

1-1-2009

## **Biomass Pretreatment For Increased Anhydrosugars Yield During Fast Pyrolysis**

Qi Li

Follow this and additional works at: <https://scholarsjunction.msstate.edu/td>

---

### **Recommended Citation**

Li, Qi, "Biomass Pretreatment For Increased Anhydrosugars Yield During Fast Pyrolysis" (2009). *Theses and Dissertations*. 888.

<https://scholarsjunction.msstate.edu/td/888>

This Graduate Thesis - Open Access is brought to you for free and open access by the Theses and Dissertations at Scholars Junction. It has been accepted for inclusion in Theses and Dissertations by an authorized administrator of Scholars Junction. For more information, please contact [scholcomm@msstate.libanswers.com](mailto:scholcomm@msstate.libanswers.com).

BIOMASS PRETREATMENT FOR INCREASED ANHYDROSUGARS YIELD  
DURING FAST PYROLYSIS

By

Qi Li

A Thesis  
Submitted to the Faculty of  
Mississippi State University  
in Partial Fulfillment of the Requirements  
For the Degree of Master of Science  
In Forest Products  
in the Department of Forest Products

Mississippi State, Mississippi

December 2009

BIOMASS PRETREATMENT FOR INCREASED ANHYDROSUGARS YIELD  
DURING FAST PYROLYSIS

By

Qi Li

Approved:

---

Philip H. Steele  
Professor of Forest Products  
(Major Professor)

---

Leonard L. Ingram  
Professor of Forest Products  
(Committee Member)

---

Fei Yu  
Assistant Professor of  
Agriculture and Biological Engineering  
(Committee Member)

---

Rubin Shmulsky  
Professor of Forest Products  
Graduate Coordinator of the Department  
of Forest Products

---

George M. Hopper  
Dean of the College of Forest Resources

Name: Qi Li

Date of Degree: 11<sup>th</sup> December, 2009

Institution: Mississippi State University

Major Field: Forest Products

Major Professor: Dr. Philip H. Steele

Title of Study: BIOMASS PRETREATMENT FOR INCREASED  
ANHYDROSUGARS YIELD DURING FAST PYROLYSIS

Pages in Study: 78

Candidate for Degree of Master of Science

Production of liquid fuels is a high national priority to provide transportation fuels. Production of liquid bio-fuels from biomass has been identified as a viable goal over the next decades. Fast pyrolysis is the rapid thermal degradation of lignocellulosic biomass in the absence of oxygen. Levoglucosan, which can be hydrolyzed and fermented into bio-ethanol, is produced during the pyrolysis process of the cellulose contained in biomass. Pure cellulose results in the production of levoglucosan of more than 50% by feedstock weight while woody biomass typically produces about 3% during pyrolysis. Researchers have performed significant research into methods to increase yields of levoglucosan and other associated anhydrosugars during pyrolysis. Most research has focused on mild acid pretreatment of biomass feedstocks prior to pyrolysis. Such treatment demineralizes and removes hemicellulose that appears to hinder the production of levoglucosan during pyrolysis. The objective of this study is to move beyond simple acid pretreatment to increase pyrolytic anhydrosugars yields during fast pyrolysis.

**Key words:** bio-fuel, pyrolysis, levoglucosan, anhydrosugars, lignocellulosic biomass.

## ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my major professor Dr. Philip H. Steele for his continuous guidance, advice and support. I would also like to thank Drs. Leonard L. Ingram and Dr. Fei Yu for their guidance and service as committee members. Deep appreciation is due for all the professors of the Department of Forest Products for their guidance during my study in this program. Special thanks to Dr. EL Barbary Hassan and Mr. Brian Mitchell of the Department of Forest Products for their valuable help.

Finally, I would like to extend special words of appreciation to the most important persons in my life: my husband An Mao, my father Gengxin Li, my lovely mother Huizhen Liu and my sister Lan Li for their endless love and selfless support.

## TABLE OF CONTENTS

ACKNOWLEDGEMENTS.....	ii
LIST OF TABLES .....	v
LIST OF FIGURES .....	vi
CHAPTER	
I. INTRODUCTION .....	1
II. PY-GC/MS STUDY OF THE CHEMICAL PRODUCTS FROM FAST PYROLYSIS OF DILUTE ACID PRETREATED LIGNOCELLULOSIC BIOMASS.....	4
2.1. Background.....	4
2.1.1. Biomass Thermal Conversion by Fast Pyrolysis .....	4
2.1.2. Biomass Pretreatment to Increase Anhydrosugars Yield from Fast Pyrolysis.....	7
2.1.3. Mechanism and Kinetics of Thermal Degradation of Cellulose and Cellulosic biomass .....	16
2.1.4. Hydrolysis of Levoglucosan .....	20
2.2. Experimental .....	22
2.2.1. Materials .....	22
2.2.2. Biomass pretreatment .....	22
2.2.3. Py-GC/MS analysis.....	23
2.2.4. Inductively coupled argon plasma spectrometry .....	24
2.3. Results and Discussion .....	24
2.3.1. Pyrolysis temperature and time optimization results of pine wood flour .....	24
2.3.2. Optimization of pretreatment of pine wood flour results.....	26
2.3.3. Minerals content test results and its affect on levoglucosan yield.....	28
2.4. Conclusions.....	30
LITERATURE CITED.....	32

III. EXPLORATORY STUDY OF ULTRASOUND ASSISTED DILUTE ACID PRETREATMENT TO FURTHER INCREASE ANHYDROSUGARS YIELD DURING FAST PYROLYSIS.....	48
3.1. Background.....	48
3.2. Experimental.....	50
3.2.1. Materials .....	50
3.2.2. Biomass pretreatment .....	50
3.2.3. Py-GC/MS analysis.....	50
3.2.4. Inductively coupled argon plasma spectrometry .....	51
3.2.5. Elemental analysis .....	51
3.2.6. X-ray diffraction analysis .....	51
3.3. Results and Discussion .....	52
3.3.1. Optimization of ultrasound assisted phosphoric acid pretreatment of pine wood flour results .....	52
3.3.2. Comparing sonicated and non-sonicated results in terms of minerals content and levoglucosan yields .....	55
3.3.3. Elemental analysis and X-ray diffraction spectrometry analysis results .....	56
3.4. Conclusions.....	57
LITERATURE CITED.....	58

## APPENDIX

A. PY-GC/MS CHROMATOGRAM OF RAW PINE WOOD FLOUR .....	68
B. PY-GC/MS CHROMATOGRAM OF ULTRASOUND ASSISTED PHOSPHORIC ACID PRETREATED PINE WOOD FLOUR.....	70
C. MASS SPECTRA AND CHEMICAL STRUCTURE OF MAJOR PRODUCTS FROM FAST PYROLYSIS OF DILUTE ACID PRETREATED PINE WOOD FLOUR (LIBRARY SPECTRA AND SAMPLE SPECTRA).....	72

## LIST OF TABLES

2.1	Mineral contents of control and pine wood flour pretreated under different temperatures.....	29
2.2	Mineral contents of control and pine wood flour pretreated with different phosphoric acid concentrations.....	29
2.3	Mineral contents of control and pine wood flour pretreated for different time period levels.....	29
3.1	Elemental analysis results of control and pretreated pine wood flour samples.....	56



## LIST OF FIGURES

2.1	Two competitive pathways of degradation of cellulose (Soares et al. 1995).....	17
2.2	Levoglucosan fragmentation mechanism (Shafizadeh 1980).....	19
2.3	Hydroxyacetaldehyde formation (Richards and Zheng 1991).....	19
2.4	The acid-catalyzed hydrolysis of levoglucosan to glucose (Olson et al. 2007) .....	21
2.5	Py-GC/MS products distributions from raw pine wood flour by spectral area percentage for pyrolysis temperatures of 300, 450 and 500°C for a heating rate of 10°C/ms for 10 s .....	38
2.6	Py-GC/MS products distributions from raw pine wood flour by spectral area percentage for pyrolysis temperatures of 450°C for a heating rate of 10°C/ms for 5 and 10 s .....	39
2.7	Py-GC/MS products distributions from pyrolysis of pretreated pine wood flour by spectral area percentage for three different phosphoric acid concentrations (0.5, 1, and 2 wt. %) at 100°C for 1 hour .....	40
2.8	Py-GC/MS products distributions from pyrolysis of pretreated pine wood flour by spectral area percentage for three different phosphoric acid concentrations (0.5, 1, and 2 wt. %) at 100°C for 1 hour .....	41
2.9	Py-GC/MS products distributions from pyrolysis of pretreated pine wood flour by spectral area percentage with 1% phosphoric acid at 100°C for three different time levels (1, 2, and 3 hours) .....	42
2.10	Py-GC/MS products distributions from pyrolysis of pretreated pine wood flour by spectral area percentage with 1% phosphoric acid at 100°C for three different time levels (1, 2, and 3 hours) .....	43
2.11	Py-GC/MS products distributions from pyrolysis of pretreated pine wood flour by spectral area percentage with 1% phosphoric acid at three different temperatures (60, 80, and 100°C) for 1 hour .....	44

2.12	Py-GC/MS products distributions from pyrolysis of pretreated pine wood flour by spectral area percentage with 1% phosphoric acid at three different temperatures (60, 80, and 100°C) for 1 hour .....	45
2.13	Py-GC/MS products distributions from pyrolysis of pretreated pine wood flour with three different inorganic acids (phosphoric acid, sulfuric acid, and hydrochloric acid) .....	46
2.14	The relationship between levoglucosan yield from pyrolysis of pretreated pine wood flour and minerals content of pretreated pine wood flour .....	47
3.1	Py-GC/MS products distributions from pyrolysis of ultrasonic pretreated pine wood flour by spectral area percentage with three different phosphoric acid concentration levels (0, 0.5, and 1 wt. %) at 100% ultrasonic amplitude for 30 minutes .....	59
3.2	Py-GC/MS products distributions from pyrolysis of ultrasonic pretreated pine wood flour by spectral area percentage with three different phosphoric acid concentration levels (0, 0.5, and 1 wt. %) at 100% ultrasonic amplitude for 30 minutes .....	60
3.3	Py-GC/MS products distributions from pyrolysis of ultrasonic pretreated pine wood flour by spectral area percentage for three pretreatment time period levels (10, 20 and 30 minutes) with 0.5% phosphoric acid at 100% ultrasonic amplitude.....	61
3.4	Py-GC/MS products distributions from pyrolysis of ultrasonic pretreated pine wood flour by spectral area percentage for three pretreatment time period levels (10, 20 and 30 minutes) with 0.5% phosphoric acid at 100% ultrasonic amplitude.....	62
3.5	Py-GC/MS products distributions from pyrolysis of ultrasonic pretreated pine wood flour by spectral area percentage with 0.5% phosphoric acid at three different ultrasonic amplitude levels (20, 60, and 100%) for 30 minutes.....	63
3.6	Py-GC/MS products distributions from pyrolysis of ultrasonic pretreated pine wood flour by spectral area percentage with 0.5% phosphoric acid at three different ultrasonic amplitude levels (20, 60, and 100%) for 30 minutes.....	64
3.7	Py-GC/MS products distributions from pyrolysis of pretreated pine wood flour with three different pretreatment methods .....	65
3.8	Minerals contents of pretreated pine wood flour with three different pretreatment methods.....	66

3.9	Comparison of crystallinity of control sample and two pretreated pine wood flour samples .....	67
-----	--	----

## CHAPTER I

### INTRODUCTION

Production of liquid transportation fuels is a high national priority. Production of liquid bio-fuels from biomass has been identified as a viable goal over the next decades. Several biofuels routes to production of liquid fuels have been developed over the years, mainly including gasification of biomass to syngas for conversion to synthetic diesel fuel, pyrolysis of biomass to bio-oils, direct liquefaction, conversion of plant oils to biodiesel, and release of sugars for fermentation to ethanol (Bin Yang et al. 2008).

For production of fermentable sugars from biomass, pretreatment operations are essential to the process and these have a very important impact on costs and performance of the entire system. Because there are various pretreatment technologies that have been developed, the specific choice of pretreatment should be targeted for low-cost, low environmental impact, and advanced pretreatment processes for producing high sugars yields. Current cellulosic ethanol processes require extensive washing, treatment of chemical waste, and specialized pressurized and corrosion resistant reactors.

An economic analysis of three lignocellulose-to-ethanol conversion technologies: fast pyrolysis integrated with a fermentation step, simultaneous saccharification and fermentation (SSF), dilute sulfuric acid hydrolysis and fermentation was conducted by So and Brown (1999). The estimated production cost of ethanol was \$1.57, \$1.28, and \$1.35

per gallon for fast pyrolysis, SSF, and acid hydrolysis, respectively. An ethanol production yield of 95 gal/ ton feedstock (DM) was estimated for the fast pyrolysis route. This study concluded that fast pyrolysis integrated with a fermentation step is comparable with the other two processes and suggested that it should be considered for further development (So and Brown 1999).

Fast pyrolysis is the rapid thermal degradation of lignocellulosic biomass in the absence of oxygen. The pyrolysis process results in the production of a liquid product termed pyrolysis oil, or more frequently, bio-oil. Typical liquid bio-oil yield is 65 to 70%; Byproducts are approximately 20% char and 15% noncondensable gases. Levoglucosan is produced during the pyrolysis process of the cellulose contained in biomass. Pure cellulose results in the production of more than 50% by feedstock weight while woody biomass typically produces about 3% during pyrolysis. Researchers have shown that inhibitors contained in the non-cellulosic component of lignocellulosic biomass reduce the production of levoglucosan during fast pyrolysis.

Researchers have performed significant research into methods to increase yields of levoglucosan and other associated anhydrosugars during pyrolysis. They have also speculated on the basic chemical mechanisms that underlie the formation of levoglucosan during pyrolysis. There has been some success in both increasing levoglucosan yields via hydrolysis or demineralizing pretreatments and some of the hypotheses put forward appear to be partial explanations as to the true chemical reactions that result in levoglucosan formation during pyrolysis. Most research has focused on mild acid pretreatment of biomass feedstocks prior to pyrolysis. Such treatment demineralizes or

removes hemicellulose that appears to hinder the production of levoglucosan during pyrolysis.

The objective of this research was to move beyond simple acid pretreatment to increase pyrolytic anhydrosugars production and to remove additional barriers to further increasing yields. Dilute acid pretreatment is expected to be more effective when assisted by ultrasonic energy and by using smaller particle size of biomass because these improvements can increase the surface area of feedstock particle that may be attacked by the acid catalyst. Feedstock surface area is expected to be increased by reducing particle size prior to pretreatment or by opening up the given particle size by treatments that may fractionate it to open up available surface area.

Therefore, the key objective is to increase the efficacy of the acid pretreatment step that has been proven successful by previous researchers. Efficacy is expected to be attempted by increasing access of acid catalyst to the feedstock cellular structure by application of ultrasonic technique to increase the intensity of acid/biomass interaction as well as to increase the initiate greater activity of the acid as it interacts with the feedstock material.

## CHAPTER II

### PY-GC/MS STUDY OF THE CHEMICAL PRODUCTS FROM FAST PYROLYSIS OF DILUTE ACID PRETREATED LIGNOCELLULOSIC BIOMASS

#### **2.1. Background**

##### **2.1.1. Biomass Thermal Conversion by Fast Pyrolysis**

Fast pyrolysis produces a liquid product known as pyrolysis oil or bio-oil. The required pyrolysis conditions for fast pyrolysis are rapid application of a temperature of 400 to 650°C and the absence of oxygen. This temperature range results in the decomposition of the biomass cell structure into their molecular components. At these moderate temperatures a fraction of biomass is converted to approximately 10 to 15% syngas by pyrolysis but the majority is converted to pyrolysis oil (60 to 75%) or char (15%). Bio-oil chemical properties vary with the feedstock type pyrolyzed but woody biomass typically produces a mixture of 30-percent water, 30-percent phenolics, 20-percent aldehydes and ketones, 15-percent alcohols and 10-percent miscellaneous compounds (Bridgewater et al. 1999).

Commercial pyrolysis reactors obtain most of the heat for their energy-intensive process from the byproducts of bio-oil production. Some of the 15% char and 10% syngas generated during pyrolysis are typically combusted to provide the heat energy

required to dry biomass and for production of pyrolysis heat. Biomass is typically dried to the approximate 10% moisture content level needed for pyrolysis. This moisture content level results in 20-30% water production in the bio-oil. Biomass moisture contents above approximately 10% will produce bio-oils containing prohibitively high water content values. Pyrolysis exit gas is composed of CO<sub>2</sub>, CO, CH<sub>4</sub>, and small amounts of hydrogen and oxygen. All but CO<sub>2</sub> are available to combust to produce heat and this is the typical practice for providing additional energy for pyrolysis reactor heating.

Rapid decomposition of the biomass (< 2 sec residence time) is required to produce maximum liquid yields. Heating rate is usually from 600°C/sec to 10,000°C/sec. The rapidity of the thermal biomass decomposition results in the production of a condensate that is not at thermodynamic equilibrium at normal storage temperatures (Diebold 2000). Bio-oil viscosity increases over time, as the many chemical compounds comprising the stored bio-oil chemically interact in various ways to move toward thermodynamic equilibrium. Increased molecular weight resulting from these reactions is the main causative agent in the viscosity increase over time (Scahill et al. 1997).

A major factor initiating the reactions toward increased bio-oil viscosity is the reactivity of the numerous oxygenated compounds responsible for the fact that the mass of a typical bio-oil is comprised of up to 45% by weight of oxygen. In addition to variable viscosity over time bio-oil has other negative properties that have hindered conversion into bio-fuels. Bio-oil pH is low, ranging from about 2.5 to 3.1. Higher heating value (HHV) is relatively low at less than one-half the value of No. 2 fuel oil or 40% of the value of petroleum diesel.



Considerable research has been performed to apply various treatments to use raw bio-oil as a bio-fuel without upgrading. Czernik and Bridgewater (2005) have provided a recent review of these attempts to use raw bio-oil as a fuel. They discuss attempts at furnace and burner/boiler systems but conclude that “better quality bio-oil available at an attractive price is necessary for commercial, large-scale, applications.” The authors also describe tests with raw bio-oil to fuel diesel engines, turbines and Stirling engines. Their conclusion following their review of past and current attempts to utilize raw bio-oil as a fuel is that some method of upgrading will be required to allow it to be utilized.

Pyrolysis yield and product distribution differences have been noted between experiments conducted with synthetic samples containing cellulose, hemicellulose, and lignin when compared with natural biomass with varying compositions of these components (Yang, et al. 2006). At least some of this variance is attributable to the minerals found in natural biomass, which may act as catalysts and influence the overall mix of products (Raveendran et al. 1995; Bradbury et al. 1979; Fahm et al. 2007). Extraneous inorganic materials may also be present due to contamination from soil and other materials during the collection, handling, and storage of the feedstock.

Studies have reported that the ratios of liquids, gases and chars produced during pyrolysis vary with higher levels of inorganic species contained in the feedstock. In general, the levels of char and gas increase and the liquid yield decreases. In the liquid component inorganics tend to increase the yield of glycolaldehyde and hydroxyacetone and decrease the anhydrosugars (Richards and Aheng 1991). Recognizing the sensitivity of the process to the presence of inorganics, researchers determined that pretreatments, such as acid washing, could impact the pyrolysis product distribution by altering the

feedstock material structure and composition (Piskorz et al. 1989; Dobeles et al. 2003; Shurong et al. 2007).

The heat and mass transfer requirements for performance of fast pyrolysis are strongly influenced by the nature of the lignocellulosic biomass and chars. At the particle level, the thermal degradation process can be described as: (1) heat penetration within the particle by conduction through the gas phase and the solid matrix and radiation; (2) vaporation of water and partial recondensation in the colder parts of the particle not accessed by the temperature front; (3) transport of water through the particle to the outer surface by convection and/or diffusion; (4) thermal degradation of the cellulosic and ligno-materials and production of vapors and chars; (5) transport of vapors to the outer surface through the char layer by convection and diffusion; (6) cracking of vapors in the char layer to other types of gases and char (Blasi 2002; Janxe et al. 2000; Willner and Brunner 2005). These mechanisms indicate that particle size should have a strong influence on fast pyrolysis results. Biomass moisture content also has a large influence on fast pyrolysis. The moisture level of the feedstock produces an increase in the devolatilization time and also influences char and gas production, the higher heating value and the water content of the final bio-oil (Dirmibas 2008; Westerhof et al. 2007; Diego et al. 2002).

### **2.1.2. Biomass Pretreatment to Increase Anhydrosugars Yield from Fast Pyrolysis**

When cellulose is heated to over 300°C, it undergoes various pyrolytic processes to produce, as a major component in the resultant bio-oil, an anhydrosugar known as levoglucosan (1,6-anhydro- $\beta$ -D-glucopyranose). Levoglucosan is a dehydrated glucose

containing a ketal functional group. Cellubiosan, in addition to levoglucosan, and other various anhydrosugars are produced in lesser but in additively significant quantities.

Shafizadeh (1980) analyzed the production of levoglucosan from various cellulose types from and cottonwood wood fiber. His results were given as percentage yields of each tested feedstock. At a 400-450°C temperature range the levoglucosan plus anhydrosugars yield from four pure commercial wood-based cellulose types was 42 to 56%. Yields of levoglucosan from wood, as opposed to pure cellulose, are known to be much lower. This is demonstrated in the Shafizadeh's yields of levoglucosan plus anhydrosugars of 3% for untreated cottonwood fiber and 9% for H<sub>2</sub>SO<sub>4</sub> acid treated cottonwood fiber. Complete removal of hemicellulose to produce a pure lignocellulose resulted in 37% yield of levoglucosan plus anhydrosugars.

Shafizadeh's (1980) results indicated that both wood lignin and hemicellulose content may potentially interfere with levoglucosan and anhydrosugars yield during pyrolysis. Pyrolysis of untreated pure holocellulose (lignin removed) gave only a 1% yield of levoglucosan and anhydrosugars. This indicated that hemicellulose content alone appears to strongly suppress levoglucosan plus anhydrosugar yield. When the holocellulose was treated with 1% NaOH and 1% H<sub>2</sub>SO<sub>4</sub> the yield of levoglucosan plus anhydrosugar increased to 32%. Again, the removal of hemicelluloses, which presumably occurred due to the base and acid treatments, produced a large increase in levoglucosan and anhydrosugar yield. These results indicate that presence of hemicellulose rather than lignin in wood interacts to inhibit levoglucosan and anhydrosugars yields during pyrolysis.

Shafizadeh (1980) also showed that a substantial yield of glucose was possible from the levoglucosan plus anhydrosugars produced from wood treated to remove lignin and/or hemicelluloses. A glucose yield of 49% was obtained from hydrolysis of levoglucosan plus anhydrosugars products obtained from Whatman CF 11, Lot A cellulose. In addition, a glucose yield of 46% was obtained from the hydrolysis (that presumably removed all hemicellulose content) of the 37% levoglucosan plus anhydrosugars yield from pyrolyzed cottonwood. These results indicate that obtaining considerable yield of glucose is possible from the pyrolysis product of wood pretreated to remove hemicellulose.

A study on the mechanism of the rapid pyrolysis of biomass and cellulose in a fluidized bed reactor was performed by Piskorz et al. (1986). It was proposed that at temperatures over about 450°C, and at vapor residence times of one second or less, the monomer unit of cellulose decomposed preferentially to a two-carbon and a four-carbon fragment and the two-carbon fragment rearranged to form hydroxyacetaldehyde. It was also indicated that the cellulose decomposition in wood followed the same path as that of pure cellulose during fast pyrolysis.

Radlein et al. (1987) pretreated wood and cellulose prior to fast pyrolysis. The wood or cellulose was pre-hydrolyzed in a batch reactor at 90°C using sulfuric acid concentrations of 1%, 3% and 5% with reaction times of 6 or 19 hours and liquid to solid weight ratios of 4:1 or 12:1. HPLC analyzed the composition of the acid hydrolysate and of the water extract of the pyrolysis oils. It was found that, after a mild hydrolysis, levoglucosan yield of the pretreated cellulose was sharply increased from 27.0% to 38.4% of the feed weight when pyrolyzed at 500°C. A large increase in cellobiosan yield (by

15.2%) was also observed for both the pretreated cellulose and the pretreated wood. It was estimated that the change in product distribution was due to the removal of inorganic cations during the acid treating process but this was not considered to be the only effect. It was also hypothesized that the morphology and degree of hydrogen bonding in the cellulose might also affect the composition of the pyrolytic liquids.

Scott et al. (1988) established a process for the production of fermentable sugars from cellulosic biomass comprising the step of pretreatment with a dilute sulfuric acid to dissolve hemicellulose and subsequent rapid pyrolysis at a temperature of 400°C to 600°C at atmospheric pressure with a short vapor residence time.

Piskorz et al. (1989) studied fluidized bed fast pyrolysis of poplar wood and a number of types of cellulose produced by different processes. Piskorz computed yields based on feedstock weight as the base. Both untreated and treated cellulose and poplar wood specimens were pyrolyzed at 500°C with vapor residence time of 0.46s. Biomass was pretreated with mild acid at 5% of H<sub>2</sub>SO<sub>4</sub> at 90°C for 5.5 hours. Levoglucosan and anhydrosugars were quantified in the resultant bio-oil. Highest yielding cellulose was Avicel which, when untreated, produced 26.9% levoglucosan with anhydrosugars yields at 10.1% cellobiosan, 6.5% glyoxal, and zero 1,6-anhydroglucofuranose (1,6-AGF) providing a total levoglucosan plus anhydrosugars yield of 43.5%. Treated Avicel produced 38.41 levoglucosan and 5.6, 2.1 and 7.0% of the anhydrosugars cellobiosan, glyoxal and 1, 6-AGF, respectively. Therefore, total levoglucosan and anhydrosugars yield from treated Avicel was 53.1%.

The yield of levoglucosan from pyrolyzed untreated poplar wood was 3.0%; the anhydrosugars yields were 1.3% of cellobiosan, 2.43% of 1, 6-AGF, and 2.18% of

glyoxal. Therefore, total levoglucosan and anhydrosugars yield was 8.95% for untreated poplar wood. For treated poplar wood the levoglucosan yield was 30.42% with yields of 5.68, 0.11 and, 4.50, for cellobioan, 1, 6-AGF and glyoxal respectively, for the remaining anhydrosugars giving a total anhydrosugars yield of 40.61%.

The described results indicate, as previously noted by Shafizadeh (1980), that hemicellulose presence has a strong suppressing influence on production of levoglucosan and associated anhydrosugars. This is substantiated by the yield of 43.5% of these compounds for untreated cellulose, a somewhat higher 53.1% yield for cellulose with mild acid treatment. In additions untreated poplar wood, which would contain all of its initial hemicelluloses, produced total levoglucosan plus anhydrosugars yield of only 8.95%. Mild acid treated poplar wood, which would presumably have all or a proportion of hemicellulose or contained inorganics decomposed, produced a total yield of anhydrosugars of 40.61%.

Piskorz et al. (1989) tested milder application of sulfuric acid treatment and relatively mild application of two mild acid HCl treatments (0.05% HCl) with one of the mild HCl treatments (0.05% HCl) followed by an additional H<sub>2</sub>SO<sub>4</sub> treatment. Anhydrosugars yields were measured only in terms of levoglucosan yields. The results of these treatments indicated that levoglucosan yields from HCl treatments were relatively low with the lowest yield for the mildest HCl treatment. The highest yields of levoglucosan were 27.7% and 30.1% for the H<sub>2</sub>SO<sub>4</sub> treatment alone and the H<sub>2</sub>SO<sub>4</sub> treatment following HCl treatment, respectively. The treatment described above for 5% H<sub>2</sub>SO<sub>4</sub> at 90°C for 5.5 hours provided a levoglucosan yield of 30.42% while the second H<sub>2</sub>SO<sub>4</sub> treatment was at 5% concentration for 2h treatment at 100°C. It is not surprising

that the yield for these treatments of nearly equal severity also has nearly identical yields of levoglucosan.

Piskorz et al. (1994) studied the effects of operating conditions in a fluidized bed reactor on anhydrosugar yields from poplar wood which was pre-hydrolyzed by a dilute acid to remove hemicellulose. It was found that modification of the solids in the bed by the use of additives had some effect on the composition of gas, liquid, and chars in the products but did not improve sugar yields.

Various pretreatment processes were investigated by Brown et al. (2000) to increase the pyrolytic yield of levoglucosan from herbaceous biomass. They further tested the hypothesis that alkali and alkaline earth metals contained in biomass serve as catalysts to degrade lignocellulose to char during fast pyrolysis, thereby reducing anhydrosugars yields. Three biomass pretreatment processes were evaluated in the study: acid hydrolysis, washing in dilute nitric acid, and washing in dilute nitric acid with the addition of  $(\text{NH}_4)_2\text{SO}_4$  as a pyrolytic catalyst. It was found that demineralization by using dilute nitric acid removed cations from biomass and the acid hydrolysis pretreatment yielded the highest percentages of anhydrosugars.

Scott et al. (2000) performed a preliminary study of the rates of removal of the native alkaline cations in a poplar wood by an ion exchange process by pretreatment with dilute acid. It was found that the exchange process was effective and potassium was more easily removed than calcium. It was also shown that a major amount of the alkaline cations from wood was removed by hot water washing alone. It was suggested that the deionized wood produced by this process could be used as the feed for a fast pyrolysis

process for thermal conversion of cellulose and hemicellulose to anhydrosugars in good yields.

Dobele et al. (2001) studied the effect of phosphoric acid pretreatment on the yield of levoglucosenone from pyrolysis of cellulosic materials. Five types of cellulose, with differing polymerization degree and crystallinity index were pyrolyzed. It was established that the yield of levoglucosenone was affected, not only by the properties of cellulosic raw material, but also by conditions of thermal pretreatment. It was reported that the highest yield of levoglucosenone (29% based on cellulose) was obtained by pyrolysis of microcrystalline Munktel cellulose pretreated with 3.5% of phosphoric acid at 100°C.

Pyrolysis combined with gas chromatography (Py-GC/MS) was applied by Dobele et al. (2001) to study the composition of volatile products from pyrolysis of several types commercial cellulose pretreated with varying concentrations of phosphoric acid in various concentrations. The variations in the composition of the two main volatile products, levoglucosan and levoglucosenone, were investigated, including their dependence on the crystallinity, degree of polymerization of cellulose and conditions of pretreatment with phosphoric acid e.g. pretreatment temperature. A narrow range of 75-78% of the amount of both 1,6-anhydrosaccharides regardless of the pretreatment conditions of the celluloses were observed by pyrolysis of the pretreated celluloses.

Dobele et al. (2003) studied pretreatment of biomass with phosphoric acid prior to fast pyrolysis. The influence of pretreatment parameters, including concentration of phosphoric acid, its uptake by biomass, and drying temperature, upon the pyrolysis



process of various cellulosic materials was determined. Based on the most effective pretreatment tested, the highest amount of levoglucosan obtained from birch wood was 15% after impregnation with 0.5% phosphoric acid at 100°C for 1 h. The highest yield of levoglucosenone obtained from birch wood was 17% after treatment with 2.5% phosphoric acid at 100°C for 1 h.

Dobele et al. (2005) studied the effect of phosphoric acid and  $\text{Fe}^{3+}$  ions on the levoglucosan and levoglucosenone content in volatile products obtained from cellulosic materials by Py-GC/MS. He found that the ratio of levoglucosan/levoglucosenone was affected by the concentration of the phosphoric acid with higher concentration leading to the decrease of the levoglucosan/levoglucosenone ratio. Iron was introduced into the biomass by soaking in  $\text{Fe}_2(\text{SO}_4)_3$  solution alone or in the presence of ammonium. A previous decationization of wood was demonstrated to be important for the subsequent results of  $\text{Fe}^{3+}$  ion treatment. It was reported that 44.8% levoglucosan was obtained from pyrolysis of cellulose pretreated by the ion-exchange method and 27.3% levoglucosan was obtained from pyrolysis of wood pretreated by the ion-exchange method.

Pyrolysis of cellulose was studied by Kwon et al. (2006) for practical production of levoglucosan. Two methods were examined to minimize secondary degradation of levoglucosan: conductive heating by glass bottle and radiation heating from the surface by  $\text{CO}_2$  laser beam, both under vacuum and in a nitrogen atmosphere. It was reported that glass-bottle pyrolysis under vacuum gave the highest levoglucosan yield of 50-55% in the optimum temperature range of 350°C to 410°C.

Yang et al. (2006) investigated the role of the three main components (cellulose, hemicellulose, and lignin) during pyrolysis by thermogravimetric analysis (TGA). The

pyrolysis characteristics of the three components were studied by dividing the pyrolysis process into four ranges according to the temperatures specified by each individual component. The pyrolysis of the synthesized samples containing two or three of the biomass main components indicated negligible interaction among the three components. By using statistical methods, two sets of multiple linear-regression equations were established for predicting the composition of biomass and the weight loss of biomass during pyrolysis in TGA respectively. Yang et al. (2007) also applied TGA to determine that the pyrolysis of hemicellulose and cellulose occurred first, with the weight loss of hemicelluloses occurring mainly between 220°C and 315°C and that of cellulose at 315°C to 400°C. Lignin was found to be more difficult to decompose, with the weight loss occurring in a wide temperature range (from 160°C to 900°C) and generating high solid residue.

Four reference fuels and three low-lignin grasses were subjected to pyrolysis by Fahmi et al. (2008). It was found that the mineral content, rather than lignin content, influenced pyrolysis yields of organics, char and gases. It was shown that demineralizing biomass improved oil quality and stability for high ash feedstocks.

The production of fermentable sugars from olive tree biomass was studied by Cara et al. (2008) by application of dilute acid pretreatment and further saccharification of the pretreated solid residues. Pretreatment was performed at sulfuric acid concentrations of 0.2%, 0.6%, 1.0%, and 1.4% (w/w) with temperature in the range of 170°C -210°C. An overall sugar yield was calculated including sugars generated by pretreatment and the glucose released by enzymatic hydrolysis. The highest sugar yield (36.3g sugar/ 100g raw material) was obtained when pretreating olive tree biomass at

180°C with 1% sulphuric acid concentration. This yield represented 75% of all sugars present in the initial biomass.

### **2.1.3. Mechanism and Kinetics of Thermal Degradation of Cellulose and Cellulosic Biomass**

Cellulose is the most extensively used natural polymer. A large number of studies have been published on its thermal decomposition and the application of the thermal decomposition products. Oligosaccharides were first identified in the tar fraction of polysaccharide pyrolysates by Tsuchiya and Sumi (1970). They were shown to be non-reducing and to contain a variety of linkages and ring sizes (Lomax et al. 1990). Fast pyrolysis of cellulose with a fluidized bed produced much larger amounts of oligomers, particularly the disaccharide, which, in contrast to the products of slow pyrolysis, consisted mainly of single isomers retaining the configuration of the glycosidic bond (Radlein et al. 1987). This suggested that the oligomers are primary pyrolysis products and not the result of resynthesis from levoglucosan as was proposed by Shafizadeh (Lomax et al. 1990).

Lomax et al. (1990) investigated perm ethylated derivatives of material from Curie-point pyrolysis of cellulose by using capillary gas chromatography and mass spectrometry in an attempt to identify the major ring cleavage fragments and to determine their structure. The main complete sugar peaks were identified as levoglucosan and cellobiosan. The identity of the main oligosaccharide ion series produced from in-source pyrolysis of cellulose was confirmed. It was found that the linkage structure of the original polymer was retained and the oligosaccharides terminated in a

1,6-anhydropyranose unit. The main additional ion series identified from in-source pyrolysis was shown to be a ring cleavage fragment produced by reverse aldolisation of a sugar unit, consisting of sugar units with an acetaldehyde fragment on the reducing terminus.

A decrease in the degree of polymerization with negligible production of volatiles occurs at moderate temperatures (below 250°C), whereas extensive degradation of cellulose takes place at higher temperatures, with evolution of various gases and high-boiling products (Soares et al. 1995). Two competitive pathways were proposed by Radlein et al. (1991), Antal, M. J. et al. (1980), Arseneau, D. F. (1971), Kishore, K. et al. (1982) and Bradbury, A. G. W. et al. (1979), for the process, as shown in Figure 2.1.

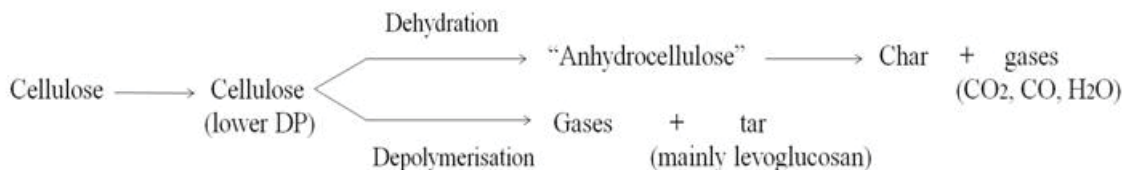


Figure 2.1 Two competitive pathways of degradation of cellulose (Soares et al. 1995)

Soares et al. showed that when the dehydration of cellulose prevailed, evolution of CO<sub>2</sub>, H<sub>2</sub>O and CO with formation of solid char was mainly observed. If depolymerisation prevailed, rather than dehydration, the bio-oil volatilization produced mostly levoglucosan (Soares et al. 1995).

Soares et al. (1995) also studied the thermal decomposition of pure cellulose by thermogravimetry, differential scanning calorimetry, thermal volatilization analysis and characterization of the degradation products. By comparing the characteristics of thermal degradation of pure cellulose and pulp paper, it was found that depolymerisation of the

pure cellulose with production of levoglucosan took place at high heating rates and that autocatalytic dehydration of the cellulose with char production predominated at low heating rates.

Although over many years much investigation has been performed to identify the chemical mechanisms underlying cellulosic pyrolytic decomposition these mechanisms remain incompletely understood. It is necessary to understand all the factors which promote product specificity and maximize yields. These factors include those physical variables which define the reaction conditions as well as the influence of pretreatments on the chemical state of the substrate.

An explanation for the formation of a lower molecular weight product (hydroxyacetaldehyde) from pyrolysis of cellulosic biomass is widely accepted, as shown in Figure 2.2. However, Richards and Zheng (1991) proposed that hydroxyacetaldehyde formed directly from cellulose by the mechanism, as shown in Figure 2.3.



The kinetics of the subsequent chemical reactions involving the products of the initial solid biomass pyrolysis was studied by Shin et al. (2001). Three primary cellulose-derived pyrolysis products (5-hydroxymethyl furfural, levoglucosan, and hydroxyacetaldehyde) were the feedstocks and kinetic studies of gas-phase pyrolysis were performed. Kinetic models were developed and reaction rates and Arrhenius parameters were presented based on the models.

#### **2.1.4. Hydrolysis of Levoglucosan**

Yu et al. (2003) investigated the acid hydrolysis of cellulosic bio-oil to glucose by the hydrolysis with 0.2 mol sulfuric acid per liter pyrolysate at 121°C for 20 min. It was found that 100% of levoglucosan in the pyrolysate was converted to glucose, which indicated that other components in the pyrolysate might have a contribution to glucose besides levoglucosan. The results also showed that the acid-hydrolyzed pyrolysate was a suitable feedstock for ethanol production by fermentation.

Helle et al. (2007) investigated the kinetic model for hydrolysis of levoglucosan and cellobiosan from pyrolysis oil to produce glucose under acidic conditions with sulfuric acid as catalyst. For levoglucosan hydrolysis, it was found that the reaction rate increased exponentially with increasing temperature from 90°C to 110°C and increasing the acid concentration from 110 mM to 500 mM had approximately the same effect as increasing the temperature from 90°C to 110°C. It was proposed that levoglucosan hydrolysis to glucose followed a first-order reaction with an activation energy of 114 KJ/mol. It was also reported that 44% of the cellobiosan was hydrolyzed initially to form

levoglucosan and glucose and the remaining cellobiosan was hydrolyzed initially to form cellobiose. Both reactions were first order reactions based on cellobiosan with the activation energy of 99 KJ/mol.

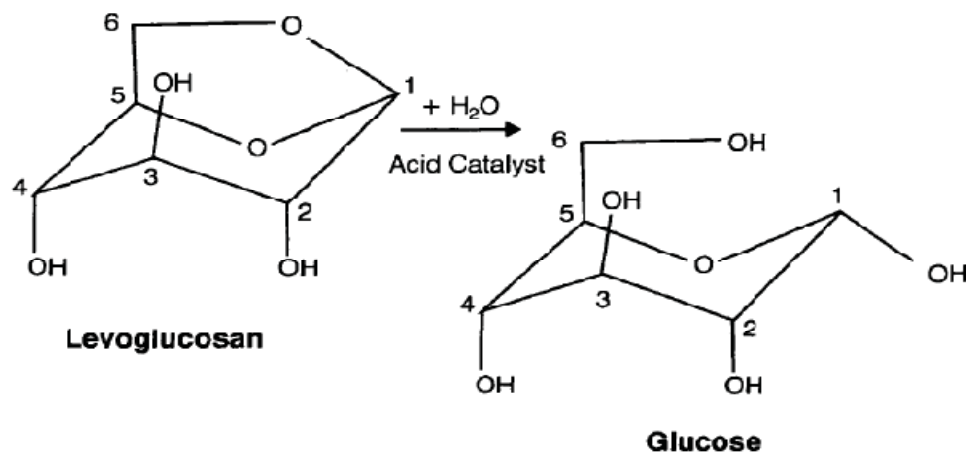


Figure 2.4 The acid-catalyzed hydrolysis of levoglucosan to glucose (Olson et al. 2007)

Olson et al. (2007) disclosed a process for producing glucose and other fermentable sugars from a liquid mixture containing anhydrosugars. The process was comprised of three steps, including water extraction of an anhydrosugar-rich fast pyrolysis bio-oil fraction, further purification of the obtained anhydrosugar-rich fraction which yielded low fermentation inhibitor concentrations, and solid-phase catalytic hydrolysis of the anhydrosugars to produce glucose and other fermentable sugars. It was reported that the preferred and recyclable solid-phase acid catalyst system for this application was a sulfonic acid-type resin or a Nafion resin under an operation temperature range of 80°C to 125°C. It was found that when reaction time was increased at 92°C, by slowing the pumping rate from 0.5 to 0.25 ml/min, levoglucosan conversion



to glucose increased to 100%. A fermentability test with *Saccharomyces* demonstrated that 90% of the glucose yielded in the hydrolyzed product was converted into ethanol. Bacteria are not able to ferment anhydrosugars but ferment simple sugars to a variety of useful products (Olson et al. 2007). Figure 2.4 shows a diagram of the acid-catalyzed hydrolysis of levoglucosan to glucose.

## **2.2. Experimental**

### **2.2.1. Materials**

Commercially available 20 mesh southern yellow pine wood flour (American Wood Fibers, Schofield, WI) was applied for this study. Three types of inorganic acids were selected as treatment reagent. Phosphoric acid, A.C.S. certified, 85% (ACROS Organics, New Jersey), sulfuric acid, extra pure, 96% (ACROS Organics, New Jersey), and hydrochloric acid, A.C.S. certified, 37.7% (Fisher Scientific, New Jersey) were diluted into the desired concentrations to pretreat the southern yellow pine wood flour samples. Distilled water was applied to rinse the samples after treatments.

### **2.2.2. Biomass pretreatment**

20 mesh southern yellow pine wood flour samples were pretreated in heated phosphoric acid aqueous solution at three acid concentrations (0.5, 1, and 2 w.t. %); for optimal acid concentration three pretreatment time period levels (1, 2 and 3 hours) were tested for three temperature levels (60, 80 and 100°C). In order to make sure that wood flour can be completely immersed into acid solution and also have sufficient contact

space with acid catalysts, solid to solution weight ratio of 1 to 20 was selected for all treatments. After the pretreatment, samples were washed with distilled water until pH=7 and then dried in the open air at room temperature for 72 h to 10% moisture content. A control sample was prepared by washing raw southern yellow pine wood flour with the same amount of distilled water as used for pretreated samples followed by drying as previously discussed. The optimal pretreatment condition determined for the phosphoric acid pretreatment was then applied for the sulfuric acid and hydrochloric acid pretreatments for comparison to determine the best inorganic acid type for pretreatment to produce increased anhydrosugars yield during fast pyrolysis.

### **2.2.3. Py-GC/MS analysis**

Pretreated biomass and control samples were tested by Py-GC/MS to obtain chemical products yield after pyrolysis. Pyrolysis of pretreated biomass and control samples were performed in a CDS 5000 pyroprobe coupled with Claurus 500 Gas Chromatography Mass Spectrometer (Py-GC/MS). The injector and the interface temperature was 225oC and 270oC respectively. A 30-meter X 0.32 mm internal diameter silica capillary column coated with 5% phenyl-methylpolysiloxane was used. The mass spectrometer was operated at an 70 eV electron impact ionization mode. The initial chromatography temperature was 40oC, with a temperature programming of 5oC/min increase to go up to 280 oC holding for 10 minutes. Runs were conducted at varied heating rates, times and temperatures under a helium atmosphere to optimize pyrolysis conditions, and Py-GC/MS reaction conditions were determined based on raw pine wood flour pyrolysis without treatments. Samples were placed in a 2 mm internal

diameter by 20 mm long quartz tube and pyrolysed in a pyroprobe containing a platinum resistance heating coil.

#### **2.2.4. Inductively coupled argon plasma spectrometry**

Pretreated and control samples were analyzed by inductively coupled argon plasma spectrometry (ICAPS) to test the dominant metal ion contents, including Ca, Mg, P, K, Na, and Zn.

### **2.3. Results and Discussion**

Py-GC/MS yields are reported in terms of area % from the GC spectrum. When samples are placed into the pyroprobe of the Py-GC/MS and heated, three types of products are formed, including volatiles, heavies, and chars. Heavies may coat out before getting to the GC column. Test results indicated that the amounts of volatiles are small compared to the total sample weight. Therefore, the area % of the volatiles reported here will also be low compared to the total sample weight. Tentative identification of pyrolysis products was performed by the EPA/NIST mass spectral database.

#### **2.3.1. Pyrolysis temperature and time optimization results of pine wood flour**

The raw pine wood flour pyrolysis experiments were performed with a limited number of pyrolysis temperature and time treatment levels based on the decomposition temperatures reviewed in the literature above. Wood thermal decomposition begins at approximately 200°C with maximum mass loss at 350°C with slow heating rate. The heating rate applied varied from 5°C/min to 10°C/min which were much slower than the

heating rates applied in this study. The fastest practical heating rate has been given as 10°C/ms by Bridgewater (2000). This rate was selected as the heating rate for this study because this study was intended to simulate fast pyrolysis. To insure that wood would thermally decompose during pyrolysis, three temperature levels (400°C, 450°C, and 500°C) were chosen to optimize the pyrolysis temperature. Following selection of the optimal pyrolysis temperature two residence times, 5 and 10s, were tested at this temperature to determine the optimal residence time.

Figure 2.5 shows the product distribution information of the raw pine wood flour at three different pyrolysis temperatures at a heating rate of 10°C/ms using Py-GC/MS analysis techniques. The main volatile products from raw pine wood flour pyrolysis at these three pyrolysis temperatures were acetic acid, furfural, levoglucosenone, 2-methoxy-4-propyl-phenol, levoglucosan,  $\alpha$ -D-Glucopyranoside, n-hexadecanoic acid and other phenolic compounds and anhydrosugars (See Appendix A). For the mass spectra and chemical structures of major products from fast pyrolysis of pine wood flour see Appendix C. Referring again to Figure 2.5, some changes were observed in the product distribution between the three pyrolysis temperatures. The production of low molecular weight compounds such as acetic acid and furfural was higher at 400°C pyrolysis temperature compared to the higher pyrolysis temperatures (450°C and 500°C). Acetic acid and furfural are considered as inhibitors for sugar fermentation. Also from Figure 2.5, 500°C temperature produced higher yield of lignin-derived phenols and n-hexadecanoic acid, with lower yield of anhydrosugars. Therefore, pyrolysis temperature of 450°C was selected as the best of the three tested.

Figures 2.6 shows the results for the 5 and 10s heating times tested at 450°C temperature applied at the previously selected heating rate of 10°C/ms. There was no obvious difference for the low molecular weight compounds yields between 5 and 10s heating times, but an great increase in the yields of levoglucosenone, levoglucosan, and  $\alpha$ -D-Glucopyranoside was observed when heating time increased from 5s to 10s. This indicates that 5s heating time is not sufficient to fracture cellulose at the 450°C. Therefore, the 10s heating time was selected as the best of those tested and the temperature and time levels selected for the Py-GC/MS experiments were 450°C applied at a rate of 10°C/ms.

### **2.3.2. Optimization of pretreatment of pine wood flour results**

The main objective of this study was to determine the best conditions for the wood pretreatment to increase the resulting anhydrosugars yield after fast pyrolysis. Figures 2.7 and 2.8 show the product types and distributions given in GC area % for the pyrolysis of pretreated pine wood flour at 450°C, a residence time of 10s and a heating rate of 10°C/ms. Pine wood flour samples were pretreated with three different phosphoric acid concentrations (0.5, 1, and 2 wt. %) at 100°C for 1 hour. Figure 2.7 shows that the yield of levoglucosan increased from 11.6% to 20.5% when the phosphoric acid concentration increased from 0.5% to 1% and only slightly increased from 20.5% to 20.92% when the phosphoric acid concentration increased from 1% to 2%. The yield of levoglucosenone was slightly decreased as the phosphoric acid concentration increased from 0.5% to 2% (Figure 2.7). The yield of furfural decreased slightly with higher acid concentration and slight increase were observed for the yields of acetic acid,

hexadecanoic acid, and 2-methoxy-4-propyl-phenol (Figure 2.8). Thus, phosphoric acid pretreatment concentration of 1 wt. % was selected as the most efficient of the three tested.

Figures 2.9 and 2.10 show the product types and distributions given in GC area % for the pyrolysis of pretreated pine wood flour at 450°C, a residence time of 10s and a heating rate of 10°C/ms. Pine wood flour samples were pretreated with 1% phosphoric acid at 100°C for three different time levels (1, 2, and 3 hours). The yields of levoglucosan and levoglucosenone slightly decreased when the treatment time increased from 1 hour to three hours (Figure 2.9). Rather, increase in the formation of low molecular weight compounds (furfural and acetic acid) and higher molecular weight compounds (hexadecanoic acid and 2-methoxy-4-propyl-phenol) were observed (Figure 2.10). Thus, increasing treatment time changed the pyrolysis product distribution by decreasing the formation of anhydrosugars and pretreatment time of 1 hour was selected as the optimal of the three tested. Therefore, 1% of phosphoric acid, 100°C, and 1 hour of pretreatment time was selected as the optimal pretreatment conditions for high anhydrosugars yield from fast pyrolysis of pine wood flour. This optimal pretreatment condition was also applied to sulfuric acid and hydrochloric acid pretreatment.

Figures 2.11 and 2.12 show the product types and distributions given in GC area% for the pyrolysis of pretreated pine wood flour at 450°C, a residence time of 10s and a heating rate of 10°C/ms. Pine wood flour samples were pretreated with 1% phosphoric acid at three different temperatures (60, 80, and 100°C) for 1 hour. The yield of levoglucosan greatly increased from 13.42% to 20.5% when the pretreatment temperature increased from 60°C to 100 °C and only slightly changes were observed for

the yields of levoglucosenone and  $\alpha$ -D-Glucopyranoside (Figure 2.11). The yield of furfural decreased with higher pretreatment temperature and no obvious changes were observed for the yields of acetic acid, hexadecanoic acid, and 2-methoxy-4-propyl-phenol. Thus, pretreatment temperature of 100°C was selected as the best of the three tested (Figure 2.12).

Figure 2.13 shows the product types and distributions given in GC area% for the pyrolysis of pine wood flour pretreated with three different acids (phosphoric acid, sulfuric acid, and hydrochloric acid). Pine wood flour samples were pretreated by 1% of three different acid solutions (phosphoric acid, sulfuric acid, and hydrochloric acid) at 100°C for 1 hour. Phosphoric acid pretreatment gave the highest yield of levoglucosan (20.5 %) and lowest yields of acetic acid and 2-methoxy-4-propyl-phenol. In contrast to phosphoric acid pretreatment, hydrochloric acid pretreatment gave the lowest yield of levoglucosan (15.8 %) and highest yields of acetic acid and 2-methoxy-4-propyl-phenol among the three different acid pretreatment. Sulfuric acid pretreatment gave levoglucosan yield of 16.23%.

### **2.3.3. Minerals content test results and its affect on levoglucosan yield**

Table 2.1 shows the mineral contents of control and phosphoric acid pretreated pine wood flour. Pine wood flour samples were pretreated with 1% phosphoric acid at three different temperatures (60, 80, and 100°C) for 1 hour. Table 2.2 shows the mineral contents of control and phosphoric acid pretreated pine wood flour. Pine wood flour samples were pretreated with three different phosphoric acid concentrations (0.5, 1, and 2 wt. %) at 100°C for 1 hour. Table 2.3 shows the mineral contents of control and

phosphoric acid pretreated pine wood flour. Pine wood flour samples were pretreated with 1% phosphoric acid at 100°C for three different time levels (1, 2, and 3 hours). From Table 2.1, 2.2, 2.3, it was found that phosphoric acid pretreatment removed most of the minerals content from raw pine wood flour. The minerals content, especially for calcium, potassium, and magnesium, was greatly decreased after phosphoric acid pretreatment.

Table 2.1 Mineral contents of control and pine wood flour pretreated under different temperatures

ppm	Ca	K	Mg	Na	P
Control	544	106.65	130.35	40.785	36.965
60 °C	65.35	81.8	4.2	51.55	18.86
80 °C	32.055	54.15	3.2	31.64	33.895
100 °C	32.845	35.48	3.325	14.29	13.895

Table 2.2 Mineral contents of control and pine wood flour pretreated with different phosphoric acid concentrations

ppm	Ca	K	Mg	Na	P
Control	544	106.65	130.35	40.785	36.965
0.5%	39.97	69.4	3.635	29.995	11.095
1%	32.845	35.48	3.325	14.29	13.895
2%	28.275	34.685	1.735	15.54	11.675

Table 2.3 Mineral contents of control and pine wood flour pretreated for different time period levels

ppm	Ca	K	Mg	Na	P
Control	544	106.65	130.35	40.785	36.965
1 hour	32.845	35.48	3.325	14.29	13.895
2 hours	248.65	51.6	57.4	33.22	14.045
3 hours	259.38	53.71	56.9	34.26	14.27



Figure 2.14 shows the relationship between levoglucosan yield from pyrolysis of pretreated pine wood flour and minerals content of pretreated pine wood flour. Pine wood flour samples were pretreated by 1% of three different acid solution (phosphoric acid, sulfuric acid, and hydrochloric acid) at 100°C for 1 hour. It was found that pretreated pine wood flour with lower minerals content gave higher levoglucosan yield after pyrolysis. Figure 2.14 shows a negative relationship between levoglucosan yield and minerals content of pretreated pine wood flour.

## **2.4. Conclusions**

Past researchers determined that complete thermal decomposition of wood at the low heating rates occurs at approximately 350°C. We chose 450°C to perform pyrolysis of pine wood flour in order to insure the complete thermal decomposition of wood components. A high heating rate of 10°C/ms was selected for this study in order to simulate fast pyrolysis. We performed Py-GC/MS studies of fast pyrolysis of raw pine wood flour to investigate the optimal pyrolysis condition for high yield of anhydrosugars and low yields of acetic acid and furfural. It was found that the best temperature and time levels of those tested for the Py-GC/MS experiments were 450°C applied at a rate of 10°C/ms. Py-GC/MS studies of pretreated pine wood flour were also performed to investigate the optimal pretreatment condition for high yield of anhydrosugars. The optimal pretreatment condition of pine wood flour for high yield of anhydrosugars was determined for 1% phosphoric acid at 100 °C for 1 hour, which produced 20.5% of levoglucosan. Inductively coupled argon plasma spectrometry (ICAPS) was used to test the dominant metal ion contents of control and pretreated pine wood flour samples,

including Ca, Mg, P, K, Na. It was found that demineralization of pine wood flour by mild acid pretreatment increased levoglucosan yield from 1.8% for untreated sample and 20.5% for pretreated sample. Pretreated pine wood flour with lower minerals content gave higher levoglucosan yield after fast pyrolysis.

## LITERATURE CITED

Blasi, C. D. Modeling intra- and extra-particle processes of wood fast pyrolysis. *AIChE Journal* (2002), 48, 2386-2397.

Bradbury, A.G.W., Y. Sakai, and F. Shafizadeh. A kinetic model for pyrolysis of cellulose. *Journal of Applied Polymeric Science* (1979), 23, 3271-3280.

Bridgewater, A., C. Czernik, J. Diebold, D. Meker and P. Radlein. 1999. *Fast Pyrolysis of Biomass: A Handbook*. CPL Scientific Publishing Services, Ltd. Newbury, UK. 188p.

Brown, Robert C., D. Radlein, J. Piskorz. Pretreatment processes to increase pyrolytic yield of levoglucosan from herbaceous feedstocks. *ACS Symposium Series* (2001), 784(Chemicals and Materials from Renewable Resources), 123-132.

Cara, C., E. Ruiz, J. M. Oliva, F. Saez, E. Castro. Conversion of olive tree biomass into fermentable sugars by dilute acid pretreatment and enzymatic saccharification. *Bioresource Technology* (2008), 99(6), 1869-1876.

Das, Piyali, A. Ganesh, P. Wangikar. Influence of pretreatment for deashing of sugarcane bagasse on pyrolysis products. *Biomass and Bioenergy* (2004), 27(5), 445-457.

Datar, Rohit, J. Huang, P. Maness, A. Mohagheghi, S. Czernik, E. Chornet. Hydrogen production from the fermentation of corn stover biomass pretreated with a steam-explosion process. *International Journal of Hydrogen Energy* (2007), 32(8), 932-939.

Demirbas, A. The influence of temperature on the yields of compounds existing in bio-oils obtained from biomass samples via pyrolysis. *Fuel Processing Technology* (2007), 88(6), 591-597.

Demirbas, A. Partial hydrogenation effect of moisture contents on the combustion oils from biomass pyrolysis. *Energy Sources* (2008), 30, 508-515.

Diebold, J.P. 2000. A review of the chemical and physical mechanisms of the storage stability of fast pyrolysis bio-oils. Rep. NREL/SR-570-27613, National Renewable Energy Laboratory. Golden, CO. 51p.

Dien, Bruce S., Hans-Joachim G. Jung, Kenneth P. Vogel, Michael D. Casler, JoAnn F. S. Lamb, L. Iten, Robert B. Mitchell, G. Sarath. Chemical composition and response to dilute-acid pretreatment and enzymatic saccharification of alfalfa, reed canarygrass, and switchgrass. *Biomass and Bioenergy* (2006), 30(10), 880-891.

Dobele, G., G. Rossinskaja, T. Dizhbite, G. Telysheva, D. Meier, O. Faix. Application of catalysts for obtaining 1,6-anhydrosaccharides from cellulose and wood by fast pyrolysis. *Journal of Analytical and Applied Pyrolysis* (2005), 74(1-2), 401-405.

Dobele, G., T. Dizhbite, G. Rossinskaja, G. Telysheva, D. Meier, S. Radtke, O. Faix. Pre-treatment of biomass with phosphoric acid prior to fast pyrolysis. A promising method for obtaining 1,6-anhydrosaccharides in high yields. *Journal of Analytical and Applied Pyrolysis* (2003), 68-69, 197-211.

Dobele, G., G. Rossinskaja, G. Telysheva, D. Meier, S. Radtke, O. Faix. Levoglucosenone - a product of catalytic fast pyrolysis of cellulose. *Progress in Thermochemical Biomass Conversion*, [Conference], 5th, Tyrol, Austria, Sept. 17-22, 2000 (2001), Meeting Date 2000, 2, 1500-1508.

Dobele, G., D. Meier, O. Faix, S. Radtke, G. Rossinskaja, G. Telysheva. Volatile products of catalytic flash pyrolysis of celluloses. *Journal of Analytical and Applied Pyrolysis* (2001), 58-59, 453-463

Fabbri, D., C. Torri, V. Baravelli. Effect of zeolites and nanopowder metal oxides on the distribution of chiral anhydrosugars evolved from pyrolysis of cellulose: An analytical study. *Journal of Analytical and Applied Pyrolysis* (2007), 80(1), 24-29.

Fabbri, D., L. Marynowski, M.J. Fabianska, M. Zaton, and B.R. Simoneit. Levoglucosan and other cellulose markers in pyrolysates of Miocene lignites: geochemical and environmental implications. *Environ Sci Technol* (2008), 42, 2957-63.

Fahmi, R., A. V. Bridgwater, I. Donnison, N. Yates, J. M. Jones. The effect of lignin and inorganic species in biomass on pyrolysis oil yields, quality and stability. *Fuel* (2008), 87(7), 1230-1240.

Helle, Steve, N. M. Bennett, K. Lau, J. H. Matsui, S. J. B. Duff. A kinetic model for production of glucose by hydrolysis of levoglucosan and cellobiosan from pyrolysis oil. *Carbohydrate Research* (2007), 342(16), 2365-2370.

Hillman, M. E. D., W. J. Huffman, E. S. Liggins, E. Stambaugh. Gasohol production from thermochemical conversion of biomass to ethanol. U.S.4523928 (1985), 14 pp.

Hosoya, T., H. Kawamoto, S. Saka. Cellulose-hemicellulose and cellulose-lignin interactions in wood pyrolysis at gasification temperature. *Journal of Analytical and Applied Pyrolysis* (2007), 80(1), 118-125.

Hosoya, T., H. Kawamoto, S. Saka. Thermal stabilization of levoglucosan in aromatic substances. *Carbohydrate Research* (2006), 341(13), 2293-2297.

Janxe, A.M.C., R.W.J. Westerhout, and W. Prins. Modelling Flash Pyrolysis of a Single Wood Particle. *Chemical Engineering and Processing* (2000), 39, 239-252.

Jensen, P. A., B. Sander, K. Dam-Johansen. Pretreatment of straw for power production by pyrolysis and char wash. *Biomass and Bioenergy* (2001), 20(6), 431-446.

Kawamoto, H., W. Hatanaka, S. J. Saka. *Anal. Appl. Pyrolysis* (2003), 70, 303-313.

Kenealy, William, E. Horn, M. Davis, R. Swaney, C. Houtman. Vapor-phase diethyl oxalate pretreatment of wood chips : part 2. Release of hemicellulosic carbohydrates. *Holzforschung* (2007), 61(3), 230-235.

Kenealy, W., E. Horn, C. Houtman. Vapor - phase diethyl oxalate pretreatment of wood chips: part 1. Energy savings and improved pulps. *Holzforschung* (2007), 61(3), 223-229.

Kim, S., M. T. Holtzapfle. Delignification kinetics of corn stover in lime pretreatment. *Bioresource Technology* (2006), 97(5), 778-785.

Kim, S., M. T. Holtzapfle. Lime pretreatment and enzymatic hydrolysis of corn stover. *Bioresource Technology* (2005), 96(18), 1994-2006.

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

Kim, T. H., Y. Y. Lee. Pretreatment and fractionation of corn stover by ammonia recycle percolation process. *Bioresource Technology* (2005), 96(18), 2007-2013.

Kim, T. H., F. Taylor, K. B. Hicks. Bioethanol production from barley hull using SAA (soaking in aqueous ammonia) pretreatment. *Bioresource Technology* (2008), 99(13), 5694-5702.

Kwon, G., S. Kuga, K. Hori, M. Yatagai, K. Ando, N. Hattori. Saccharification of cellulose by dry pyrolysis. *Journal of Wood Science* (2006), 52(5), 461-465.

Lomax, J. A., J. M. Commandeur, P. W. Arisz, J. J. Boon. Characterization of oligomers and sugar ring-cleavage products in the pyrolyzate of cellulose. *Journal of Analytical and Applied Pyrolysis* (1991), 19, 65-79.

Negro, M. J., P. Manzanares, J. M. Oliva, I. Ballesteros, M. Ballesteros. Changes in various physical / chemical parameters of *Pinus pinaster* wood after steam explosion pretreatment. *Biomass and Bioenergy* (2003), 25(3), 301-308.

Piskorz, Jan, D. S. A. G. Radlein, D. S. Scott, S. Czernik. Pretreatment of wood and cellulose for production of sugars by fast pyrolysis. *Journal of Analytical and Applied Pyrolysis* (1989), 16(2), 127-142.

Piskorz, Jan, D. Radlein, D. S. Scott. On the mechanism of the rapid pyrolysis of cellulose. *Journal of Analytical and Applied Pyrolysis* (1986), 9(2), 121-137.

Piskorz, Jan, D. Radlein, D. S. Scot. Thermal conversion of cellulose and hemicellulose in wood to sugars. *Adv. Thermochem. Biomass Convers.*, [Ed. Rev. Pap. Int. Conf.], 3rd (1994), Meeting Date 1992, 2 1432-1440.

Radlein, D. S. A. G., J. Piskorz, A. Grinshpun, D. S. Scott. Fast pyrolysis of pre-treated wood and cellulose. *Preprints of Papers - American Chemical Society, Division of Fuel Chemistry* (1987), 32(2), 29-35.

Radlein, D., J. Piskorz, D. S. Scott. Fast pyrolysis of natural polysaccharides as a potential industrial process. *Journal of Analytical and Applied Pyrolysis* (1991), 19 , 41-63.

Raveendran, K., A. Ganesh, and K.C. Khilar. Influence of mineral matter on biomass pyrolysis characteristics. *Fuel* (1995), 74, 1812-1822.

Richards, G.N. and G. Zheng. Influence of metal ions and of salts on products from pyrolysis of wood: applications to thermochemical processing of newsprint and biomass. *Journal of Applied Pyrolysis* (1991), 21, 133-146.

Scahill, J.W., J.P. Diebold and C. Feik. 1997. Removal of residual char fined from pyrolysis vapors by hot gas filtration. In: *Developments in Thermochemical Biomass Conversion*, A.V. Bridgwater and D.G.B. Boocock, eds. Blackie Academic and Professional, London, pp. 256-266.

Scott, D. S., J. Piskorz. Process for the production of fermentable sugars from biomass. U.S.4880473 (1989), 6 pp.

Scott, D. S., L. Paterson, J. Piskorz, D. Radlein. Pretreatment of poplar wood for fast pyrolysis: rate of cation removal. *Journal of Analytical and Applied Pyrolysis* (2001), 57(2), 169-176

Shafizadeh, Fred. A comprehensive pyrolytic process for conversion of wood to sugar derivatives and fuels. Proceedings of the Annual Meeting - American Section of the International Solar Energy Society (1980), 3(Sect. 1), 122-129

Shin, E.-J., M. R. Nimlos, R. J. Evans. Kinetic analysis of the gas-phase pyrolysis of carbohydrates. Fuel (2001), 80(12), 1697-1709.

Shurong, W., L. Yanfen, L. Quian, L. Zhongyang, and C. Kefa. Experimental study of the influence of acid wash on cellulose pyrolysis. Frontiers of Chemical Engineering (2007), 1, 35-39.

Singh, A. K., S. D. Fernando, R. Hernandez. Base-catalyzed fast transesterification of soybean oil using ultrasonication. Energy & Fuels (2007), 21(2), 1161-1164.

Soares, S., G. Camino, S. Levchik. Comparative study of the thermal decomposition of pure cellulose and pulp paper. Polymer Degradation and Stability (1995), 49(2), 275-283.

So, K. S., R. C. Brown. Economic analysis of selected lignocellulose-to-ethanol conversion technologies. Applied Biochemistry and Biotechnology (1999), 77(9), 633-640.

Sun, Fubao, H. Chen. Enhanced enzymatic hydrolysis of wheat straw by aqueous glycerol pretreatment. Bioresource Technology (2008), 99(14), 6156-6161.

Sun, Ye, J. J. Cheng. Dilute acid pretreatment of rye straw and bermudagrass for ethanol production. Bioresource Technology (2005), 96(14), 1599-1606.

Westerhof, R.J.M., N.J.M. Kuipers, S.R.A. Kersten and W.P.M. van Swaaij. Controlling the water content of biomass fast pyrolysis oil. Industrial Engineering and Chemical Research (2007), 46, 9238-9247.

Willner, T., and G. Brunner. 2005. Pyrolysis kinetics of wood and wood components. Chemical Engineering Technology, vol. 28, pp. 1212- 1225.

Wilke, C. R., G. Mitra. Conversion of cellulosic materials to sugar. U.S.3972775 (1976), 6 pp.

Xiao, Y. M., Q. Wu, Y. Cai, X. F. Lin. Ultrasound-accelerated enzymatic synthesis of sugar esters in nonaqueous solvents. Carbohydrate Research (2005), 340(13), 2097-2103.

Yang, Bin, C. E. Wyman. Pretreatment: the key to unlocking low-cost cellulosic ethanol. Biofuels, Bioproducts & Biorefining (2008), 2(1), 26-40.

Yang, H., R. Yan, H. Chen, D. H. Lee, C. Zheng. Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel* (2007), 86(12-13), 1781-1788.

Yang, H., R. Yan, H. Chen, C. Zheng, D.H. Lee, D. T. Liang. In-depth investigation of biomass pyrolysis based on three major components: hemicellulose, cellulose and lignin. *Energy & Fuels* (2006), 20(1), 388-393.

Yang, H., R. Yan, H. Chen, C. Zheng, D.H. Lee, and D. T. Liang. Influence of mineral matter on the pyrolysis of palm oil wastes. *Combustion and Flame* (2006), 146, 605-611.

Yu, Z., H. Zhang. Ethanol fermentation of acid-hydrolyzed cellulosic pyrolysate with *Saccharomyces cerevisiae*. *Bioresource Technology* (2003), 90(1), 95-100.



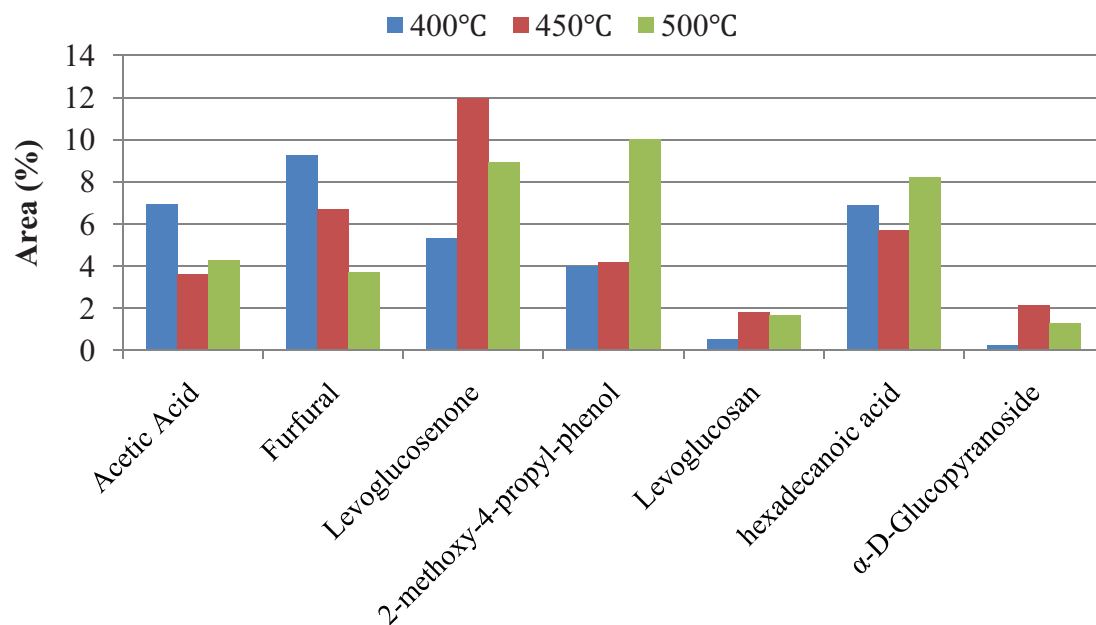


Figure 2.5 Py-GC/MS products distributions from raw pine wood flour by spectral area percentage for pyrolysis temperatures of 300, 450 and 500°C for a heating rate of 10°C/ms for 10 s.

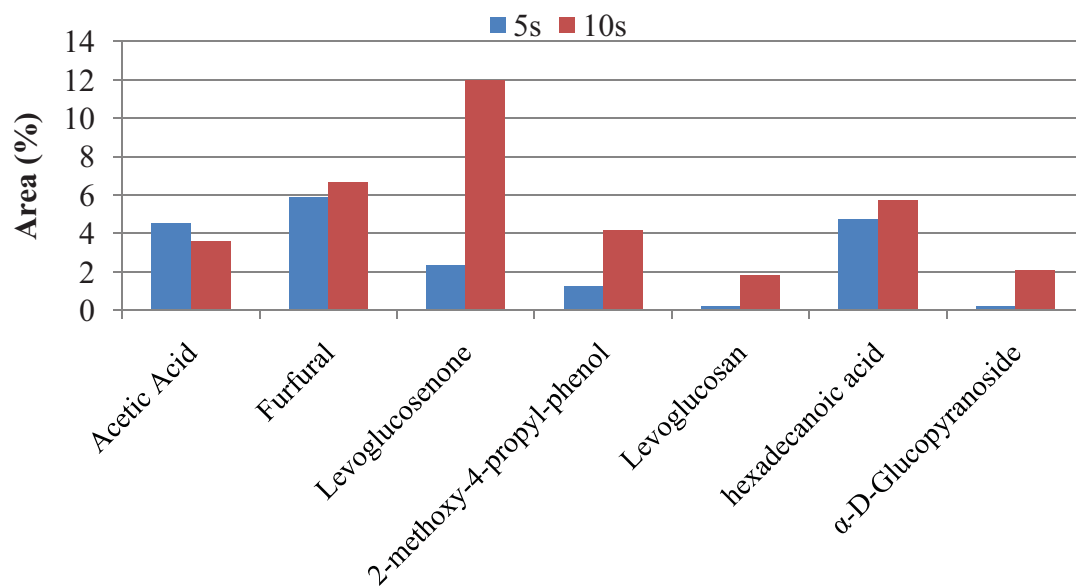


Figure 2.6 Py-GC/MS products distributions from raw pine wood flour by spectral area percentage for pyrolysis temperatures of 450°C for a heating rate of 10°C/ms for 5 and 10 s.

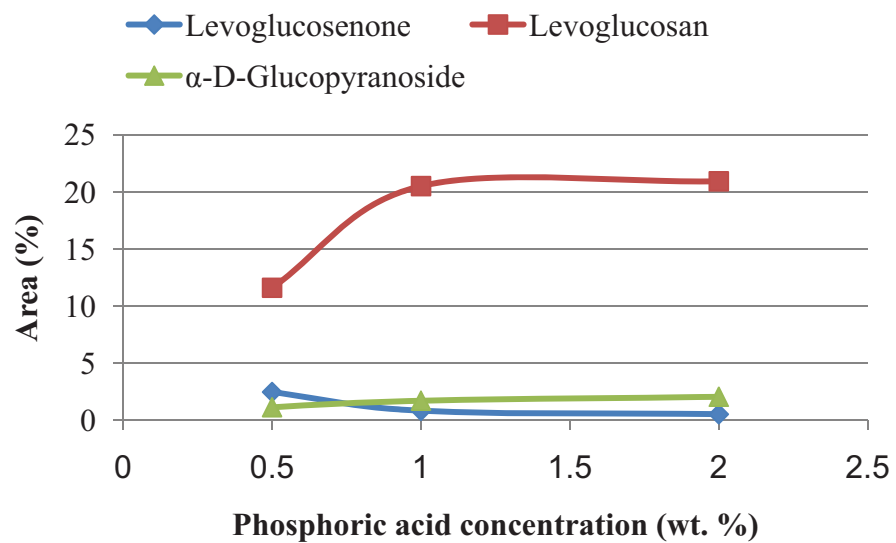


Figure 2.7 Py-GC/MS products distributions from pyrolysis of pretreated pine wood flour by spectral area percentage for three different phosphoric acid concentrations (0.5, 1, and 2 wt. %) at 100°C for 1 hour.

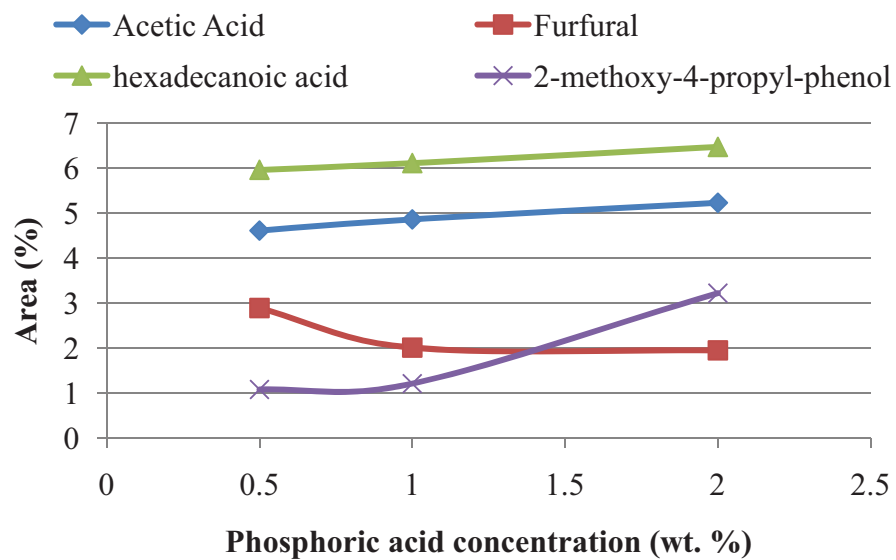


Figure 2.8 Py-GC/MS products distributions from pyrolysis of pretreated pine wood flour by spectral area percentage for three different phosphoric acid concentrations (0.5, 1, and 2 wt. %) at 100°C for 1 hour.

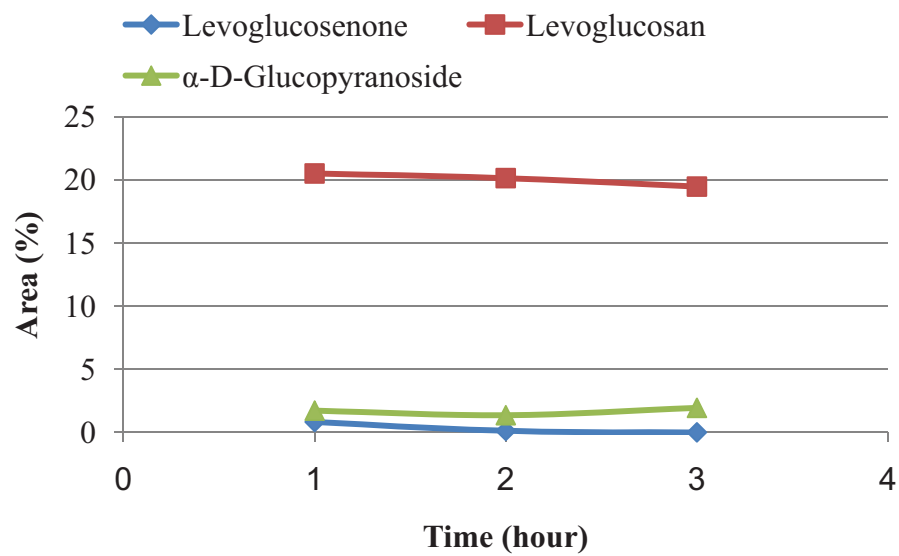


Figure 2.9 Py-GC/MS products distributions from pyrolysis of pretreated pine wood flour by spectral area percentage with 1% phosphoric acid at 100°C for three different time levels (1, 2, and 3 hours).

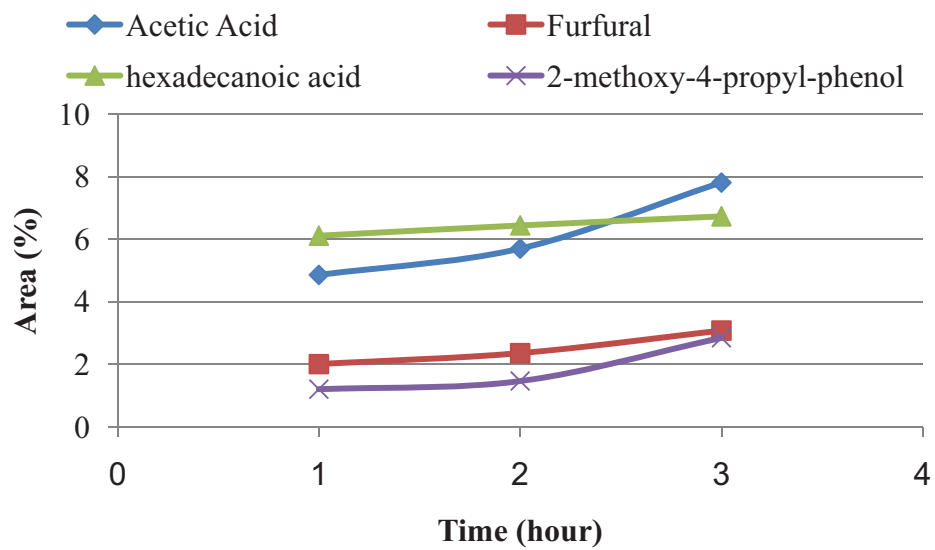


Figure 2.10 Py-GC/MS products distributions from pyrolysis of pretreated pine wood flour by spectral area percentage with 1% phosphoric acid at 100°C for three different time levels (1, 2, and 3 hours).

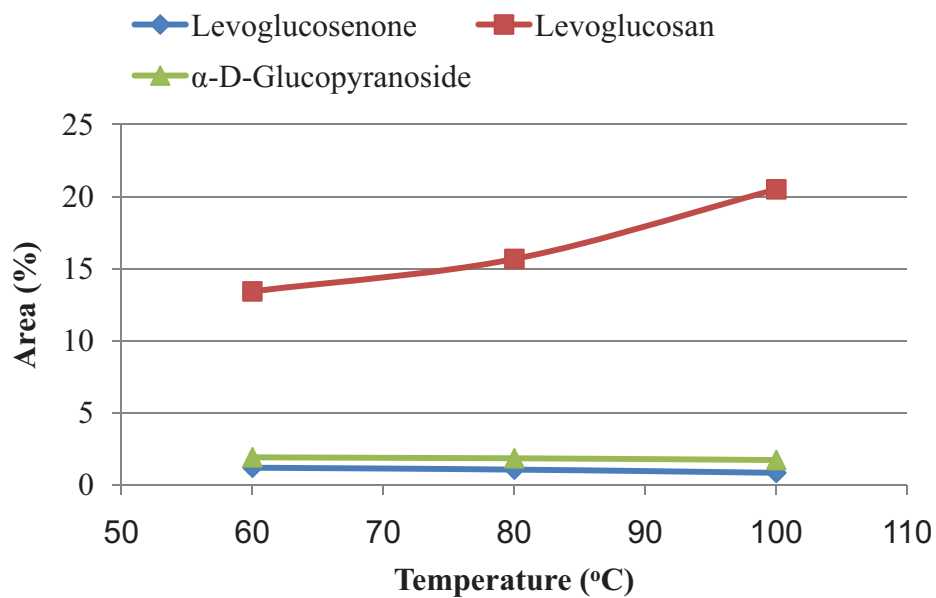


Figure 2.11 Py-GC/MS products distributions from pyrolysis of pretreated pine wood flour by spectral area percentage with 1% phosphoric acid at three different temperatures (60, 80, and 100°C) for 1 hour.

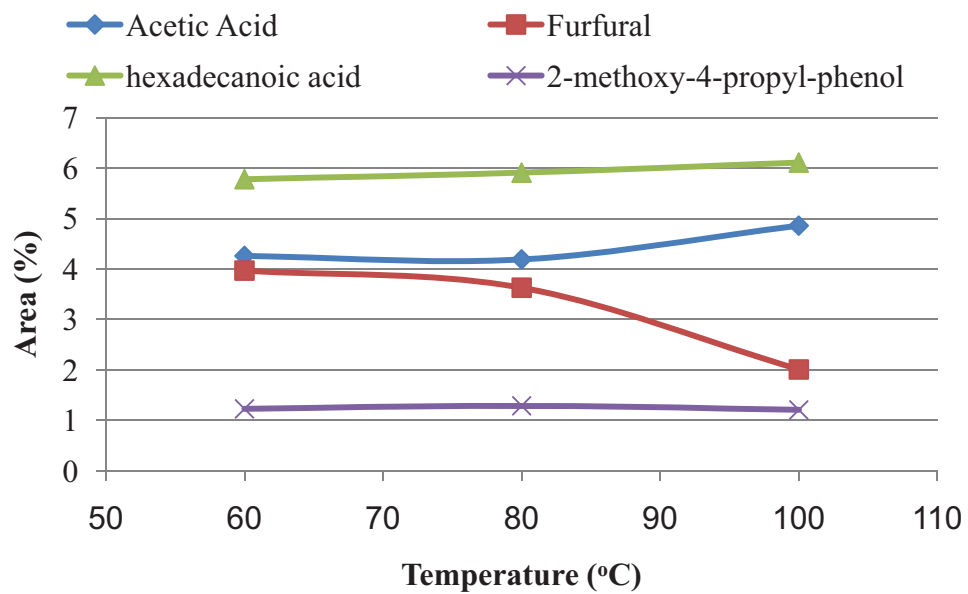


Figure 2.12 Py-GC/MS products distributions from pyrolysis of pretreated pine wood flour by spectral area percentage with 1% phosphoric acid at three different temperatures (60, 80, and 100°C) for 1 hour.



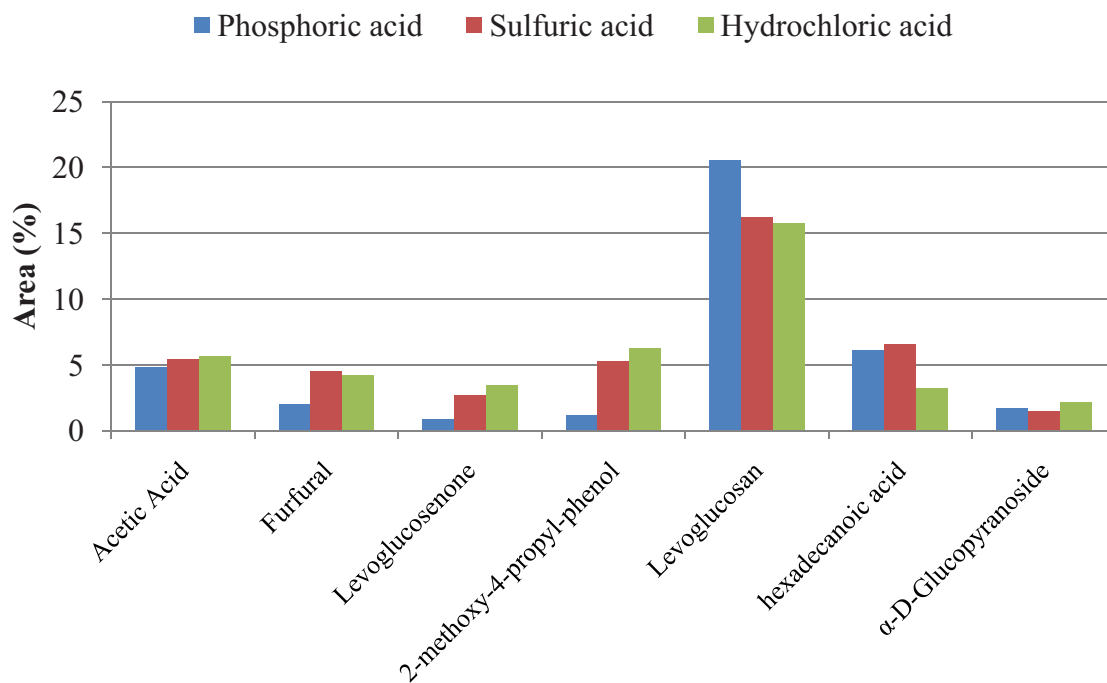


Figure 2.13 Py-GC/MS products distributions from pyrolysis of pretreated pine wood flour by spectral area percentage with three different inorganic acids (phosphoric acid, sulfuric acid, and hydrochloric acid).

Pine wood flour samples were pretreated by 1% of three different acid solutions (phosphoric acid, sulfuric acid, and hydrochloric acid) at 100°C for 1 hour.

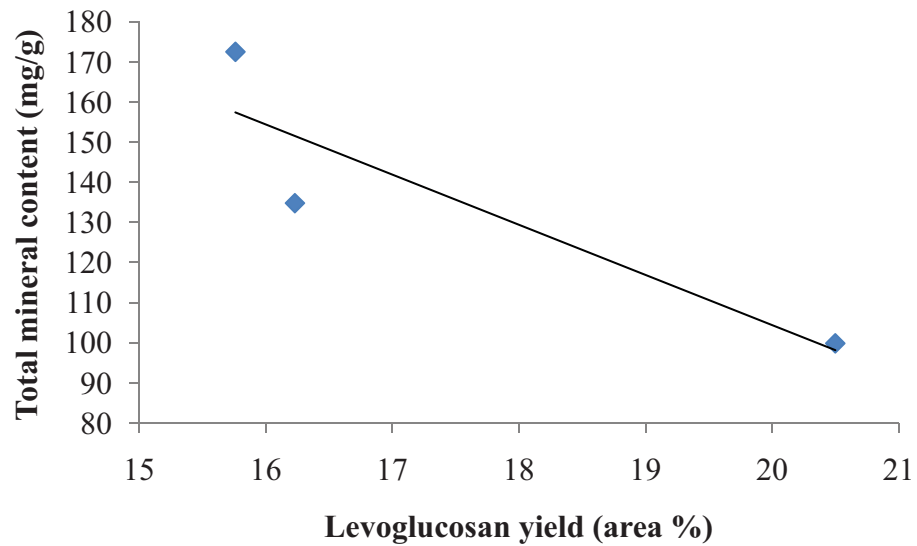


Figure 2.14 The relationship between levoglucosan yield from pyrolysis of pretreated pine wood flour and minerals content of pretreated pine wood flour.

Pine wood flour samples were pretreated by 1% of three different acid solution (phosphoric acid, sulfuric acid, and hydrochloric acid) at 100°C for 1 hour.

CHAPTER III  
EXPLORATORY STUDY OF ULTRASOUND ASSISTED DILUTE ACID  
PRETREATMENT TO FURTHER INCREASE ANHYDROSUGARS  
YIELD DURING FAST PYROLYSIS

**3.1. Background**

Application of ultrasound technology to achieve biomass cellular disintegration to increase material surface area has been recently described in a thorough review of the technology application to the food industry (Vilkhu et al. 2008). Cellular disintegration resulting in size reduction combined with intraparticle diffusion was identified as the mechanisms that allowed increased access by solvents, and/or catalysts, to the sonicated cellular material. This increased access appears to be responsible for the increased rates of chemical product extractions observed by practitioners. Researchers have employed ultrasound to lignocellulosic biomass feedstocks to improve the extractability of hemicellulose (Ebringerova et al. 2002), cellulose (Pappas et al. 2002), and lignin (Sun et al. 2002; Fengel et al. 1984) or to produce cellulosic fiber from used paper (Scott et al. 1995; Sell et al. 1995).

Toma et al. (2006) employed ultrasound to improve the enzymatic hydrolysis of lignocellulosic materials in a two-stage process. First-stage sonication was applied to increase biomass surface area through cellular disintegration to smaller particles with

increased surface area. Second-stage ultrasound was then applied to the pretreated biomass to increase hydrolysis rate during enzymatic treatment. Direct sonication at 20 kHz increased glucose yield by 93%.

A method comprising applying ultrasonic energy to a biomass to increase ethanol production rates and yields has been disclosed by Kinley and Krohn (2005). This invention employed the use of ultrasonic energy as a pretreatment step, either alone or in combination with any conventional pretreatment methods. Following conventional reduction of feedstock particle size by grinding the biomass water is added to produce slurry that is then sonicated in a pretreatment process to produce further particle size reduction and disaggregation of cellular structure. During this treatment a mild hydrolysis of a portion of the cellulose and hemicellulose components is claimed by the inventors. A second sonication is then applied to improve the typical acid-catalyzed hydrolysis performed on biomass during ethanol production. This treatment employed acid at a concentration necessary “to hydrolyze the hemicellulose fraction and decrystallize the cellulose into an amorphous state.” Alternatively, the hydrolysis treatment was achieved by enzyme catalysis also energized by sonication treatment described by the inventors (Kinley and Krohn 2005). However, the inventors performed only limited experiments to prove their process. Pretreatment of switchgrass slurry with only water added was sonicated for 0, 5 and 15 min followed by ethanol production from the slurry by simultaneous saccharification and fermentation or 7 days. Results showed that ethanol efficiency increased from 11.6 to 24.4% for 5 min sonication treatment but declined to 22.8% for the 15 min sonication treatment. In a second experiment the inventors found that 15 min of sonication of a pretreatment biomass slurry rendered cellulose about 21-24%

more digestible. Reduction to practice of inventor's other conceived sonication applications were not discussed.

No references to research performed to increase anhydrosugars yields via sonication prior to fast pyrolysis were found.

## **3.2. Experimental**

### **3.2.1. Materials**

Materials were the same as previously described in chapter II.

### **3.2.2. Biomass pretreatment**

20 mesh southern yellow pine wood flour samples were pretreated in phosphoric acid aqueous solutions in a sonicator (Hielscher-Ultrasound Technology, Germany) at three acid concentrations (0, 0.5, and 1 w.t. %); for optimal acid concentration three pretreatment time period levels (10, 20 and 30 minutes) were tested for three amplitude levels (20, 60 and 100%). The solid to solution weight ratio of 1 to 20 was selected (the same as in Chapter II) for all the ultrasound assisted dilute acid treatments. After the pretreatment, samples were washed with distilled water until pH=7 and then dried in the open air at room temperature for 72 h to 10% moisture content. Control sample was prepared by the same method as described in chapter II.

### **3.2.3. Py-GC/MS analysis**

Py-GC/MS analysis was performed as previously described in chapter II.

#### **3.2.4. Inductively coupled argon plasma spectrometry**

ICP analysis was performed as previously described in chapter II.

#### **3.2.5. Elemental analysis**

Elemental analysis was conducted for carbon, hydrogen and oxygen content of pretreated and control samples. The elemental analysis combustion process can directly determine the amount of carbon, hydrogen, nitrogen. The amount of oxygen present was calculated by deducting the amounts of hydrogen and carbon from the total amount. A CE-440 Elemental Analyzer (Exeter Analytical Inc., Chelmsford, MA) was used in this study. The samples to be analyzed were weighed into disposable tin capsules. The sample was injected into a high temperature furnace and combusted in pure oxygen under static conditions. At the end of the combustion period, a dynamic burst of oxygen was added to ensure total combustion of all inorganic and organic substances. An initial exothermic reaction occurred raising the temperature of combustion to over 1800°C.

#### **3.2.6. X-ray diffraction analysis**

X-ray diffraction spectrometry (XRD) characterized the crystallographic structure of control and pretreated wood flour solid samples. XRD is a common method for determining crystallinity in crystalline materials. An effect of the finite crystallite sizes is seen as a broadening of the peaks in an X-ray diffraction.

### **3.3. Results and Discussion**

Py-GC/MS study was performed on the ultrasound assisted phosphoric acid pretreated pine wood flour. 20 mesh southern yellow pine wood flour samples were pretreated in phosphoric acid aqueous solutions in a sonicator (Hielscher-Ultrasound Technology, Germany) at three acid concentrations (0, 0.5, and 1 w.t. %); for optimal acid concentration three pretreatment time period levels (10, 20 and 30 minutes) were tested for three amplitude levels (20, 60 and 100%). Py-GC/MS yields are reported in terms of area % from the GC spectra. Tentative identification of pyrolysis products was done using the EPA/NIST mass spectral database. Elemental analysis was conducted for carbon, hydrogen and oxygen content of control and ultrasonic pretreated pine wood flour samples. Inductively coupled argon plasma spectrometry (ICAPS) was used to test the dominant metal ion contents of control and pretreated pine wood flour samples. Finally, XRD spectrometry was applied to characterize the crystallographic structure of control and selected pretreated wood flour solid samples.

#### **3.3.1. Optimization of ultrasound assisted phosphoric acid pretreatment of pine wood flour results**

The main objective of this study was to determine the best conditions for the ultrasound assisted phosphoric acid pretreatment of pine wood flour to increase the efficiency of pretreatment. In traditional pretreatment methods, biomass is pretreated in heated acid or basic solution. In this study, ultrasound was the energy input method instead of the simple heating method.

Figures 3.1 and 3.2 show the product types and distributions given in GC area% for the pyrolysis of ultrasonically pretreated pine wood flour at 450°C, a residence time of 10 s and a heating rate of 10°C/ms. Pine wood flour samples were pretreated with three different phosphoric acid concentration levels (0, 0.5, and 1 wt. %) at 100% ultrasonic amplitude for 30 minutes. The yield of levoglucosan greatly increased from 2.39% to 19.6% when the phosphoric acid concentration increased from 0% to 0.5% and slightly increased from 19.6% to 21.7% as the phosphoric acid concentration increased from 0.5% to 1% (Figure 3.1). No obvious change was observed for the yield of  $\alpha$ -D-Glucopyranoside and a slight decreasing trend was observed for the yield of levoglucosenone (Figure 3.1). Decreasing trends were observed for the yields of furfural and 2-methoxy-4-propyl-phenol (Figure 3.1). It was indicated that 0.5% of phosphoric acid concentration was sufficient to remove most of the minerals in the raw pine wood flour because no appreciable increase of levoglucosan yield was observed as the phosphoric acid concentration increased from 0.5% to 1%. Therefore, 0.5% of phosphoric acid concentration was selected as the optimal concentration of the three tested.

Figures 3.3 and 3.4 show the product types and distributions given in GC area% for the pyrolysis of ultrasonic pretreated pine wood flour at 450°C, a residence time of 10 s and a heating rate of 10°C/ms. Pine wood flour samples were pretreated for three pretreatment time period levels (10, 20, and 30 minutes) with 0.5% phosphoric acid at 100% ultrasonic amplitude. Figure 3.3 shows that the yield of levoglucosan increased in an almost linear trend from 5.98% to 19.6% when the pretreatment time increased from 10 minutes to 30 minutes. No obvious changes were observed for the yields of levoglucosenone and  $\alpha$ -D-Glucopyranoside as the pretreatment time increased from 10



minutes to 30 minutes (Figure 3.3). Figure 3.4 shows that slightly decreasing trends were observed for the yields of furfural and 2-methoxy-4-propyl-phenol and no obvious changes were observed for the yields acetic acid and hexadecanoic acid as the pretreatment time increased from 10 minutes to 30 minutes. Thus, pretreatment time of 30 minutes was selected as the best of the three tested.

Figures 3.5 and 3.6 show the product types and distributions given in GC area% for the pyrolysis of ultrasonic pretreated pine wood flour at 450°C, a residence time of 10 s and a heating rate of 10°C/ms. Pine wood flour samples were pretreated in the sonicator with 0.5% phosphoric acid at three different ultrasonic amplitude levels (20, 60, and 100%) for 30 minutes. The yield of levoglucosan increased from 2.31% to 19.6% when the ultrasonic amplitude increased from 20% to 100% and slightly decreasing trend was observed for the yield of levoglucosenone (Figure 3.5). Figure 3.6 also shows that an increase in the formation of acetic acid (from 3.6% to 5.2%) and a decrease in the formation of furfural and 2-methoxy-4-propyl-phenol were observed when the ultrasonic amplitude increased from 20% to 100% (from 5.8% to 1.9% for furfural and from 4.0% to 0.98% for 2-methoxy-4-propyl-phenol). Thus, increasing ultrasonic amplitude for ultrasound assisted phosphoric acid pretreatment changed the pyrolysis product distribution by increasing the formation of levoglucosan and ultrasonic amplitude of 100% was selected as the optimal of the three tested. Therefore, 0.5% of phosphoric acid, 30 minutes, and 100% ultrasonic amplitude was selected as the optimal sonicated pretreatment conditions for high anhydrosugars yield from fast pyrolysis of pine wood flour.

### **3.3.2. Comparing sonicated and non-sonicated results in terms of minerals content and levoglucosan yields**

Figure 3.7 shows the product types and distributions given in GC area% for the pyrolysis of pine wood flour pretreated with three different methods. Two methods were applied to compare sonicated and unsonicated optimal anhydrosugars production. A third method was applied to compare the 1% phosphoric acid optimal unsonicated pretreatment to a sonicated pretreatment with the same 1% acid application. Method 1 was pretreatment with 1% phosphoric acid at 100°C heated solution for 1 hour. Method 2 was pretreatment with 0.5% phosphoric acid at 100% ultrasonic amplitude for 30 minutes. Method 3 was pretreatment with 1% phosphoric acid at 100% ultrasonic amplitude for 30 minutes. Among these three pretreatment methods, Method Three gave the highest levoglucosan yield of 21.7%. However, Method Two gave levoglucosan yield of 19.6%, comparable to method one giving levoglucosan yield of 20.5%. This indicates that ultrasound assisted phosphoric acid pretreatment enhanced the pretreatment efficiency by producing almost the same yield of levoglucosan from pyrolysis as simple phosphoric acid pretreatment, using half percentage of phosphoric acid concentration and half of the pretreatment time period. Figure 3.8 shows the minerals content of pine wood flour pretreated by the three methods described above. Figure 3.8 again indicates a direct negative relationship between levoglucosan yield and minerals content of pretreated pine wood flour. Pretreated pine wood flour with lower minerals content gave higher levoglucosan yield after pyrolysis.

### 3.3.3. Elemental analysis and X-ray diffraction spectrometry analysis results

Three pine wood flour samples (control, sample pretreated with Method 1, and sample pretreated with Method 3) were selected for elemental analysis. Table 3.1 summarizes the elemental analysis results of the selected samples. No appreciable difference was observed for carbon, hydrogen, and oxygen contents of the three samples. This indicated that no obvious changes in the chemical components (cellulose, hemicelluloses, and lignin) of pine wood flour occur after dilute phosphoric acid pretreatment except for minerals content.

Table 3.1 Elemental analysis results of control and pretreated pine wood flour samples

Sample name	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Oxygen (%)
Control	45.66	5.81	0.42	48.11
1 w.t. % phosphoric acid treatment	44.92	5.96	0.55	48.57
Ultrasound assisted 1 w.t. % phosphoric acid treatment	45.17	5.86	0.49	48.48

The same samples as those selected for elemental analysis were selected for XRD spectrometry analysis. JADE Software calculated the crystallinity in percentage based on the XRD spectra. Figure 3.9 shows that the crystallinity of the pine wood flour sample pretreated by Method 1 was nearly the same as that of the control sample (43.7% for the sample pretreated by Method 1, and 42.4% for the control). The crystallinity of the pine wood flour sample pretreated by Method 3 increased to 60.2%, compared with the crystallinity of the control sample of 42.4%. This indicated that ultrasonic pretreatment breaks down some of the amorphous structure (hemicelluloses and a small part of cellulose structure) of pine wood flour into smaller fragments, leaving the crystalline

structure intact but exposed. The exposure of cellular structure clearly assisted in increasing anhydrosugars production during fast pyrolysis.

### **3.4. Conclusions**

In order to increase the efficiency of pretreatment for high anhydrosugars yield during fast pyrolysis, an ultrasonic technique was introduced into combination with traditional dilute acid pretreatment. The optimal sonicated pretreatment conditions for high anhydrosugars yield from fast pyrolysis of pine wood flour was 0.5% of phosphoric acid, 30 minutes, and 100% ultrasonic amplitude. It was found that ultrasound assisted phosphoric acid pretreatment produced the same yield of levoglucosan but required only half of the phosphoric acid and pretreatment time required for simple mild acid pretreatment. Minerals were proved to be inhibitors to the formation of pyrolytic anhydrosugars. No obvious difference was observed for carbon, hydrogen, and oxygen contents of pine wood flour after pretreatment, which indicated that no obvious changes in the chemical components (cellulose, hemicelluloses, and lignin) of pine wood flour occur after dilute phosphoric acid pretreatment except for minerals content. The efficacy of dilute acid pretreatment was attempted by increasing access of acid catalyst to the feedstock cellular structure by application of ultrasonic technique to increase the intensity of acid/biomass interaction as well as to increase the initiate greater activity of the acid as it interacts with the biomass material.

## LITERATURE CITED

Ebringerova A., Z. Hromadkova. Effect of ultrasound on the extractability of corn bran hemicelluloses. *Ultrason. Sonochem* (2002), 9(4), 225-229.

Fengel D., G. Wegener. *Wood: chemistry, ultrastructure, reactions*. Walter de Gruyter, Berlin. New York. 1984: 52.

Kinley, M. T., B. Krohn. Biomass conversion to alcohol using ultrasonic energy. *U.S. Pat. Appl. Publ.* (2005), 23 pp.

Pappas C., P. A. Tarantilis, I. Daliani, T. Mavromoustakos, M. Polissiou. Comparison of classical and ultrasound-assisted isolation procedures of cellulose from kenaf (*Hibiscus cannabinus* L.) and eucalyptus (*Eucalyptus rodustrus* Sm.). *Ultrason. Sonochem* (2002), 9(1), 19-23.

Scott W. E., P. Gerber. Using ultrasound to deink xerographic waste. *TAPPI J* (1995), 78, 125-130.

Sell, N. J., J. C. Norman, D. Jayaprakash. Deinking secondary fiber using ultrasound. *Progress in Paper Recycling*. 1995: 28-34.

Sun R. C., J. Tomkinson. Comparative study of lignins isolated by alkali and ultrasound-assisted alkali extractions from wheat straw. *Ultrason. Sonochem* (2002), 9(2), 85-93.

Toma, M., H. Bandow, M. Vinatoru, Y. Maeda. Ultrasonically assisted conversion of lignocellulosic biomass to ethanol. *AIChE Annual Meeting, Conference Proceedings*, San Francisco, CA, United States, Nov. 12-17, 2006 (2006), 701a/1-701a/7.

Vinatoru M, M. Toma, T. J. Mason. Ultrasonically assisted extraction of bioactive principles from plants and their constituents, in: T. J. Mason (Ed.), *Advances in Sonochemistry*, vol. 5, JAI Press. 1999: 209-248.

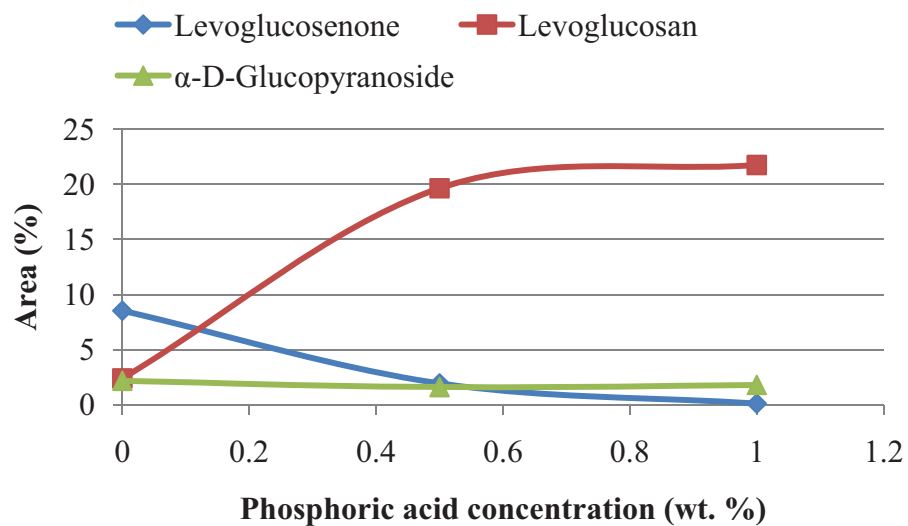


Figure 3.1 Py-GC/MS products distributions from pyrolysis of ultrasonic pretreated pine wood flour by spectral area percentage with three different phosphoric acid concentration levels (0, 0.5, and 1 wt. %) at 100% ultrasonic amplitude for 30 minutes.

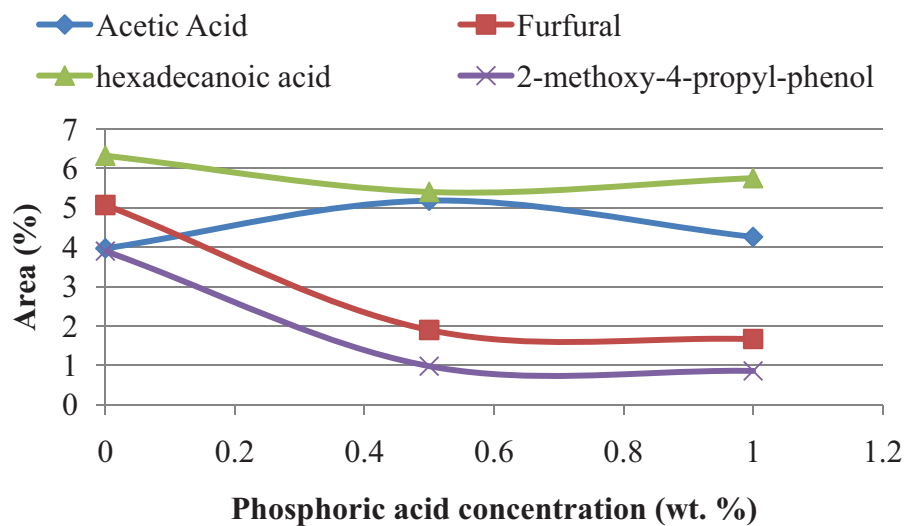


Figure 3.2 Py-GC/MS products distributions from pyrolysis of ultrasonic pretreated pine wood flour by spectral area percentage with three different phosphoric acid concentration levels (0, 0.5, and 1 wt. %) at 100% ultrasonic amplitude for 30 minutes.

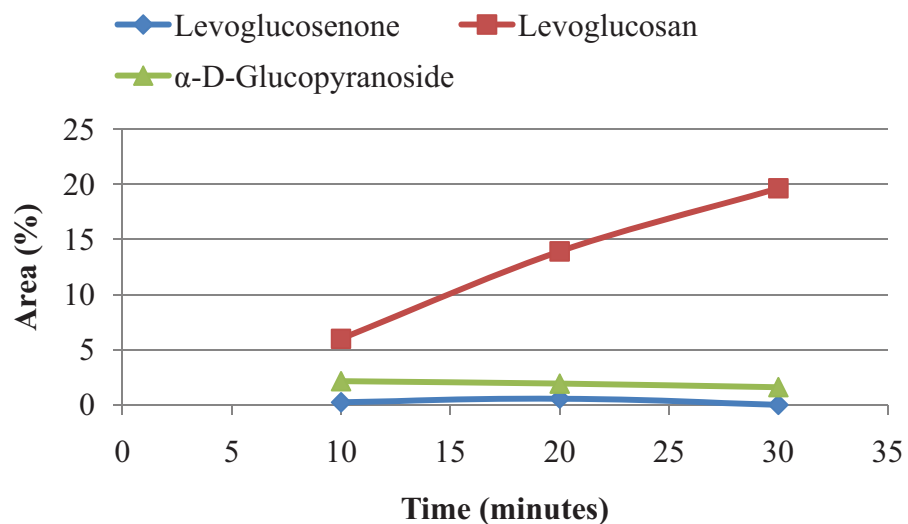


Figure 3.3 Py-GC/MS products distributions from pyrolysis of ultrasonic pretreated pine wood flour by spectral area percentage for three pretreatment time period levels (10, 20 and 30 minutes) with 0.5% phosphoric acid at 100% ultrasonic amplitude.



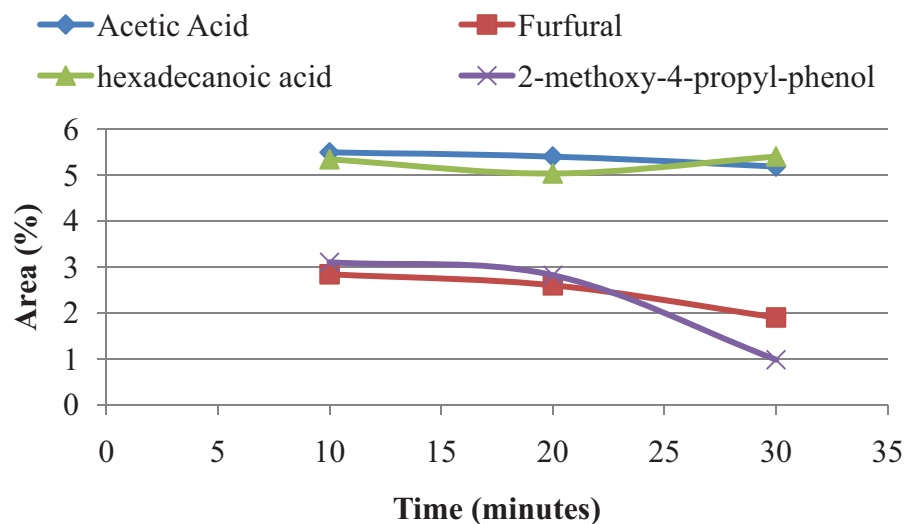


Figure 3.4 Py-GC/MS products distributions from pyrolysis of ultrasonic pretreated pine wood flour by spectral area percentage for three pretreatment time period levels (10, 20 and 30 minutes) with 0.5% phosphoric acid at 100% ultrasonic amplitude.

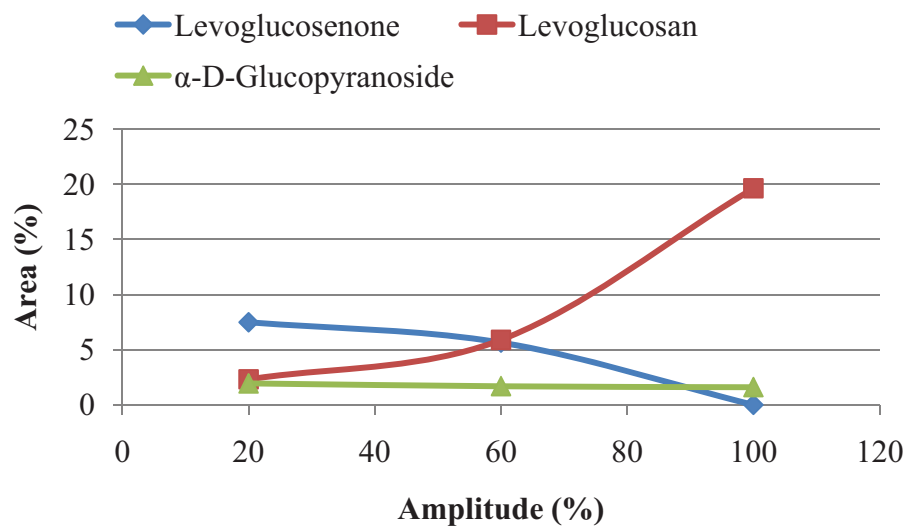


Figure 3.5 Py-GC/MS products distributions from pyrolysis of ultrasonic pretreated pine wood flour by spectral area percentage with 0.5% phosphoric acid at three different ultrasonic amplitude levels (20, 60, and 100%) for 30 minutes.

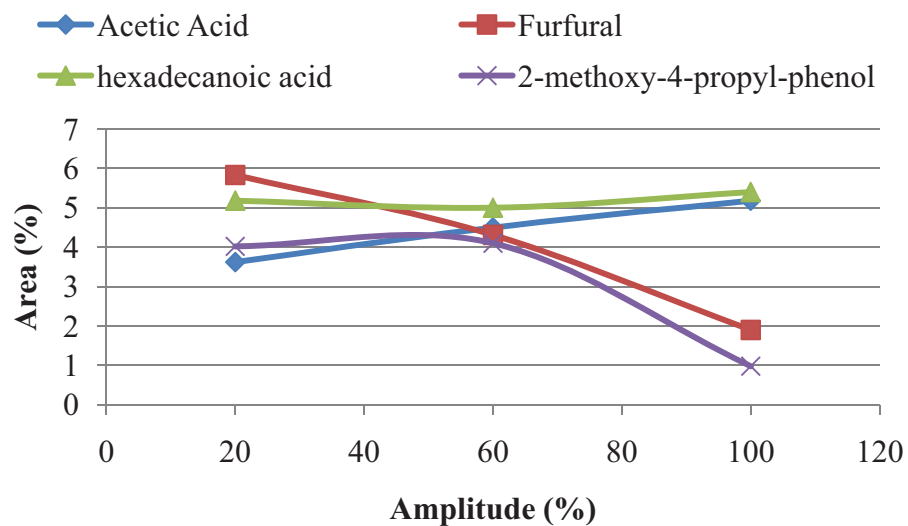


Figure 3.6 Py-GC/MS products distributions from pyrolysis of ultrasonic pretreated pine wood flour by spectral area percentage with 0.5% phosphoric acid at three different ultrasonic amplitude levels (20, 60, and 100%) for 30 minutes.

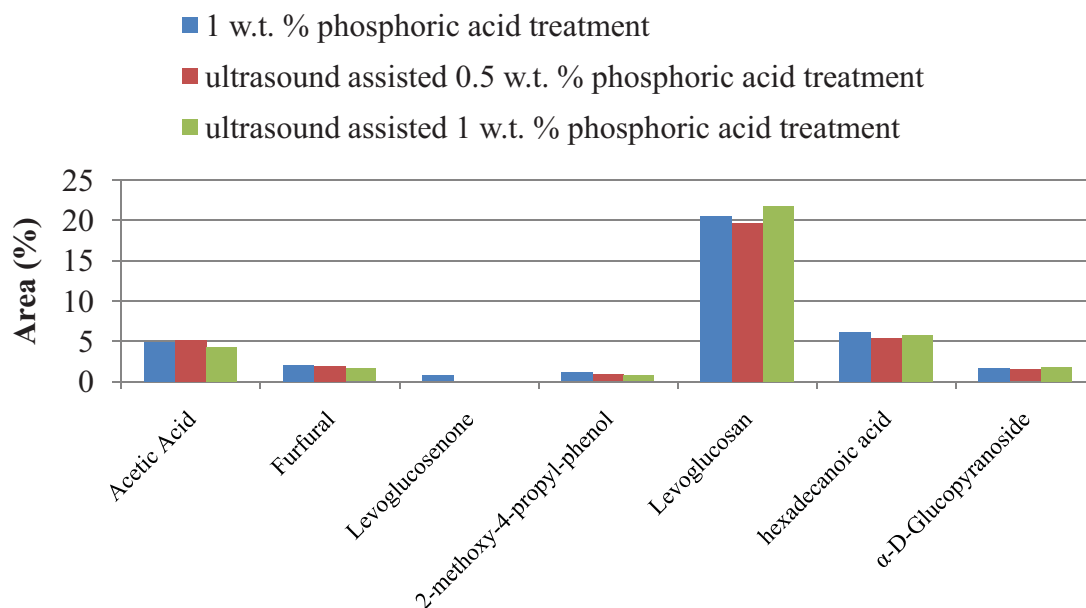


Figure 3.7 Py-GC/MS products distributions from pyrolysis of pretreated pine wood flour by spectral area percentage with three different pretreatment methods.

Method 1 was 1% phosphoric acid at 100°C heated solution for 1 hour. Method 2 was 0.5% phosphoric acid at 100% ultrasonic amplitude for 30 minutes. Method 3 was 1% phosphoric acid at 100% ultrasonic amplitude for 30 minutes.

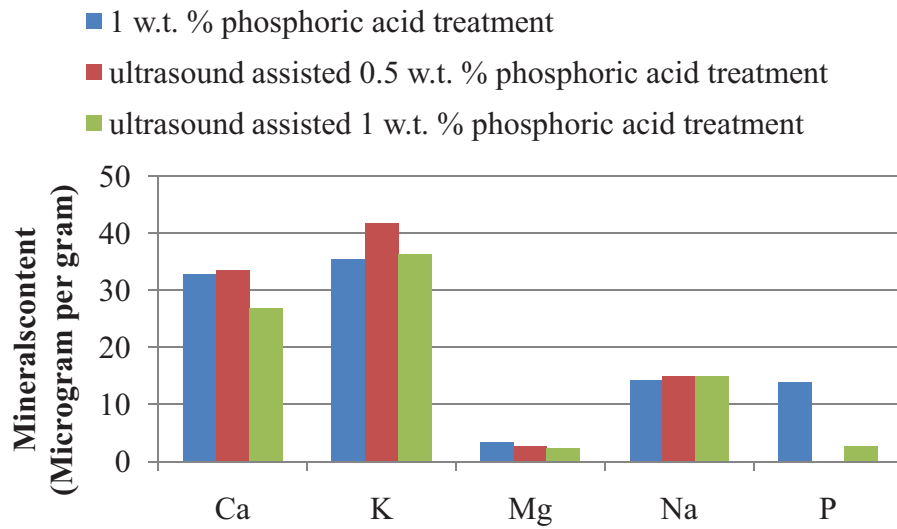


Figure 3.8 Minerals contents of pretreated pine wood flour with three different pretreatment methods.

Method 1 was 1% phosphoric acid at 100°C heated solution for 1 hour. Method 2 was 0.5% phosphoric acid at 100% ultrasonic amplitude for 30 minutes. Method 3 was 1% phosphoric acid at 100% ultrasonic amplitude for 30 minutes.

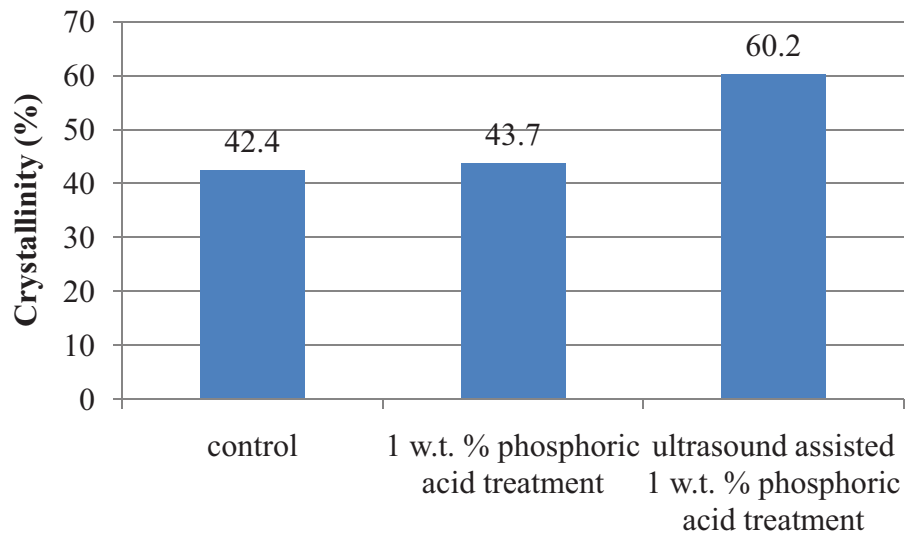


Figure 3.9 Comparison of crystallinity of control sample and two pretreated pine wood flour samples.

Control sample was prepared by washing raw southern yellow pine wood flour with the same amount of distilled water as used for pretreated samples and then dried in the open air at room temperature for 72 h to 10% moisture content. Method 1 was 1% phosphoric acid at 100°C heated solution for 1 hour. Method 3 was 1% phosphoric acid at 100% ultrasonic amplitude for 30 minutes.

APPENDIX A

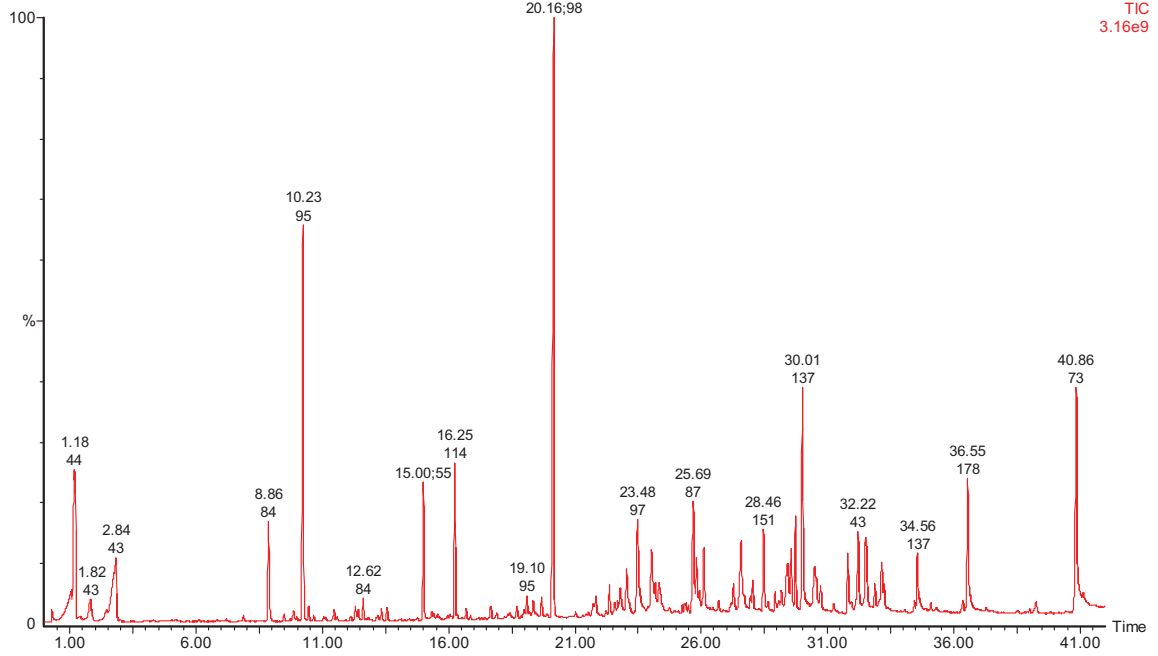
PY-GC/MS CHROMATOGRAM OF RAW PINE WOOD FLOUR

PW T1  
Pine Wood T1

Pine Wood T1

01-Jul-2008

Scan EI+  
TIC  
3.16e9





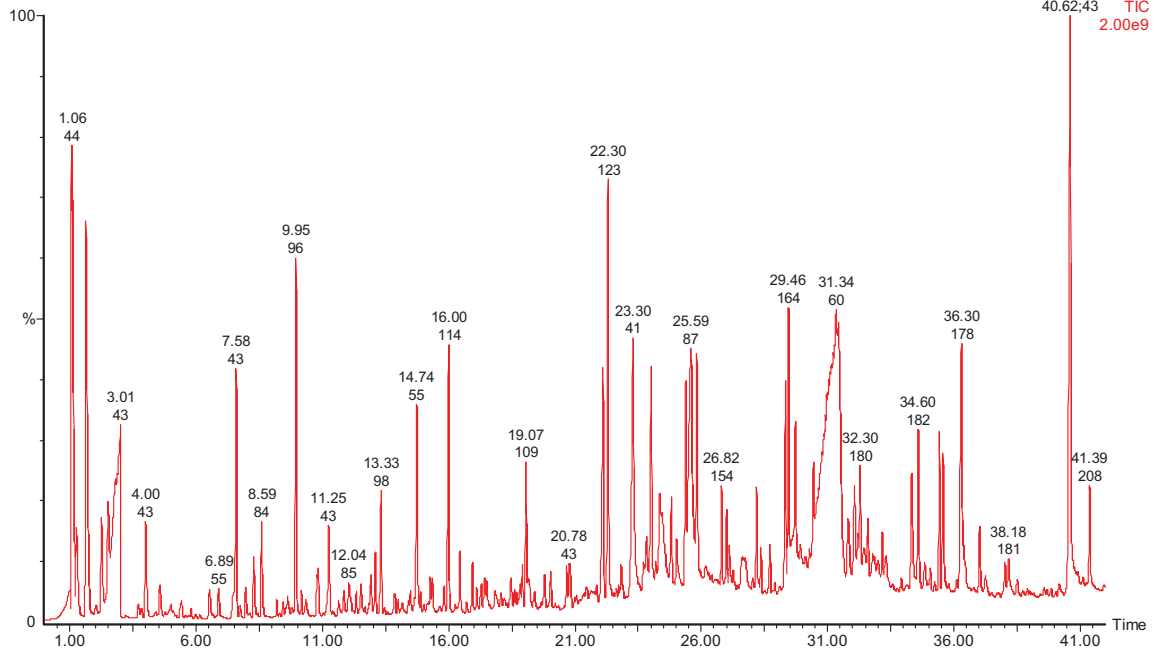
APPENDIX B

PY-GC/MS CHROMATOGRAM OF ULTRASOUND ASSISTED PHOSPHORIC ACID  
PRETREATED PINE WOOD FLOUR

091208 pre-so  
091208 pre-soni-7

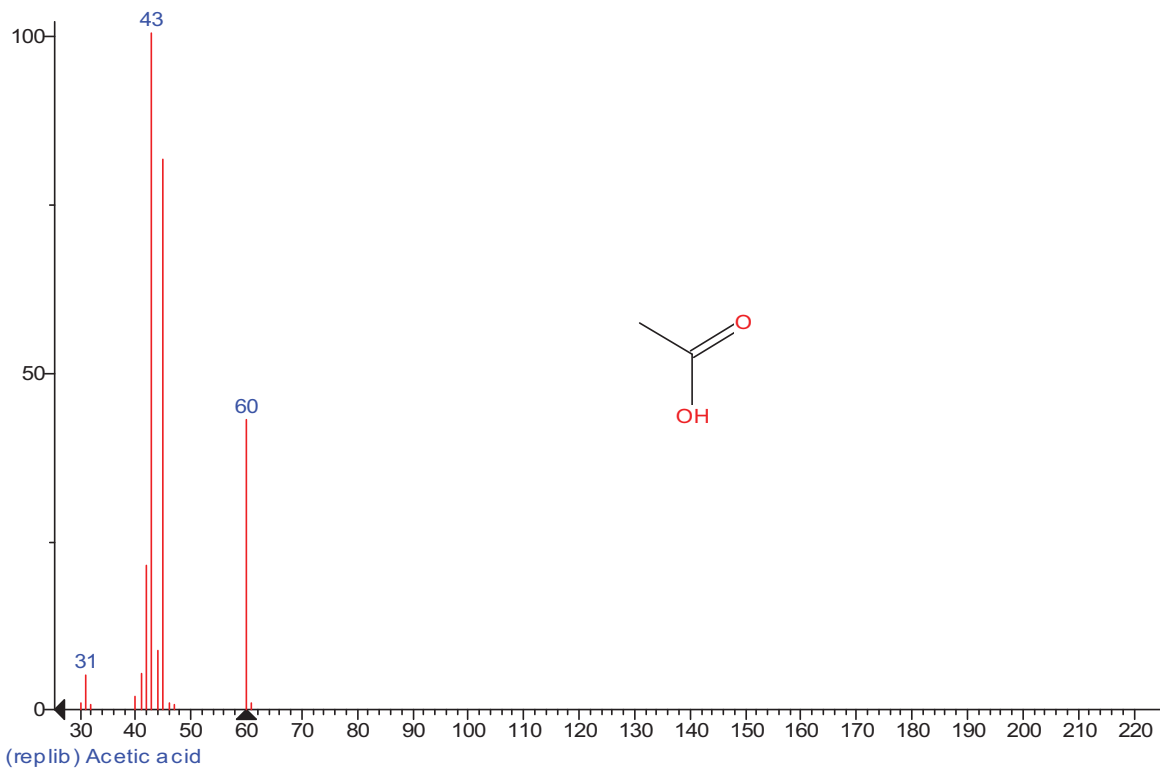
091208 pre-soni (for auger)-7

14-Oct-2008  
Scan E1+  
TIC  
2.00e9



APPENDIX C

MASS SPECTRA AND CHEMICAL STRUCTURE OF MAJOR PRODUCTS FROM  
FAST PYROLYSIS OF DILUTE ACID PRETREATED PINE WOOD FLOUR  
(LIBRARY SPECTRA AND SAMPLE SPECTRA)

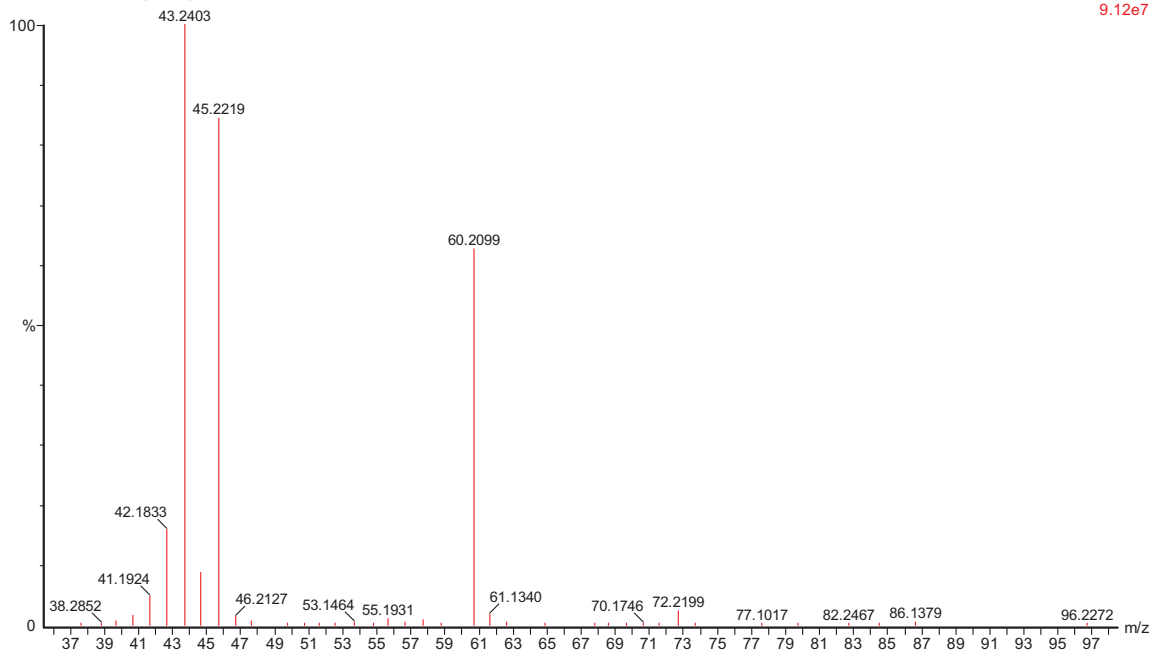


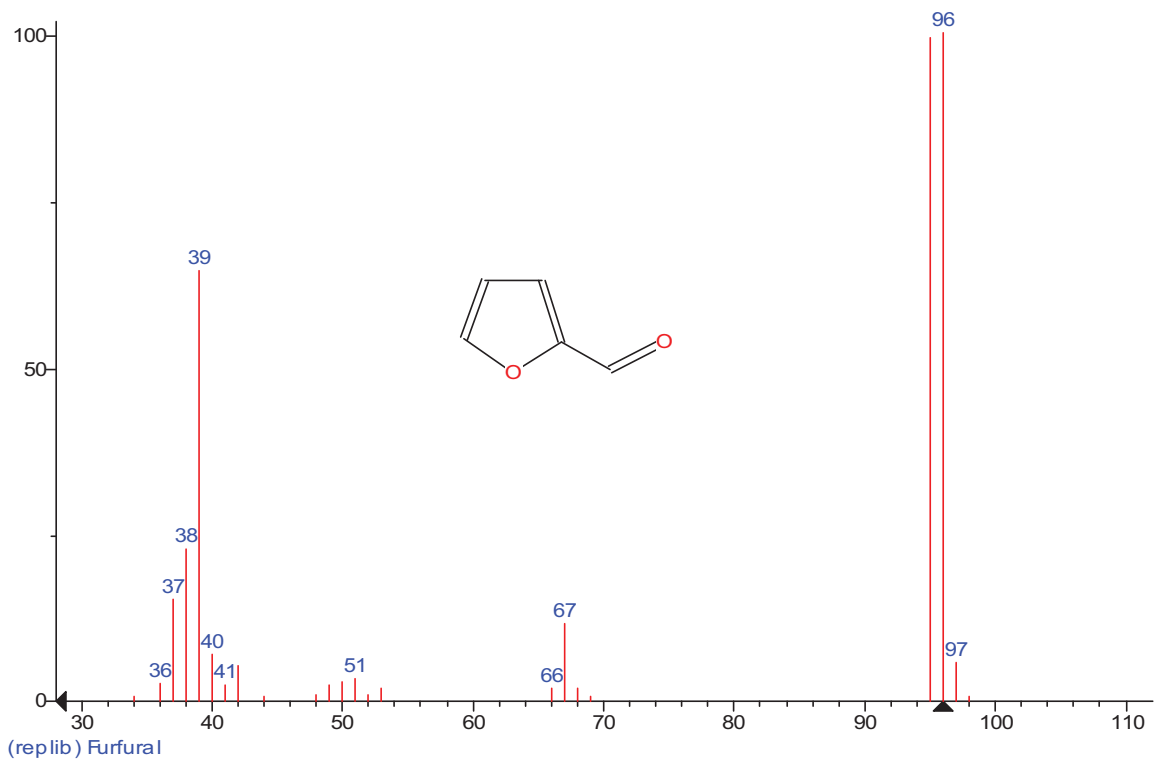
**Pine Wood T1**

Pine Wood T1 548 (2.772)

10 Sec. @ 450C, 01-Jul-2008 + 16:11:08

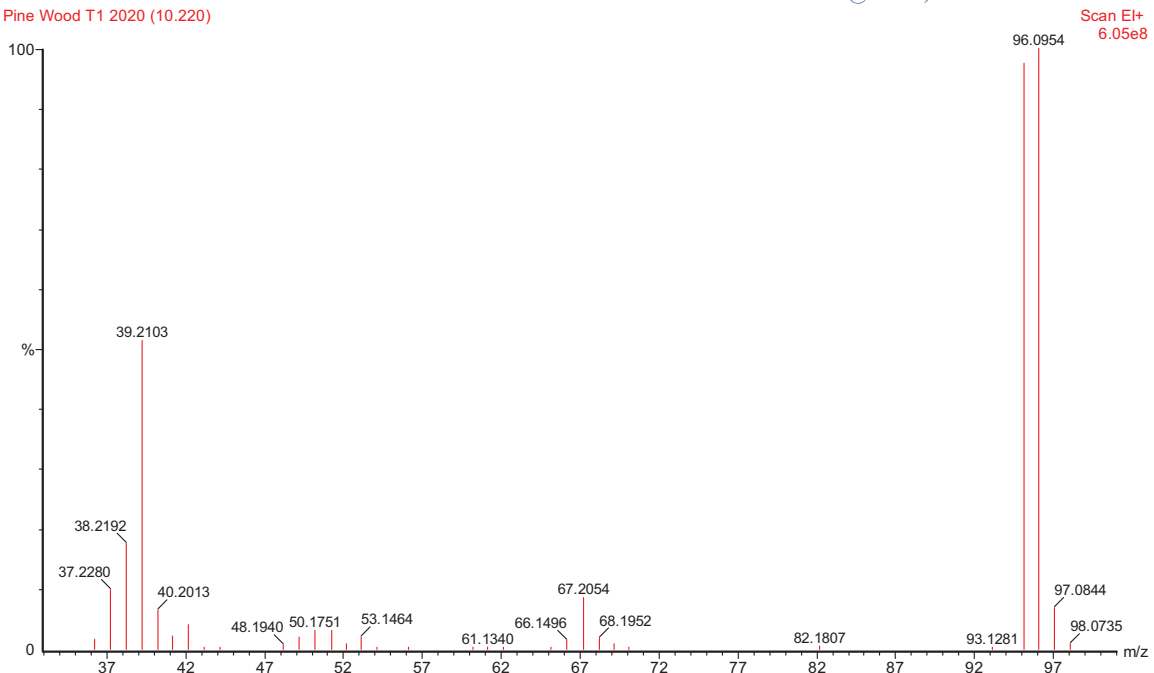
Scan EI+  
9.12e7

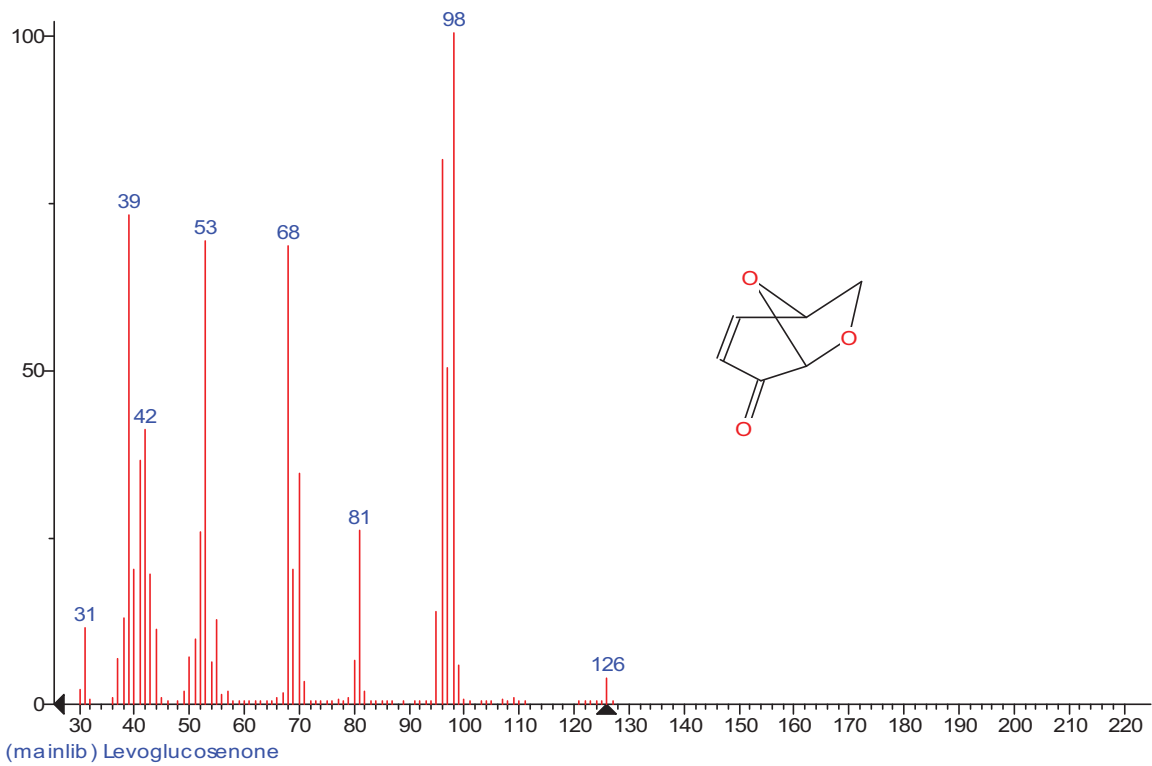




Pine Wood T1  
Pine Wood T1 2020 (10.220)

10 Sec. @ 450C, 01-Jul-2008 + 16:11:08



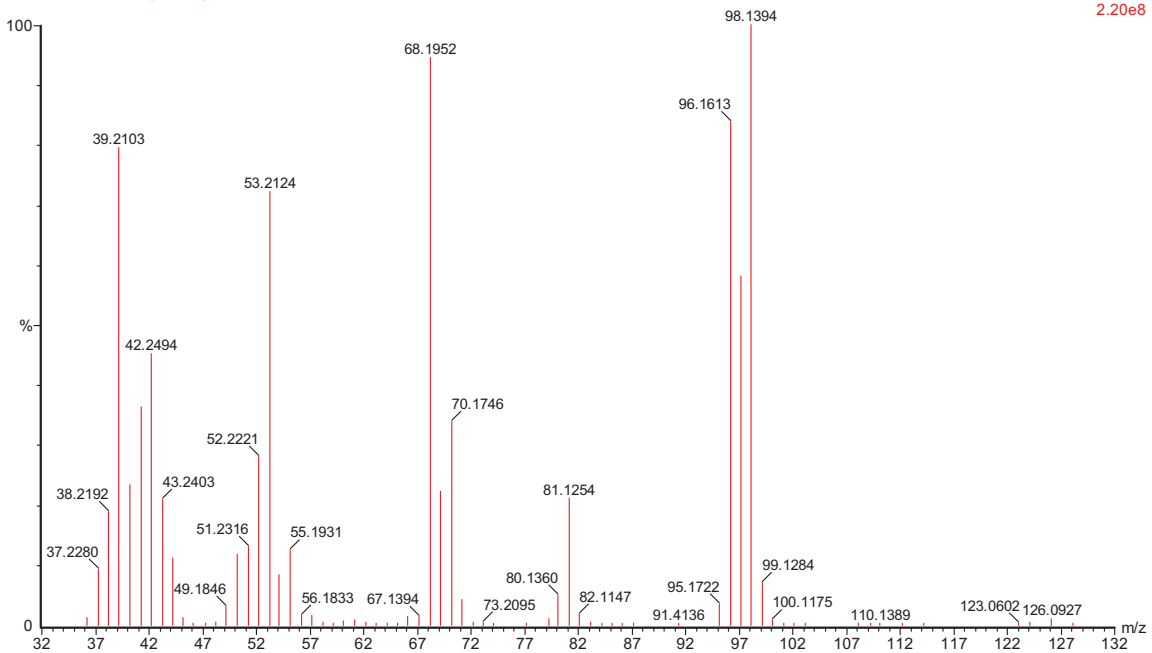


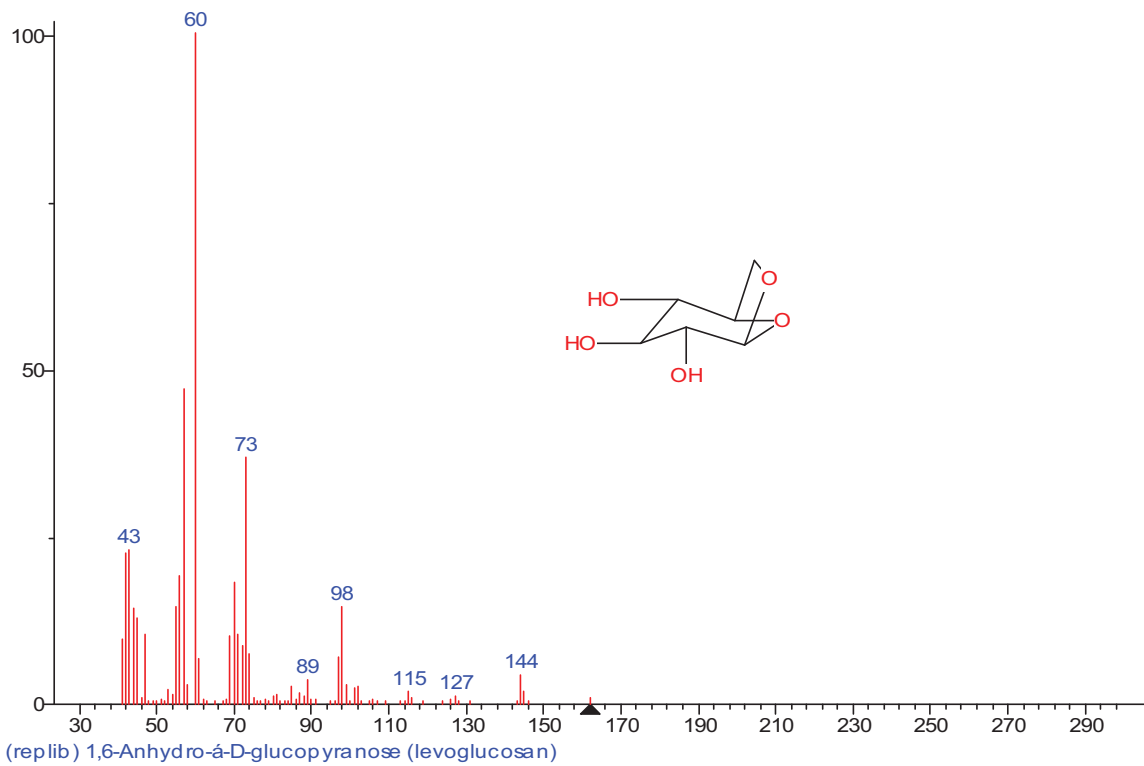
**Pine Wood T1**

Pine Wood T1 3977 (20.118)

10 Sec. @ 450C, 01-Jul-2008 + 16:11:08

Scan EI+  
2.20e8



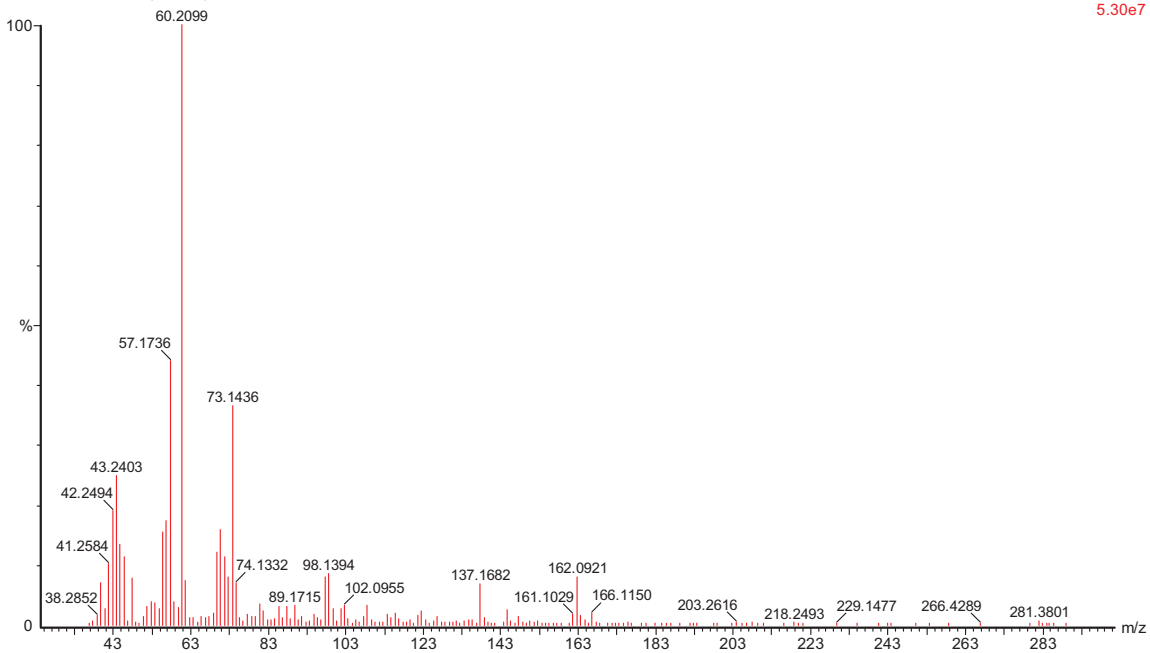


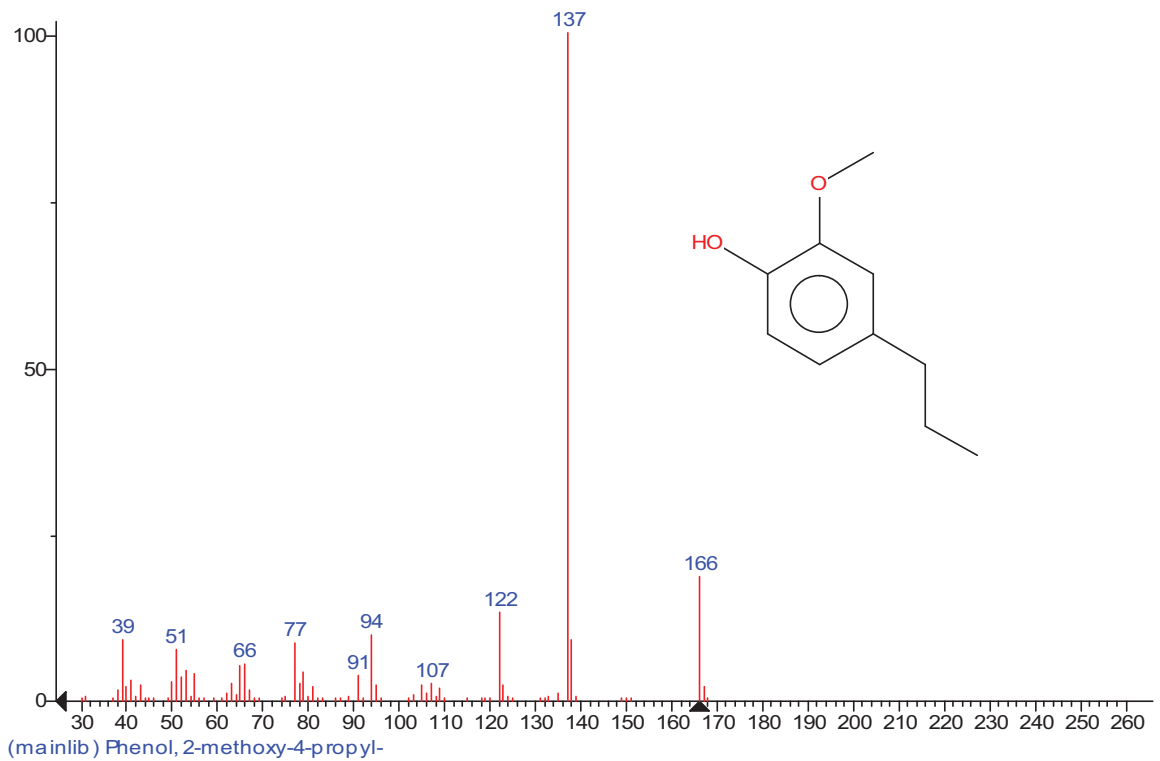
**Pine Wood T1**

Pine Wood T1 6036 (30.512)

10 Sec. @ 450C, 01-Jul-2008 + 16:11:08

Scan EI+  
5.30e7

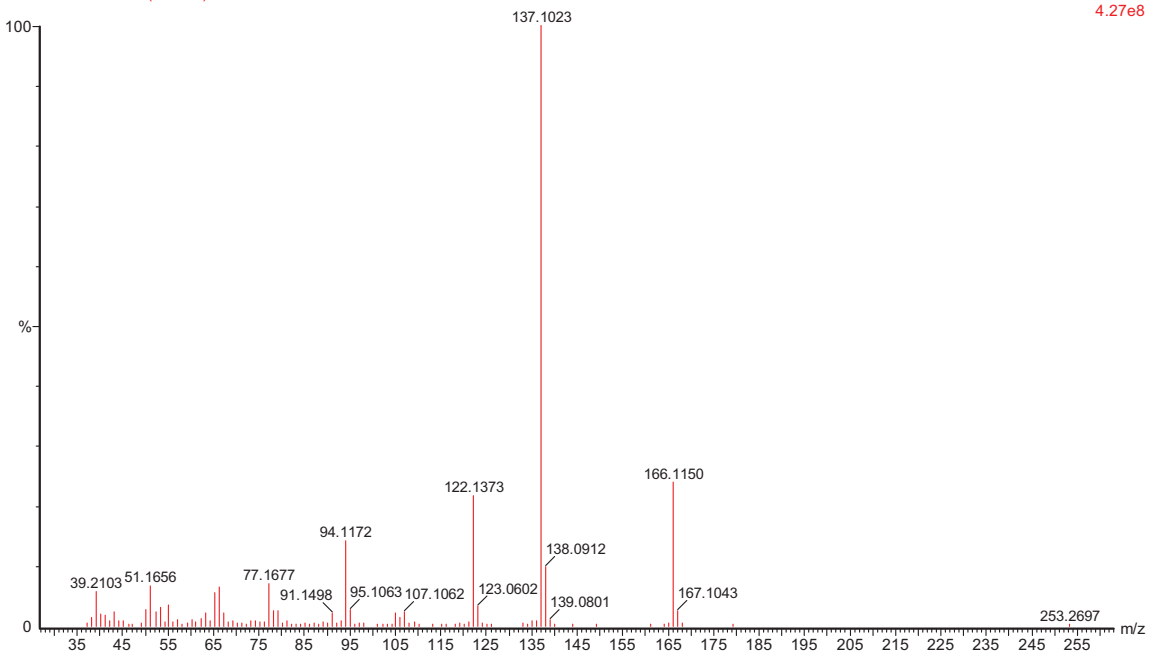




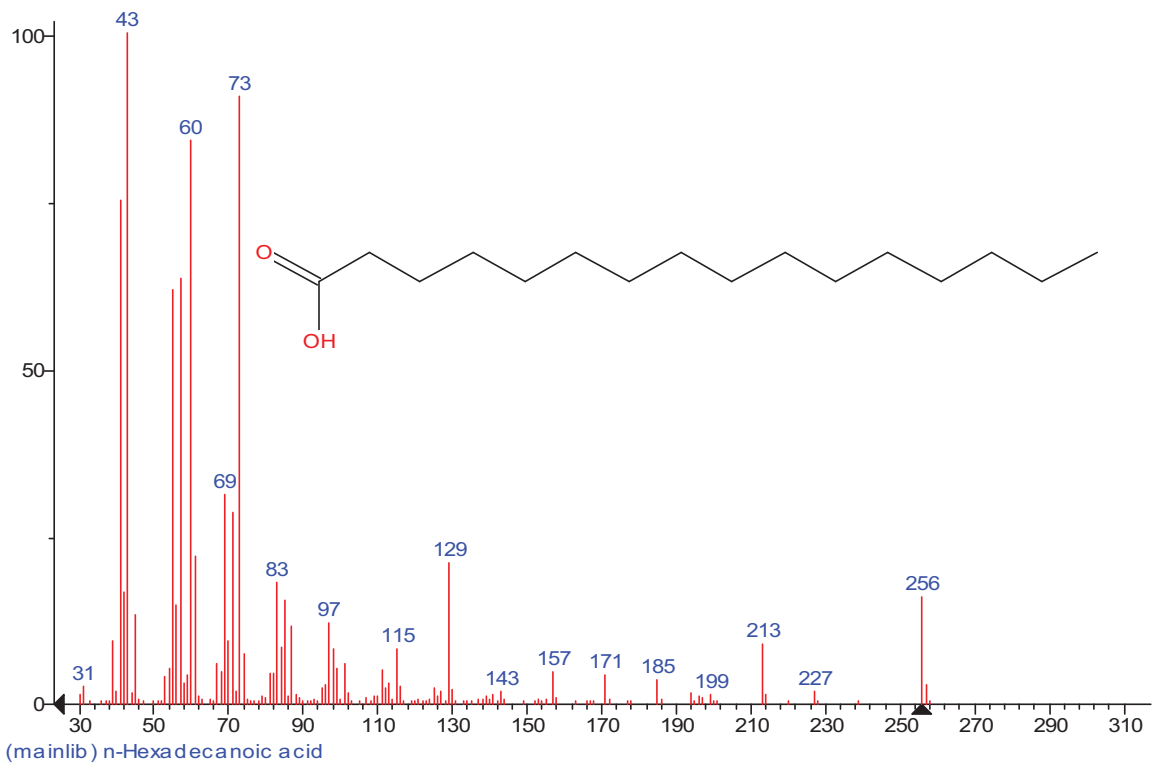
**Pine Wood T1**  
 Pine Wood T1 5937 (30.013)

10 Sec. @ 450C, 01-Jul-2008 + 16:11:08

Scan EI+  
 4.27e8







**Pine Wood T1**

Pine Wood T1 8088 (40.865)

10 Sec. @ 450C, 01-Jul-2008 + 16:11:08

Scan E1+  
8.99e7

