2013

Pyrolytic sugars from cellulosic biomass

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Pyrolytic sugars from cellulosic biomass

by

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A dissertation submitted to the graduate faculty

in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Biorenewable Resources and Technology

Program of Study Committee:

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Iowa State University

Ames, Iowa

2013

Dedication

I dedicate this work to my mom and dad
who selflessly dedicated their lives to bring the best out of their children. I also dedicate this work to my wife and daughter
whose unflinching support made this work possible.

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ACKNOWLEDGEMENT

I take this opportunity to thank many wonderful people who contributed to this work and supported me through my PhD at Iowa State University. I consider the opportunity to work with Dr. Robert Brown as a great privilege in my life. I thank him for providing me with invaluable guidance on this research project and on my graduate study. I thank Dr. Song-Charng Kong for being my co-major professor and for his timely guidance and support. I thank Dr. Brent Shanks, Dr. Steven Hoff and Dr. Terry Meyer for serving in my Program of Study Committee and for providing excellent guidance on my research.

I profusely thank my colleagues at CSET who have helped me in carrying out many of the experiments and also in honing my research ideas, especially Dustin Dalluge for his outstanding contributions to this work. I thank Pushkaraj Patwardhan, Lysle Whitmer, Katy Brewer, Kaige Wang, Marjorie Rover, Patrick Johnston, Sunitha Sadula, Dr. Xianglan Bai and Ryan Smith for their help and support. I thank the undergraduate students for helping me with the reactor and analytical works. Without the help of all these people this work would not have been possible.

I thank my family back in India, and my wife and daughter for their great support and the inspiration that they are to me!

Finally, I thankfully acknowledge the financial support from ConocoPhillips Company and the US Department of Energy for this work.

ABSTRACT

Sugars are the feedstocks for many promising advanced cellulosic biofuels. Traditional sugars derived from starch and sugar crops are limited in their availability. In principle, more plentiful supply of sugars can be obtained from depolymerization of cellulose, the most abundant form of biomass in the world. Breaking the glycosidic bonds between the pyranose rings in the cellulose chain to liberate glucose has usually been pursued by enzymatic hydrolysis although a purely thermal depolymerization route to sugars is also possible. Fast pyrolysis of pure cellulose yields primarily levoglucosan, an anhydrosugar that can be hydrolyzed to glucose. However, naturally occurring alkali and alkaline earth metals (AAEM) in biomass are strongly catalytic toward ring-breaking reactions that favor formation of light oxygenates over anhydrosugars.

Removing the AAEM by washing was shown to be effective in increasing the yield of anhydrosugars; but this process involves removal of large amount of water from biomass that renders it energy intensive and thereby impractical. In this work passivation of the AAEM (making them less active or inactive) using mineral acid infusion was explored that will increase the yield of anhydrosugars from fast pyrolysis of biomass. Mineral acid infusion was tried by previous researchers, but the possibility of chemical reactions between infused acid and AAEM in the biomass appears to have been overlooked, possibly because metal cations might be expected to already be substantially complexed to chlorine or other strong anions that are found in biomass. Likewise, it appears that previous researchers assumed that as long as AAEM cations were in the biomass, they would be catalytically active regardless of the nature of their complexion with anions.

On the contrary, we hypothesized that AAEM can be converted to inactive or less active salts using mineral acids. Various biomass feedstocks were infused with mineral (hydrochloric, nitric, sulfuric and phosphoric acids) and organic acids (formic and acetic acids) followed by analytical pyrolysis on a micropyrolyzer/GC/MS/FID system. It was found that sulfuric and phosphoric acids are very effective in passivating the AAEM thereby increasing the yield of anhydrosugars. An excellent correlation was discovered between the amount of acid required to obtain the maximum yield of anhydrosugars and the amount of AAEM contained in the biomass feedstock. In the micro-scale studies, up to 56% of the cellulose contained in the biomass was converted into anhydrosugars which is close to the 57% conversion obtained from pure cellulose pyrolysis.

It is known that LG polymerization and subsequent charring occur at temperatures above 275°C depending on the vapor pressure of LG in the gas stream. A study of pyrolysis of acid-infused biomass feedstocks at various temperatures revealed that LG recovery is best at lower temperatures than the conventional pyrolysis temperature range of 450-500°C.

Pyrolysis of acid-infused biomass failed in a continuous fluidized bed reactor due to clogging of the bed. The feedstock formed vitreous material along with the fluidizing sand that was formed from poor pyrolysis of lignin. However, more investigation of this phenomenon is a subject for future work. Pyrolysis experiments on an auger type reactor were successful in producing bio-oils with unprecedented amounts of sugars. Though there was increase in charring when compared to the control feedstock, pyrolysis of red oak infused with 0.4 wt% of sulfuric acid produced bio-oil with 18wt% of sugars.

One of the four fractions of bio-oil collected contained most of the sugars, which shows significant potential for separating the sugars from bio-oil using simple means. This work points towards a new pathway for making advanced biofuels viz. upgrading pyrolytic sugars from biomass that could compete with enzymatic sugars from biomass.

CHAPTER 1. OVERVIEW

1.1. Introduction

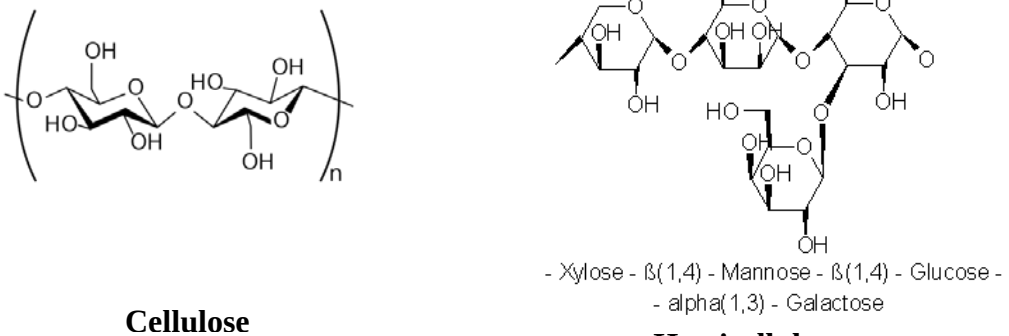
Biofuels have gained importance in the present circumstances of high energy prices and the uncertainty of energy supply for many countries in the world. Fossil fuels are limited in quantity and are not renewable. Their utilization increases the amount of carbon dioxide in the atmosphere which is considered to be one of the causes of global warming and climate change. Biofuels on the other hand utilize renewable carbon that is captured from the atmosphere by the plants that makes them carbon neutral or less carbon emitting. Biofuels also provide energy security for countries that have large area of land available for cultivation of energy crops.

While biofuels provide carbon neutral fuels and energy security, it is equally important to maintain the food security of nations around the world. Instead of competing with food producing crops for raw materials, the biofuel industry should use plant biomass feedstocks that are not used for producing food. In this aspect, cellulosic biomass from agricultural and forestry wastes and energy crops such as switchgrass are excellent feedstocks for biofuel production. In the present work such feedstocks were used. The path taken here was to convert the carbohydrates contained in biomass into sugars that can be upgraded into transportation fuels.

Currently, sugars are the feedstocks for many of the advanced biofuel programs based both on biological and catalytic conversion processes (Huber et al. 2006; Wyman et al. 2007). Naturally occurring sugars are limited in availability while cellulose, which is a

polymer of sugar monomers, is the most abundant naturally occurring polymer in the world. In principle, it is possible to produce large quantity of sugars that is essential to produce biofuels by depolymerizing the cellulose contained in plant biomass.

Cellulose forms the structural material for the greater part of plant cell walls. It is a polymer of D-glucose units joined together by bonds from the hydroxyl group attached to the first carbon atom of one glucose unit to the hydroxyl group of the fourth carbon atom of another glucose unit (Figure 1). Plant biomass also contains hemicellulose which consists of a mixture of polysaccharides derived from both hexoses and pentoses the depolymerization of which also can produce feedstocks for biofuel production. Cellulose and hemicellulose are carbohydrates while the third component of biomass called lignin is more of aromatic rings (Figure 2).



Cellulose **Hemicellulose**

Figure 1. Structural representation of cellulose and hemicellulose

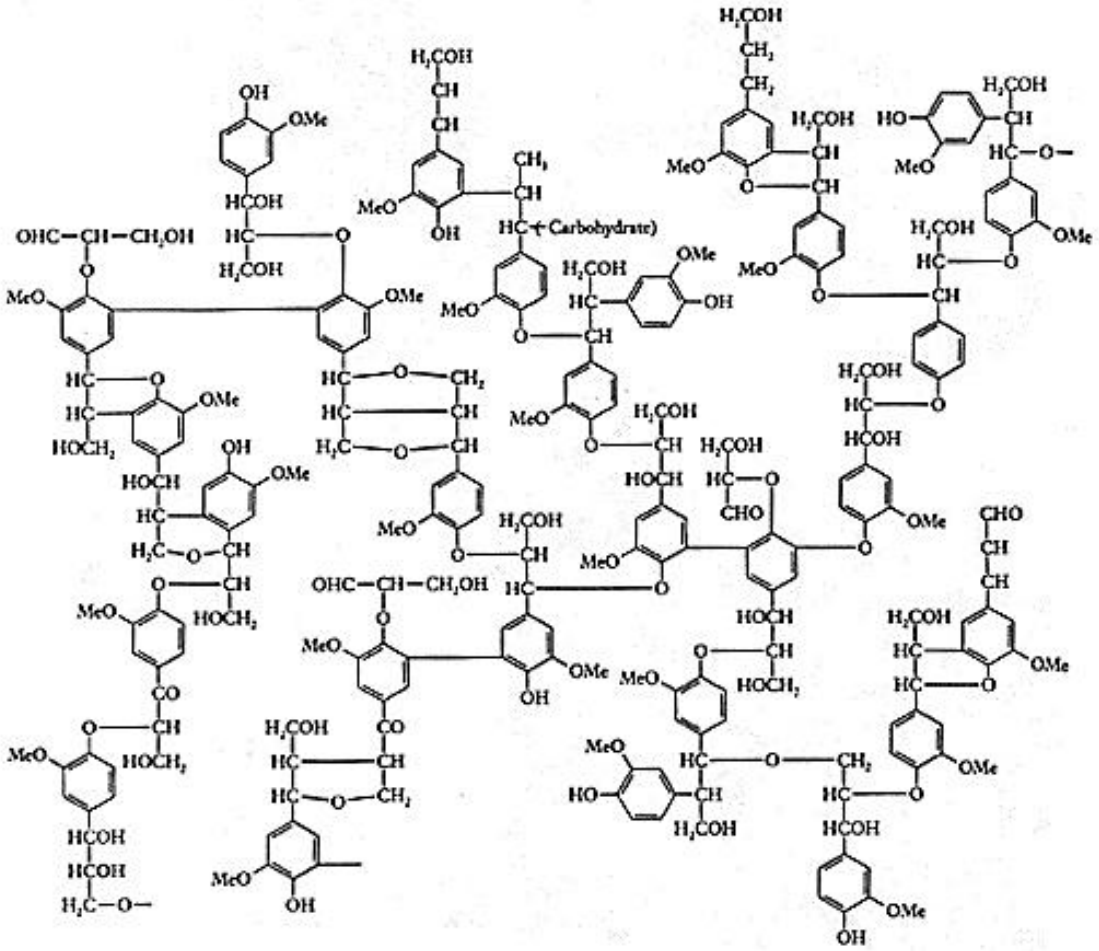


Figure 2. Structural representation of lignin

To date much of the research and development effort in advanced biofuels has focused on biological approaches that employ expensive enzymes to hydrolyze cellulose to monosaccharides (Dwivedi et al. 2009). Commonly overlooked is the prospect of using thermal processes to produce water soluble carbohydrates suitable for fermentation or catalytic upgrading. Pure cellulose readily depolymerizes during pyrolysis at temperatures of 350-600°C to yield predominately levoglucosan (LG) and other anhydrosugar derivatives of glucose. Thermal processes such as fast pyrolysis have the advantage of very fast conversion rates and simplicity of operation.

1.2. Definition of the Research Problem

Fast pyrolysis of pure cellulose yields predominantly levoglucosan and other anhydrosugars resulting from the depolymerization of cellulose. However, alkali and alkaline earth metals (AAEM) inherent in biomass catalyze pyranose ring fragmentation reactions during pyrolysis thereby decreasing the yield of sugars and increasing the yield of light oxygenates such as hydroxy acetaldehyde and acetol (DeGroot et al.1984; Patwardhan et al. 2009). Removing the AAEM by washing the biomass with water or dilute acid was shown by many researchers to be effective in increasing the yield of anhydrosugars; but this process involves removal of large amount of water from biomass that renders it energy intensive and thereby impractical (Piskorz et al. 1989; Raveendran et al. 1995).

Infusing mineral acids such as phosphoric and sulfuric acids in smaller quantities was found to be effective in increasing the yield of anhydrosugars from fast pyrolysis of biomass (Dobele et al. 1999; Dobele et al. 2003). The mechanism of activity of the mineral acids on cellulose pyrolysis in this case was poorly known and the yields reported were not significant enough for the production of sugars. The possibility of chemical reactions between infused acid and AAEM in the biomass appears to have been overlooked, possibly because metal cations might be expected to already be substantially complexed to chlorine or other strong anions that are found in biomass. Likewise, it appears that previous researchers assumed that as long as AAEM cations were in the biomass, they would be catalytically active regardless of the nature of their complexion with anions (Patwardhan et al. 2009).

We hypothesized that *the AAEM in the biomass can be passivated using mineral acid infusions because the AAEM react with mineral acids to form thermally stable salts thereby*

decreasing or eliminating their catalytic activity. We also hypothesized that *if the AAEM in biomass feedstocks are passivated, significant amount of sugars can be produced from fast pyrolysis of biomass.*

1.3. Objectives

The first objective of this study was to understand the ways in which AAEM interact with mineral acids and the mechanism of passivation Various biomass feedstocks were infused with selected acids at various concentrations followed by analytical pyrolysis carried out using a microscale analytical pyrolyzer coupled with a GC/MS/FID system. The best infusion rates were down selected for further study. At the same time, model compound studies were carried out to delineate the influence of AAEM on pyrolysis of cellulose and the effects of acids on the catalytic activity of AAEM.

The second objective was to demonstrate the efficacy of AAEM passivation during continuous pyrolysis. Based on the results from investigations of the first object, acid infused biomass was pyrolyzed in both fluidized bed and auger type pyrolysis reactors to and the resulting bio-oils were analyzed for sugar content and physico-chemical properties.

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CHAPTER 2. LITERATURE REVIEW

2.1. Introduction

This literature review explores the role of AAEM in biomass; the effect of AAEM in biomass pyrolysis; and the methods employed to mitigate the effect of AAEM on biomass pyrolysis.

2.2. Alkali and Alkaline Earth Metals (AAEM) in Biomass

Biomass contains many inorganic compounds that include naturally occurring plant nutrients and impurities carried over from the field. Plant nutrients are essential for plant growth and are classified into macronutrients and micronutrients according to the average amount contained in plants. Nitrogen, phosphorous, sulfur, potassium, magnesium and calcium are macronutrients while iron, manganese, zinc, copper, boron, molybdenum, chlorine and nickel are micronutrients (Marschner et al. 1995; Mengel et al. 2001). Most micronutrients are predominantly constituents of enzyme molecules and are thus essential only in small amounts. In contrast, most of the macronutrients are constituents of organic compounds, such as proteins and nucleic acids, or act as osmotica. The concentrations of each of these nutrient elements can vary considerably depending upon the plant species and soil conditions (Marschner et al. 1995).

Potassium and sodium are the alkali metal constituents of biomass while calcium and magnesium are alkaline earth metals in it. Sodium is a micronutrient and is found in very low concentrations in biomass, but the other three are macronutrients that are found in higher concentrations. A typical analysis result from literature is provided in Table 1 (Monti et al.

2008). It is clear that the concentrations of mineral nutrients are different in various feedstocks. It is important to note that silicon is not a plant nutrient, but it comes from the dirt that gets carried along with the biomass during harvesting. In case of herbaceous biomass, the annuals contain more inorganic material than the perennials. On the other hand, woody biomass contains less AAEM than the herbaceous ones.

Potassium is the most abundant cation in the cytoplasm (Marschner et al. 1995). Potassium is not metabolized and it forms only weak complexes in which it is readily exchangeable. It neutralizes the soluble and insoluble anions (both organic and inorganic) and maintains the pH between 7 and 8. The anions associated with potassium are NO_3^{--}, Cl^{--} and malates. Most researchers have reported potassium to be a very mobile free cation (Marschner et al. 1995; Mengel et al. 2001). However, there is alternate opinion that most of the potassium is bound to organic molecules like proteins and amino acids (Cameron et al. 1990). Calcium on the other hand is part of the cell wall bound to the uronic acids and the carbohydrates.

2.3. Influence of AAEM on Pyrolysis of Biomass

Alkali and alkaline earth metals (AAEM) alter the mechanism by which pyrolysis reactions of cellulosic materials proceeds. Cellulose pyrolysis occurs by a mechanism shown in Figure.3, which was suggested by Shafizadeh (1982) and other researchers (Bradbury et al. 1979; Piskorz et al. 1989, Scott et al. 2001). Hopkins and Antal provided evidence for direct fragmentation of cellulose (Hopkins et al. 1984).

Table 1. Typical mineral matter contents of various biomass feedstocks from literature (Monti et al. 2008)

Feedstock	ash	N	C	Al	Ca	Cl	Fe	K	Mg	Na	P	S	Si
Reed grass	32	5.2	431	196	968	5608	102	5609	1027	130	320	932	6223
Cynara	68	3	401	150	12,190	18,171	79	6467	766	12,807	1363	1740	889
Miscanthus	19	1.6	439	143	1730	7406	61	3588	857	153	154	337	4531
Switchgrass 20	26	3	435	137	1097	13,798	86	3555	1020	870	404	464	5345
Switchgrass 80	23	3.3	440	111	1197	4944	83	2628	1171	870	248	443	5301
Sweet Sorghum	50	4.4	408	152	3446	7199	112	12,991	2079	195	804	681	7013

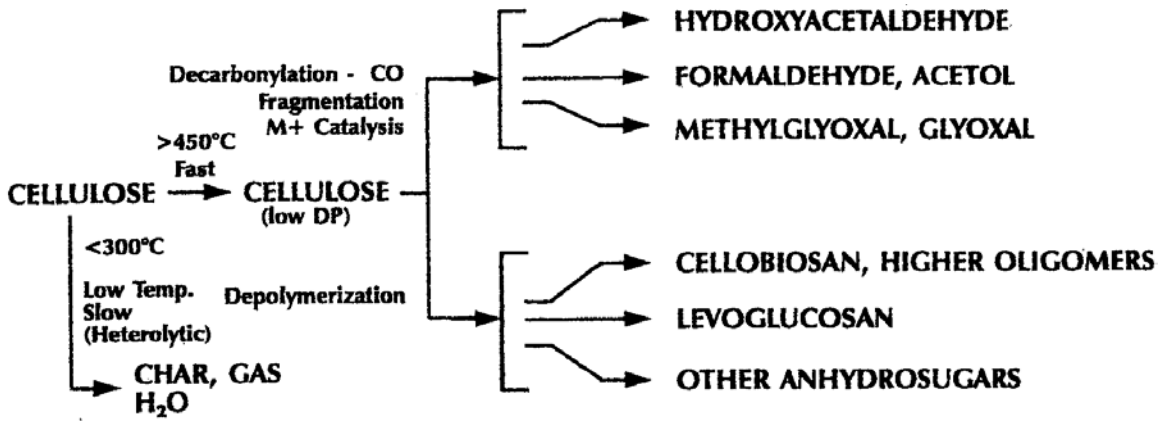

Figure 3. Schematic of the mechanism of cellulose pyrolysis (Scott et al. 2001)

Cellulose, on heating, either transforms into active cellulose that has low degree of polymerization or turns into char and water. The active cellulose further breaks down in two different pathways. In the first one, the chain breaks at the glycosidic bonds to form levoglucosan, other anhydrosugars, cellobiosan and higher sugar oligomers.

When pure cellulose is pyrolyzed, about 50 to 60 wt% levoglucosan is obtained as the depolymerization is the predominant pathway of breakdown (Shafizadeh 1982). The second pathway is of decomposition or fragmentation in which the cellulose ring opens up and breaks down into two or three carbon oxygenated compounds. The predominant products are hydroxyacetaldehyde, formaldehyde, acetol, methyl glyoxal and glyoxal.

Many researchers observed that (Pan et al. 1989; Piskorz et al. 1989; Raveendran et al. 1995) the presence of alkali and alkaline earth metals in cellulose or biomass changes the pyrolysis mechanism by catalyzing the decomposition reactions. Because of this shift in mechanism, the yield of levoglucosan is very low and the yield of light oxygenates is very high in the case of alkali catalyzed pyrolysis. Di Blasi et al. (2009a, 2009b) found that

hydroxides and carbonates of sodium and potassium impregnation to fir wood at a treatment level of 0.7-0.9wt% practically reduced the yield of levoglucosan close to zero. The char, water and non-condensible gas yield increased by about 1.3-1.5 times.

Ponder et al.(1992), Yang et al.(2006) and Patwardhan et al.(2009) suggested a mechanism of alkali catalysis of cellulose ring scission. This mechanism is shown in Figure 4. The influence of any mineral salt depends on its ionic nature, Lewis acidity/basicity and/or ability to form complexes that stabilize particular reaction intermediates.

Shafizadeh (1982) postulated that glycolaldehyde is generated by a C_2-C_3 scission of the glucose intermediate formed from levoglucosan which is in turn formed via depolymerization of cellulose; i.e., cellulose → levoglucosan → glucose → glycoldehyde + C4 fragment. Richards et al. (1987) and Pan et al. (1989) observed greater levoglucosan yields from microcrystalline cellulose and reduced glycolaldehyde yield leading to speculation that glycoldehyde must have been diverted from the reaction network prior to the formation of levoglucosan.

Recently, Patwardhan et al (2009) demonstrated that all the low molecular weight compounds, including glycolaldehyde, could be produced from cellulose pyrolysis under the conditions of minimal levoglucosan degradation, which clearly suggested the competitive nature of the primary pyrolysis reactions. The mechanism suggested by them is shown in Figure 4.

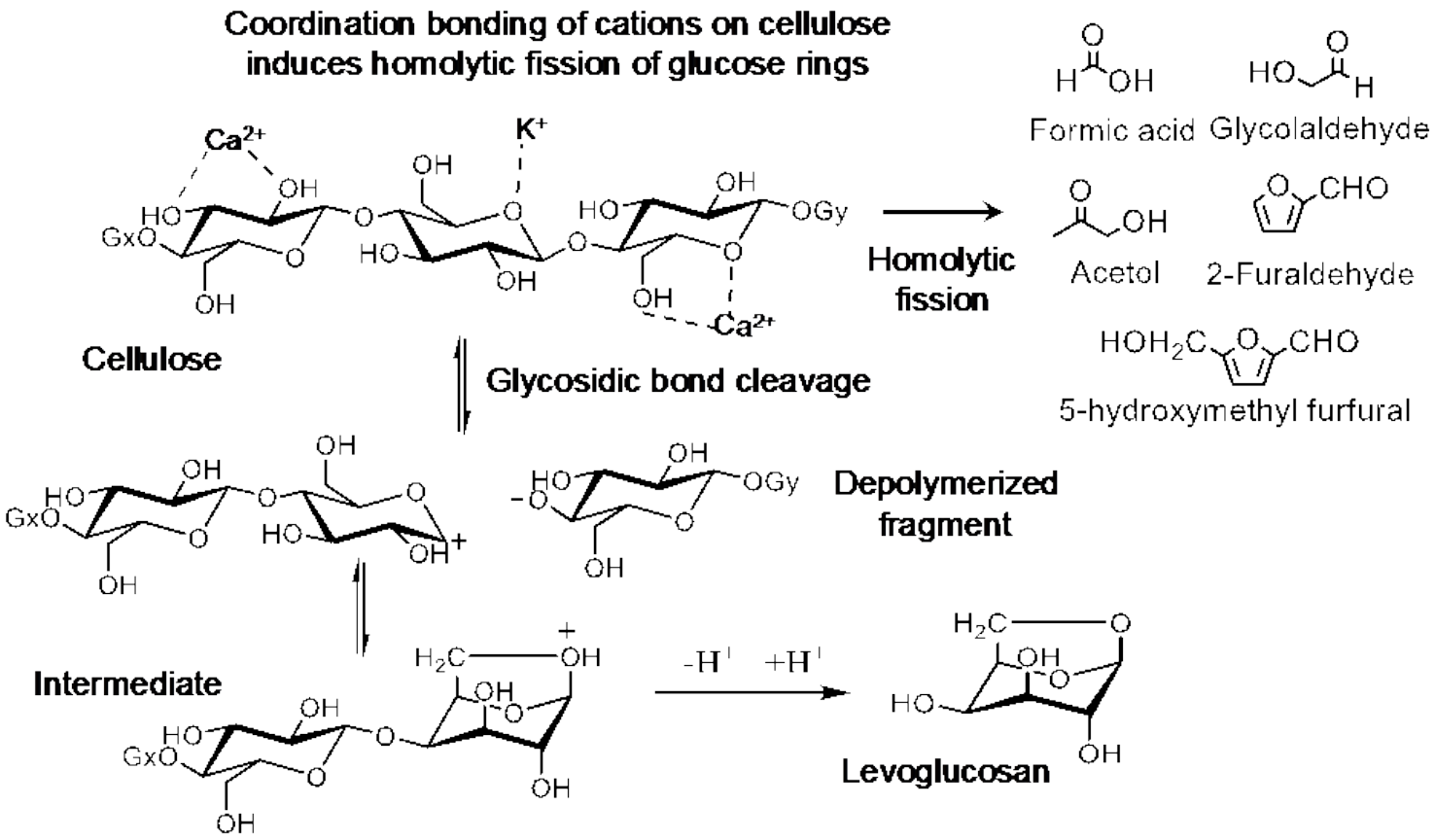

Figure 4. Mechanism of alkali catalysis on cellulose pyrolysis (Patwardhan et al. 2009)

Yang et al. (2006) proposed that the 'ionic forces' associated with the metal ions and pyranose ring interaction induces hemolytic scission of various bonds leading to different pyrolysis products. For example, scission at the C_1 or C_5 position would generate compounds containing a single carbon atom (CO2, formic acid etc), scission at the C_2 or C_4 position would produce glycoladehyde, and scission at C_3 would lead to the formation of acetol. It has been reported previously that levoglucosan is formed via heterocyclic cleavage of the glycosidic linkage.

To summarize the above hypotheses, the presence of metal ions, especially alkali and alkaline earth metals, appears to enhance the hemolytic cleavage of several bonds in the pyranose ring leading to smaller decomposition products in competition with the heterocyclic cleavage of glycosidic linkages that result in the formation of levoglucosan. Pyrolysis of

Figure 4. Mechanism of alkali catalysis on cellulose pyrolysis (Patwardhan et al. 2009)

yields because of the catalytic effect of the inherent alkali and alkaline earth metals.

2.4. Pretreatment of biomass feedstocks to improve the yield of sugars from Fast pyrolysis

Piskorz et al. (1989) showed the difference in the bio-oil composition from feedstocks with alkali and without alkali. They pretreated various cellulose samples and wood samples with mild mineral acids at the conditions of acid hydrolysis followed by a wash with distilled water. This procedure removed most of the hemicelluloses and alkali. They found that the absence of alkali increased the tar yield and reduced the char and gas yield. They also found that the bio-oil from pretreated poplar wood contained more levoglucosan (30.42 wt%) than the untreated poplar wood (3.04 wt%). In a subsequent study, they showed that most of the

potassium can be removed from woody biomass with a hot water wash while calcium requires an ion exchange with acids (Scott et al. 2001).

Brown et al. (2001) reported very high increase in the yield of levoglucosan from pretreated switchgrass. Their pretreatments involved demineralization by nitric acid wash and acid hydrolysis. They found 530% increase in the yield of levoglucosan for the demineralized samples (from 2.3 to 14.5%) and about a 960% increase in the acid hydrolyzed samples (24.2%). Though the yield of hydroxyacetaldehyde decreased drastically in the bio-oils from the pretreated feedstocks, it remained a significant component of the bio-oils. They suggested that this could be a result of residual alkali in the treated biomass feedstocks.

Fahmi et al. (2007, 2008) demineralized Lolium and Festuca grasses, switchgrass and willow by washing with deionized water. The washing removed about 70% of the alkali from the feedstocks. The samples were analyzed using a TGA and analytical pyrolysis. They found that the major alkali metals such as sodium, potassium, calcium and magnesium have a significant effect in both pyrolysis and combustion, as shown by effects on temperature of maximum degradation, rate of degradation, chemical degradation mechanisms and yields of products. They obtained increased levoglucosan yield (from 3.25 wt% to 13.5 wt%) and decreased hydroxyacetaldehyde (from 19.0 wt% to 15.8 wt%) from the washed feedstocks when compared to the raw feedstocks (Figure 5).

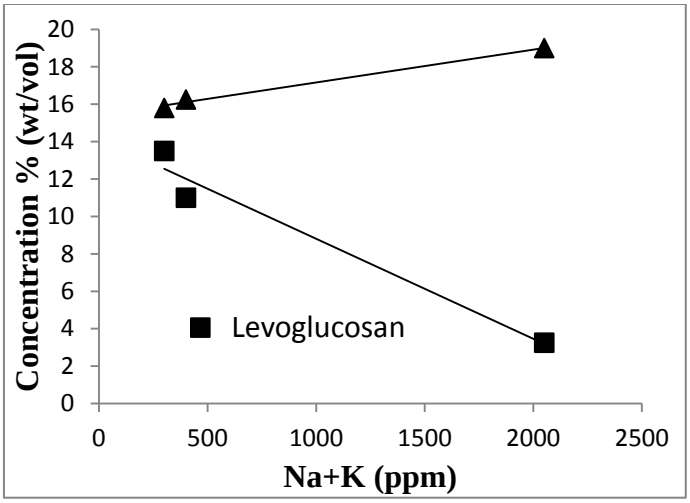

Figure 5. The yield of levoglucosan and hydroxyacetaldehyde compared to Na and K contents for washed and unwashed willow samples (Fahmi et al. 2008)

Mourant et al.(2011) showed by washing of mallee wood sample with water and a dilute acid that AAEM species exist in the wood in two different forms: water-soluble and water-insoluble but acid-soluble. The pyrolysis of the washed wood in a fluidized-bed reactor gave similar yields of bio-oil and biochar. The removal of AAEM species, especially the acid-soluble AAEM species, led to significant increases in the yields of sugars and lignin-derived oligomers, accompanied by decreases in the yields of water and light organic compounds in the bio-oil (Figure 6).

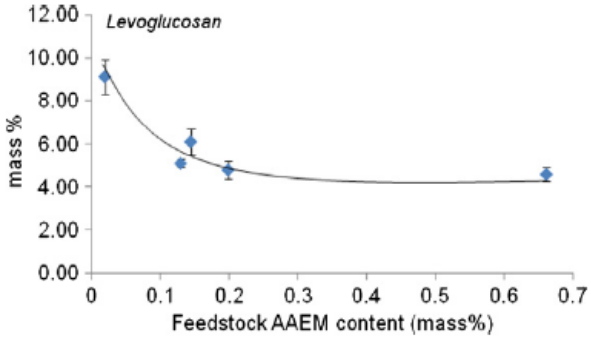

Figure 6. Yield of levoglucosan obtained by Mourant et al. from mallee wood with respect to its AAEM content (Mourant et al. 2011)

Oudenhoven et al.(2012) demonstrated that washing pine wood with an acetic aqueous solution, containing organic acids (mainly acetic acid) produced and concentrated within the pyrolysis process, prior to drying and pyrolyzing the biomass, effectively removes the alkali ions initially present in biomass (Figure 7). Subsequent pyrolysis of the feedstock resulted in increased yield of levoglucosan. To obtain the highest levoglucosan yield additional rinsing was required after acid washing, to rinse out the washing liquid containing the dissolved minerals.

They also used a simulated pyrolysis fraction to wash the biomass for comparison. Pyrolysis of the acid washed biomass resulted in an increased oil yield and a decreased water and char production. The selectivity towards levoglucosan increased strongly (17 wt% yield on biomass intake). The yield from the biomass washed with the simulated fraction was 17.6 wt% which was similar to that obtained from the washed biomass. Besides the well-known effect of alkali ions on the cellulose decomposition, the decomposition products obtained from lignin also changed.

In an effort to increase the yield of sugars from fast pyrolysis, Li et al. (2012) pretreated pinewood particles with 0.1 wt% aqueous phosphoric acid solution. The pinewood particles were immersed in an aqueous solution of 0.1 wt% phosphoric acid (sample/solution weight ratio = 1:10) and heated to 100 ◦C for 1 h in a water bath. Following phosphoric acid pretreatment, pinewood samples were washed with distilled water until reaching neutral pH to avoid residual acid in the feed. The pinewood particles were then oven dried at 105 ◦C to below 3 wt% moisture content. Washing reduced the total AAEM content (Na, K, Ca and Mg) of the feedstock from 136 ppm to 31 ppm.

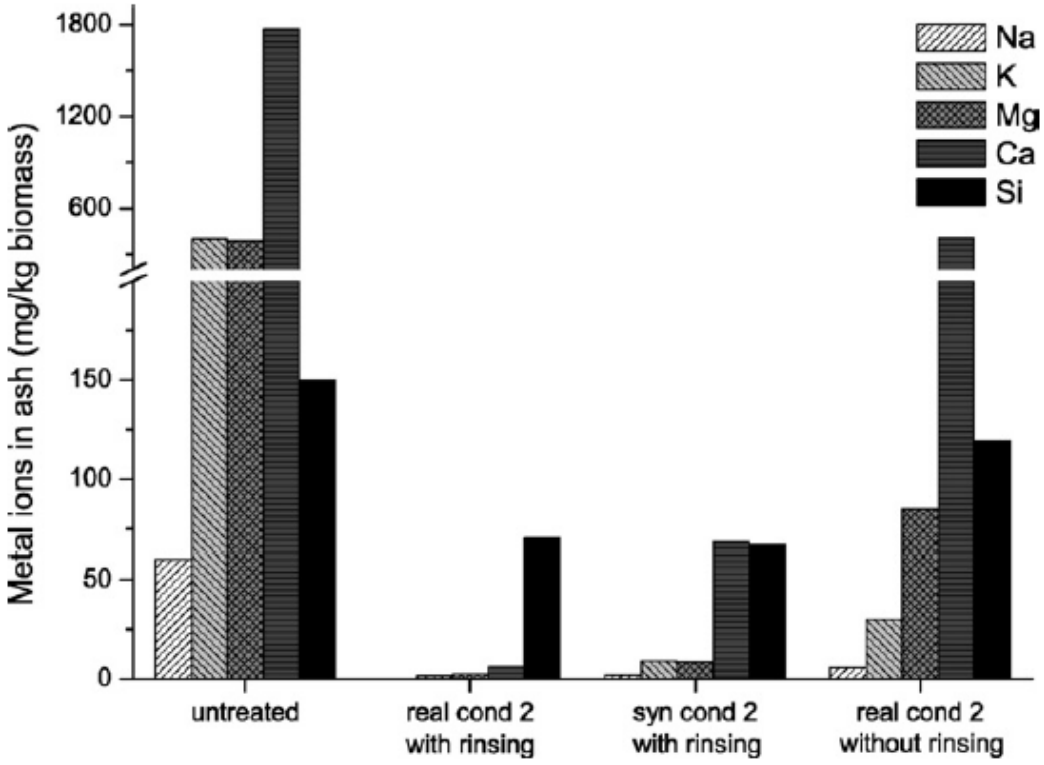

Figure 7. Concentrations of various alkali species and silicon in pine wood (on dry biomass basis) before and after different acid washing (Oudenhoven et al. 2012)

In their study, fast pyrolysis reactions of untreated and treated pinewood were conducted in an auger type pyrolysis reactor. Figure 8 shows the schematic of the pyrolysis reactor used by them.

The pyrolysis vapor then moved through the pipe into a condenser train where it was condensed to liquid bio-oil. Just prior to entry into the condensers, injection nozzles sprayed fine ambient water droplets (25°C) into the hot pyrolytic vapor stream at a spraying rate of 8 ml min^{-1}. The pyrolysis reactor, the cross pipe for passage of the pyrolysis vapors to the reactor and the injection device location are shown in Figure 8. The initially formed vapor temperature was about 30°C below the set pyrolysis temperature (450°C).

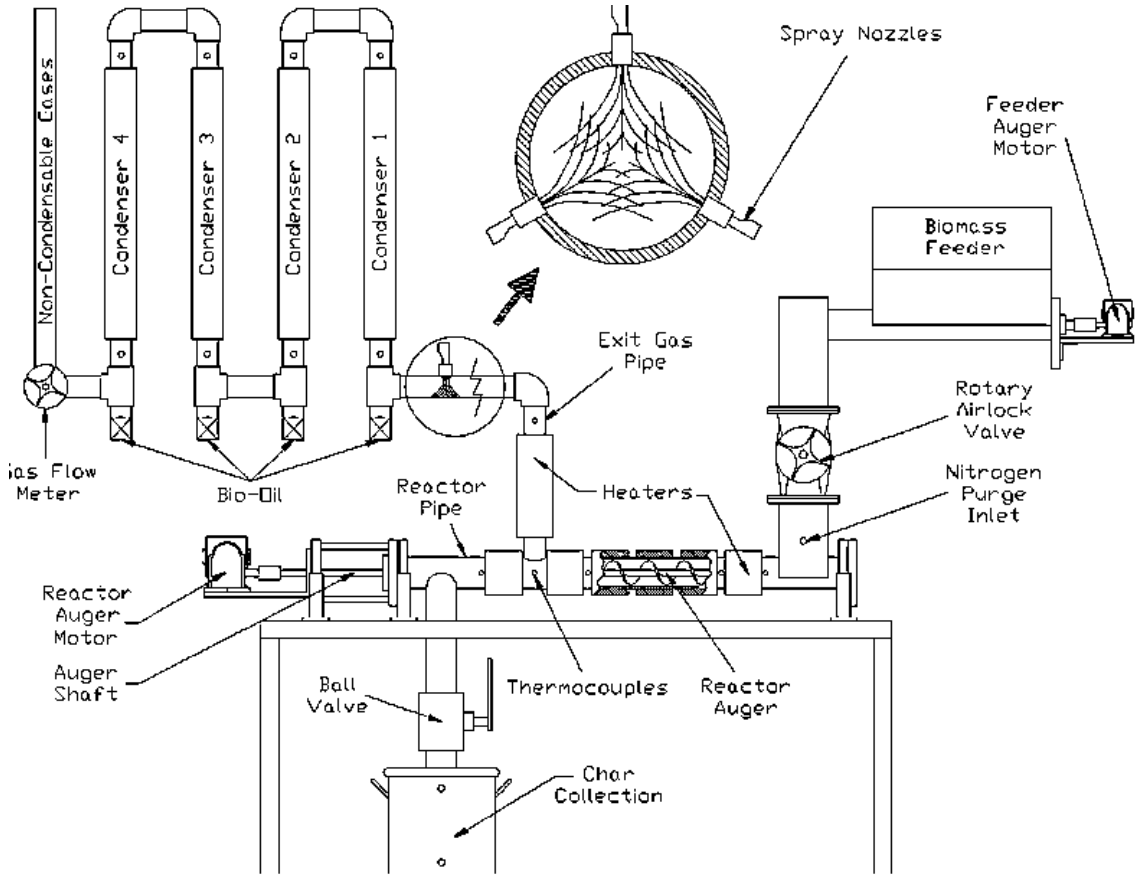

Figure 8. Schematic of the pyrolyzer reactor and the water spray equipment used by (Li et al. 2012)

As a result of direct exposure to the water spray, the initial pyrolysis vapor was quenched rapidly and cooled to below 300°C. The quenched pyrolysis vapor exited the reactor pipe into a water-cooled first condenser where its temperature dropped to about 75–80°C. A second condenser lowered the temperature to 25–35°C and aerosol (fog-like) water continued into the third and fourth condenser maintained almost the same temperature as the second condenser (25–35°C). Liquid condensate was collected from the exits of all four

condensers and combined to be analyzed as a whole bio-oil sample. The control and pretreated feedstocks were pyrolyzed with and without the water spray.

The pretreated pinewood with spray gave the significantly highest concentrations of levoglucosan in the bio-oil organic portion (16.43 wt%), followed by pretreated pinewood without spray of 12.57 wt% of levoglucosan (Figure 9).

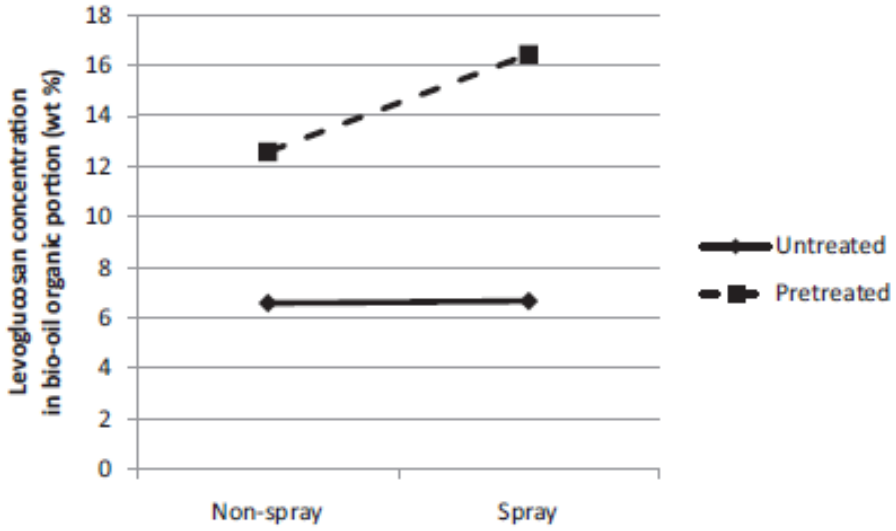

Figure 9. Yield of LG from untreated and pretreated wood obtained by (Li et al. 2012)

Both treatments of untreated pinewood with spray and untreated pinewood without spray had the significantly lowest concentrations of levoglucosan in the bio-oil organic portions (6.58 wt% for untreated pinewood without spray; 6.66 wt% of levoglucosan for pretreated pinewood without spray).

The spray treatment was not effective on untreated pinewood in terms of increasing levoglucosan yield. They concluded that the ineffectiveness of the spray might be because untreated pinewood contained high mineral content compared to pretreated pinewood and

those minerals had been proved to serve as catalyst during fast pyrolysis causing levoglucosan decomposition. In combination with dilute acid pretreatment, addition of water spray to the pyrolysis vapor significantly increased levoglucosan concentration by 30.7% in the resultant bio-oil organic portion compared to the yield for dilute acid pretreatment alone.

The increase in LG concentration in the organic portion of the bio-oil by about 30% looks impressive, but on the basis of the wt% of biomass used, the yields did not show much promise. The yields were:

- Untreated : 3wt%
- Untreated with spray : 3wt%
- Treated without spray : 6wt%
- Treated with spray : 7wt%.

The explanation they gave for the increased yield of LG was that the water spray quenched the pyrolysis vapor and suppressed the decomposition of levoglucosan into lower molecular weight species in both the vapor stream and during condensation. On the contrary the same could be happening from the suppression of LG polymerization into oligomers as described by (Kawamoto et. al. 2003, 2009).

Hassan et al. (2012) carried out similar pretreatments and a membrane separation of the sugars from the resultant bio-oil. Biomass was mixed with an aqueous solution of phosphoric acid at various ratios. The concentration of phosphoric acid in this study ranged, 1–5 wt% based on the weight of biomass, and the ratio of biomass to pretreatment solution was (1:3, 1:5 and 1:7). Biomass and pretreatment solution were mixed in a mixer for 30 min at room

temperature to allow complete mixing of wood and pretreatment solution. Biomass slurry was then transferred to a heat resistant polypropylene plastic bag and placed in an oven for pretreatment at 100°C for an hour. After pretreatment, biomass was filtered from the pretreatment solution using 40 mesh size stainless steel container, washed with distilled water and dried at 100°C in a drying oven till the moisture content reached 5–7%. After drying, the biomass samples were kept in sealed plastic buckets until used for pyrolysis.

The above phosphoric acid treatment of green pinewood, which is similar to dilute acid wash, prior to fast pyrolysis process considerably increased the sugar yield from15% without pretreatment to 25% at the optimum pretreatment conditions (phosphoric acid concentration, 1% and pretreatment liquor ratio 1:5) in the aqueous fraction of the bio-oil. However, the quantity of the aqueous fraction of the bio-oil produced from the whole bio-oil is unclear from their paper. Hence the amount of sugars produced expressed as wt% of the biomass pyrolyzed could not be determined. They applied a solvent separation technique to remove the lignin derivatives from the sugar fraction and then separated the sugars using a membrane. They found that the solvent separation step enhanced the selectivity of the membrane towards monosugars.

Though the above studies with demineralized feedstocks provided valuable results on the effect of alkali on biomass pyrolysis and proved that minerals can be removed by simple water wash or mild acid wash, it is impractical to wash biomass feedstocks before pyrolysis. Biomass can hold a lot of water when washed and removing this water can be energy intensive and too expensive for a process that is intended to produce fuels and chemicals.

Due to the same reasons, such methods of demineralization and pyrolysis are currently not in commercial use for improving the yield of sugar or bio-oil quality.

On the other hand, infusing mineral acids at low concentrations (from 0.5 to 10 wt% of biomass) has been shown to be effective in increasing the yield of leveoglucosan and other anhydrosugars. It is notable that these works have considered the effect of acid independent of the alkali catalyzed pyrolysis.

Dobele et al. (2003) infused phosphoric acid into various cellulose feedstocks at concentrations of 0.05-3.0% by weight. They mixed the samples with aqueous acid solution and then filtered the solution and the sample was dried. The amount of acid absorbed by the sample was determined by titrating it with sodium hydroxide. On pyrolysis of these samples, they found that the yield of levoglucosan and levoglucosenone (LGnone) increased to certain concentrations of acid and then decreased (Figure 10).

They suggested that the mechanism by which the acids increase the levoglucosan is predominantly acid catalysis and reduction in the degree of polymerization of the cellulose. They also suggested that the ability of lignin to scavenge the free radicals cause the increase of levoglucosan yield and when acid concentrations beyond 2 wt%, this activity is decreased and then the pyrolysis proceeds via dehydration reactions leading to decrease in LG and increase in levoglucosenone. These hypotheses are not proven beyond doubts and are discussed later in the study. It is evident that the authors have not looked into the effect of alkali on pyrolysis and the possible interaction between the alkali and acid.

Dobele et al. (2005) in a later work used phosphoric acid and an iron catalyst in order to increase the yield of levoglucosan and other anhydrosugars. They infused iron as ferric sulfate solution. They concluded that theacid and ferric sulfate increase the yield of levoglucosan by catalyzing the cellulose depolymerization. In this study also, they have not looked into the alkali content of the feedstocks and the possible effect of alkali catalysis.

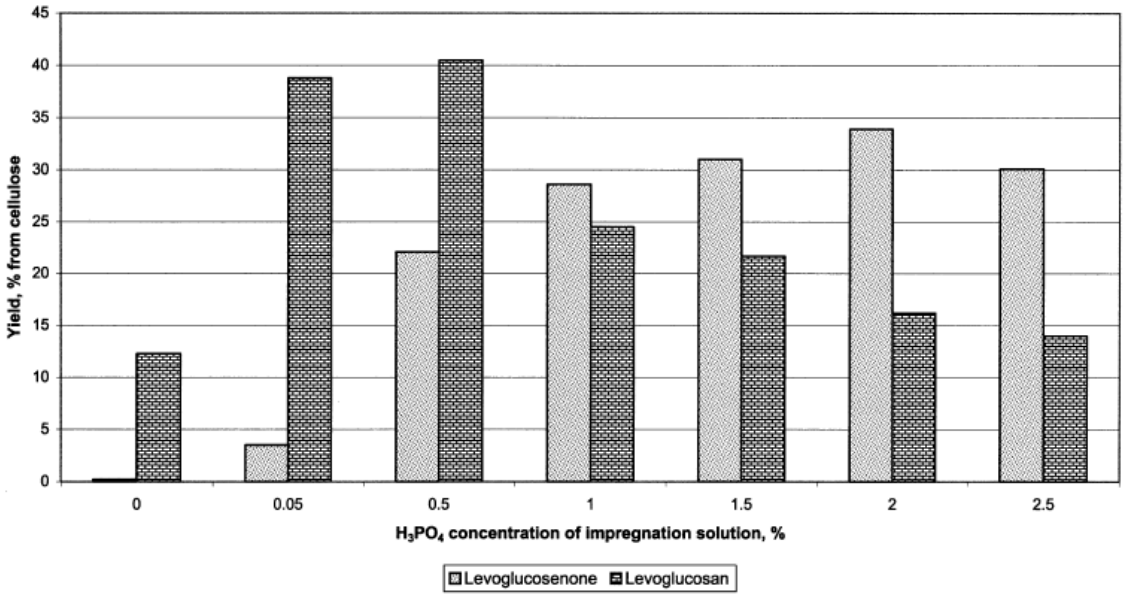

Figure 10. The yield of levoglucosan and levoglucosenone obtained by Dobele et al. from cellulose treated with phosphoric acid (Dobele et al., 2003)

Contradicting results from that of Dobele et al. (2003) were reported by Wang et al. (2006). They pretreated cellulose with hydrochloric acid and sulfuric acid by soaking in acid solutions for 2 hours. Samples were washed with deionized water and dried. On pyrolysis of these samples, they found that acid wash decreased the degree of polymerization of cellulose and altered the product distribution of cellulose pyrolysis by dehydration and cross linking reaction. The existence of high concentration of acid catalyzed the dehydration and cross

linking reaction intensively and led to higher production of char and water. It also caused lower production of tar. The yield of levoglucosan decreased with an increase of acid concentration. They concluded that acid residue had an intensive catalysis on the dehydration and cross linking reaction, which led to lower production of levoglucosan.

Similar results were published by Fu et al. (2008) after they carried out pyrolysis of phosphoric acid treated raw and chromated copper arsenate treated pine wood feedstocks (Figure 11).

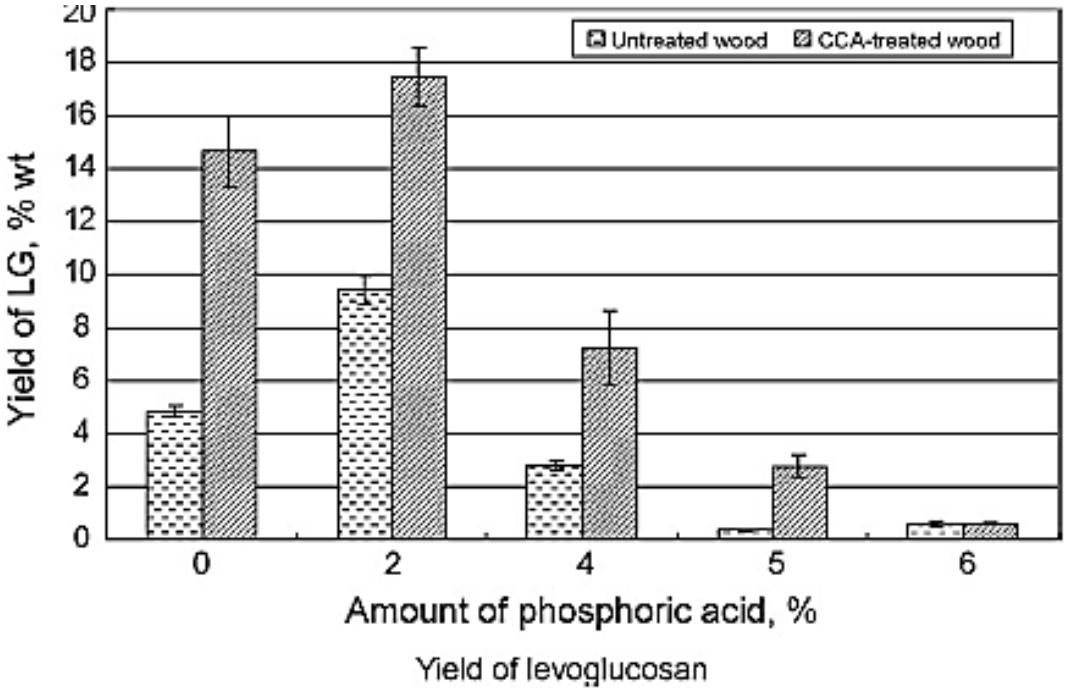

Figure 11. The yield of levoglucosan obtained by Fu et al. from wood and CCA treated wood further treated with phosphoric acid (Fu et al. 2008)

They found pretreatment of wood with phosphoric acid significantly alters the pyrolysis kinetics and products distribution leading to lower yields of tar and an increase in char formation. The yield of LG was found to increase with increase in acid concentration up to 2 wt% and then decrease in the presence of higher concentrations of phosphoric acid

(Figure 11). On the other hand, the yield of LGnone increased with increase in acid concentration for the range tested (Figure 12). However, the authors have not provided any reasoning for this result.

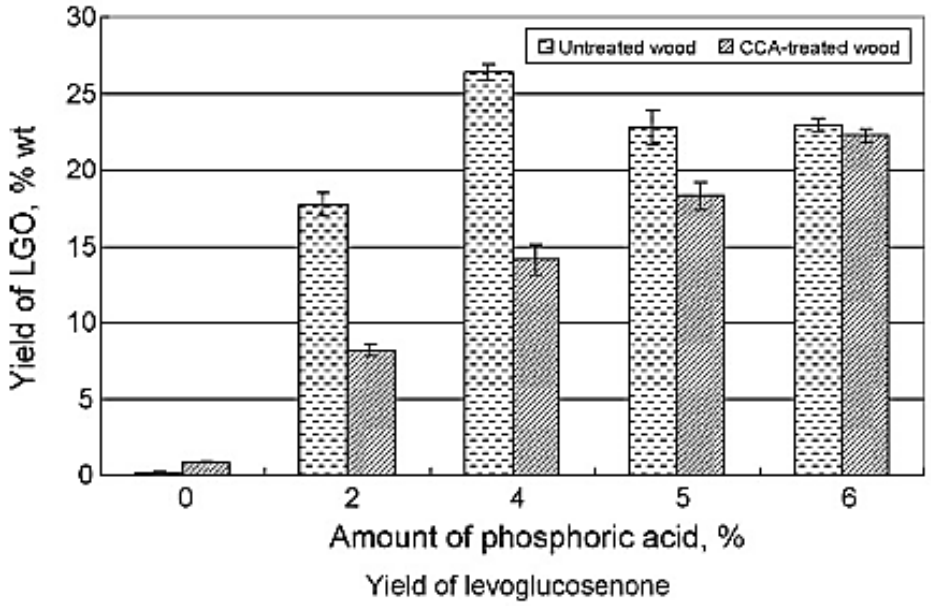

Figure 12. The yield of levoglucosenone obtained by Fu et al. from wood and CCA treated wood further treated with phosphoric acid (Fu et al. 2008)

From the literature, it is evident that pretreatment studies were carried out in order to understand their effects on bio-oil composition. While some of them looked into the possibility of increasing the yield of a particular compound such as levoglucosan, others were looking at the overall yield and quality of bio-oil.

Mineral acid infusion has been shown to increase the yield of levoglucosan from biomass at lower concentrations and that of levoglucosenone at higher concentrations. The conventional view is that the acids are breaking down the cellulose chain thereby reducing the degree of

polymerization and then catalyzing the breakage of the glycosidic bonds in cellulose causing the increase in the yield of levoglucosan. However, there is no mention of the catalytic effect of alkali on biomass pyrolysis in any of the above works that can be a factor in the effectiveness of pretreatments.

As discussed before, alkali in biomass catalyze the defragmentation reactions that produce light oxygenates thereby reducing the levoglucosan yield. By making the AAEM inactive or less active using the pretreatments it is possible to improve the yield of sugars. The researchers who studied the pyrolysis of acid infused biomass feedstocks totally ignored the possibility of acids acting on the alkali because of the common notion that the AAEM in biomass existed as salts that are stable enough not to react with mineral acids. Likewise, it appears that previous researchers assumed that as long as AAEM cations were present in the biomass, they would be catalytically active regardless of the nature of their complexion with anions (Patwardhan et al. 2009). Hence, it is important and intriguing to understand the mechanism of acid activity on biomass pyrolysis if we are to develop a process to increase the yield of levoglucosan and other anhydrosugars.

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CHAPTER 3. EXPERIMENTAL METHODS AND MATERIALS

3.1. Introduction

In order to understand the effects of acid infusions on pyrolytic yields of anhydrosugars pyrolysis experiments were performed on a micro-scale batch pyrolyzer and on bench scale continuous pyrolysis reactors.

3.2. Micro-scale batch pyrolysis

3.2.1. Materials

Both woody biomass (red oak and loblolly pine) and herbaceous biomass (switchgrass and cornstover) were investigated in this study, which provided a wide range of naturally occurring AAEM concentrations. Typically, woody biomass contains less than 500 ppm of total AAEM while herbaceous biomass can contain more than ten times this amount. In addition, model compounds made from cellulose also were used to study the underlying mechanisms.

3.2.1.1. Structural Composition of Biomass: The structural composition was determined by extracting the cell wall and subsequent analysis of cellulose, hemicellulose, and lignin content. Five hundred grams of each biomass sample were dried and milled to 212-500 μm size. The plant material was homogenized in 80% (v/v) ethanol using a Polytron Homogenizer (Fisher, USA) at high speed for 2-3 minutes. Homogenate was heated for 1h at 80°C, cooled down to room temperature and centrifuged at 12000G for 30 min.

Pellets were resuspended in 80% ethanol and the procedure was repeated. Pellets were washed three times with 85% acetone and air dried. Dry pellets were suspended in 0.5% aqueous sodium dodecyl sulfate (SDS) overnight, the residue was recovered and washed with water by filtration, washed with a 1:1 mixture of chloroform and methanol, rinsed with acetone and air-dried. Resulting cell wall material (CW) was used for analyses.

Cellulose content was determined by treatment of CW (10 mg) with acetic-nitric reagent (80% acetic acid: concentrated nitric acid, 10:1). Unhydrolyzed pellets were washed several times with water followed by acetone, air-dried and weighed. Cellulose content was calculated in percentage of total cell wall. The hemicellulose content was estimated by hydrolysis of CW with 2M trifluoroacetic acid (TFA). Unhydrolyzed pellets were washed several times with water followed by acetone, air-dried and weighed. Acid soluble hemicellulose content was calculated in percentage of total cell wall.

Lignin content was determined using the acetyl bromide assay according to (Fukushima et al. 2004). One milligram of CW was placed in a glass vial and 2 ml 25% acetyl bromide was added. Samples were incubated at 50°C for 2 hours, with occasional mixing. After cooling, 1 ml of reaction mixture was transferred to a 2 ml centrifuge tube containing 2 ml of 1 N sodium hydroxide, and then 1 ml of 1 N hydroxylamine hydrochloride and 4 ml of acetic acid were added. After shaking the volume was made up to 10 ml with acetic acid. Optical density at 280 nm was measured against blanks (all reagents without cell wall sample), which contained all reagents except cell walls. The calculation of lignin content was carried out as outlined in Fukushima et al. (2004). Table 2 shows the structural composition of each

feedstock. Samples were tested in duplicates and the uncertainties shown are standard deviations.

3.2.1.2. AAEM Content of Biomass: The cation content of the feedstocks was determined using an Inductively Coupled Plasma Spectrometer (ICP) after preparing the biomass sample using the standard acid digestion method ASTM D6349. The measured AAEM content of each feedstock is listed in Table 2. Chlorine content of the feedstocks was determined using ion chromatography. Moisture was determined using a Mettler Toledo Thermogravimetric Analyzer (TGA) by subjecting 10 mg of sample to a nitrogen atmosphere at 105°C for 10 minutes. The resulting mass loss was assumed to be moisture. All the above tests were run in duplicates and standard deviations were determined. As shown in Table 3.1 the pretreated feedstocks were dried to similar moisture contents.

Six acids (phosphoric, sulfuric, nitric, hydrochloric, acetic and formic acids) were infused into the biomass at five different loadings (0.5, 1, 2, 5, and 10 wt%). Acid was dissolved into 15 g of water before mixing with a 5 g sample of biomass in a 250 mL beaker to insure uniform infusion of the acid into the biomass. The damp biomass was then dried in an oven at 50°C to the same moisture content as the original biomass, which took 20 hours.

3.2.1.3. Model Compounds: Some experiments were performed with model compounds to delineate the complex reactions between AAEM cations and cellulose. Commercial cellulose of 50 μm particle size obtained from Sigma-Aldrich that had an ash content of less than 0.01 wt% was infused with the respective salts and acids by dissolving the salts and acids in water and mixing with cellulose using the same procedure previously described for biomass

Table 2. Structural composition, concentrations of AAEM and chlorine, and moisture content of biomass feedstocks

Parameter Tested	Switchgrass		Cornstover		Red Oak		Loblolly Pine	
	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev
Cellulose (wt%)	33.26	2.03	28.89	2.19	41.01	0.2	32.06	0.31
Hemicellulose (wt%)	35.29	2.64	39.21	0.79	42.61	1.92	31.83	1.87
Lignin (wt%)	11.54	0.89	11.69	1.25	13.02	1.83	15.61	1.58
Potassium (ppm)	3488	71	7309	284	570	5	420	9
Sodium (ppm)	273	5	188	4	179	7	177	2
Calcium (ppm)	2752	51	2715	55	809	154	1290	84
Magnesium (ppm)	1409	33	1461	35	168	2	405	14
Chlorine (ppm)	3901	43	1782	11	407	2	355	3
Moisture in Control (wt%)	3.25	0.09	4.16	0.24	2.8	0.16	4.17	0.11
Moisture in Pretreated (wt%)	3.33	0.13	3.79	0.04	2.66	0.21	3.6	0.11

feedstocks. Ten potassium salts (acetate, chloride, formate, nitrate, phosphates, and sulfates) were separately doped to the cellulose. Four mineral acids (hydrochloric, nitric, sulfuric and phosphoric acids) and two carboxylic acids (formic and acetic acids) were used for infusion. The samples were dried in an oven at 50°C for 20 hours.

3.2.2. Methods

The micro-scale experiments were carried out on an automatic micro-pyrolyzer. The greatest advantage with such a pyrolyzer is its ability to automatically run about 24 samples per day thereby offering higher sample turnover when compared to a bench-scale pyrolysis reactor that requires about a week to run one sample.

The micro-scale pyrolyzer used in this study was a Frontier Lab Double Shot Micropyrolyzer 2020iS coupled to a Varian 450 Gas Chromatograph (GC). A Varian 320 Mass Spectrometer (MS) was used for product identification while a Varian Flame Ionization Detector (FID) was used for species quantification. A Frontier Lab 2020iS micro-pyrolyzer was used in this study. It consists of a quartz tube sitting inside a micro-furnace that is calibrated for temperatures from room temperature to 800°C. There is continuous flow of sweep gas through the quartz tube which was helium in the present study. The micro-pyrolyzer sits on top of the GC injector and the helium flows into the GC injector through a needle connected to the bottom of the quartz tube. The samples to be pyrolyzed can be inserted automatically into the quartz tube using the specially made auto-sampler and sample

cups that are made of deactivated stainless steel. Samples to be pyrolyzed are weighed along with the cup using a microbalance. Usually 400-600 micrograms of sample is taken in the cup. The cups with samples are loaded on the auto-sampler that can hold up to 44 cups at a time. A schematic of the equipment is given in Figure 13.

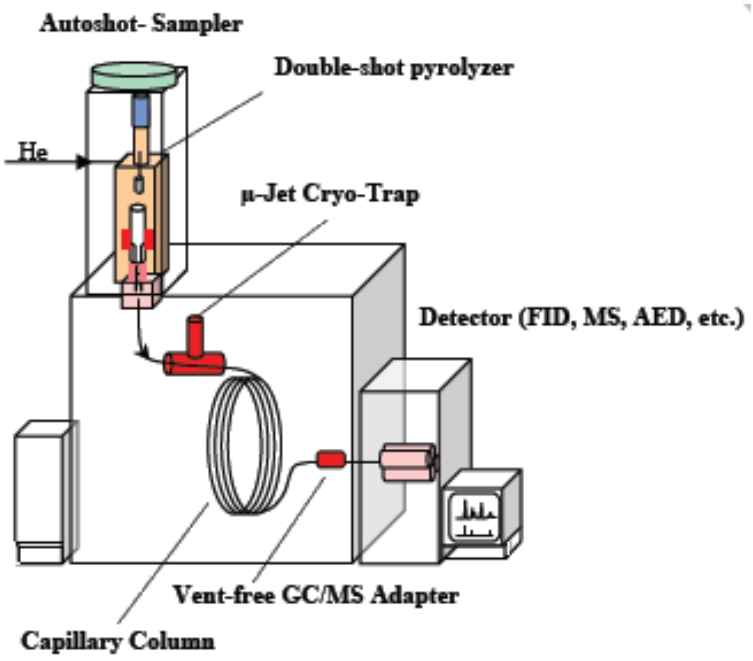

Figure 13. Schematic of micro-pyrolyzer/GC/MS

With the help of the micropyrolyzer software, a designated cup can be inserted into the quartz by the autosampler. The sample gets pyrolyzed instantly as the thermal inertia of the steel cup is very low in comparison to that of the furnace.

The micropyrolyzer (MPy) is hooked to a gas chromatograph (GC) and mass spectrometer (MS). The pyrolysis vapors from the MPy flows directly into the GC and gets separated into its components by the capillary column of the GC so that the MS can detect the constituent compounds. The GC/MS is generally used for the identification and

quantitation of volatile and semi-volatile organic compounds in complex mixtures. It can be used for the determination of molecular weights and (sometimes) elemental compositions of unknown organic compounds in complex mixtures.

In order to analyze on the GC/MS, organic compounds must be in solution for injection into the gas chromatograph. The solvent must be volatile and organic (for example, hexane or dichloromethane). Depending on the ionization method, analytical sensitivities of 1 to 100 µg per component are routine. Sample preparation can range from simply dissolving some of the sample in a suitable solvent to extensive cleanup procedures using various forms of liquid chromatography. In addition to sample preparation time, the instrumental analysis time usually is fixed by the duration of the gas chromatographic run, typically between 20 and 100 min. Data analysis can take another 1 to 20 hr (or more) depending on the level of detail necessary.

Gas chromatography involves a sample being vaporized and injected onto the head of the chromatographic column (Figure 14). The sample is transported through the column by the flow of inert, gaseous mobile phase. The column itself contains a stationary phase which is adsorbed onto the surface of an inert solid. The carrier gas must be chemically inert. Commonly used gases include nitrogen, helium, argon, and carbon dioxide. The choice of carrier gas is often dependent upon the type of detector which is used. The carrier gas system also contains a molecular sieve to remove water and other impurities.

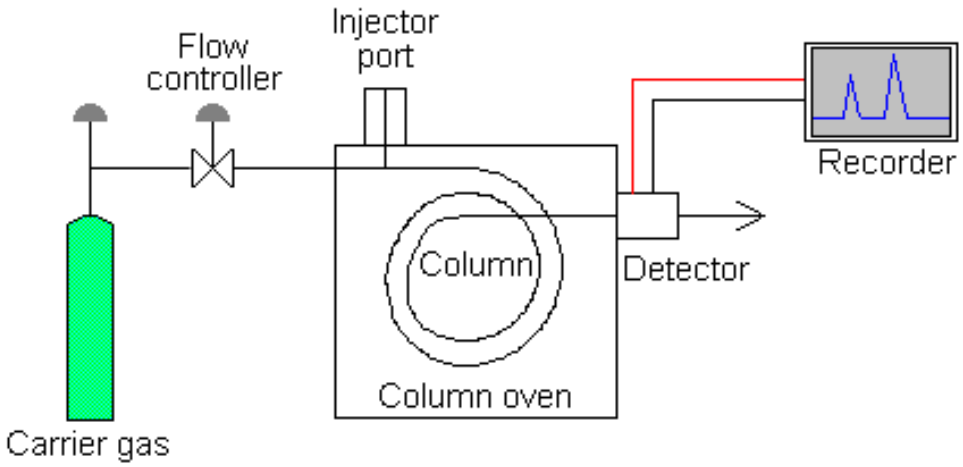

Figure 14. Schematic of GC/MS

In this study a Bruker (previously Varian Inc.) 450 GC/320 MS set up was used to analyze the pyrolysis vapors generated by the Frontier micro-pyrolyzer. The capillary column used was a Frontier Ultra Alloy deactivated stainless steel column (UA 1701, medium polarity, 60m length, 0.25 mm ID, 0.25 μm film thickness). The MS used was a single quadrapole 320 MS. Throughout the experiments, only electron ionization was used.

In the GC method, the column oven temperature range used was from 45-270°C with a ramping rate of 4°C. The total run time of the sample was 60 minutes. The MS was set to detect ions from 45 to 650 Daltons.

Experiments were performed with both cellulosic biomass that contained a wide range of naturally occurring AEEM levels and pure cellulose to which metal cations were added.

Sample weights in the range of 450-550 μg produced resolvable spectra for compounds of interest while minimizing mass transfer effects. Pyrolysis was carried out at 500°C with the interface line between the pyrolyzer and GC maintained at 320°C to prevent condensation of vapors. The volatile products were swept from the micropyrolyzer directly to the 300°C GC injector using 1 ml/min of helium as carrier gas. The typical residence time in the micropyrolyzer ranged from 20-50 ms. The column used was a Frontier Ultra Alloy 1701 (60 m length, 0.25mm ID, 0.25μm film thickness with a stationary phase of 14% phenyl and 86% polysiloxane, medium polar). The column oven started at 45°C and ramped to 300°C at 5°C/minute. A Varian 320 Mass Spectrometer operating in the range of 45 to 650 m/z was used for chemical identification. Once the important compounds in the pyrolysate were identified, a Varian flame ionization detector (FID) was used in subsequent experiments for the quantification of those compounds. Results are reported as means of triplicate runs with uncertainties estimated as one standard deviation about the mean.

The chromatograms from the GC/MS show hundreds of compounds in the volatile fraction produced by the pyrolysis of the feedstock. For ease of comprehension, forty of the major compounds found in the pyrolysis vapor as reported by (Branca et al. 2003) were identified and classified into light oxygenates, anhydrosugars, furans and phenols. The light oxygenates consist of hydroxyacetaldehyde, formic acid, acetic acid and ketones. The anhydrosugars consist of levoglucosan (LG), levoglucosenone (LGnone) and glucofuranoses. Furfural and other furan compounds were classified as furans while all the phenolic compounds were classified as phenols.

3.2.2.1. Method for the Study of Temperature Dependence of LG: In the experiments to investigate the temperature dependence of LG yield, the feedstocks of switchgrass, red oak, corn stover and loblolly pine were infused with sulfuric and phosphoric acids using the same method as described above. 5g each of them were pretreated with phosphoric and sulfuric acids separately by diluting the acid with deionized water and wetting it. The amounts of phosphoric and sulfuric acids used are shown in Table 3. These were the optimum amounts to obtain the maximum yields of LG as determined from the initial micro-scale study. The pretreated feedstocks were dried in an oven at 50°C for 20 hrs.

Table 3. The amount of acid added to biomass feedstocks to obtain Maximum yield of LG

Feedstock	Amount of acid added (wt%)	
	Phosphoric	Sulfuric
Switchgrass	2.00	1.75
Red Oak	0.60	0.40
Corn Stover	4.00	3.00
Loblolly Pine	0.90	0.60

Analytical pyrolysis was carried out on a micropyrolyzer/GC/FID system at various temperatures. Each sample was pyrolyzed at 300, 350, 400, 450 and 500°C separately with the interface line between the pyrolyzer and GC maintained at 320°C to prevent condensation of vapors. Same instrumentation as described above was used for the analytical pyrolysis. The chromatograms were analyzed only for the quantification of the anhydrosugars. Results are reported as means of triplicate runs with uncertainties estimated as one standard deviation about the mean.

3.4. Continuous pyrolysis reactor experiments

3.4.1. Materials

Biomass for the continuous pyrolysis experiments was ground using a Retsch Type SM2000 Heavy-Duty Cutting Mill with a 750μm screen. The resulting ground feedstock was sieved using a W.S. Tyler Ro-Tap sieve shaker with screens that allowed separation of the desired size range of 212-500μm.

The method of acid infusion into the biomass used in the batch micro-scale experiments was scaled-up to prepare the 3 kg quantities of biomass needed for continuous pyrolysis experiments. 12 g of sulfuric acid was diluted in 9 kg of water and mixed with ground biomass using a paddle mixer in a five-gallon plastic pail. The wet biomass was dried in an oven at 50°C for about 5 days with frequent turning and homogenizing to achieve a final moisture content of 7.99 wt% (close to the moisture content of the control feedstock, which was 8.94 wt%).

3.4.2. Methods

Two kinds of continuous flow pyrolyzers were used in the experiments. The first was a laboratory-scale fluidized bed pyrolyzer that consisted of a biomass feeder, a fluidized bed reactor, two particulate cyclones in series, and a multi-stage bio-oil recovery system. The original configuration of the reactor is shown in Figure 15.

The modified configuration used for the present study which is different from the original configuration in the bio-oil collection system is shown in Figure 16. The biomass feeder consisted of a hopper pressurized with nitrogen to about 20 kPa to prevent oxygen entering

the system. An injection auger transported approximately 100 g/hr of biomass from the hopper into the reactor. Nitrogen was injected into the biomass feeder at 2 SLPM (standard liters per minute) to prevent the backflow of hot gases and purge the biomass feeder. The fluidized bed reactor was constructed from a 316-stainless steel tube, 0.30 m long and 38.1 mm in diameter. Approximately 100 g of sand with average particle size of 0.512 mm was used as fluidization media.

The reactor was fluidized with 8 SLPM of nitrogen (a very high flow rate of nitrogen is essential for the fluidization of the sand and biomass which is 100 SLPM/kg of biomass). Gas residence time between the surface of the fluidized bed and the inlet to the cyclones was approximately 0.5 s. Further details on the construction of the pyrolyzer are found in (Kasperbauer 2009).

The bio-oil collection system in the original configuration had two water cooled condensers followed by an ESP and an ice bath. On the other hand, the modified system utilized liquid nitrogen to quench the pyrolysis vapors, which were then directed to an electrostatic precipitator (ESP). The quench operated at 90°C in order to form aerosols from the heavier bio-oil compounds while preventing the majority of the water and light compounds from condensing into the first stage fraction. A shell and tube heat exchanger operated at a wall temperature of -10°C was used to condense the remainder of the bio-oil vapors including much of the water and light oxygenates. A more detailed description of the bio-oil collection system can be found in Daugaard et al. (2011).

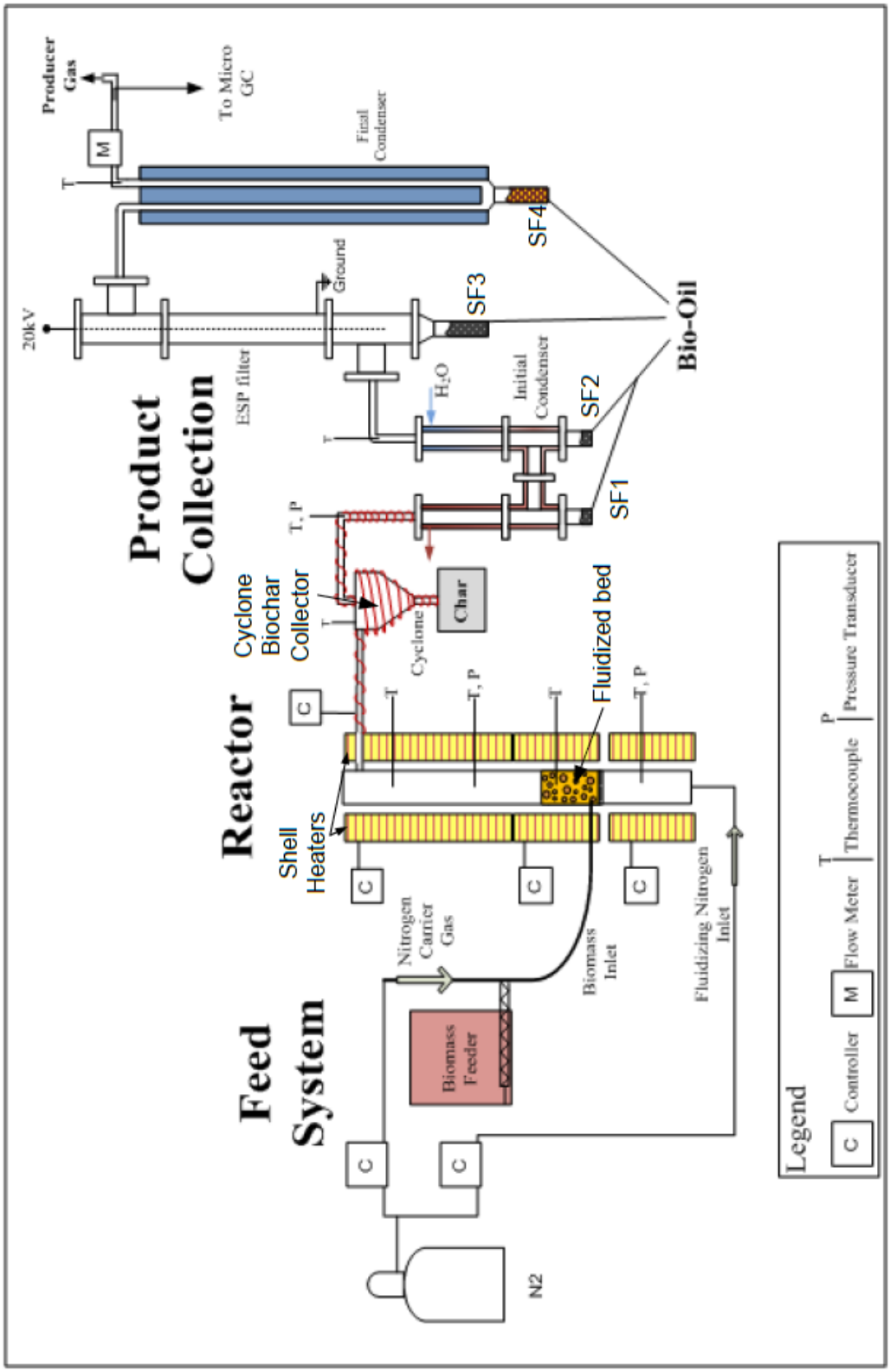

Figure 15. Process-flow diagram of fluidized bed pyrolysis reactor and product collection (Kasperbauer 2009)

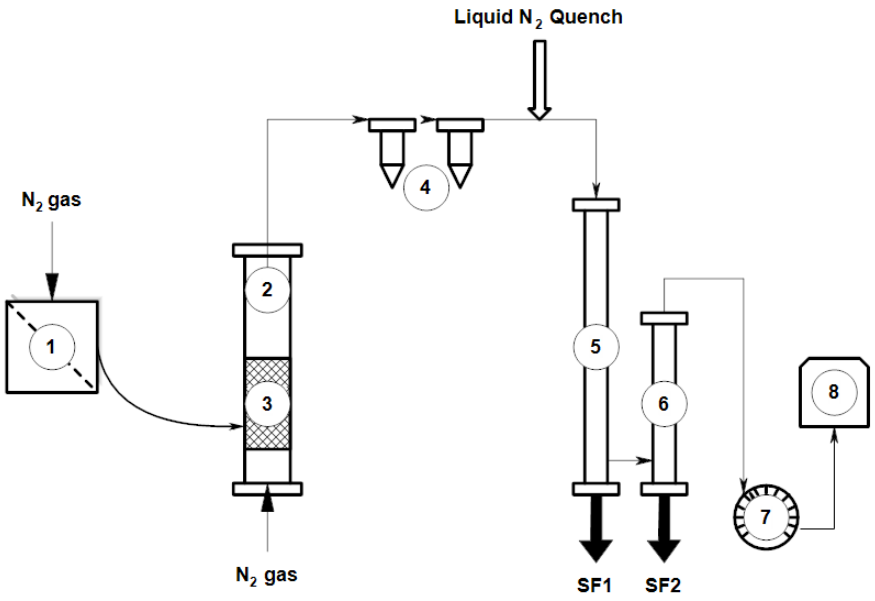

Figure 16. Schematic of the fluidized bed reactor: 1. Biomass Feeder; 2. Fluidized Bed Reactor; 3. Sand Bed; 4. Cyclone Char Separators; 5. ESP: Electrostatic Precipitator; 6. Condenser; 7. Non-condensed Gas Flow-meter; and 8. Micro GC.

The second continuous flow pyrolyzer was a laboratory-scale auger pyrolyzer consisting of a biomass feeder; a heat carrier system; a dual-screw auger reactor, and a bio-oil recovery system. The original configuration of the reactor is shown in Figure 17 and the modified configuration used in this study which is different in the heat carrier system is shown in Figure 18. The biomass feeder consisted of a hopper and an injection auger that transported 0 to 1.0 kg/hr of biomass to the reactor.

The heat carrier system consisted of a hopper to hold 0.5 mm nominal diameter steel shot used as the heat carrier media. In the original system, the heat carrier was heated in a vertical heater tube followed by a metering auger. In the modified system two horizontal augers operated in series and wrapped in heating tape to raise the temperature of the steel shot to 550° C as it is conveyed to the pyrolysis reactor.

The steel shot feed rate could be varied from 0 to 20 kg/hr by varying the speed of the conveying augers. The pyrolysis reactor consisted of long, steel trough containing two counter-rotating augers. Biomass was dropped into the “front end” of the trough and hot steel shot added just downstream of this location. The dual augers facilitated efficient mixing of biomass and steel shot and the rapid heat transfer between the two.

At the back end of the reactor the steel shot and the char produced from the pyrolyzed biomass exited the reactor and dropped into a char catch. The heat carrier augers, the biomass feed system and the pyrolysis reactor were slightly pressurized with nitrogen gas to prevent air infiltration. This gas flow rate was in the range of 3 to 5 SLPM (in this case the flow rate in various experiments were in the range of 6 to 20 SLPM/kg of biomass).

Pyrolysis vapors were swept out of the reactor into two series cyclone separators that removed approximately 99% of char particles entrained in the gas flow. Pyrolysis vapors and aerosols in the gas flow then passed to the bio-oil recovery system, which consisted of two stages of condensation, an electrostatic precipitator (ESP), and a final stage of condensation.

The first condenser was kept at a wall temperature of 60-65°C to collect “heavy ends” while the second was kept at 10-15°C to collect water and “light ends.” The ESP was kept at room temperature (20-25°C) to recover aerosols from the gas stream. The third condenser was placed in an ice bath with wall temperature of about 0°C to assure complete collection of condensable compounds

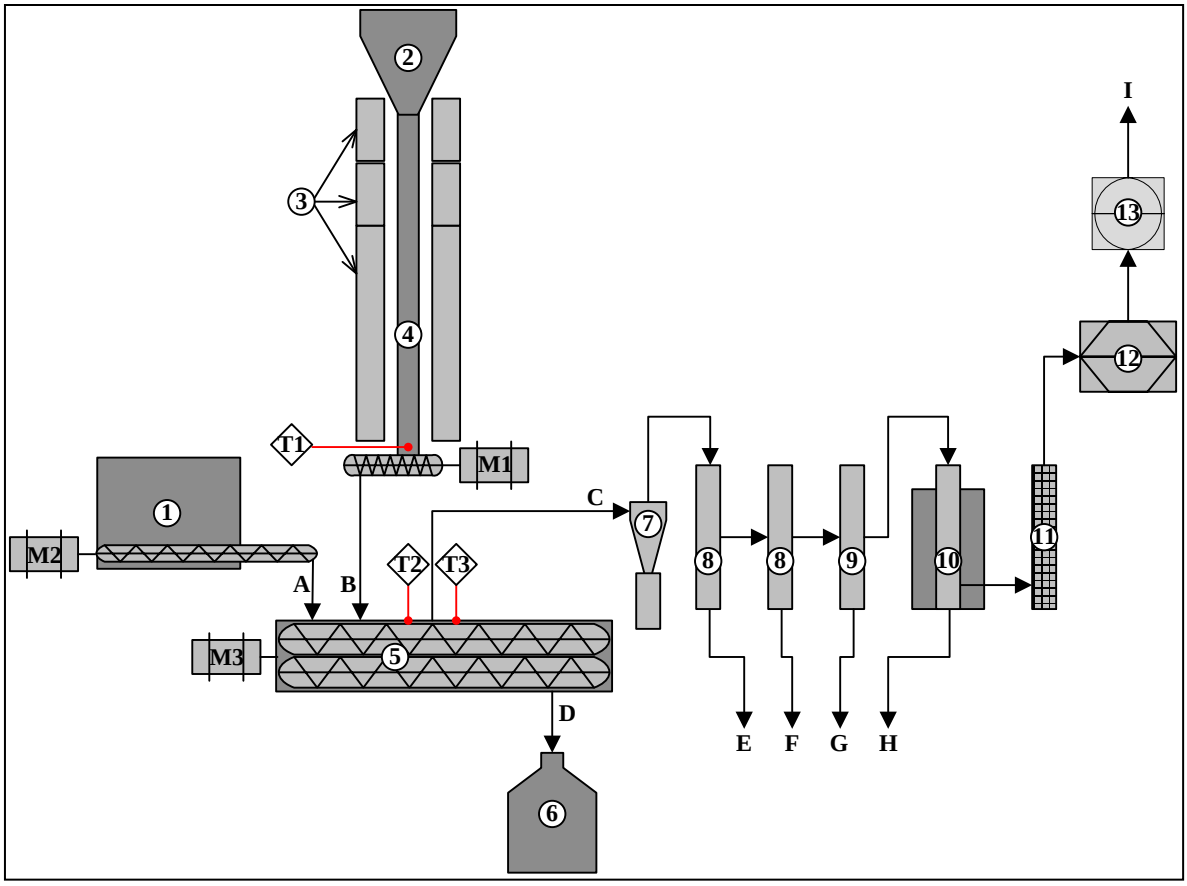

Figure 17. Laboratory scale fast pyrolysis auger reactor system schematic (Components: 1. biomass feeder; 2. heat carrier hopper; 3. electric heater; 4. heated pipe; 5. reactor; 6. solids canister; 7. cyclone; 8. water cooled condenser; 9. ESP; 10. condenser in ice bath; 11. desiccant tube; 12. micro-GC; 13. dry gas meter. Material flows: A. biomass inlet; B. heat carrier inlet; C. reaction products; D. solids outlet (heat carrier and char); E., F, G, and H. bio-oil stages 1-4; I. non-condensable gas (to vent); Temperatures: T1 - heat carrier inlet temperature; T2 - outlet vapor temperature 1; T3- outlet vapor temperature 2. Motors: M1 - heat carrier metering; M2 - biomass metering; M3 - reactor mixing augers) (Brown et al. 2012)

Char from the auger pyrolyzer was collected in a char catch along with the steel shot. Char was sieved from the steel shot for the purposes of obtaining mass balances on the reactor. In some experiments, char was found to form clumps around the steel shot. In these instances, the char-shot clumps were ground to release the shot from the char and then sieved

to separate the two. The accuracy of char measurements and mass balances was compromised when char and shot agglomerated because the two were not easily separated.

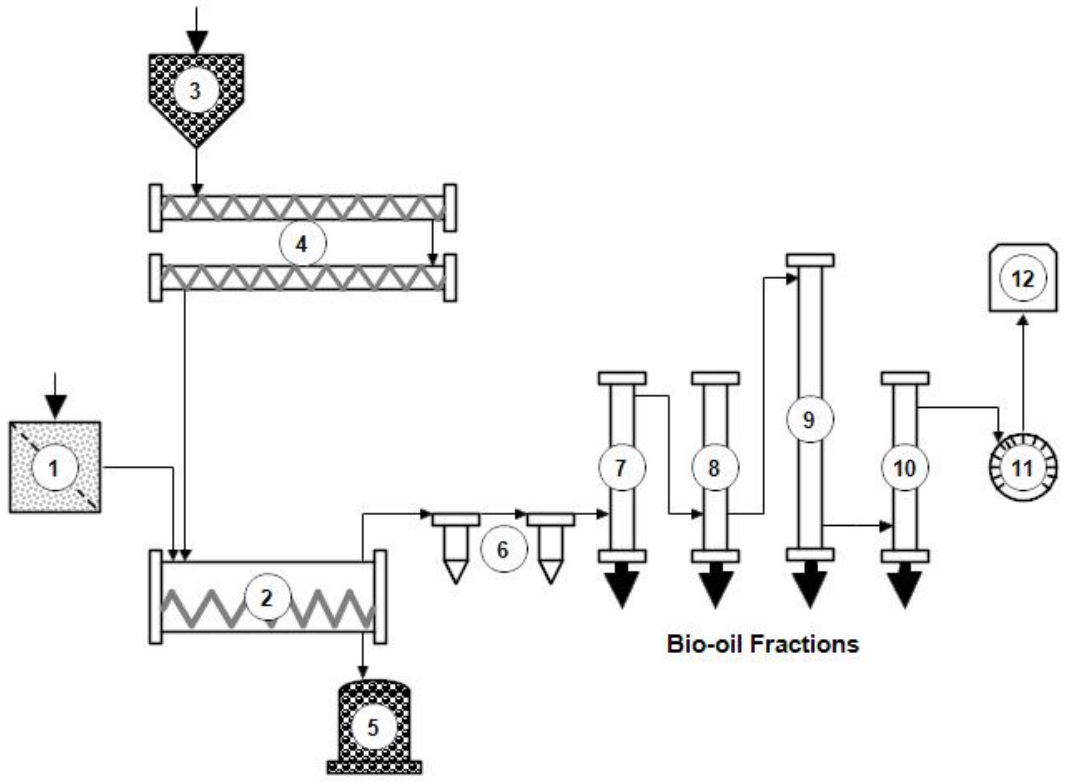

Figure 18. Schematic of the auger reactor: 1. Biomass Feeder; 2. Auger Reactor; 3. Heat Carrier Feeder; 4. Heat Carrier Heater; 5. Heat Carrier and Char Catch; 6. Cyclone Char Catch; 7. Condenser 1 (C1); 8. Condenser 2 (C2); 9. ESP: Electrostatic precipitator; 10. Condenser 3 (C3); 11. Non-condensable Gas Flow-meter; ;and 12. Micro GC.

The non-condensable gas from the reactor was analyzed in-situ using a Varian micro gas chromatograph. During pyrolysis runs, gas samples were taken every three minutes and analyzed using three separate columns. Concentrations were recorded for nitrogen, hydrogen, methane, propane, carbon monoxide, and carbon dioxide. Total non-condensable gas flow

rate was measured using a rotameter. Further details on the auger pyrolyzer system are found in Brown et al. (2012).

3.4.3. Analytical Methods: Sugars in the bio-oil samples were quantified using High Pressure Liquid Chromatography (HPLC) after acid hydrolysis (Johnston et al. 2112). When the current work was in progress, this method was under development due to which there is significant uncertainty in the results of quantification of sugars using this method. Levoglucosan and cellobiosan standards were purchased from Carbosynth (Compton, Berkshire, UK) and had purities of ≥99.0. Glucose and xylose standards were purchased from Thermo Fisher Scientific (Waltham, MA) and had purities ≥98.0%. All samples and standards solutions were prepared using ultrapure 18.2 mega Ohm deionized water from a Barnstead E-Pure system (part of Thermo Fisher Scientific, Waltham, MA). The sulfuric acid used was certified 10 N with an assay of (9.95-10.05) from Thermo Fisher Scientific.

The anhydro and other polymeric/oligomeric sugars in the fast pyrolysis bio-oil were acid hydrolyzed with 400 mM H_2SO_4 at 125°C for 44 min to monomeric sugars such as glucose. Hydrolysis conditions used were based off the previous work of (Bennett et al. 2009). The sulfuric acid used was certified 10 N with an assay of 9.95-10.05 from Fisher Scientific. Aliquots of 6 mL of 400 mM H_2SO_4 and 60 mg of bio-oil were added to sealed glass vials. Pure compounds of levoglucosan and cellobiosan were hydrolyzed under the same conditions as the samples to establish complete hydrolysis conditions and used as reference standards.

The HPLC system used for the experiment was a Dionex Ultimate 3000 LC system (Sunnyvale, CA) with a quaternary analytical pump and a Shodex Refractive Index (RI) Detector (New York, NY). The analytical column used was 300 mm X 7.7 mm 8µm particle size HyperRez XP Carbohydrate (p/n 69008-307780). The guard column used for the HyperRez was a Carbohydrate H+ cartridge (p/n 69008-903027) with the guard holder (p/n 69208-90327). The instrument parameters for the HyperRez were as follows: the mobile phase was ultrapure 18.2 mega Ohm deionized water with a flow rate of 0.2 mL/min and a column temperature was set at 55°C.

Moisture was measured using Karl-Fischer titration per ASTM D6305. The water insoluble fraction of the bio-oil was determined using a method developed in-house. Bio-oil was dissolved in water at 80°C and mixed thoroughly using a vortex mixer for 1 minute. The mixture was sonicated for 30 minutes and then centrifuged for 20 minutes at 2500 rpm. The water soluble fraction was removed using a 2 micron filter. The filter and the centrifuge tube were dried and weighed to obtain the weight of the water insoluble fraction.

Acid number was determined using a Modified Acid Number (MAN) method, which excludes the very weak acid (phenolic) content of the oil, as described by Pollard et al. (2012). Potentiometric titration with a Metrohm 798 Titrino was used to perform MAN analysis. The titrant was 0.1 M KOH in 2-propanol per ASTM D664. This modified ASTM D664 method uses 75 ml methanol for the solvent with the bio-oil sample dissolved in 5 ml dimethylformamide (DMF) versus the ASTM D664 solvents: 50% toluene, 49.5% 2-propanol, and 0.5% water.

The composition of the organic content of the bio-oil was analyzed using a Varian Saturn 3800 gas chromatograph coupled with a Varian 2200 mass spectrometer (GC/MS) as described in (Pollard et al. 2012). The analysis was performed with a Varian capillary column CP8722 that was 60 m in length, 0.25 mm inner diameter and with a 0.25 mm film thickness with a helium flow rate of 1.0 ml/min. The oven temperature was programmed at 45°C for 4 min to 235°C at a heating rate of 3°C/min (63.3 min) and held at 235°C for 13 min. The injector temperature was held at 250°C and the GC/MS interface was kept at a constant temperature of 235°C.

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CHAPTER 4. RESULTS AND DISCUSSION

4.1. Pyrolytic sugars from cellulosic biomass

The results of analytical pyrolysis of switchgrass infused with mineral and organic acids are shown in Figure 19. With the exception of the nitric acid, 2 wt% additions of mineral acids increased yields of LG from less than 2 wt% for untreated switchgrass to 10 – 15 wt%. Increases in LG were accompanied by decreases in light oxygenates, which would be expected if AAEM-catalyzed ring fragmentation decreased with respect to thermally-induced cleavage of glycosidic bonds. Also, mineral acid infusions roughly doubled the production of furans, which are dehydration products of LG, compared to the control. Phenolic compounds, derived from the lignin content of switchgrass, did not show much effect from the acid infusions.

Among the mineral acids, the order of decreasing effect was H_2SO_4>H_3PO_4>HCl>HNO_3, which does not correspond to the pKa of the acids. Significantly, HNO_3 behaved differently from the other mineral acids. In fact, the effect of HNO_3 was closer to that of the carboxylic acids, none of which strongly influenced yields. These results would be difficult to understand if the main role of the infused acid was to catalyze dehydration reactions of cellulose during pyrolysis. However, if the infused acids are reacting with AAEM to reduce their catalytic activity, then differences among the acids are more readily understood. All six acids are expected to react with most or all of the AAEM in biomass, which is thought to exist as chlorides or nitrates and/or to be weakly complexed with plant polymers (Marschner 1995, Barker et al. 2007). However, the salts

resulting from the reaction of acids with AAEM will behave differently upon heating. Three of the mineral acids form chlorides, phosphates, and sulfates that are either thermally stable or form other salts that are thermally stable at typical pyrolysis temperatures (400-500°C). These large anions are likely to shield the AAEM cations from effectively reacting with plant carbohydrates.

Nitric acid and the two carboxylic acids, on the other hand, form nitrates, formates, and acetates, respectively, that are known to decompose at pyrolysis temperatures, liberating AAEM to catalyze ring fragmentation in cellulose (and similarly in hemicellulose). The formation of thermally stable salts appears to be the key to understanding the AAEM passivation phenomenon; otherwise it is difficult to explain why a strong mineral acid like nitric acid would show little catalytic activity toward cellulose depolymerization and dehydration compared to other mineral acids.

Treatment level also reveals differences among the acids. As shown in Figure 20, sulfuric acid and phosphoric acid pretreatments produce prominent maxima in LG yields near 2 wt% acid infusions. Hydrochloric acid also substantially increased the yield of LG, but did not display a prominent maximum. Nitric acid and the two carboxylic acids did not show any variation in LG yield. This behavior is consistent with the hypothesis that infused acids react with AAEM cations to form salts that reduce the catalytic activity of the metal cations, allowing thermal depolymerization to anhydrosugar to dominate over cellulose decomposition to light oxygenates. Acid addition beyond that required to scavenge the metal cations would be available to catalyze polymerization and/or dehydration of LG, explaining the existence of an optimal acid infusion level. Excess hydrochloric acid, which has a

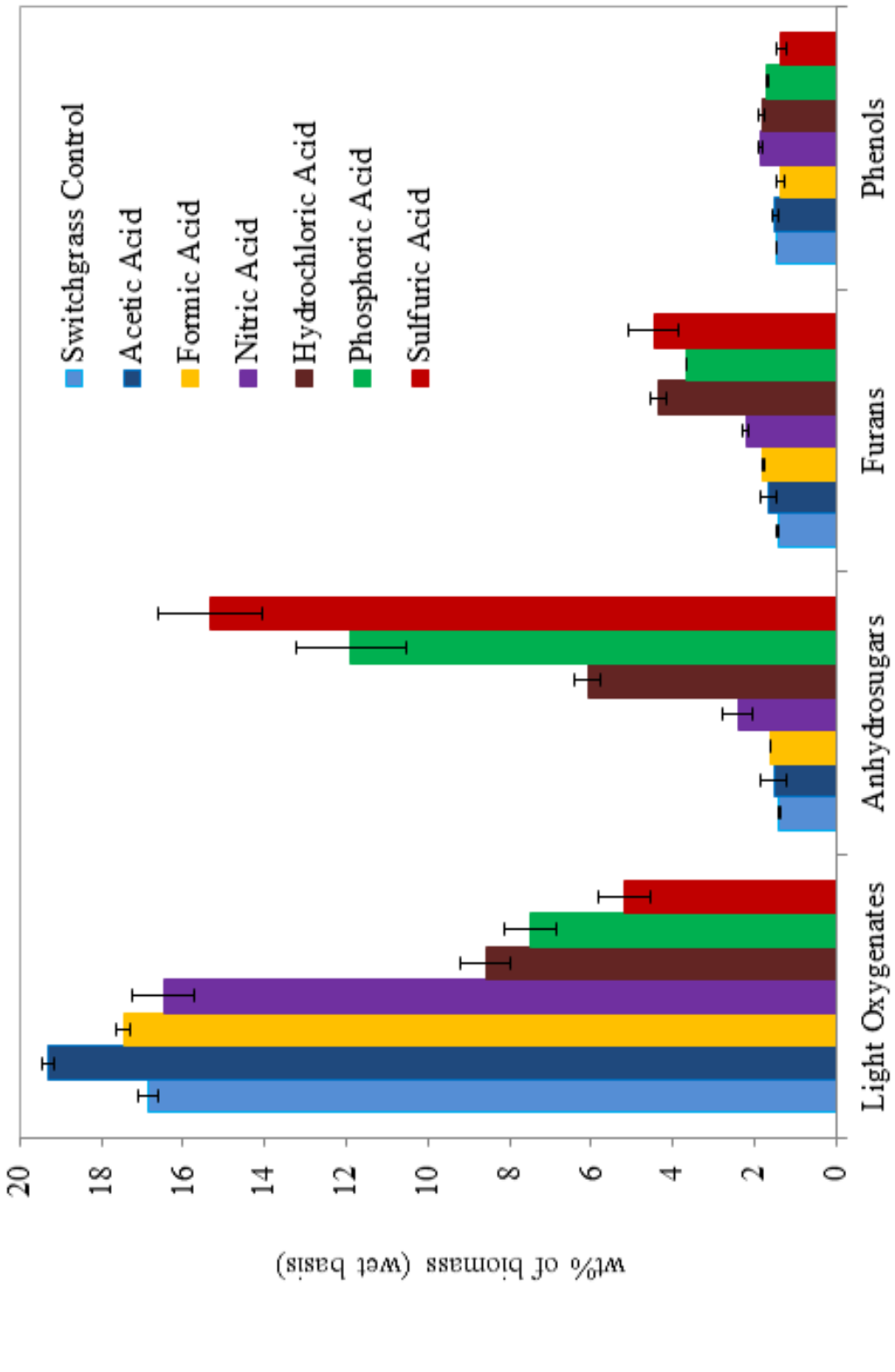

Figure 19. Yield of volatile compounds for the pyrolysis of switchgrass at 500°C after pretreatments with 2 wt%

significantly lower boiling point (<108° C) than either sulfuric acid (337° C) or phosphoric acid (158° C), might be expected to more readily vaporize during biomass pyrolysis, reducing its opportunity to catalyze polymerization and/or dehydration of LG.

The occurrence of maxima for sulfuric acid and phosphoric acid treatments can also be qualitatively explained by the acid catalyst hypothesis of Dobele and coworkers (Dobele et al. 1999, 2003, 2005): low levels of infused acid facilitates the depolymerization of cellulose to LG although eventually the concentration of acid becomes high enough to promote acid-catalyzed dehydration of the produced LG.

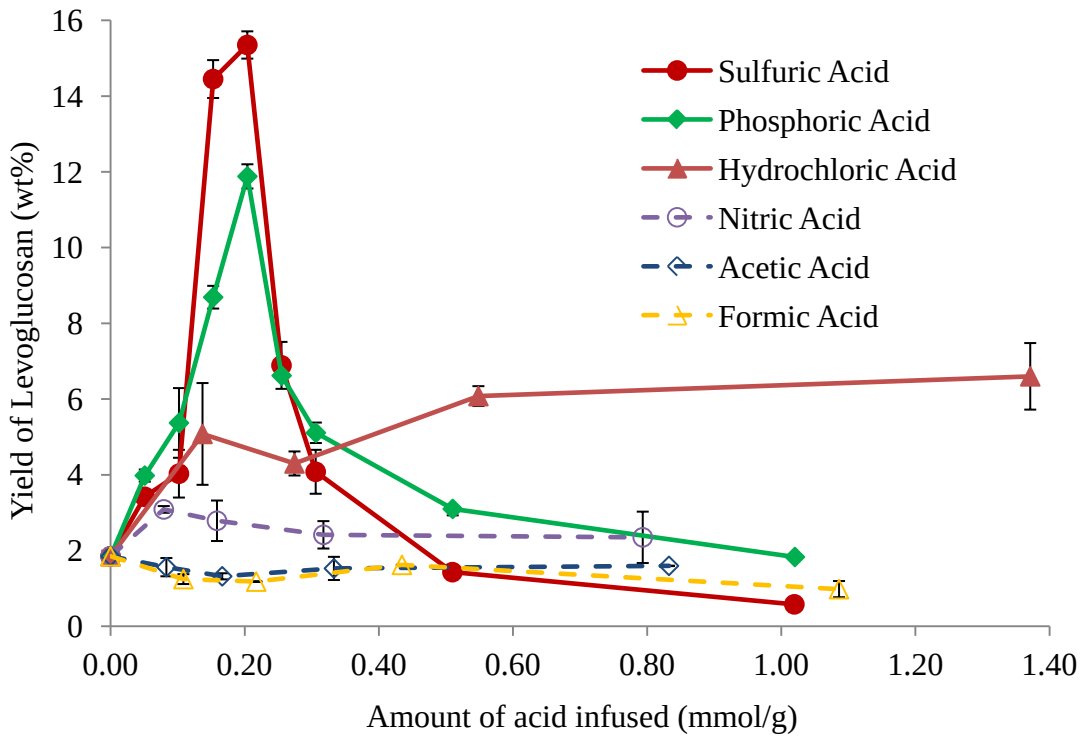

Figure 20. Yield of anhydrosugars from the pyrolysis of acid infused switchgrass at 500°C (closed symbols and solid lines: acids that produce thermally stable salts; open symbols and dashed lines: acids that produce thermally unstable salts).

However, one would expect the other acids, nitric acid in particular, to show similar behavior. The fact that they did not suggests that the acid catalyst hypothesis of Dobele cannot explain the observed phenomena.

Further evidence against the Dobele hypothesis (Wang et al. 2006) is the absence of a maximum in the yield of LG for the pyrolysis of acid-infused, AAEM-free cellulose. As shown in Figure 21, LG yield decreased monotonically with increasing infusions of sulfuric and phosphoric acids into otherwise pure cellulose. Why the peak in LG concentration should be absent in this experiment is wholly unexplained by the Dobele hypothesis. In these experiments LGone appeared as a pyrolysis product (Figure 19), but not in sufficient quantities to explain the disappearance of LG via dehydration. Although it can be argued that the effect of acid is to catalyze the fragmentation of pyranose rings, it can also catalyze the polymerization of LG, which subsequently dehydrates to char and furans (Bai et al. 2012).

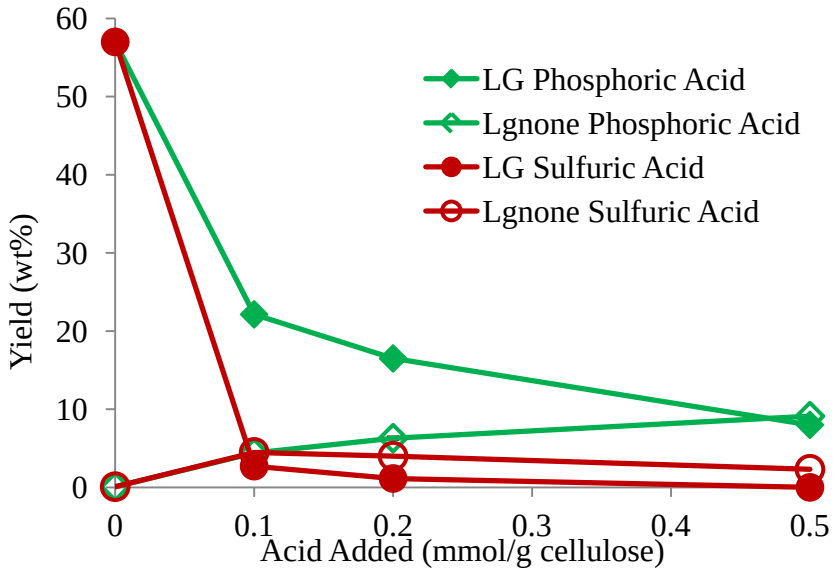

Figure 21. The yield of LG and LGnone from pyrolysis of pure cellulose at 500°C

The yield of LG from pyrolysis of pure cellulose at 500°C monotonically decreases with increasing levels of infused sulfuric or phosphoric acid. Levoglucosenone (Lgnone), a dehydration product of LG, increases but not sufficiently to explain the disappearance of LG.

If acid infusions of biomass are in fact converting naturally-occurring AAEM into thermally stable salts, then it should be possible to simulate the phenomenon in pure cellulose for which AAEM has been added. For this experiment, it was important to add AAEM in a form similar to naturally-occurring AAEM in biomass, which is thought to be associated with nitrate and chloride anions or coordination bonded to plant polymers (Marschner 1995, Barker et al. 2007). Although chlorides would be thermally stable during pyrolysis, it occurs at relatively low molar quantities in most kinds of biomass. Neither AAEM nitrates nor organically bound AAEM are thermally stable at pyrolysis temperatures.

After discarding the acid-catalyst hypothesis, experiments were carried out to test our hypothesis of passivating the AAEM. Potassium chloride, thought to be one of the most common components of the biomass inorganic matter, was impregnated into cellulose at 0.2 mmols of KCl per gram of cellulose. This cellulose was further treated with varying quantities of phosphoric acid. The results are shown in Figure 22.

It was found that the phosphoric acid reduced the effect of KCl and increased the yield of LG by about 30%. On the other hand, in the case of switchgrass, the increase in the yield of LG was from 1.8 wt% to 9 wt% which was 400%. From this experiment, it was concluded that there is another much larger cause for the increase in the yield of LG when

switchgrass was infused with phosphoric acid and also that potassium chloride does not necessarily represent the alkali in biomass.

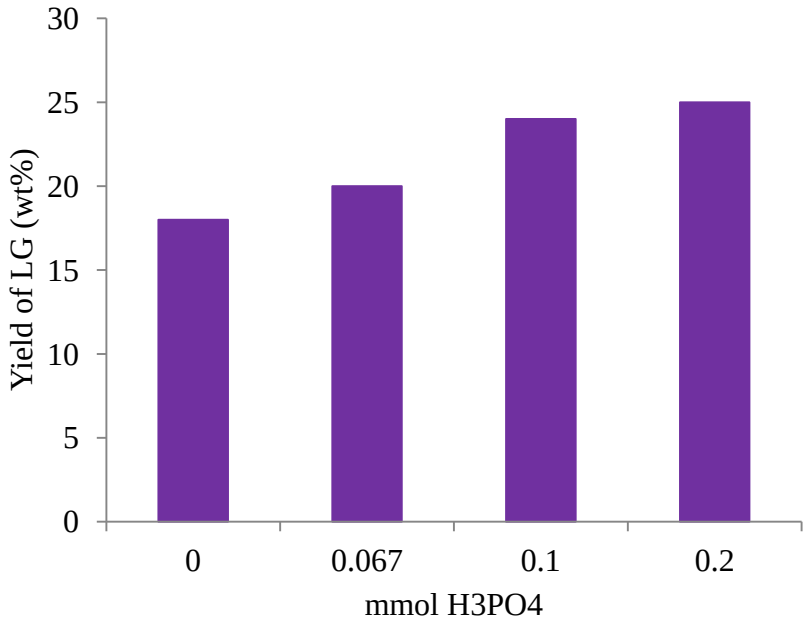

Figure 22. Yield of LG from cellulose infused with KCl and H3PO4

A literature review revealed that most of the potassium in biomass is in the form of free ions that are associated with anions such as NO_3^{--}, Cl^{--} and organic functional groups such as mallates while most of the calcium is bound to the cell wall carbohydrates (Marschner 1995, Barker 2007). These cations can possibly react with the acids and form inactive or less catalytically active salts. From this information, it was inferred that using alkali and alkaline earth metal chlorides as a representative of biomass alkali is not a good choice. By examining the results of the acid pretreatments closely again, it was noticed that nitric acid pretreatment did not increase anhydrosugars yield while hydrochloric acid did. Hydrochloric acid cannot react with KCl, but it can react with KNO_3. On the other hand, nitric acid cannot further react with KNO_3. From these results, it can be inferred that there

was considerable amount of alkali nitrates in the switchgrass used that was contributing to the alkali catalysis of the pyrolysis. Also, nitrate salts are not thermally stable at the pyrolysis temperature of 500°C.

In order to determine if alkali nitrates were reacting with the acids and reducing its catalytic effect, experiments were carried out by impregnating cellulose with KNO_3 at 0.2 mmol/g of cellulose. This sample was further infused with phosphoric acid at various concentrations. As shown in Figure 23, the LG yield is severely affected (from 58% to 3.5%) when pure cellulose was infused with KNO_3 which implied that KNO_3 was highly catalytically active. When treated with phosphoric acid, the yield improved with the amount of acid added until about 0.15 mmol/g cellulose, and then decreased. It can be inferred that the acid participates in some reaction with the alkali and forms a less active salt. At concentrations higher than 0.15 mmol/g of cellulose, it is possible that the reaction was not complete and the left over acid catalyzes the dehydration reaction thereby reducing the LG yield.

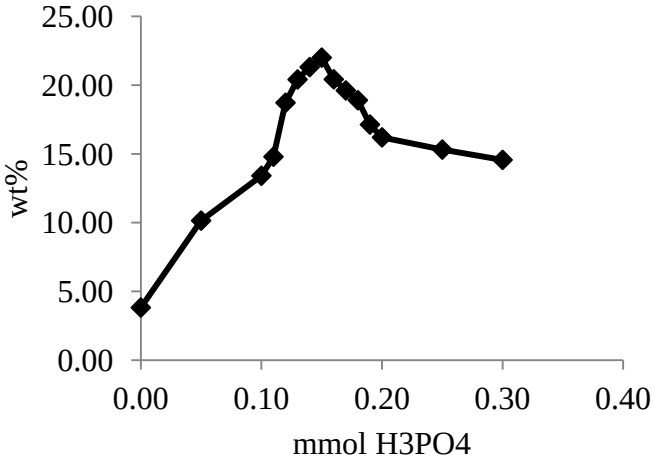

Figure 23. LG yield from cellulose doped with KNO3, subsequently treated with H3PO4

It is likely that phosphoric and sulfuric acids result in a double displacement reaction at the pyrolysis temperature that forms potassium phosphates and sulfates respectively. For this reaction to increase LG yield, potassium phosphates and sulfates should be less catalytically active compared to potassium nitrate.

At the same time, biomass contains organically bound AAEM that could form thermally stable salts on mineral acid infusion. In the experiments to simulate organically bound naturally-occurring AAEM in biomass, separate samples of potassium nitrate and potassium acetate doped cellulose were prepared by adding 0.20 mmol/g of the respective salts into cellulose. The doped cellulose was then infused with either sulfuric or phosphoric acid in the range of 0 to 0.25 mmol/g and pyrolyzed at 500°C. As shown in Figure 24, salt-treated cellulose produced less than 3.5 wt% LG if pyrolyzed without acid.

Levoglucosan yield from alkali-treated cellulose increased significantly when infused with mineral acids. The infusion of H_2SO_4 into alkali-treated cellulose increased LG to levels comparable to that for pure cellulose (59 wt%). The effect was smaller for infusion of H_3PO_4 into alkali-treated cellulose, but still yielded about 25 wt% LG. These results are in qualitative agreement with Figure 18, which reveals H_2SO_4 to be more effective than H_3PO_4 in enhancing LG yields from biomass. The fact that this experiment was able to simulate the effect of acid pretreatments on biomass strongly supports the AAEM passivation hypothesis.

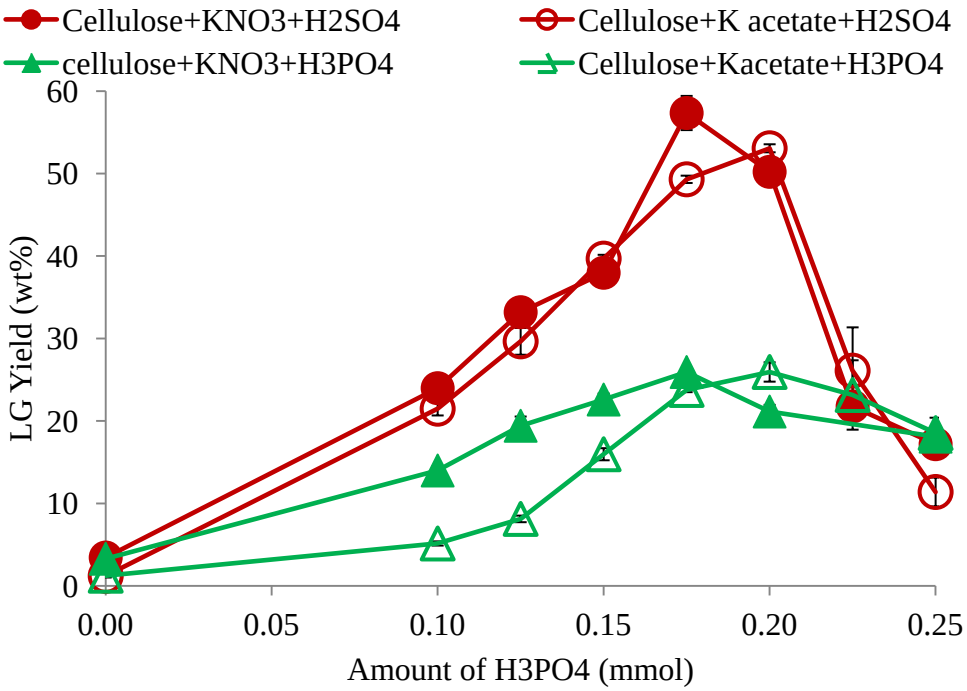

Figure 24. Levoglucosan yield vs. acid infusion level for pyrolysis at 500°C of cellulose doped with 0.2 mmol potassium nitrate and potassium acetate per gram of cellulose

Regardless of the acid used, the optimal acid/K molar ratio for KNO_3 and CH_3COOK treated cellulose was 1.0. The first degree dissociation constant of sulfuric acid is very large while the second degree dissociation constant is in the order of 10^{-2} (Francis 2011). The first degree dissociation constant of phosphoric acid is in the order of 10^{-2} while second and third degree dissociation constants are in the order of 10^{-7} and 10^{-12} (Francis 2011).

From Figure 4.1.4 and these dissociation constants, it seems likely that the salts formed are mostly potassium monohydrogen sulfate ($KHSO_4$) and potassium dihydrogen phosphate (KH_2PO_4). Upon heating, $KHSO_4$ forms potassium pyrosulfate ($K_2S_2O_7$) that further decomposes to form thermally stable potassium sulfate (K_2SO_4) (Sadtler et al. 1918). On the other hand, KH_2PO_4 decomposes to potassium metaphosphate ([KPO_3]n), which is thermally stable (Averbuch-Pouchot 1996).

To investigate whether there were differences in the catalytic activity of various AAEM salts, pure cellulose was doped with 0.2 mmol/g of potassium in the form of the various salts that might form from mineral acid infusions. These included K_2SO_4, $KHSO_4$, tripotassium phosphate (K_3PO_4), K_2HPO_4, KH_2PO_4, potassium pyrophosphate ($K_4P_2O_4$), KNO_3, KCl, CH_3COOK, and potassium formate (HCOOK). These samples were pyrolyzed without acid infusions at 500°C.

As shown in Figure 25, the order of decreasing LG yields was: $KHSO_4$ > KH_2PO_4 > K_2SO_4 > KCl > K_3PO_4 > K_2HPO_4 > $K_4P_2O_4$ > KNO_3 > HCOOK > CH_3COOK.

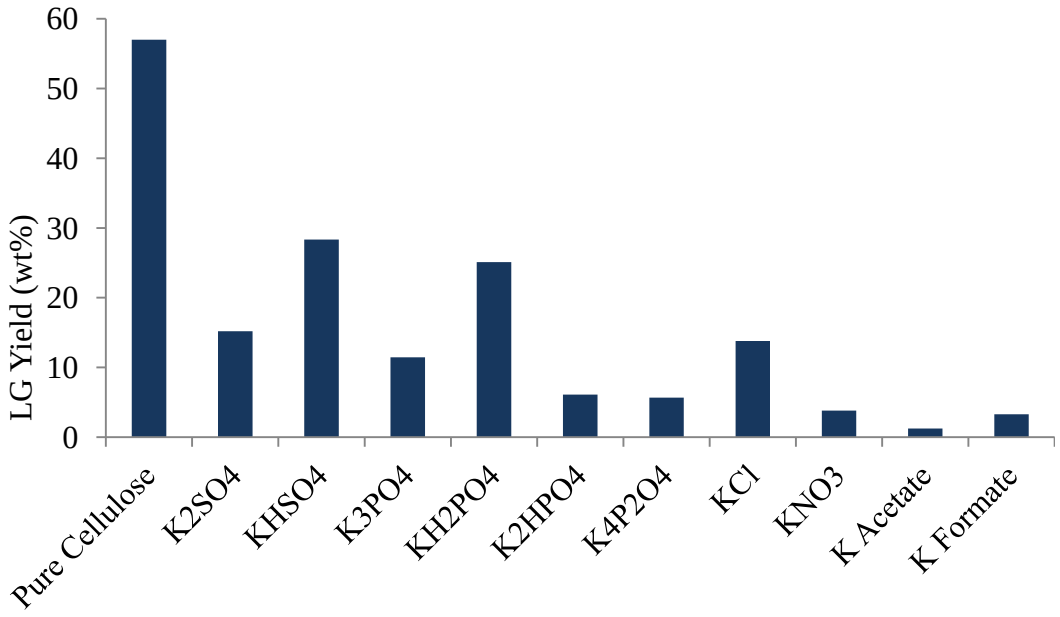

Figure 25. Comparison of LG yield for pyrolysis at 500°C of pure cellulose and cellulose doped with various potassium salts

This result is consistent with the variations in the efficacy of acid infusions (H_2SO_4 > H_3PO_4 > KCl > HNO_3) although differences among the various forms of sulfates and phosphates are more difficult to explain. Significantly, all of the salts greatly reduced LG yields compared to pure cellulose, which suggests that passivation of alkali does not fully

explain the effect of acid infusions on LG yields. The highest yielding salts ($KHSO_4$ and KH_2PO_4) are hydrogen donors, although they are much weaker acids than the mineral acids infused into biomass.

The fact that neither acids nor thermally stable salts acting alone can produce LG yields from cellulose comparable to that achieved from acid infused biomass suggests that the addition of acid to biomass not only converts AAEM into catalytically inactive salts but exchanges hydrogen ions into the biomass where they catalyze the depolymerization of cellulose to LG. To test this hypothesis, cellulose was prepared in three ways: without pretreatment; pretreated with 0.2 mmol/g of $KHSO_4$ (a suspected product salt); and 0.2 mmol/g each of $KHSO_4$ and HNO_3. If the hypothesis is correct, then the loss of LG yield observed in the presence of salt will be substantially restored by the addition of acid (Figure 26).

In fact, as shown in Figure 26, addition of acid in the presence of $KHSO_4$ increased LG yield, which might not have been suspected from the effect of acid on pure cellulose (Figure 19). As shown in Figure 27, LG yield decreased as the pH of the sample increased, suggesting that acid catalysis also plays a role in enhancing LG yield from cellulose, at least in the presence of the salts formed during AAEM passivation. Based on Figure 16, it would appear that acid catalysis might contribute to 20% of the enhancement in LG yield upon acid infusion in biomass while AAEM passivation contributes the balance of the enhancement. Considering that mineral acids appear to catalyze pyranose ring fragmentation in pure cellulose and glycosidic bond breakage in the presence of AAEM suggests that AAEM

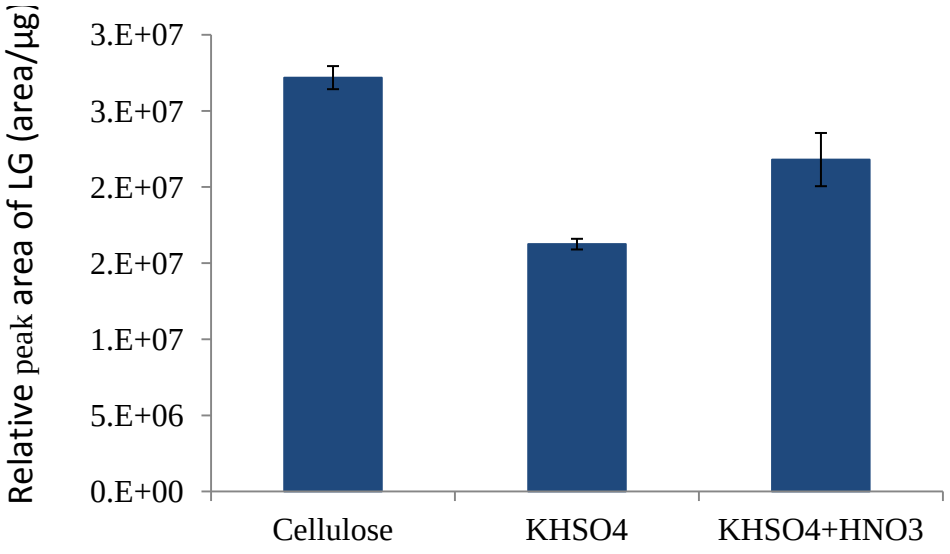

Figure 26. The effect of combined salt and acid pretreatment on yield of LG from cellulose (pretreatment levels were 0.2mmol/g KHSO4 and 0.2mmol/g HNO3 followed by pyrolysis at 500^{0}C)

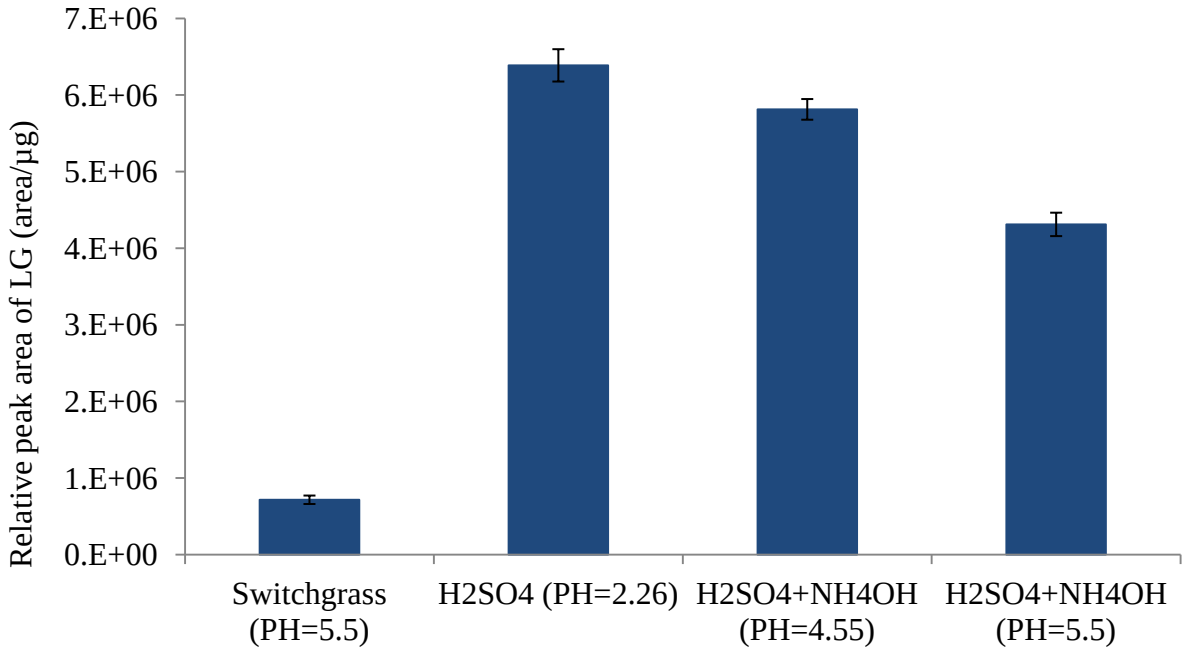

Figure 27. The effect of pH on the pyrolysis yield of LG for acid-infused switchgrass (H2SO4 was infused at 0.2mmol/g; pH adjustment was made with NH4OH; pyrolysis was performed at 500^{0}C)

cations react with mineral acids to form weak acids that buffer the pH of acid infused biomass. Buffering is important for specific (vs general) acid catalysis, in which a proton is transferred to a substrate in a rapid pre-equilibrium reaction followed by the rate limiting reaction of the protonated substrate to form the final products (Larson et al. 1994).

For specific acid catalysis, the rate of reaction is controlled by pH rather than acid concentration, thus buffering will strongly influence the outcome of the reaction. Oxygen is particularly suitable as a substrate because its high electronegativity promotes fast proton transfer (Larson et al. 1994), thus specific acid catalysis is a likely mechanism for glycosidic bond breakage. Both $KHSO_4$ and KH_2PO_4 are weak acids:

1. $KHSO_4 \Leftrightarrow H^+ + KSO_4^-$
2. $KH_2PO_4 \Leftrightarrow H^+ + KHPO_4^-$

Thus, the addition of strong mineral acids are expected to react with naturally occurring AAEM in biomass to form acid salts that buffer the system at pH levels that favor glycosidic bond breakage.

These previous results suggest that for a given sample of biomass there exists an optimum acid pretreatment level that depends upon the amount of AAEM (specifically potassium, sodium, calcium and magnesium) in the sample. This was investigated by determining the optimal infusions of sulfuric and phosphoric acids for a diverse set of biomass feedstocks (red oak, loblolly pine, switchgrass, and cornstover) containing a wide range of AAEM content (see Table 4).

Table 4. Acid required to convert AAEM into various salts to the amount of acid added to achieve maximum LG yields for Pyrolysis of biomass at 500°C

		Stoichiometric acid requirement to produce prospective anions (mmol/g)					Acid consumed for max LG yield (mmol/g)	
Feedstock	**Adjusted metal valency* (mmol/g)**	**$H_2PO_4^{-1}$**	**HPO_4^{-2}**	**PO_4^{-3}**	**HSO_4^{-1}**	**SO_4^{-2}**	**H_3PO_4**	**H_2SO_4**
Cornstover	**0.40**	**0.40**	**0.20**	**0.13**	**0.40**	**0.20**	**0.41**	**0.30**
Switchgrass	**0.24**	**0.24**	**0.12**	**0.08**	**0.24**	**0.12**	**0.20**	**0.18**
Loblolly Pine	**0.11**	**0.11**	**0.055**	**0.037**	**0.110**	**0.055**	**0.082**	**0.061**
Red Oak	**0.065**	**0.065**	**0.033**	**0.022**	**0.065**	**0.033**	**0.061**	**0.041**

*Total valency of metal minus valency of chlorine in biomass (K + Na + 2Ca + 2Mg – Cl)

As shown in Figures 28-31, all four feedstocks showed prominent maxima in LG yields vs. the amount of infused acid.

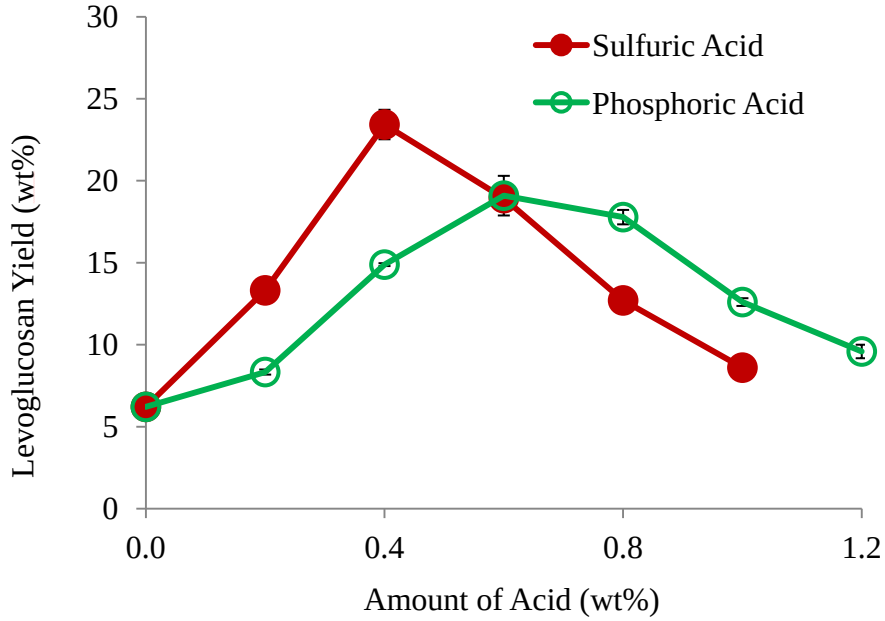

Figure 28. Yield of LG from pyrolysis of red oak at 500°C as a function of the amount of infused phosphoric and sulfuric acids

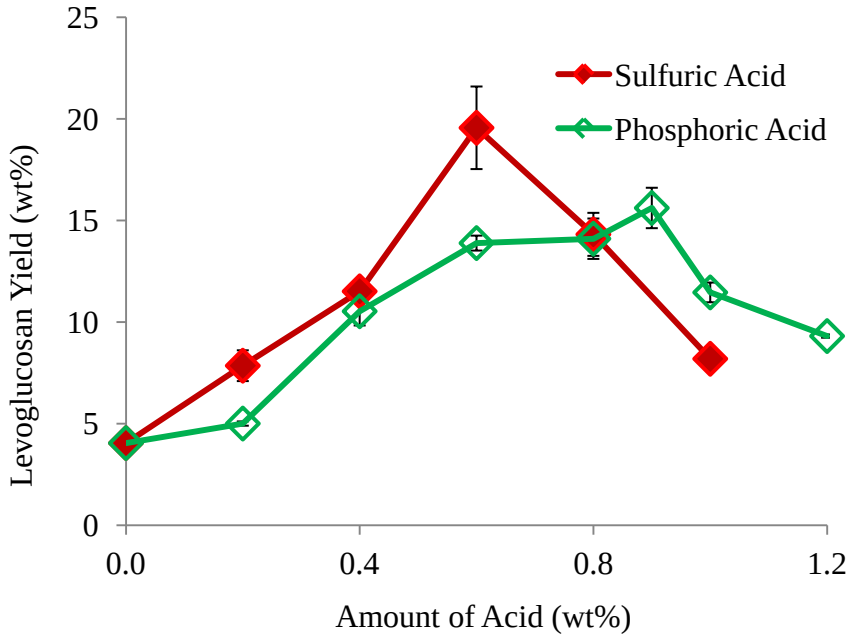

Figure 29. Yield of LG from pyrolysis of loblolly pine at 500°C as a function of the amount of infused phosphoric and sulfuric acids

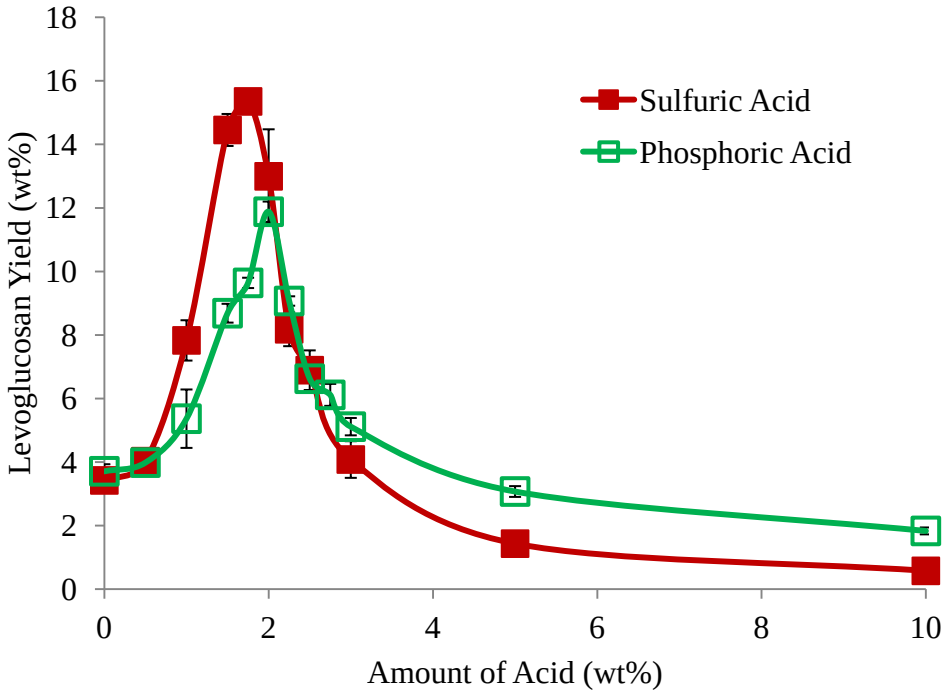

Figure 30. Yield of LG from pyrolysis of switchgrass at 500°C as a function of the amount of infused phosphoric and sulfuric acids

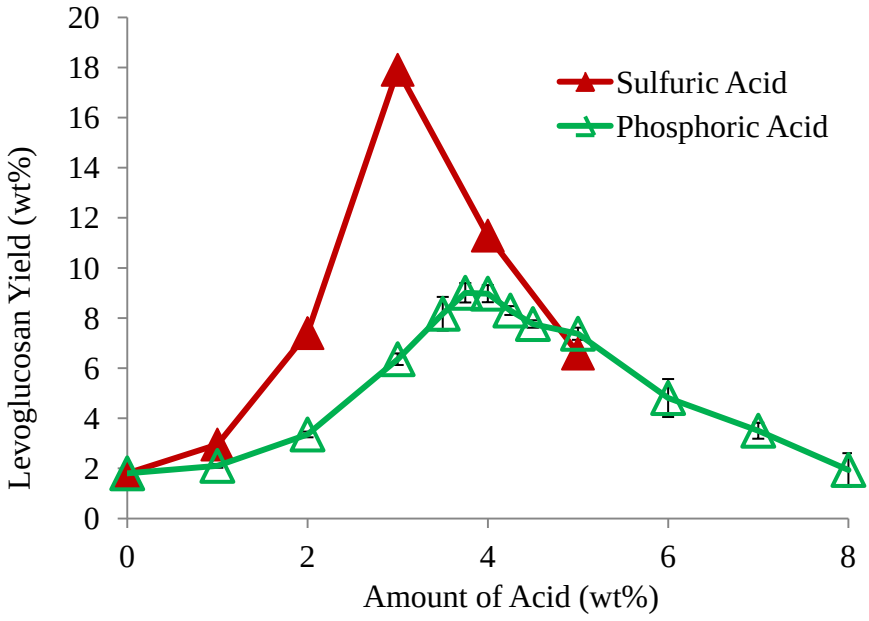

Figure 31. Yield of LG from pyrolysis of cornstover at 500°C as a function of the amount of infused phosphoric and sulfuric acids

For each acid these maxima were plotted against the total valency of the AAEM in the biomass (i.e., mmol of K+Na+2Ca+2Mg). As shown in Figure 32, linear plots were obtained for both phosphoric and sulfuric acids, with correlation coefficients of 0.89 and 0.95, respectively.

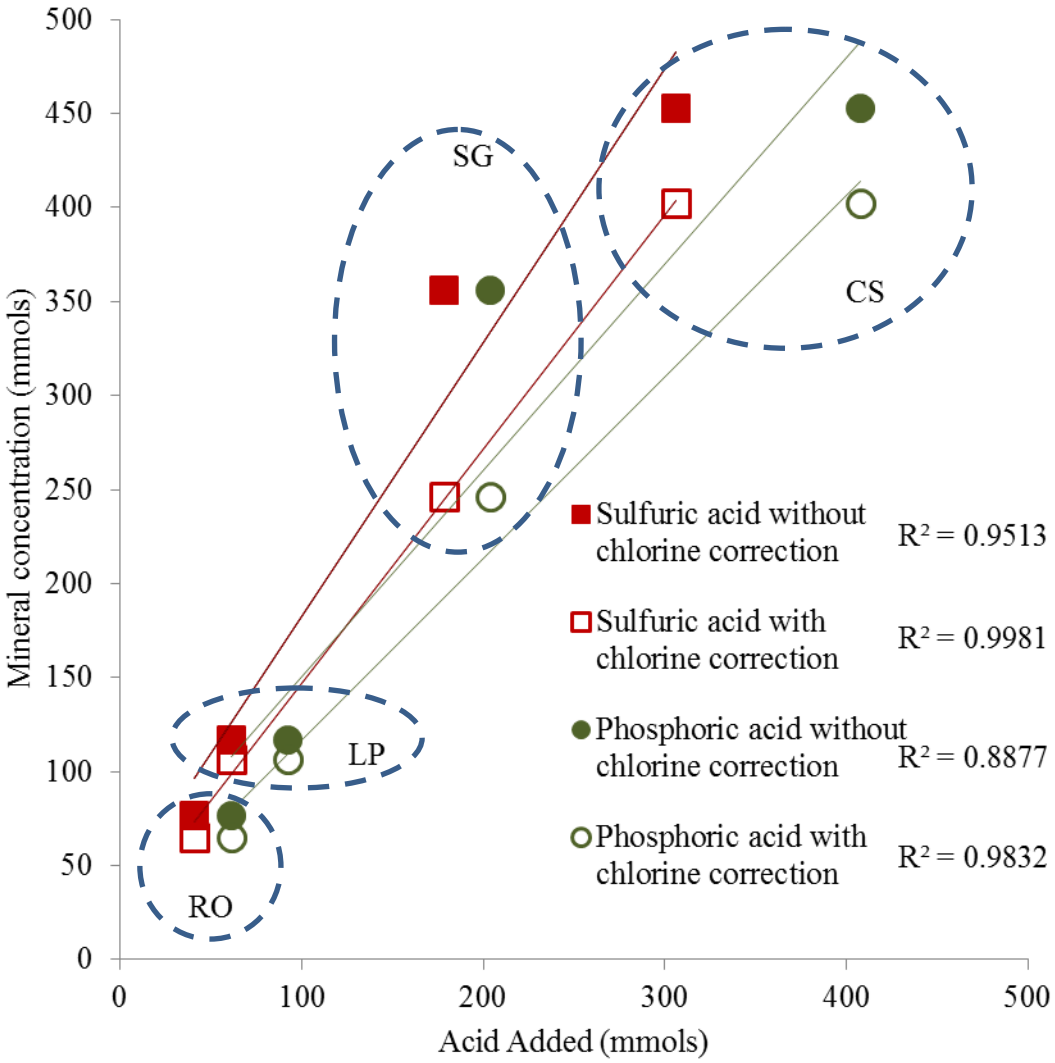

Figure 32. Correlation between total AEEM valency (K+Na+2Ca+2Mg) or chlorine corrected AAEM valency (K+Na+2Ca+2Mg-Cl) of biomass and the optimal addition of phosphoric or sulfuric acid for maximum yield of LG from pyrolysis at 500°C (RO: Red oak, LP: Loblolly Pine, SG: Switchgrass, CS: Corn Stover)

Chlorine (Cl) in the biomass is expected to strongly bond to AAEM, reducing the amount of acid required to achieve maximum LG yields. To correct for this effect, Figure 30 also includes plots of total valency of AAEM reduced by the valency of the Cl in the biomass (i.e., mmol of K+Na+2Ca+2Mg-Cl). The correlation coefficients improved to 0.9981 and 0.9832 for sulfuric acid and phosphoric acid respectively.

The amount of acid consumed in these experiments gives some indication of the specific salts formed. Table 4 compares the amount of sulfuric and phosphoric acid required to achieve maximum LG yields to the amount of these acids to produce sulfates, hydrogen sulfate, phosphates, monohydrogen phosphates, and dihydrogen phosphates. For all four biomass feedstocks the amount of sulfuric and phosphoric acid consumed was far more than required to form neutral sulfates and phosphates, suggesting the formation of acid salts.

The potential of acid infusions is defined as the weight percent of cellulose in the biomass multiplied by the experimentally observed maximum yield of LG for pure cellulose (59 wt%). The effectiveness of acid infusions is defined as the actual yield of LG from acid infused biomass divided by the potential yield of LG from the cellulose contained in that biomass sample. As shown in Table 5, the effectiveness of acid infusions to enhance LG yields were greater than 83% and ranged as high as 99.7%.

This study reveals a simple method for the pyrolytic production of sugars without the use of enzymes or catalysts. The process, which requires only small quantities of mineral acids to form thermally stable acid salts from naturally occurring AAEM in biomass, can dramatically increase levoglucosan yields upon pyrolysis.

Table 5. Effectiveness of acid infusions in producing LG from Pyrolysis of biomass at 500°C

		H_3PO_4 Infusion		H_2SO_4 Infusion	
Feedstock	Potential LG Yield[1] (wt%)	LG Yield (wt%)	Effectiveness[2] (%)	LG Yield (wt%)	Effectiveness[2] (%)
Switchgrass	20.7	11.9	64.5 ± 1.7	15.4	83.4 ± 2.0
Cornstover	18.4	9.0	43.4 ± 1.9	17.9	86.3 ± 7.2
Red Oak	25.0	19.1	76.6 ± 4.8	23.4	94.0 ± 3.6
Loblolly Pine	20.4	15.6	79.6 ± 4.3	19.6	99.7 ± 8.8

[1] Potential yield = wt% celluose in biomass x wt% LG yield for pure cellulose

[2] Effectiveness of acid diffusion = actual LG yield/potential yield

These salts not only passivate AAEM that normally catalyzes fragmentation of pyranose rings but buffer the system at pH levels that favor glycosidic bond breakage. It appears that AAEM passivation contributes to 80% of the enhancement in LG yield while the buffering effect of the acid salts contributes to the balance of the enhancement.

4.2. Temperature dependence of levoglucosan yield from fast pyrolysis of Acid infused biomass

In the micro-scale pyrolysis experiments we have previously seen that infusion of mineral acids into lignocellulosic biomass converts alkali and alkaline earth metals into thermally-stable salts, reducing their catalytic activity during fast pyrolysis (Kuzhiyil et al. 2012). The suppression of metal-catalyzed ring breaking reactions allows depolymerization to dominate the pyrolytic decomposition of cellulose, resulting in enhanced yields of levoglucosan (LG) in batch pyrolysis trials lignocellulosic of biomass.

In the absence of AAEM, cellulose thermally depolymerizes to liquid LG, which has a small but measureable vapor pressure at pyrolysis temperatures, allowing it to vaporize and exist in the reaction zone. However, as reported by Kawamoto et. al. (2003, 2009) and Bai et al. (2012), LG also begins to polymerize and char at temperatures above 270°C, suggesting a competition between evaporation and charring of LG during pyrolysis. Since acid-infused biomass expresses a large amount of levoglucosan compared to untreated biomass when pyrolyzed, the optimal temperature for LG production may be lower than traditionally assumed (500°C). Thus, to maximize yields of LG from acid infused biomass, pyrolysis at lower temperatures may be possible. The temperature dependence of LG yield from acid infused biomass pyrolysis was explored through pyrolysis experiments using a micropyrolyzer/GC/FID.

The yields of LG from the pyrolysis of biomass in the temperature range of 300°C to 500°C are compared for untreated switchgrass control (SG) and switchgrass infused with phosphoric acid (SG-PA) and sulfuric acid (SG-SA). As shown in Figure 33, the LG yields for the (untreated) switchgrass control increased from 0.94 wt% at 300°C to 1.66 wt% at 350°C. At higher temperatures, in the range of 350°C to 500°C, LG yield was approximately constant at 2 wt%.

The yields from switchgrass pretreated with phosphoric acid (SG-PA) and sulfuric acid (SG-SA) were significantly higher than for the control experiments at all temperatures tested (300°C to 500°C). For SG-PA, LG yield increased from 6.7% to 11.1% in going from 300°C to 350°C above which the LG yield appeared almost constant. Similarly, the LG yield

for SG-SA increased from 13.79 wt% at 300°C to 17.03 wt% at 375°C, above which the LG yield appeared almost constant.

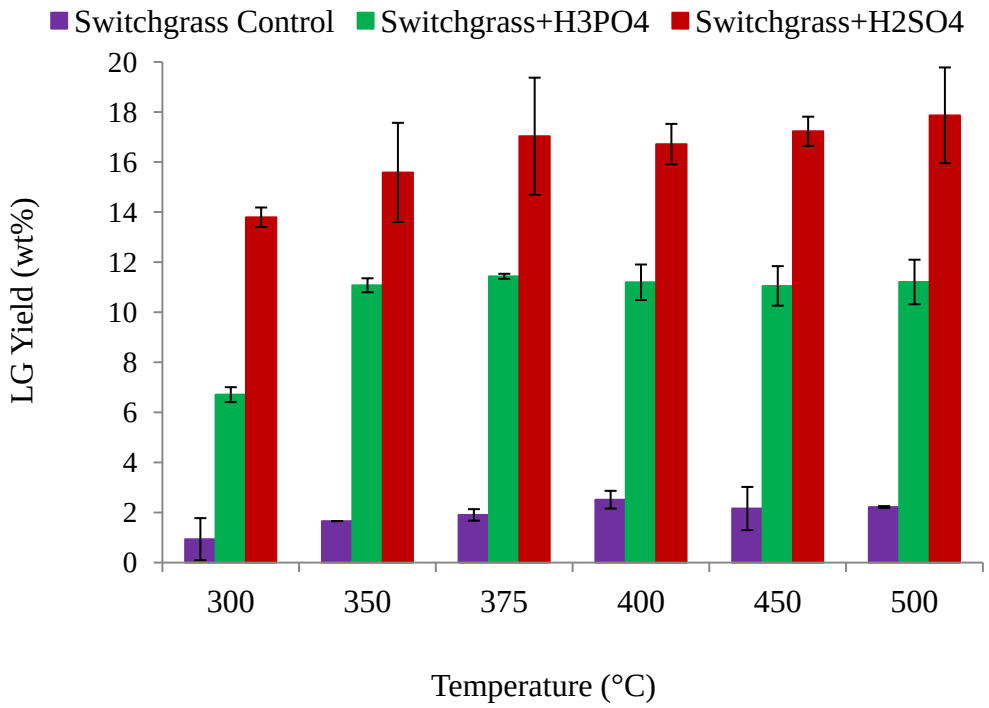

Figure 33. LG yield from pyrolysis of switchgrass: control and infused with phosphoric acid (2.0 wt%) and sulfuric acid (1.75 wt%)

To test the statistical significance of these results, a single factor ANOVA of the LG yields from SG-PA and SG-SA in the temperature range of 350°C to 500°C was carried out. As shown in Table 6, in this temperature range the F values are lower than the F critical values, indicating no statistical significance in the differences in LG yields from SG-PA and SG-SA in the temperature range of 350-500°C.

Table 6. Single factor ANOVA of switchgrass feedstocks over a temperature Range of 350-500°C

Feedstock	F	F Critical
SG	2.20	3.48
SG-PA	0.10	3.48
SG-SA	0.89	3.48

These results suggest that the pyrolyzer could be operated at a wide range of temperature of 350-500°C to obtain similar yield of LG from SG-PA and SG-SA.

For red oak, pyrolysis of the control at 300°C yields almost no LG, which increased to about 5 wt% in the temperature range of 350°C to 500°C (Figure 34) respectively.

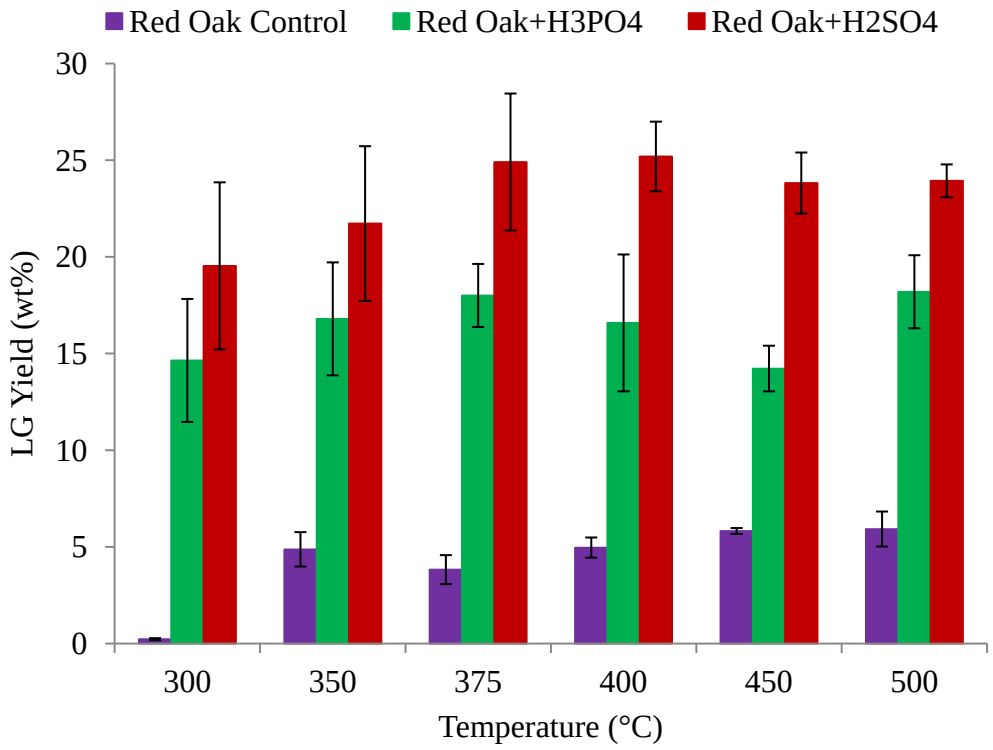

Figure 34. LG yield from red oak: control and infused with phosphoric acid (0.6 wt%) and sulfuric acid (0.4 wt%)

Pyrolysis of red oak infused with phosphoric acid (RO-PA) and sulfuric acid (RO-SA) produced almost 15 wt% and 20 wt% of LG at 300°C. At 350°C and above, the LG yields were almost constant at 18.2 wt% and 25.2 wt% for RO-PA and RO-SA.

As shown in Table 7, single factor ANOVA reveals no statistically significant differences in LG yield with temperature in the range of 350-500°C for either RO-PA or RO-SA.

As shown in Figure 35, the yield of LG from the loblolly pine control was very low (< 0.5 wt%) at 300°C, increasing to 3.07 wt% at 350°C and further increasing to 4.87 wt% at 500°C.

Table 7. Single factor ANOVA of red oak feedstocks over a temperature Range of 350-500°C

Feedstock	F	F Critical
RO	4.46	3.48
RO-PA	1.25	3.11
RO-SA	1.42	3.11

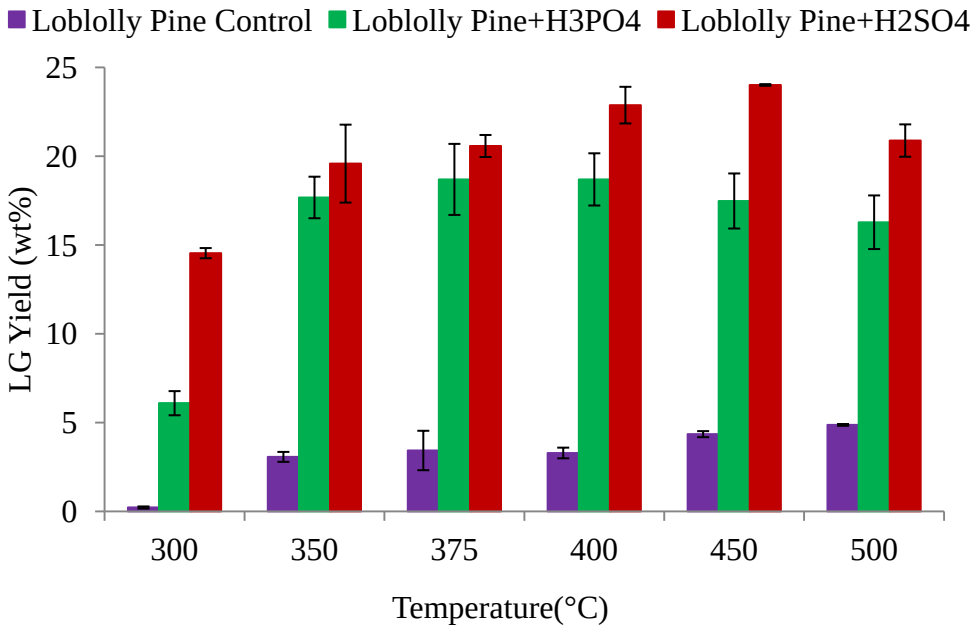

Figure 35. LG yield from loblolly pine: control and infused with phosphoric acid (0.9 wt%) and sulfuric acid (0.6 wt%)

Infusion of phosphoric acid yielded 6.09 wt% of LG at 300°C that increased to 18.69 wt% at 350°C. At higher temperatures there was no further increase in yield or it slightly decreased. Infusion of sulfuric acid yielded 14.54 wt% LG at 300°C that increased to 19.58 wt% at 350°C and 24.01 wt% at 450°C.

A single factor ANOVA was performed on the loblolly pine data (see Table 8). Analysis of the data for the untreated loblolly pine (control) indicates statistically significant differences in LG yield as a function of temperature although the differences in yield are generally small. Differences in yields of LG from LP-PA in the range of 350-500°C are not statistically significant. On the other hand, there is a statistically significant difference in LG yields among the LP-SA experiments in the temperature range of 350-500°C. It appears that the maximum yield of LG from sulfuric-acid infused loblolly pine occurs between 450 and 500°C.

Table 8. Single factor ANOVA of loblolly pine feedstocks for the temperature Range of 350-500°C

Feedstock	F	F Critical
LP	7.54	3.48
LP-PA	1.11	3.48
LP-SA	3.85	3.48

The study showed that LG yields from acid infused lignocellulosic biomass was almost constant in the temperature range of 350-500°C. For acid-infused switchgrass and red oak, the maximum LG yields occurred between 350-375°C. For loblolly pine the highest yield of LG occurred at 450°C. Thus, depending upon feedstock, it might be possible to operate at much lower temperatures than previously thought for pyrolysis to achieve maximum yields of LG from acid-infused biomass.

However, experiments on conventional fluidized bed and auger reactors failed to pyrolyze both control and acid-infused feedstocks. The reason for the failure was inferred to be poor heat transfer into the feedstocks. In order to take advantage of the finding that LG recovery is the best at lower temperatures of 300-350°C, there may be a need for unconventional way of pyrolysis.

4.3. Continuous production of sugars from the pyrolysis of pretreated Lignocellulosic biomass

Experiments were carried out to demonstrate the continuous production of sugar-rich bio-oil from the fast pyrolysis of acid-infused biomass. Two of the most common types of pyrolyzers were employed: a fluidized-bed reactor and auger reactor. The study evaluated the operability of the two systems, the properties of the bio-oil, and the yields of sugar.

Both untreated red oak (control) and acid-infused red oak were pyrolyzed separately in a laboratory-scale fluidized bed reactor at 500°C to produce bio-oils. The results of these 3-hour trials are found in Table 9. For the untreated biomass (control), the bio-oil yield was 67 wt%, char yield was 13.2 wt%, and non-condensable gas yield was 15.6 wt%. For the acid infused biomass, yields were similar: 67 wt% for bio-oil, 13.2 wt% for char, and 15.6 wt% for non-condensable gas. These are comparable to other reports in the literature for woody biomass pyrolyzed in fluidized beds (Mohan et al. 2006; Pollard et al. 2012).

Subsequently, the acid-infused red oak was pyrolyzed in the fluidized bed reactor at identical conditions as the previous run. During the three hours of operation, bed temperature remained relatively constant, but the rate of bio-oil collection visibly declined during the course of the trial. Gas production was so unsteady as to prevent its reliable measurement. Bio-oil yield was 45.1 wt%, which was low compared to 67 wt% achieved for the control feedstock. On inspection of the cyclone catch, it was found that no char was collected, which is extremely unusual for lignocellulosic feedstocks.

Table 9. Mass balance of products from pyrolysis of control and acid treated red oak on Fast pyrolysis in the fluidized bed reactor

Products	Control (wt%)	Acid Infused (wt%)
Bio-oil	67.0	45.1
Char	13.2	Not Known
Gas	15.6	Not Known
Unaccounted	4.2	--

Upon completion of the trial, it was found that the fluidized bed contained large agglomerates consisting of char and sand. Careful examination of the char agglomerates showed them to be smooth textured, as if formed from the solidification of molten material (Figure 36). The origin of this vitreous char is unclear, but it could have been formed from the polymerization and dehydration of levoglucosan released upon pyrolysis of the pretreated biomass (Bai et al. 2012) or from polymerization and dehydration of lignin-derived compounds that failed to devolatilize in the presence of passivated AAEM or mineral acid (Dalluge et al. 2011).

Whether the fall-off in bio-oil production rate during the course of the experiment translated into increased char yields or gas yields was impossible to ascertain. Char production rate could not be monitored because char accumulated in the reactor instead of being elutriated and steadily collected in the cyclone catch. Gas temperature and composition, from which gas production rate were calculated, was too unsteady over time, to make this determination.

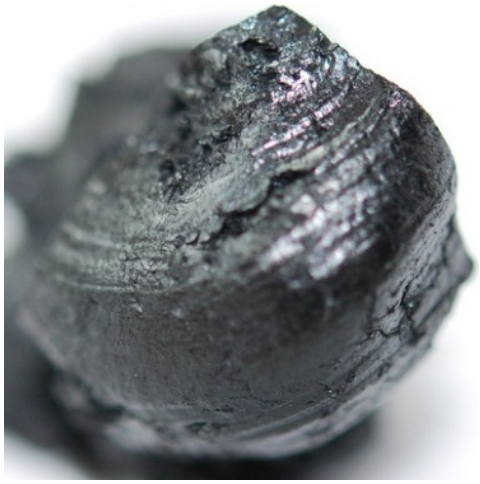

Figure 36. Vitreous char recovered from the fluidized bed reactor after pyrolyzing acid-infused red oak

Subsequent attempts to pyrolyze acid-infused red oak in the fluidized bed were no more successful than the first trial in reaching steady state operation. These trials also produced unusually low bio-oil yields and agglomerated bed material. Nevertheless, oil collected during the first test of the acid treated red oak contained 18.2 wt% sugar compared to only 4.12 wt% for the bio-oil from untreated red oak. Although this high sugar yield is unprecedented for pyrolysis of lignocellulosic biomass, further tests in the fluidized bed reactor were abandoned because of the difficulty in achieving steady-state operating conditions due to char accumulation in the bed.

In an effort to overcome the char agglomeration problem, we attempted to pyrolyze the acid-infused feedstock in an auger type reactor. In this system, the heat carrier and pyrolyzing biomass are actively conveyed through the reactor by the rotating auger, so any char formed is continuously removed from the reactor. As a result, new biomass fed into the reactor always encounters fresh heat carrier. Because of this continuous conveyance of

solids, we anticipated that the charring of lignin or sugars would not affect the pyrolysis of the fresh biomass.

In the first trials of the auger reactor both untreated and acid infused red oak were fed at 0.5 kg/hr, hot steel shot was fed at 10 kg/hr, and the sweep flow rate of nitrogen gas was set at 3 SLPM, and pyrolysis temperature was held at 500°C, which are typical operating conditions for this reactor. The auger reactor was successfully operated at steady conditions for 3 hours. As shown in Table 6, bio-oil yields were similar for untreated and acid-infused feedstock (65.1 wt% and 67 wt%, respectively).

However, in contrast to the fluidized bed trials, the sugar yield from the acid treated red oak was only marginally higher than for the untreated red oak (6.1 wt% vs. 4.7 wt%). As occurred in the fluidized bed trials, acid-infused feedstock produced large amounts of agglomerated char although it was imbedded with steel shot and the augers were able to continuously convey it out of the reactor. This char, like that from the fluidized bed trials, had the appearance of having solidified from a molten mass.

We hypothesized that the low sugar yields from acid-infused feedstock in the auger trials compared to the fluidized bed trials was the result of its use of relatively low sweep gas-to-biomass ratio (SG/B) compared to the fluidized bed (6 SLPM/kg vs. 100 SLPM/kg). It is well known that char yields are inversely proportional to the amount of sweep gas used in a pyrolyzer (Brown 2009). Kawamoto et al. (2003, 2009) showed that the vapor pressure of levoglucosan directly influences its oligomerization reactions. Although the saturation vapor pressure of anhydrosugars is relatively low even at pyrolysis temperatures, the amount of anhydrosugars released from untreated biomass during pyrolysis is also low and they can

readily evaporate as they are formed. The amount of anhydrosugar released upon pyrolysis of acid infused biomass might be so large as to impede its rapid evaporation, which instead would rapidly repolymerize and dehydrate to char (Bai et al. 2012).

To test this hypothesis, the biomass feed rate for both untreated and acid infused red oak was reduced to 0.25 kg/hr and the sweep gas flow rate was increased to 4 SLPM. These changes increased the SG/B to 16 SLPM/kg, still well short of the ratio employed in the fluidized bed pyrolyzer, but 170% higher than the initial attempt. Two replications were performed for each biomass (Table 10). All trials were successfully run at steady conditions for 3 hours. The average bio-oil yields for untreated and acid infused biomass were 67.0 wt% and 65.3 wt%, respectively, which are essentially indistinguishable.

On the other hand, the sugar yields were 4.95 wt% and 17.4 wt% for the untreated and acid infused biomass, which is almost a three-fold increase as a result of pretreating the biomass. The yield of non-condensable gas from the acid-infused biomass for pyrolysis at this higher SG/B was slightly reduced to 13.1 wt%. The char yield did not change significantly.

Encouraged by these results, we further increased the sweep gas flow to 5 SLPM to achieve a SG/B of 20 SLPM/kg. The sugar yield for the acid infused biomass decreased to 11.9 wt%. The reasons for this decrease are unclear, but are likely due to the small headspace in the auger reactor, which was originally designed to minimize the amount of sweep gas needed for its operation.

Table 10. Pyrolysis Conditions and Mass balances of the control and acid-infused red oak on the auger reactor

Feedstock	**Red Oak Control**		**Red Oak Control**		**Red Oak 0.4wt% H2SO4**		**Red Oak 0.4wt% H2SO4**		**Red Oak 0.4wt% H2SO4**	
N2 flow rate (SLPM)	3.0		4.0		3.0		4.0		5.0	
N2/Biomass feed ratio (SLPM/kg)	6.0		16.0		6.0		16.0		20.0	
Yields	Average	Std.Dev.	Average	Std.Dev.	Average	Std.Dev.	Average	Std.Dev.	Average	Std.Dev.
Bio-Oil (wt%)	65.1	--	67.0	2.4	65.2	1.2	65.3	0.4	62.5	3.4
Gas (wt%)	23.7	--	20.9	1.0	15.2	0.8	13.1	1.6	18.2	1.1
Char (wt%)	11.2	--	12.2	1.4	19.6	0.4	21.7	2.0	19.3	2.4
Mass closure	100.0	--	100.0		100.0		100.0		100.0	
Bio-Oil in Fractions	% oil	--	% oil		% oil		% oil		% oil	
C1	53.6	--	59.0	8.8	64.9	0.4	54.8	0.4	45.7	2.7
C2	26.1	--	8.9	8.0	10.4	2.9	5.1	0.0	9.4	4.9
ESP	18.8	--	28.9	0.8	23.0	2.6	37.3	0.1	39.6	7.7
C3	1.5	--	3.2	0.0	1.7	0.7	2.7	0.5	5.3	0.2
Total Oil	100.0	--	100.0		100.0		100.0		100.0	
% yield of sugars	4.7	--	5.0	0.3	6.1	0.2	17.4	0.7	11.9	0.6

However, when attempting to maximize sugar production, the flow of large amounts of sweep in through the small cross section of this reactor likely entrains biomass particles and reduces their contact time with the heat carrier, which is essential for complete pyrolysis. The small headspace is not inherent in the design of an auger reactor, which suggests that sugar yields could be further increased by reducing the velocity of the sweep gas while increasing its volumetric flow rate. Although such a configuration change would increase the residence time of anhydrosugar vapors in the hot zone of the pyrolysis reactor, once vaporized, levoglucosan is known to be relatively stable (Patwardhan et al. 2011).

The maximum yield of sugar obtained with the auger reactor was 17.4 wt%. Since the cellulose content of the red oak was 41 wt%, approximately 42% of the cellulose content of the red oak was converted to sugars. On total carbohydrate basis the yield is about 21%.

Non-condensable gas yield was also influenced by acid infusion of the biomass prior to pyrolysis. Untreated biomass yielded about 20 wt% gas while pretreatment reduced gas yield to only about 13 wt%. This 35% reduction in gas yield is a direct result of the passivation of AAEM, which is known to promote both gas and char formation during pyrolysis (DeGroot et al. 1984).

The distribution of sugar in the four stages of the bio-oil collection system reveals that the anhydrosugar exists as both vapors and aerosols, at least downstream of the pyrolysis reactor. As shown in Figure 37, the sugar is recovered almost completely in the first stage (condenser operated at 60-65°C) and the third stage (ESP) for both the untreated and acid-infused feedstocks. The first stage cools the gas stream sufficiently to condense anhydrosugars (principally levoglucosan) and phenolic monomers (Patwardhan et al. 2011)

derived from pyrolyzed lignin on the walls of the condenser or to form a fume of (liquid) anhydrosugar and polymerized phenolic compounds. The practical implementation of a process to separate the sugars and phenolic oligomers in stages 1 and 3 is the subject of a separate study (Rover et al. 2013).

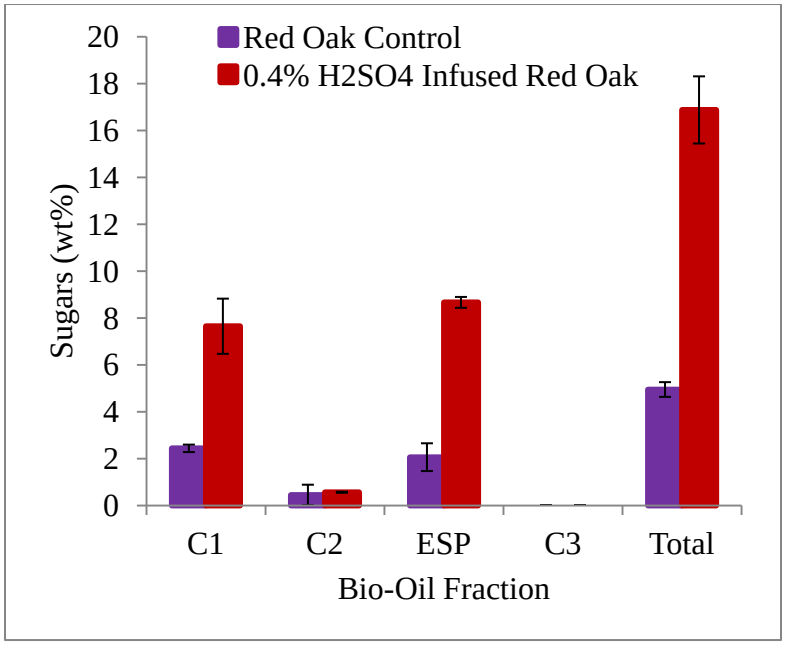

Figure 37. Sugar content of the bio-oil fractions from control and acid-infused red oak (C: Condenser, ESP: Electrostatic precipitator)

From the current knowledge of passivation and the observations of the fast pyrolysis process described above, it is clear that the pyrolysis reaction of cellulose and hemicellulose proceeds predominantly through the depolymerization pathway. Considering the char yields from the acid-infused biomass and the texture of the char from failed and normal pyrolysis runs we hypothesized that the lignin pyrolysis is negatively affected by the passivation process or the presence of mineral acid in the feedstock. To test this hypothesis, we determined the moisture content, modified acid number (MAN) and water insoluble content in the bio-oils produced from the acid-infused and control feedstocks.

The bio-oil from the control feedstock had total moisture content of 19.3 wt% while the bio-oil from the acid-infused feedstock had a total moisture content of 18.9 wt% on a biomass weight basis. With the passivation of alkali, the alkali-catalyzed ring scission of cellulose and hemicellulose will decrease as will the char formation; so the water formation from the polysaccharides should decrease as well. The present results show that moisture content of bio-oils from both the untreated and acid-infused red oak is similar (Figure 38).

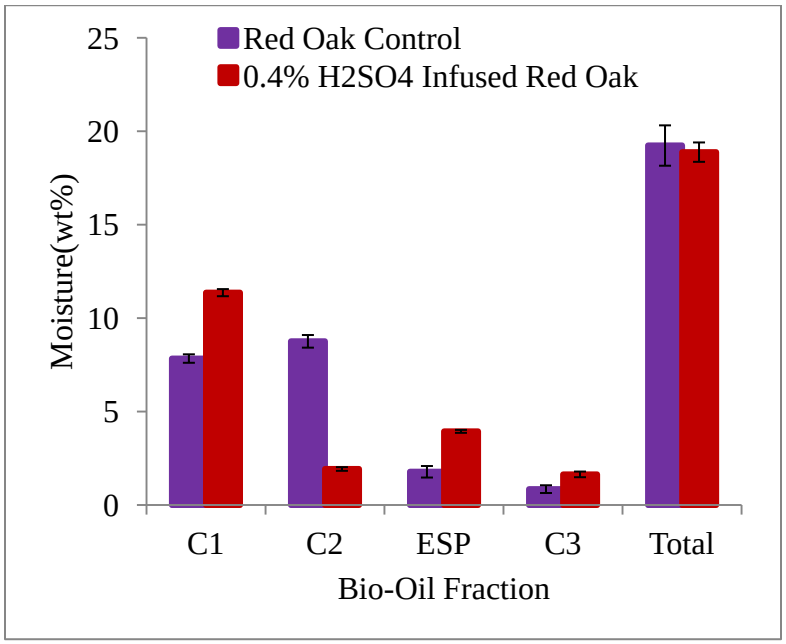

Figure 38. Moisture content of the fractions of bio-oils normalized to total bio-oil weight from control and acid-infused red oak (C: Condenser, ESP: Electrostatic precipitator)

This result suggests that though there may be a decrease in water formation from carbohydrates in the passivated feedstock, there may be increased char and water formation from lignin, which would contribute to similar water content from both the control and treated feedstocks. Though the overall water contents are almost equal, the distribution of the moisture into the bio-oil fractions is different in each case. The moisture content of C1 and ESP increase while that of C2 decreases considerably when compared to the control

feedstock. It is possible that the sugars are absorbing moisture, causing the increase in moisture contents of the first and third fractions, which contain most of the sugars produced from the acid-infused feedstocks. (The acid-infused feedstock also produced more water in the C3 fraction, but the difference is not significant as this fraction collected much smaller quantities of bio-oil than the other fractions.)

MAN: In the case of the bio-oil from the acid-infused feedstock, a reduction in acidity is anticipated because passivation increases sugar yields and decreases light oxygenates that are acidic. As can be seen from Figure 39, the Modified Acid Number (MAN) of the first and fourth fractions decreases significantly.

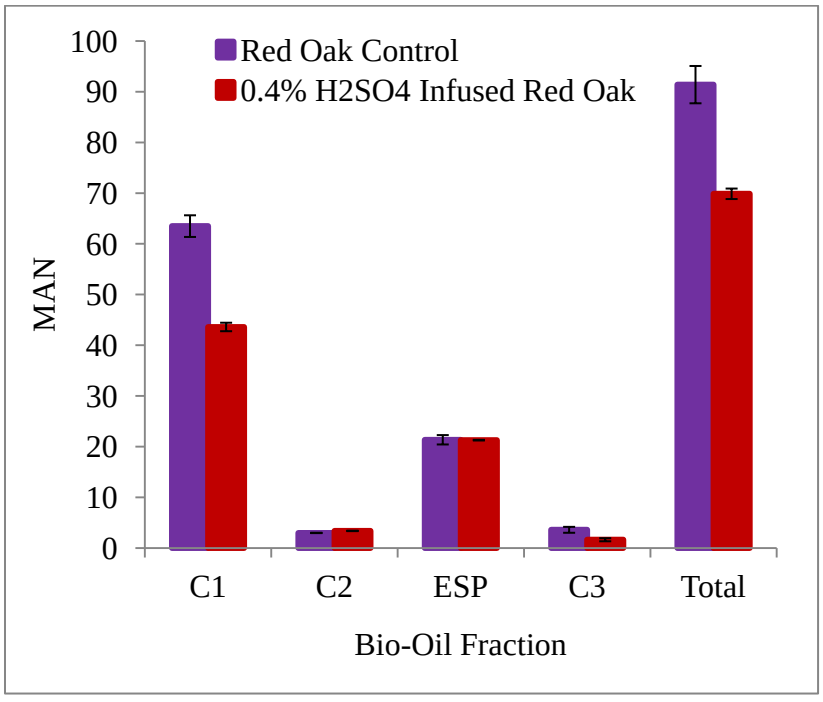

Figure 39. Modified acid number (MAN) of the fractions of bio-oils from control and acid-infused red oak (C: Condenser, ESP: Electrostatic precipitator)

Maximum reduction occurs in the first fraction because of the large quantity of this fraction. Fraction 4, which is comprised mostly of acidic compounds, dropped its acidity

considerably. The overall MAN of the bio-oil from acid-infused feedstock was 71 compared to 91 for the bio-oil from control feedstock, a 21% decrease. The decrease in acidity of the bio-oil makes it much less corrosive and storage-friendly. On the other hand, the pyrolysis of lignin is not supposed to produce any acidic products, so this result does not provide any insight into the pyrolysis of lignin.

The water insoluble portion of the bio-oil consists of the oligomers derived from lignin. As shown in Figure 40, the water insoluble content decreases in the acid-infused red oak when compared to the control. The insolubles decrease from 10.7 to 4.8 wt% in the case of C2 and from 25.6 to 16.2 wt% in the case of ESP, which results in an overall decrease from 12.7 to 10.8 wt%. This decrease in insoluble content read along with the increase in char yield supports the hypothesis that passivation affects the pyrolysis of lignin.

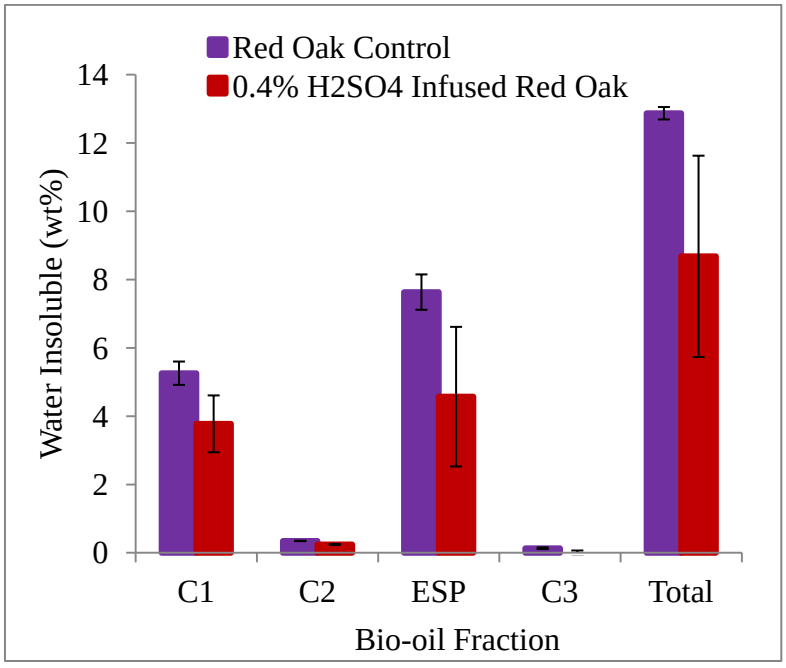

Figure 40. Water insolubles of the fractions of bio-oils from control and acid-infused red oak (C: Condenser, ESP: Electrostatic precipitator)

The vitreous crumps found in the char obtained from every run of the acid-infused feedstock pointed towards this inference. It is possible that the passivation of AAEM is decreasing their ability to catalyze the breaking down of the lignin chains in a similar way to their effect on the cellulose rings. However, this phenomenon calls for further investigation, the knowledge of which will help design better pyrolyzers and a more efficient pyrolysis process.

In summary, the process being developed offers a novel pathway toward the production of drop-in biofuels from lignocellulosic feedstocks. In this study, the acid-infused red oak yielded 240% more sugars than untreated feedstock. While the sugar yields of 41% of the cellulose content are below those of enzymatic hydrolysis of lignocellulosic feedstocks, which vary from 55-96 wt% of the theoretical yields (Wyman et al. 2009), the present process does not require enzymes, is simpler, and faster than the hydrolysis processes. Moreover, our previous studies on the micro-scale pyrolyzer showed a yield of 23.4 wt%, which indicates that the yield of 17 wt% obtained from the present process might be improved with further optimization. This work demonstrates the potential for fast pyrolysis of biomass to be used in the commercial production of sugars suitable for upgrade to drop-in biofuels.

In the thermochemical process was development using the fluidized bed and auger type pyrolysis reactors, the former reactor was not suitable for acid-infused feedstock due to agglomeration of the bed. The auger type pyrolysis reactor with optimized running conditions was found suitable to produce bio-oils from acid-infused feedstock, which yielded 240% more sugars than the untreated feedstock. The acid-infused feedstock pyrolysis

produced char clumps that pointed towards incomplete pyrolysis of lignin. The hypothesis that acid-infusion negatively affects lignin pyrolysis was supported by less amount of water insoluble content in the bio-oil. The MAN of the bio-oil produced from the acid-treated feedstock was significantly lower than that from the control feedstock which indicates a pyrolysis reaction predominantly in the depolymerization pathway. The lower MAN corresponds to less corrosivity of the bio-oil. Overall, the current process offers excellent prospects for the use of biomass feedstocks to produce sugars that could be upgraded to drop-in transportation fuels.

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CHAPTER 5. CONCLUSIONS AND FUTURE WORK

The alkali and alkaline earth metals (AAEM) inherently contained in biomass feedstocks catalyze the pyroanose ring fragmentation during fast pyrolysis thereby yielding more light oxygenates and less of anhydrosugars. It was shown that the catalytic activity of AAEM can be passivated by infusing mineral acids into the biomass feedstocks and the yield of anhydrosugars can be improved from 20% of the theoretical yields to 100% of the theoretical yields from fast pyrolysis of biomass. Excellent correlations, R^2 coefficients exceedding 0.98, were discovered between the amount of acid required to obtain the maximum yield of anhydrosugars from the fast pyrolysis of biomass feedstocks and the amount of AAEM contained in them, corrected for chlorine content. This stoichiometric correlation proves that there is chemical reaction occurring between the acids and AAEM. The correlation can be used to determine the amount of acid to be used for a biomass feedstock to obtain maximum yield of anhydrosugars once its AAEM content is determined.

Most mineral acids are capable of forming thermally stable salts at the pyrolysis temperature of 500°C although there effectiveness in increasing sugar yields varied. Sulfuric acid was found to be capable of improving the yield up to 100% of the theoretical yield while phosphoric could get a yield of 80%. Hydrochloric acid was moderately effective with a yield of 40% of the theoretical yield. The acids such as nitric, acetic and formic were not effective as the salts that they can form are not thermally stable at the pyrolysis temperature.

A micro-scale study over a temperature range of 300-350°C showed that the yield of levoglucosan was very similar at much lower temperatures than the conventional pyrolysis

temperature. However, there is practical difficulty in achieving complete fast pyrolysis of the feedstocks on fluidized bed and auger type reactors.

Scaling up from the microscale study, it was found that a fluidized bed was not effective for continuous processing of acid infused biomass due to fouling by enhanced char production. However, an auger type pyrolyzer was able to continuous process acid infused biomass and produce bio-oil containing very high sugar content. Bio-oil with a sugar content of 18wt% on biomass basis was produced from 0.4wt% sulfuric acid-infused red oak on the auger type pyrolyzer. Decrease in modified acid number and water insolubles of the bio-oils shows that the pyrolysis reactions in the case of passivated biomass have shifted towards depolymerization as opposed to the ring fragmentation that dominates pyrolysis of untreated biomass.

Future Work

From the fundamental studies carried out in this work, it was evident that the mineral acids passivated alkali by forming thermally stable salts. At the same time it was observed that the passivation increased the yields of levoglucosan to as much 100% of the actual yields obtained from pure cellulose. This is higher than observed when adding thermally stable salts to pure cellulose. The phenomenon could be an effect of the synergistic action of weak acids produced during the displacement reactions between the acids and AAEM on the glycosidic bonds. Additional studies are required to better understand the underlying chemical mechanisms.

The yields of sugars from the passivated woody biomass feedstocks were close to that for pure cellulose. On the other hand, the maximum yields of levoglucosan from passivated

herbaceous biomass were in the range of 80-85% of the yield for pure cellulose. This phenomenon suggests that covalent bonds between AAEM and polysaccharides in herbaceous and woody biomass are more catalytically active than simply added salts. More work needs to be done to understand this phenomenon, which could lead to improved yield of sugars from herbaceous biomass. This is particularly important because many of the potential energy crops are herbaceous biomass containing high levels of intrinsic AAEM.

In this work, the effect of passivation on hemicellulose pyrolysis was not studied. As biomass contains about 30-35 wt% of hemicellulose, obtaining sugar from it is important. It is recommended to carry out passivation study on hemicellulose similar to the demonstrations in this work with cellulose.

During the pyrolysis of acid-infused feedstocks on the auger type reactor it was found that clumps were formed that looked more like molten lignin. This phenomenon was poorly understood. It is possible that the acid infusion is changing the mechanism of lignin pyrolysis. Lignin monomers tend to reoligomerize during pyrolysis reactions and mineral acids are capable of catalizing such reactions. Clear understanding this phenomenon could lead to better process development and improved yield of bio-oil.

During the continuous pyrolysis trials on the auger reactor, it was observed that the vapor pressure of levoglucosan was critical to efficiently collecting it in the bio-oil. Removing the vapors from the char as soon as they formed is the key to levoglucosan yield. An auger reactor with different outlets for the vapors may be tried to change the vapor residence times in the reactor.

The auger reactor that was used for the study was not optimized for the best yield. Streamlining the heat carrier feed system and optimizing the parameters can greatly improve the yield of bio-oil. Also, incorporating ISU's proprietary cold-quench bio-oil collection system in to the reactor system may help collect most of the sugars in one fraction which in turn will make separation of the sugars from bio-oil much easier.