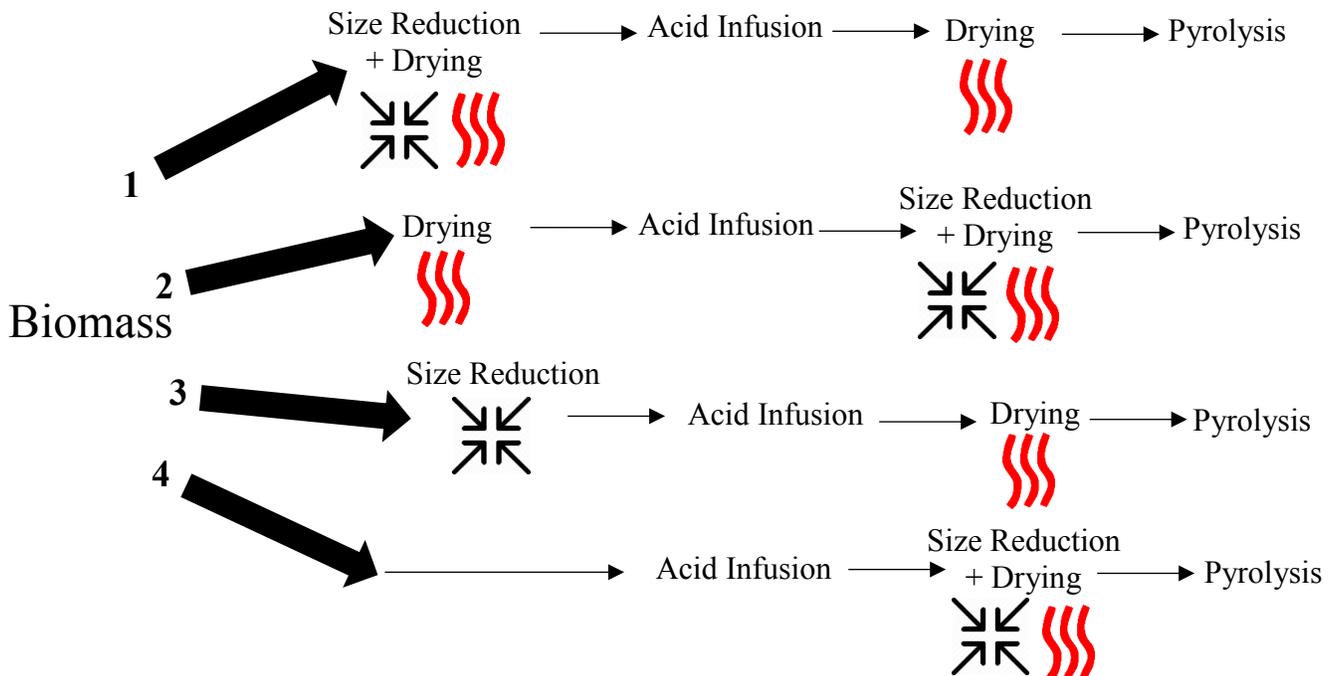


Figure 11: Various pretreatment pathways to obtain acid infused biomass for pyrolysis.

Table 2: Pretreatment parameters for the acid infusion of cornstover.

Diffusion Time (min)	Biomass to Water Ratio	Cornstover Mass (g)	Particle Size (mm)	Acid Mass (g)	Spray Time (min)	
					30 mL/min	200 mL/min
60	2:1	400	3.17	13.2	7.11	-
60	4:3	400	6.35	13.2	10.44	-
60	1:1	400	1.59	13.2	13.77	-
30	1:1	400	3.17	13.2	13.77	-
30	2:1	400	6.35	13.2	7.11	-
2	2:1	400	1.59	13.2	-	1.07
2	4:3	400	3.17	13.2	-	1.57
2	1:1	400	6.35	13.2	-	2.07
30	4:3	400	1.59	13.2	10.44	-

Analytical Methods

Inductively Coupled Plasma Mass Spectrometry and X-Ray Fluorescence Spectroscopy

The sodium, magnesium, potassium, and calcium, content of the cornstover were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The standard acid digestion method ASTM D6349 was used to digest these samples prior to ICP-MS analysis with an ISTU-4 standard. Untreated feedstock samples were also sent in to Test America to be tested for chlorine by X-Ray Fluorescence spectroscopy (XRF).

Thermogravimetric Analysis (TGA)

A Mettler Toledo Thermogravimetric Analyzer (TGA) was used to determine the moisture, volatiles, ash, and fixed carbon content of the feedstock. The method used was the same as described for the carboxylic acid washed samples. Each sample was tested at least in triplicate.

CHAPTER IV

RESULTS & DISCUSSION

Recycled Bio-oil Fraction Wash

Two different types of pretreatment were incorporated in this study with red oak as the feedstock. The effectiveness of an acid passivation was compared to washes involving a carboxylic acid rich aqueous fraction of bio-oil produced from a fast pyrolysis process. The aim of the wash was to decrease the amount of sulfuric acid necessary to passivate the remaining AAEMs in the biomass. The results of the four separate processes, SF5/6 wash, SF5/6 wash with a water rinse, SF5/6 wash and sulfuric acid passivation, and sulfuric acid passivation, are considered below. Error bars on the figures represent 95% confidence intervals from at least 3 replicates.

Removal of AAEMs

The untreated red oak contained relatively high amounts of calcium and potassium, and smaller concentrations of magnesium, sodium, and chlorine. The concentrations of the AAEMs as determined by ICP and XRF in the biomass samples is summarized in Figure 12. The initial wash removed 48% of the calcium and over 85% of the magnesium was removed from the biomass. Sodium was also reduced significantly from the wash, 93% was washed out. However, the wash was less effective at removing potassium and chlorine. Potassium levels only decreased by about 26% as a result of the wash. Although, the untreated biomass had a large standard deviation for potassium; two samples had higher potassium concentrations while the third had a much smaller amount that could not be quantified. This may explain why the

water soluble AAEM appears to have not been washed out. There was a slight increase in the chlorine content, which could be a result of the sampling process causing slight variances in AAEM content. Considering 9 ppm is a very small difference, the wash had little effect if any on the chlorine in the red oak.

When the wash was followed by a water rinse the total AAEM content was decreased further. Calcium was reduced to approximately one third of the amount of the untreated red oak and magnesium and sodium were undetectable by ICP analysis. Potassium was also significantly reduced, 94% of the average amount in untreated red oak was removed. Chlorine content was not determined for the wash with a water rinse incorporated. Overall, the wash was more effective at removing AAEMs when followed by a water rinse, but the wash did remove significant amounts of calcium, magnesium, and sodium.

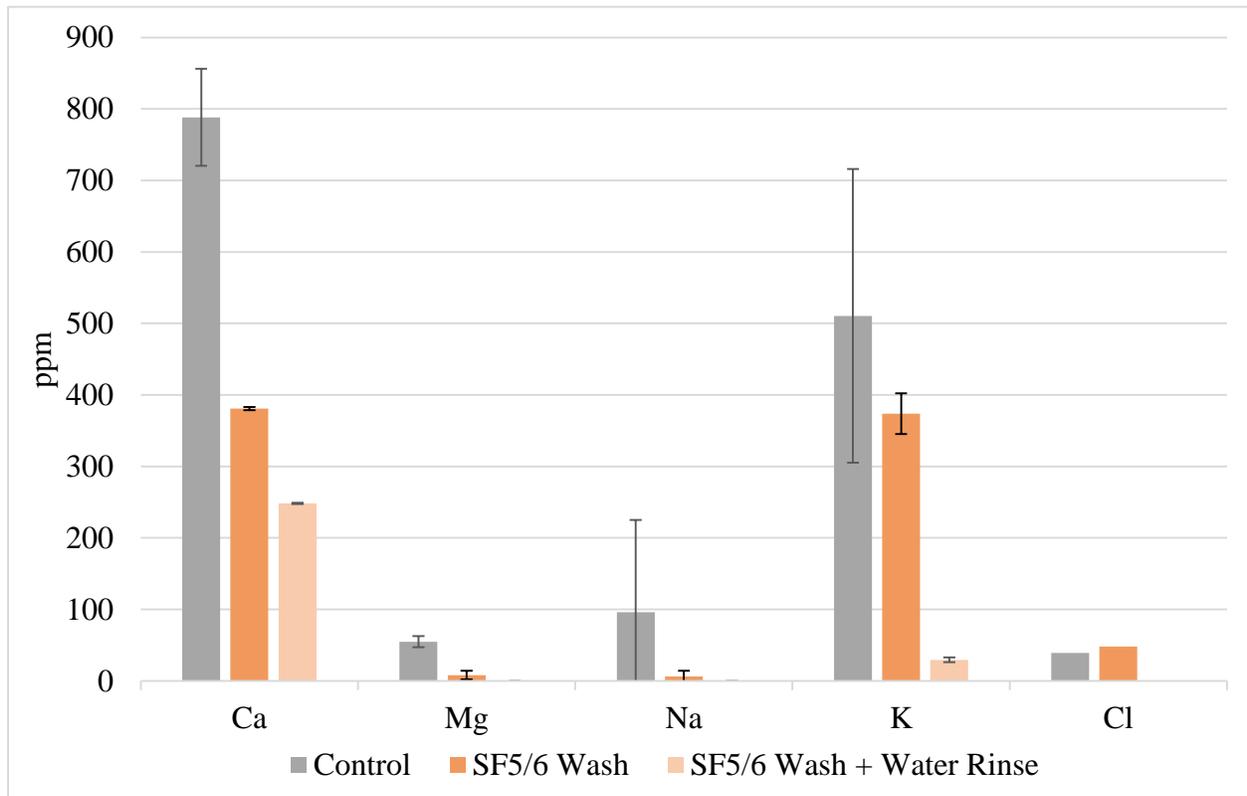


Figure 12: AAEM content of red oak samples.

Pyrolysis products of red oak

Yields of levoglucosan for the red oak with varying washing or infusion treatments ranged from 2.47 to 20.8 wt% on a dry biomass basis. The levoglucosan yields of the various samples are summarized in Figure 13. The aqueous fraction wash was the least effective. Levoglucosan yields were decreased from 3.32 wt% for untreated to 2.47 wt%. However, when a water rinse was incorporated, levoglucosan yields were as high as 13.3 wt%. This significant increase may be due to the removal of a majority of the AAEMs present in the biomass. Oudenhoven et al. [21] also noted that a similar pyrolytic bio-oil wash did not have as large of an impact on levoglucosan yields unless a water rinse was incorporated to remove the washing solution, but nevertheless yields increased. Considering that a 1:1 biomass to washing solution ratio was used, a majority of the wash was likely absorbed into the biomass and may have led to decreased levoglucosan yields.

Upon determining the AAEM content remaining following the aqueous fraction wash, the sulfuric acid necessary to passivate the remaining AAEM was calculated. In this case the levoglucosan yields were decreased from 13.3 to 9.84 wt%. This result was unexpected based on previous research where dilute acid passivation typically greatly increases levoglucosan yields. It may be possible that too much acid was used causing the biomass to be very acidic, which may cause fragmentation during pyrolysis. On the other hand, when untreated red oak was passivated with sulfuric acid the average levoglucosan yield was 20.8 wt%. In this study, sulfuric acid passivation pretreatment was by far the most effective at increasing levoglucosan yields from red oak. Assuming red oak contains around 40 wt% cellulose and 60% of pure cellulose is converted to levoglucosan, the sulfuric acid passivation in this study enabled red oak to reach approximately 87% of its theoretical levoglucosan yield.

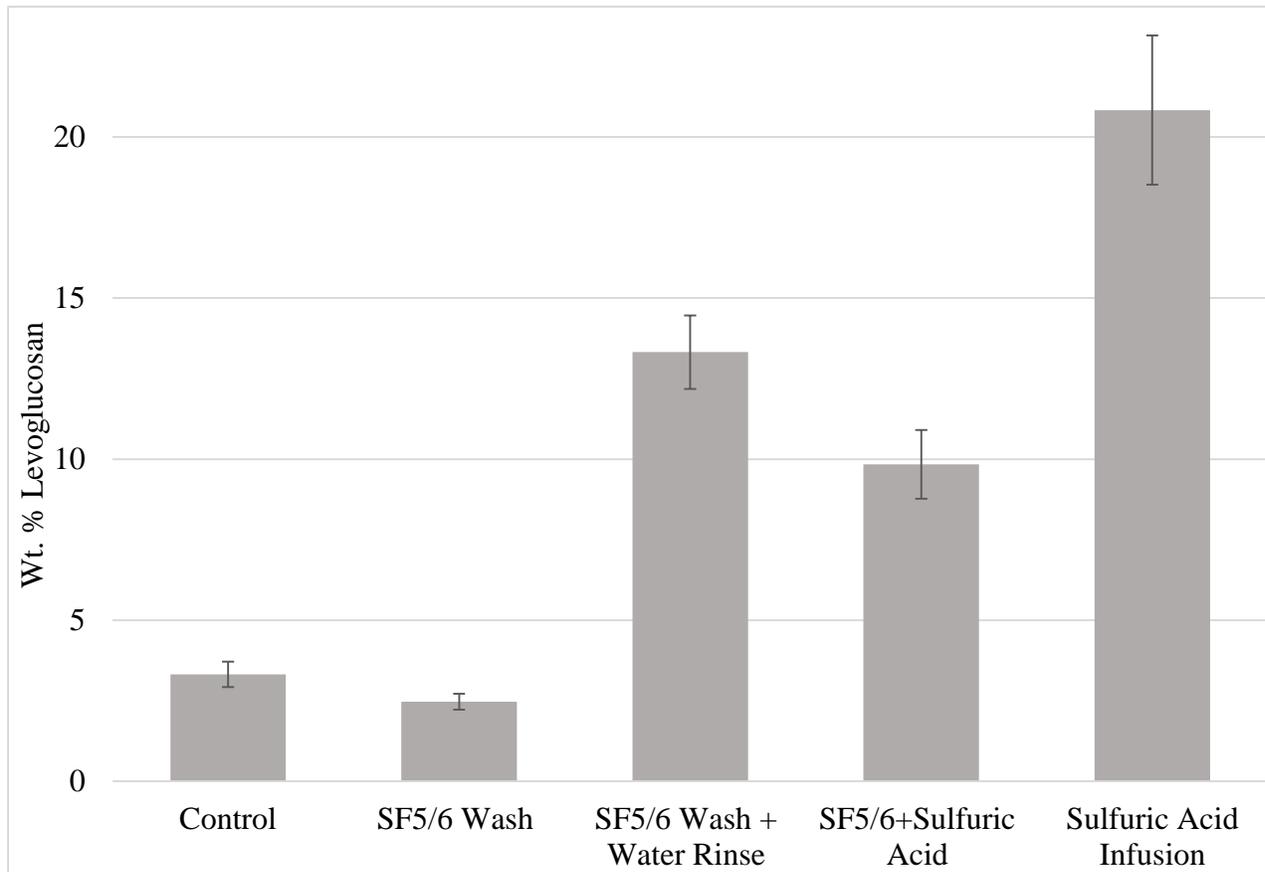


Figure 13: Levoglucosan yields of untreated and various pretreated red oak samples.

This study demonstrates that levoglucosan yields are not increased solely by removing the AAEMs in the biomass. It may also be possible that removing all of the AAEMs in biomass is critical for cellulose to attain 100% of its potential levoglucosan yields. This would require large volumes of washing solutions and thus resources for filtering as well as increased drying times. While washes that remove most of the AAEMs do lead to increased levoglucosan yields, passivation appears to have greater potential in terms of efficiently increasing yields, especially considering the large amount of water and energy for removing AAEMs. The recycled pyrolytic bio-oil used in this study was also not effective unless a water rinse was incorporated, further supporting an optimized dilute acid passivation pretreatment.

Optimization of Cornstover Passivation

The RSM designed to test the three variables in the sulfuric acid passivation of cornstover, involved 9 separate batches in the paddle mixer. All micropyrolysis experiments of these batches were performed with at least 10 replicates. The error bars in the figures represent the 95% confidence interval for the 10 trials. To determine which pretreatment parameters led to statistically significant differences in levoglucosan yields a Student T-Test was performed. A p-value of 0.05 or less showed a statistically significant difference in the means at a 95% confidence interval and a p-value less than 0.10 indicated a statistically significant difference at a 90% confidence interval. P-values obtained from JMP for the various parameters are given in Table 3. Based on their low p-values, particle size, biomass to water ratio (amount of water), and the quadratic effect of particle size were chosen to model a regression for the prediction of levoglucosan yields in JMP. The equation for the regression is:

$$\begin{aligned} \text{Predicted Levoglucosan Yield} = & -2.22 + [0.945 \times ((\text{Particle Size} - 0.156) / \\ & 0.0938)] + [-2.18 \times ((\text{Amount of Water} - 300) / 100)] + [((\text{Particle Size} - \\ & 0.156) / 0.0938) \times ((\text{Particle Size} - 0.156) / 0.0938) \times (-0.0126)]. \end{aligned}$$

The surface profile of the regression is seen in Figure 14. The regression model predictions were compared to experimental levoglucosan yields from each of the 9 trials. The experimental and predicted values are given in Table 4. Figure 15 represents the actual levoglucosan yields by the predicted yields, which gave a R^2 value of 0.927.

Table 3: P-values for various interaction parameters.

Parameter	P-value
Particle Size	0.0308
Amount of Water	0.0558
Diffusion Time	0.8238
Particle Size*Particle Size	0.0165
Particle Size*Amount of Water	0.9072
Amount of Water * Amount of Water	0.5159
Particle Size*Diffusion Time	0.7986
Amount of Water *Diffusion Time	0.1802

Table 4: Quantification of levoglucosan yields.

Sample	Diffusion Time (min)	Biomass to Water Ratio	Particle Size (mm)	Levoglucosan Yields from Pyrolysis		Predicted Levoglucosan Yields (Wt%)
				Wt% (dry basis)	Standard Deviation	
Control	-	-	-	0.834	0.216	-
1	60	2:1	3.17	17.1	2.43	17.3
2	60	4:3	6.35	6.05	0.781	5.04
3	60	1:1	1.59	5.39	0.889	7.10
4	30	1:1	3.17	14.2	1.53	12.9
5	30	2:1	6.35	7.00	0.879	7.21
6	2	2:1	1.59	10.7	2.03	11.5
7	2	4:3	3.17	14.0	2.68	15.1
8	2	1:1	6.35	2.07	0.322	2.86
9	30	4:3	1.59	11.8	1.93	9.28

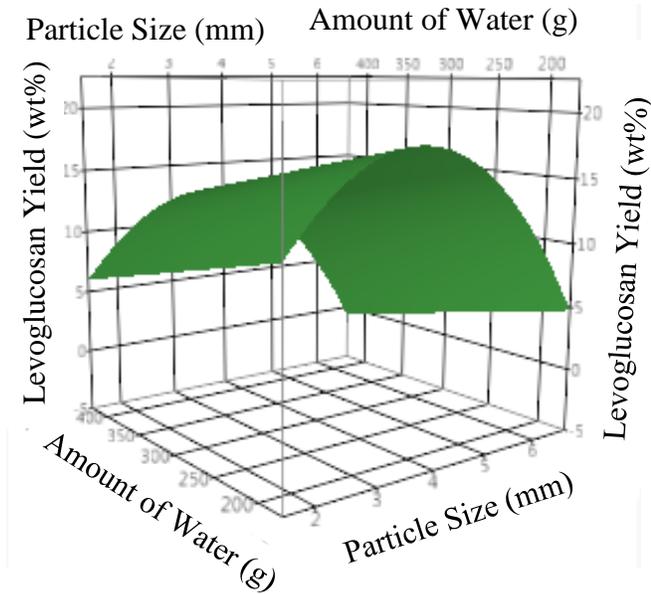


Figure 14: Surface profile for prediction of levoglucosan yields.

Biomass particle size

Of the particle sizes tested, the 3 trials involving 3.17 mm cornstover were found to yield the highest amounts of levoglucosan overall, 14.0 to 17.1 wt%. The lowest levoglucosan yields were observed with 6.35 mm particles; all three of the trials not attaining over 7.0 wt% levoglucosan. The 1.59 mm particles fared slightly better, but the highest observed levoglucosan yield was 11.8 wt%. Thus, it appears that 3.17 mm cornstover may be optimal for acid infusion. Overall, these results may suggest that when such low quantities of water are used for acid passivation, larger particles, such as 6.35 mm, are not ideal, as the acid may not be able to infuse all the way into the biomass to passivate the AAEMs. On a larger scale reactor, this effect may become less apparent, but further investigation is needed in order to examine if larger particles would yield low quantities of levoglucosan in this case. Considering the rather small standard deviations (0.322 to 0.879) in yields of the ball milled 6.35 mm treated particles, this suggests

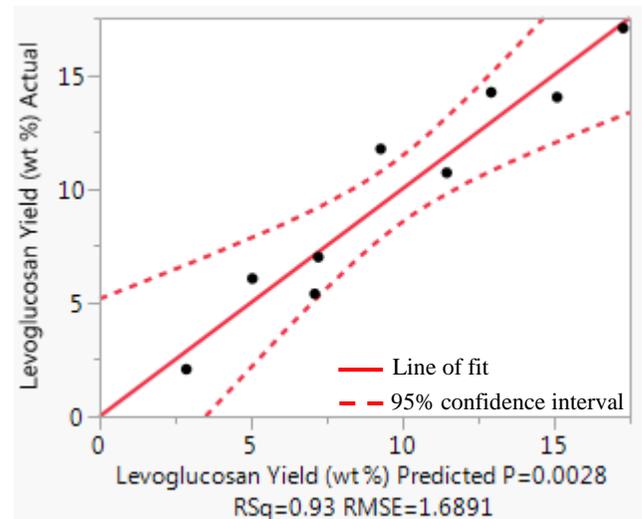


Figure 15: Comparison of experimental and predicted levoglucosan yields.

that a great majority of the particle was not exposed to the acid, leading to an overall low average of levoglucosan yields. On the other hand the 1.59 mm particles might then be expected to obtain higher yields of levoglucosan than the 3.17 mm particles, since the acid can easily infuse all the way to the center of the particle. The fact that this is not the case may be due to some particles receiving too much acid which has been observed to have a negative impact on levoglucosan yields [15]. This trend may be related to the rather narrow range for the optimal wt% of acid necessary to passivate the AAEMs, as seen in Figure 9. Each individual particle needs to receive the proper amount of acid on average to reduce the effect of the AAEMs. Thus, this study hypothesizes that an optimal particle size may be necessary to achieve maximum levoglucosan yields for low amounts of water, but further experiments to ensure reproducibility are necessary.

Figures 16 and 17 display the observed quadratic effect on levoglucosan yields when decreasing particle size. Figure 16 also shows a rather unpredictable effect of diffusion time for each particle size based on the experimental results, suggesting that the biomass to water ratio is more influential than diffusion time, especially when varying the particle size. Figure 17 represents the predicted levoglucosan yields from the regression model and demonstrates that decreasing the amount of water incorporated in the pretreatment process has a similar linear effect for each particle size. Particle size and the quadratic effect of the particle size were factors included in the regression model fit to the data to predict levoglucosan yields, given that their p-values were 0.0308 and 0.0165 respectively. These low p-values suggest that the two parameters have a strong influence on levoglucosan yields.

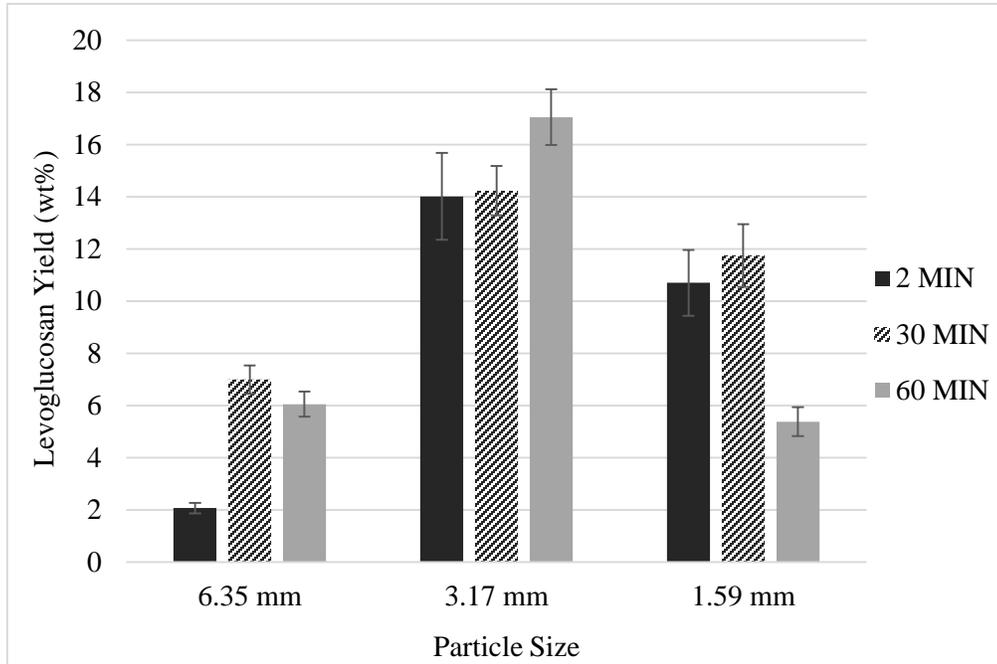


Figure 16: Levoglucosan yields for differing particle sizes with varying diffusion times.

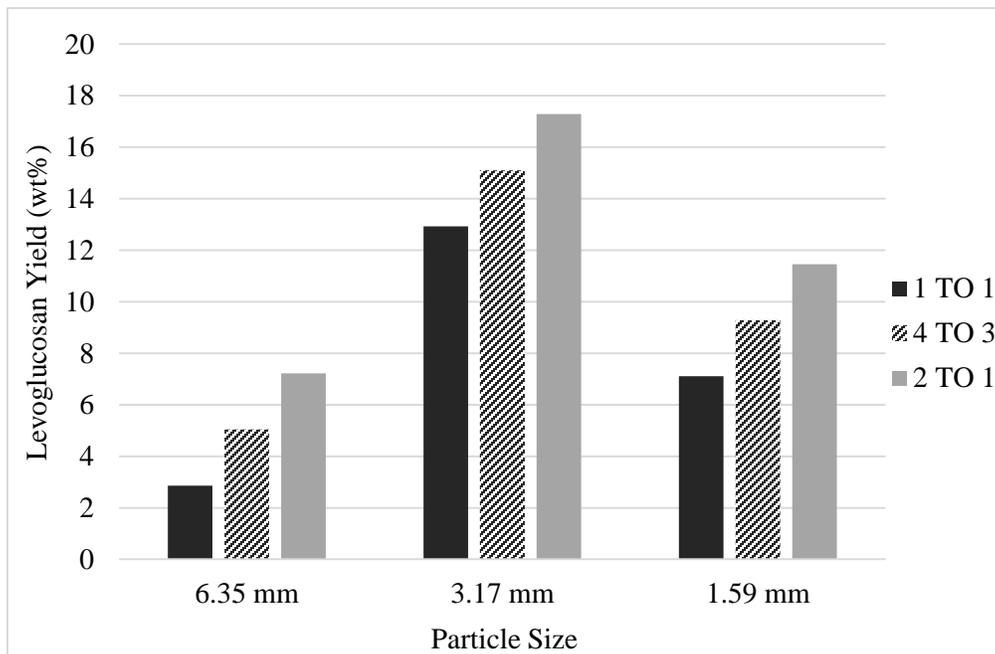


Figure 17: Predicted levoglucosan yields as a function of particle size and biomass to water ratio.

Biomass to water ratio

There may be a linear trend of increased levoglucosan yields as the amount of water incorporated in the pretreatment process decreases. This effect is seen in Figure 18 for each particle size. With an exception being the 2:1 biomass to water ratio for the 1.59 mm particle size (diffusion time of 2 min). The yield may be slightly lower than for the 4:3 biomass to water ratio for the 1.59 mm particles due to a small effect of the lowest diffusion time not allowing sufficient infusion when such small amounts of water are used. A small effect due to the 2 minute diffusion parameter is also seen for the 3.17 mm cornstover infused at a 4:3 ratio. The biomass to water ratio (amount of water) was also included as a parameter in the regression model because of its low p-value, 0.0558. When the predicted values from the regression model are plotted the linear trend is more visible as seen in Figure 19.

The biomass to water ratios tested in this pretreatment process, 2:1, 4:3, and 1:1, use very low amounts of water compared to literature. In the reviewed literature, biomass to washing solution ratios ranged from 1:1 to as high as 1:100. Not only do low amounts of water mean fewer inputs and potentially decreased drying energy, but excess water appears to be more harmful to levoglucosan yields than helpful, when an efficient mixing device is incorporated. Using half as much water as the biomass resulted in levoglucosan yields over 17 wt%. These low quantities of water were feasible due to the paddle mixer that allowed the acid to be evenly distributed and the biomass to be thoroughly mixed.

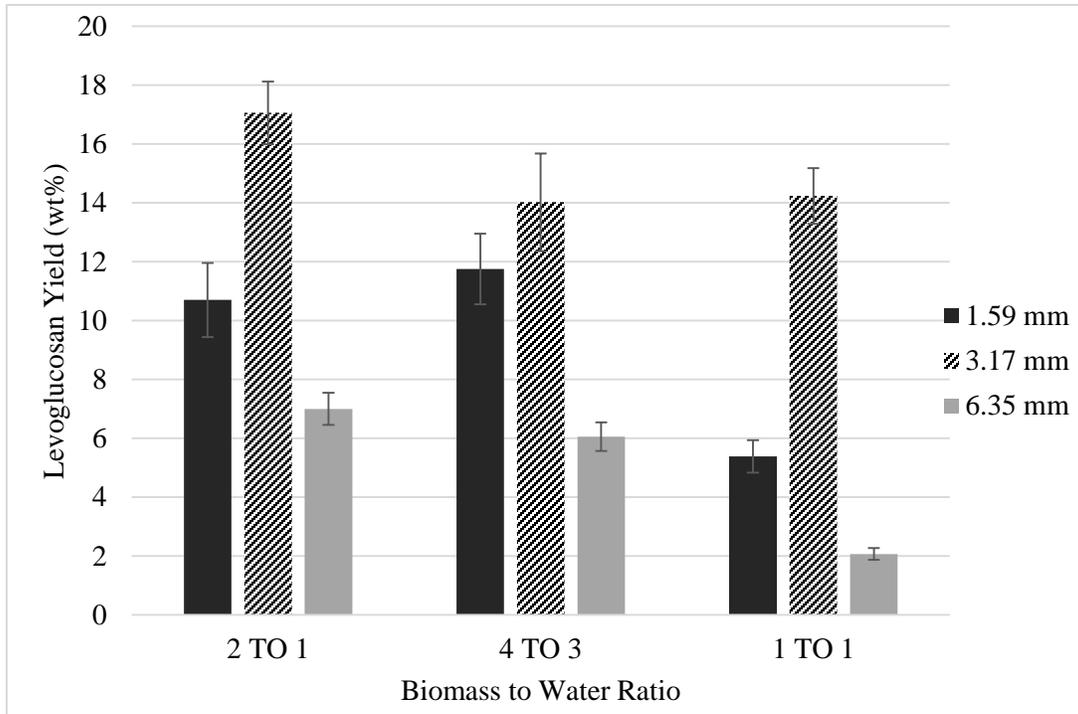


Figure 18: Experimental levoglucosan yields for various biomass to water ratios (including the effect of diffusion time).

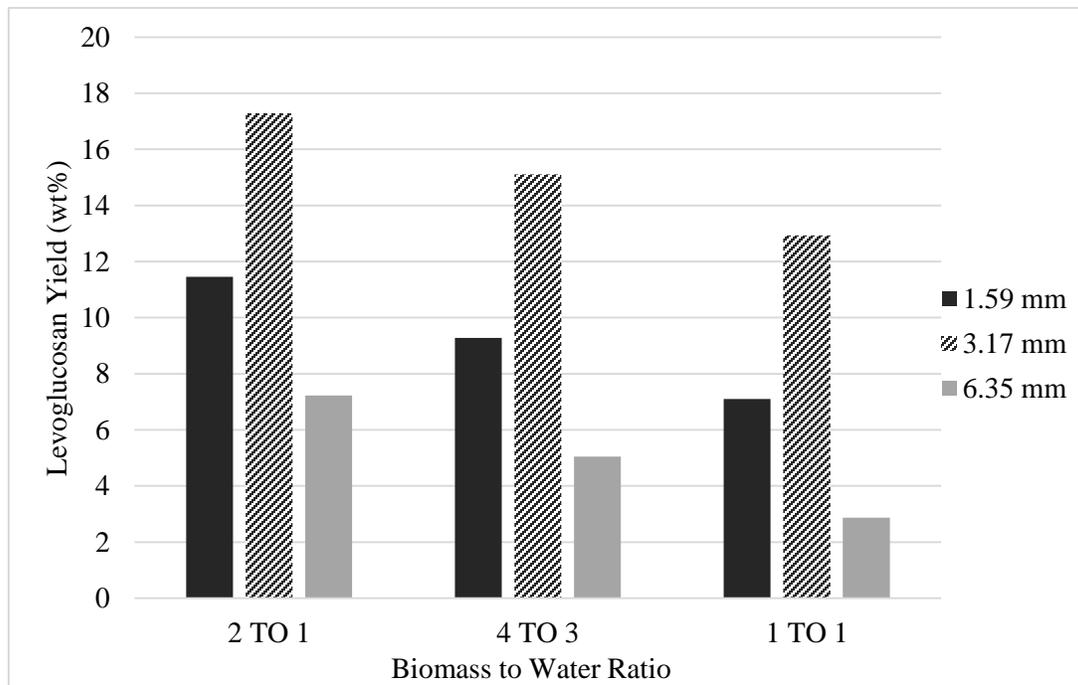


Figure 19: Predicted levoglucosan yields for various biomass to water ratios.

Diffusion time

Overall, diffusion time did not have a statistically significant effect on levoglucosan yields based on the Student T-Test. As shown in Figure 20 increasing diffusion time had varying impacts on the different particle sizes. The 6.35 mm and 1.59 mm particles had no visible trends when diffusion time was increased. The varying effects may be due to the different biomass to water ratios incorporated. One possibly significant trend is the general increase in levoglucosan yields as diffusion time increased for the 3.17 mm particles. In this case yields were increased slightly for longer diffusion times, but the shortest diffusion time still yielded levoglucosan higher than 14 wt%, greater than any yields attained by the other 2 particle sizes. Thus, it may be concluded that proper diffusion time may be a factor in further increasing levoglucosan yields when other parameters, like the particle size and biomass to water ratio, are optimized.

Although not determined statistically significant, diffusion time was also added to the regression model in order to examine its effect. This new regression model only slightly increased the R^2 value from 0.927 to 0.929, and the optimal levoglucosan yield, occurring at a 2:1 biomass to water ratio for 3.17 mm particles, increased from 17.3 to 17.5 wt%. Thus, the diffusion time was not found to be significant for increasing levoglucosan yields in the acid infusion of cornstover, the small difference is within the confidence interval. This can be seen graphically in Figure 21 where the predicted slope of the line for diffusion time as a function of levoglucosan yield is very close to zero.

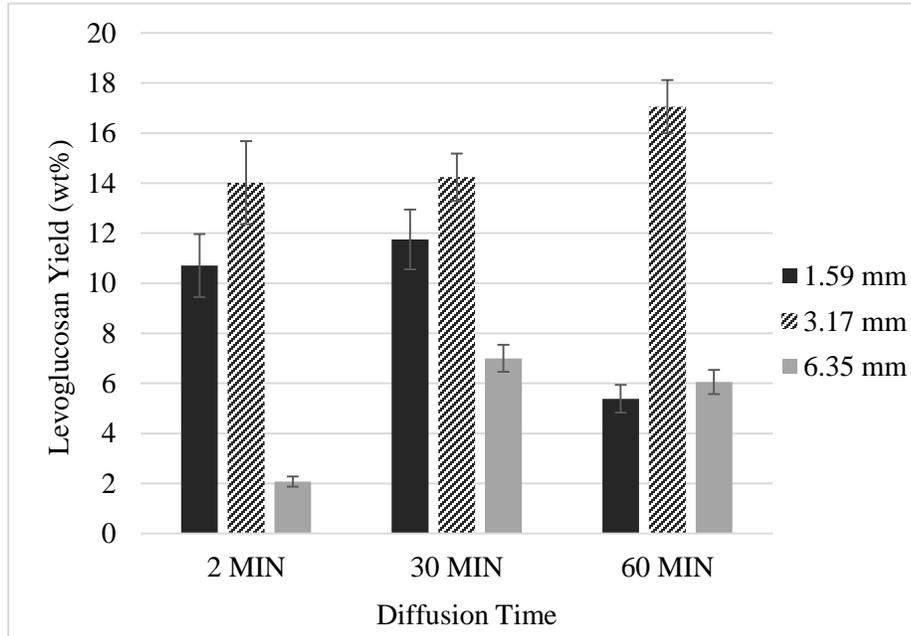


Figure 20: Impact of increasing diffusion time for various particle sizes and biomass to water ratios.

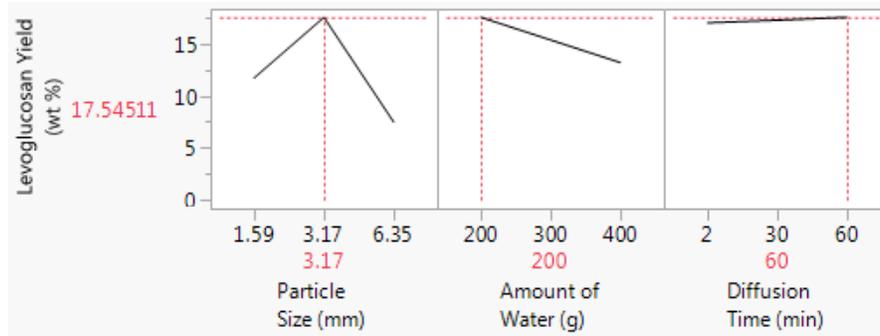


Figure 21: Parameters for optimized levoglucosan yield (17.5 wt%) for a regression model involving the effect of particle size, the quadratic effect of particle size, biomass to water ratio, and diffusion time.

CHAPTER V

CONCLUSIONS & FUTURE WORK

Conclusions

Many pretreatment methods to increase the quality of products produced from fast pyrolysis have previously been investigated. The effect of acid and water washes has been examined, most involving the use of large quantities of solution, even if dilute. Almost all of the washing methods also require a water rinse to neutralize the sample prior to pyrolysis. Although typically effective at increasing levoglucosan yields and decreasing the less desirable products, these methods require the consumption of excess water. It may be possible to wash biomass with “waste” products produced from pyrolysis, followed by a water rinse, but this process still needs further refinement for it to be considered an efficient method. Passivation seems to be a more viable option than attempting to rid the biomass of its inherent high amounts of AAEMs. Many aspects of this process have previously been studied such as the type of acid used and the amount of acid necessary, but this study shows that further improvement of the process is possible. The aim of this study was to determine methods to optimize the pretreatment process by decreasing the amount of water necessary to distribute the acid to the particles, reducing energy inputs for particle size reduction (by a design of experiments that only requires one size reduction step), and determining the amount of time the acid needs to infuse into the biomass.

In the preliminary study for the pretreatment of red oak, acid passivation alone led to the largest increase in levoglucosan yields. Levoglucosan yields increased from 3.3 to 20.8 wt%. Following these results, an optimization study was conducted for the passivation of cornstover, which, when untreated, has levoglucosan yields as low as 1 wt% from micropyrolysis. The study concluded that while the particle size and biomass to water ratio are influential parameters in the

pretreatment process, diffusion time does not have a very large impact on the effectiveness of the pretreatment. It was found that the 3.17 mm cornstover yielded the best results in each of the three trials that it was included in. Each individual particle needs to receive the proper amount of acid on average to reduce the effect of the AAEMs. When minimizing the water used for passivation 3.17 mm particles appear to be optimal for cornstover, but further studies may be required to determine if this is the case for other feedstocks as well. Based on experimental results, decreasing the amount of water in the pretreatment process also helped increase levoglucosan yields. The small amounts of water are sufficient in this study due to the designed mixing device that does not simply dump the dilute acid onto the biomass and mix it, but slowly sprays the solution onto the biomass. This ensures that most of the particles are uniformly wet by the solution. Thus, it is essential to have proper methods for infusion in order to incorporate low quantities of water. Overall, when pretreatment was carried out at the concluded optimal conditions, 3.17 mm, 2:1 biomass to water ratio, for 60 minutes, levoglucosan yields as high as 17 wt% were obtained.

Future Work

Many inputs in pretreatment processes can be further reduced, making pretreatment an attractive process for increasing the quality of bio-oil. It is important to incorporate other feedstocks to investigate if there are similar trends for particle size, diffusion time, and biomass to water ratios. Although this study concluded that under the other conditions tested, 3.17 mm cornstover was the optimal particle size, this parameter might be different for other feedstocks. Testing other feedstocks may help determine if there is another factor during the infusion process, such as the sorption capacity of the feedstock.

The initial moisture content of the feedstock is another variable worth considering. The initial moisture content of the biomass in the cornstover study was around 8 wt%. If the moisture content was higher diffusion time may become a significant factor given that the biomass might not absorb water as quickly. Variable initial moisture content may also change the amount of water necessary for the pretreatment process; lesser amounts of water may be feasible when the initial moisture content is higher, such as cornstover received directly from the field. This passivation optimization study should also be repeated at a kilogram scale in order to determine the impacts on the pyrolysis reactor used, as well as the amount of bio-oil produced and the product yields in the bio-oil, especially other sugars. Feeding difficulties might also be encountered when moving to a kilogram scale reactor which would need to be dealt with.

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