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Investigation of Volatile Products from Wood Pyrolysis

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INVESTIGATION OF VOLATILE PRODUCTS FROM WOOD PYROLYSIS

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By
Prabhavathi Gade

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INVESTIGATION OF VOLATILE PRODUCTS FROM WOOD PYROLYSIS

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I would like to thank God for all his blessings. I owe my deepest gratitude to my family members, who have been a constant source of love, concern, support and strength forever. I am grateful to my friends for helping me to get through the difficult times and for all the emotional support and caring they provided.

Finally, I dedicate my thesis to my parents, my sister Sunitha and my husband.

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INVESTIGATION OF VOLATILE PRODUCTS FROM WOOD PYROLYSIS

Prabhavathi Gade   December 2010   55 Pages

Directed by: Dr. Eric D Conte

Department of Chemistry   Western Kentucky University

In this research we are following the thermo-chemical degradation of wood in the absence of oxygen. The objectives are to evaluate the influence of heating rates on pyrolysis products obtained from wood pyrolysis and to evaluate the influence of acid pre-treatment on pyrolysis products. Depending on the wood heating rates, pyrolysis can be categorized as Flash pyrolysis, Fast pyrolysis, and Slow pyrolysis. We have evaluated the volatile products obtained at different heating rates and the volatile products obtained from sulfuric acid pre-treatment by using gas chromatography- mass spectrometry (GC-MS). We have also performed thermo-gravimetric analysis (TGA) of raw wood samples and sulfuric acid pre-treated wood samples of Yellow Pine to determine the changes in weight in relation to change in temperature.

Our results indicated that by using the Flash, Fast, and Slow heating rates, the overall volatile products obtained from wood pyrolysis (i.e. the overall list of all the compounds obtained from different temperature ranges in wood pyrolysis by using different heating rates) were the same, but the volatile products obtained at different temperature ranges like Room temperature-300°C, 300°C - 400°C, and 400°C -500°C in Flash, Fast, and Slow pyrolysis were different. Most of the volatile products obtained from the pyrolysis of untreated wood were phenols. Our results also indicated that the

pretreatment of wood with sulfuric acid alters the charcoal properties and releases

gaseous products including furan derivatives that are useful as fuels or fuel additives. The

sulfuric acid (10%) pretreatment of wood followed by slow pyrolysis produced maximum

yield of charcoal, indicated by the lowest mass % decrease of 58.234. The production of

furan derivatives increased by using sulfuric acid pre-treatment, which is a good

improvement for the production of Furanics, the furan based biofuels. The furan based

biofuels are of increasing research interest because of their significant advantages over

the first generation biofuels. The thermogravimetric analysis (TGA) results indicated that

the acid pre-treatment altered the decomposition rate of pyrolysis and lowered the onset

of temperature for decomposition.

The use of thermal degradation of plants for creating chemicals and fuels is seeing

renewed interest across the globe as it is considered carbon-neutral and it uses a

renewable feedstock. The information obtained from this research work will also be

valued by industries, such as charcoal and activated carbon producers, which currently

perform biomass pyrolysis, by allowing them to form approaches that optimize their

energy use and minimize waste.

I. INTRODUCTION

When wood is pyrolyzed at higher temperatures in absence of oxygen, the wood will retain its shape and will give off a wood gas in an exothermic reaction. The solid portion remaining from wood pyrolysis is charcoal (carbonized wood) and the crude condensate of the gases produced from wood pyrolysis is called pyroligneous acid, which mainly consists of an aqueous phase and an organic phase. The research presented in this thesis is mainly focused on investigating the volatile by-products from wood pyrolysis and on demonstrating beneficial alterations through the chemical pretreatment of the wood.

<u>Background:</u>

Renewable biomass is an important energy source, with future potentials as fossil fuels are depleted. With a few exceptions, the cost of producing energy from fossil fuels is more than the same amount of energy supplied through biomass conversion. The major scientific interest in developing new technologies for the conversion of renewable biomass into sustainable energy and chemical materials is mainly due to environmental, political, and economic concerns of our dependence on petroleum. Currently, biomass is the only source of carbon with the potential to supply a significant fraction of the energy and chemical intermediates needed for the world economy. However, biomass is generally poorly suited for direct energy use, so under pyrolysis conditions, pyroligneous acid (pyrolysis oil) can be produced. Fortunately, thermo chemical processes can convert biomass into stable physical or stable chemical forms that can be used in higher

efficiency energy conversion processes developed for liquid petroleum and charcoal.[1, 2] Amongst the thermo chemical processes, pyrolysis is mostly preferred because of its ability to optimize process conditions and produce high energy density pyrolytic oils in addition to derived charcoal, with high fuel-to-feed ratios.[3, 4]

Wood Pyrolysis goes through different steps, including exothermic step which produces three types of products: gases, heavy oil fractions, and char fractions. The condensable gases and the heavy oil fractions from the pyrolytic breakdown of wood contain a large number of chemical substances which can be used as substitutes for conventional fuels or as intermediates for substitutes for conventional fuels. Depending on the heating rates and the residence times at particular temperatures, pyrolysis process can be categorized into flash, fast and slow pyrolysis processes. When wood is pretreated with sulfuric acid (dehydrating agent) and then subjected to pyrolysis, it produces more mass yield of charcoal.[5, 6] The general reactions which undergo during the pyrolysis of wood can be categorized as primary reactions and secondary reactions. The primary reactions mainly involve the fragmentation and dehydration reactions. At temperatures lower than 300°C, dehydration is dominant, involving reduction in molecular weight, evolution of water, carbon monoxide, and carbon dioxide and the formation of char. At temperatures higher than 300°C, fragmentation predominates, involving the depolymerization of biomass to characteristic primary tar units.[7] In the category of secondary reactions, the products obtained from the primary reactions may repolymerize or undergo further fragmentation reactions like cracking and reforming or react with free radicals to form secondary products.[7]

Cellulose is the most common form of photosynthetically fixed carbon. Currently, biofuel is mainly produced from biological degradation of starch, which is broken down into sugars, which are then fermented to give ethanol. But the degradation of cellulose into its individual sugar components and its fermentation is a very slow and expensive process. To avoid the breakdown and fermentation of cellulose, Mascal and Nikitin have developed a simple process for the direct conversion of cellulose into furan-based organic liquids called "furanics", which are suitable as fuels.[8, 9] These furan derivatives are the key substances that provide new avenues for the development of cost effective routes for the production of biofuels and chemical intermediates.

In this research work, the common North American yellow pine wood has been selected as a representative sample of coniferous type of woods. The work presented in this thesis has investigated the volatile by-products obtained by using different categories of pyrolysis processes of yellow pine wood and has also undertaken a study on the sulfuric acid pretreatment of wood pyrolysis, aiming at the production of furan derivatives.

History:

Carbonization of wood for the manufacture of charcoal and destructive distillation has been practiced since the beginning of history. The Egyptians, Greeks, and Romans carbonized wood for embalming purposes and the filling of joints in wooden ships. During the ancient times wood charcoal was used for removal of odors, medicinal purposes, domestic cooking fuel, the making of gun powder, and the refining of ores. The industrial revolution brought a heavy demand for charcoal, especially for the reduction of iron ores.[10, 11] The wood distillation was started in the late 1800's with collection of

byproducts like - crude pyroligneous acid and non condensable gases. The pyroligneous

acid was refined to make acetate of lime, methanol, and tar. The wood industry was the

precursor of the petrochemical industry. Before petrochemical production, most of the

industrially important organic chemicals were obtained from wood distillation. Most of

the wood distillation plants were closed by 1950, because the petroleum based products

had taken over the markets dominated by wood distillation products.[12] By the late 1900's,

our dependence on petroleum was increasing enormously. Currently, the environmental,

political, and economic concerns of this increased dependence on petroleum brought back

the importance of wood distillation products and charcoal. It seems like, in the future,

wood will be the only source of carbon with the potential to supply the energy and

chemical intermediates needed for the world economy.

Biomass regaining its central position as feedstock:

Renewable Biomass resources have been the primary industrial and consumer

feed stocks from the beginning of human history. But coal, natural gas and petroleum

have replaced them in the past 150 years as sources for energy and chemicals. These

fossil resources are diminishing day by day and petroleum production is unlikely to meet

the growing human needs in the near future. Moreover, the growing concerns about

global warming are demanding the renewable and sustainable sources of energy.[13] The

advantage of biomass is that it is a CO_2 – neutral feedstock. In 2000, the Biomass

Technical Advisory Committee in the United States stated that 20% of petroleum

transportation fuels have been substituted with fuels from biomass.[14] Currently, the only

largest producing renewable liquid fuel is ethanol from corn (staple food), but it suffers

from several limitations like low energy density, high volatility, and contamination by the

absorption of moisture from the atmosphere.[15] To alleviate this concern , numerous methods are being developed towards the utilization of lignocellulosics for liquid biofuels.[14]

The lignocellulosic feedstock mainly consists of three groups of polymers: cellulose, hemicellulose, and lignin. The cellulose and hemicellulose groups of polymers comprise the carbohydrate fraction of compounds, which is currently being focused by the biofuel technologies.[14] The lignin group of polymers consists of poly(aromatic) moieties from phenylpropanoid building blocks.[14] They produce some tarry substances, which are not advantageous in the field of biofuels. But these lignin group of polymers may be used for the production of some chemicals.

Today the advances in conversion technology using catalytic stages is increasing the potential of the biomass resources to produce renewable carbon sources for transportation fuels and chemicals.[13] For the replacement of petroleum feed stocks with biomass, conversion of carbohydrates from biomass into a variety of furan based chemicals is required, whose importance is explained in the later part of this section. The disubstituted furans produced from carbohydrates (obtained from biomass) using different catalytic strategies can be used as liquid transportation fuels. These disubstituted furans have higher energy density, higher boiling point, and are insoluble in water when compared to that of ethanol.[15] The platform chemical 5-hydroxymethylfurfural which is a dehydration product of carbohydrates also plays a key role in the transportation sector.[13] Hence the production of different furan based chemicals which are suitable for the transportation sector, diminishes the growing needs and dependence of humanity on petroleum. The applications of Bio-oil can be summarized as shown in Figure 1.1.[16]
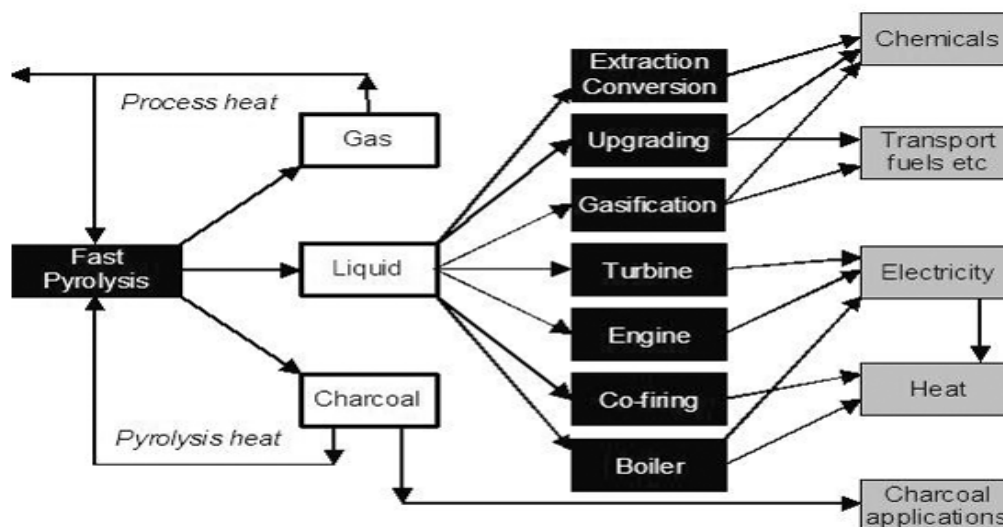
Figure 1.1. Applications of Bio-oil provided by a study on Fast pyrolysis as given in reference 16.[16]

Furanics – furan based biofuels:

      Furanics are the heteroaromatic compounds derived from the chemical intermediate hydroxymethylfurfural, $C_6H_6O_3$. Furanics, the furan based biofuels are of increasing research interest because of their significant advantages over the first generation biofuels.[17]

      Avantium successfully completed an engine test using the furan based biofuels demonstrating the potential of furanics.[17] The development of cost effective methods for the production of furan based chemicals from biomass is mainly being focused on developing second generation biofuels and bio-based chemicals. By using different catalytic strategies, Avantium has developed new and improved catalytic routes to specific furanics.[17] Tom van Aken, Chief Executive Officer of Avantium stated-

"The excellent results of the engine test support the proof of principle of our next generation biofuel, and is an essential milestone for our biofuels development program. The significant reduction of soot in the car exhaust is encouraging, as soot emissions are considered a major disadvantage of using diesel today, because of its adverse environmental and health effects. We are developing a next generation biofuel that has superior fuel properties and process economics compared to existing biofuels. The production process of Furanics has an excellent fit with existing chemical process technology and infrastructure. Ultimately our ambition is to develop biofuels that are competitive with fossil based fuels." [17]
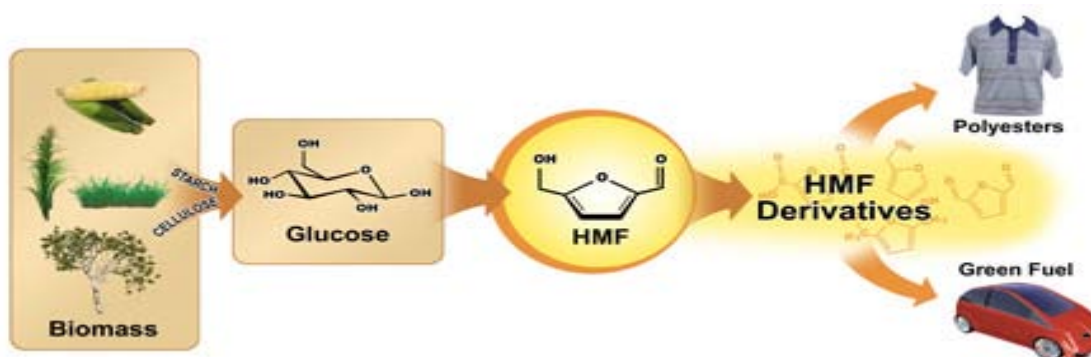
Figure 1.2. Avantium derives its Furanics fuels from the intermediate hydroxymethylfurfural. Illustration: Pacific Northwest National Laboratory [17]

Figure 1.2 clearly shows that the production of furan derivatives is very important in the field of biofuels and for the production of bio-based chemicals. The furan derivatives having higher energy density than that of ethanol are of major research interest for the production of second generation biofuels. Different catalytic processes were developed for the efficient production of furan derivatives from untreated biomass.

In the research work presented in this thesis, the focus was mainly on the production of furan derivatives from the acid pre-treated wood pyrolysis.

Pyrolysis of sulfuric acid pre-treated wood:

The first detailed study of the dilute acid treatment of wood at elevated temperatures was done by Saeman in 1945.[14] Wood containing cellulose is an important starting material for the production of carbons, including charcoal and activated carbons. The maximum carbon yield of cellulose $(C_6H_{10}O_5)_n$ is 44.4% when hydrogen and oxygen are removed as water from it. But practically when wood is subjected to higher temperatures of about 400°C, the carbon yield of cellulose is only 15% because when wood is pyrolyzed it releases some volatile products such as methanol, acetic acid, carbon dioxide and some tar substances. An improvement has been achieved in increasing the carbon yield by decreasing the heating rate to as low as 1°C/min. To achieve greater yields, dehydration is the key phenomenon in the course of pyrolysis. In the Industrial processes, addition of zinc chloride as a dehydrating agent seems to be adopted, but detailed descriptions cannot be found in the existing literatures . Whereas in laboratories, since sulfuric acid is an inexpensive and nonvolatile dehydrating agent, it was chosen to examine the effect on pyrolysis of cellulose. It has been stated that sulfuric acid treatment can be useful in increasing the mass yield of carbon and preservation of the original shapes.[18]

When the wood is treated with acid, the main reactions taking place during the process are classified into two types: (1) The cellulose and hemicelluloses group of polymers depolymerize resulting in the formation of their oligosaccharide or

monosaccharide components, and (2) The degradation of the subsequent monosaccharide products.[14] The schematic diagram of these reactions as outlined by Marzialetti, Olarte, Sievers, Hoskins, Agarwal, and Jones is shown in Figure 1.3.[14] The acid catalyzed dehydration of glucose forms levulinic acid and formic acid with a detectable intermediate, 5-hydroxy-methyl-2-furfuraldehyde (HMF). The schematic diagram of this reaction is shown in Figure 1.4.[14] Similarly acid catalyzed dehydration of xylose (pentoses) results in the formation of furfural as in Figure 1.5.[14]
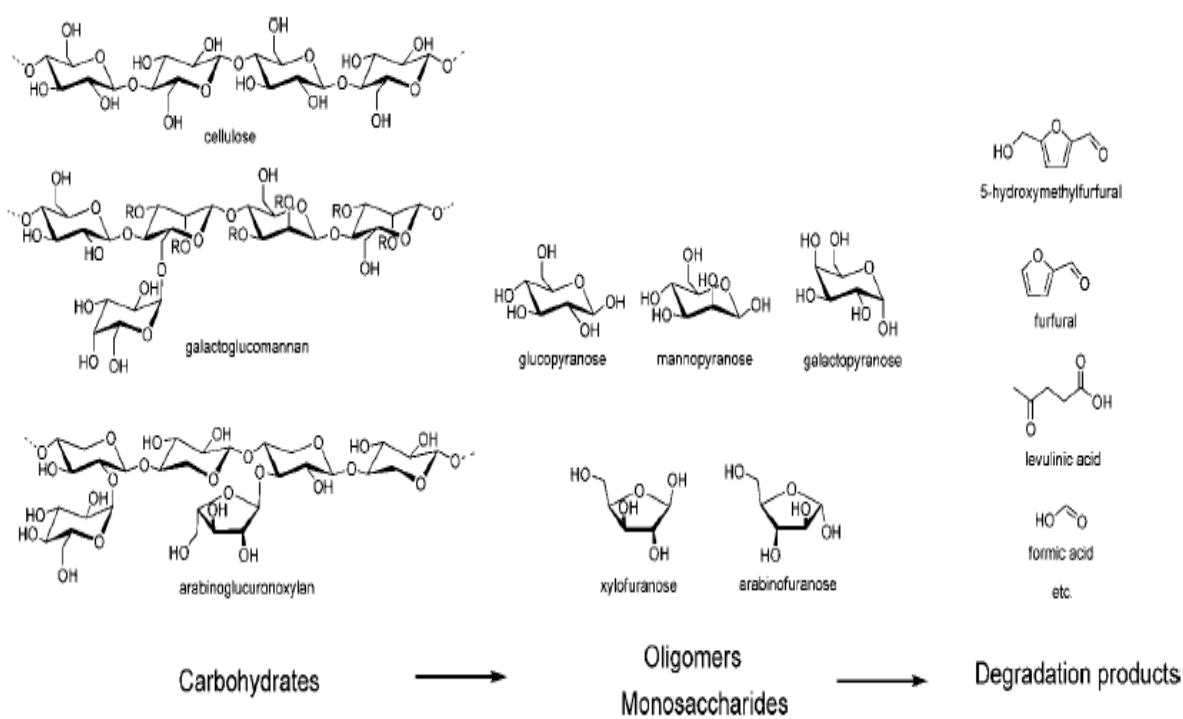
Figure 1.3. Carbohydrate Reactions in the presence of acid. [14]
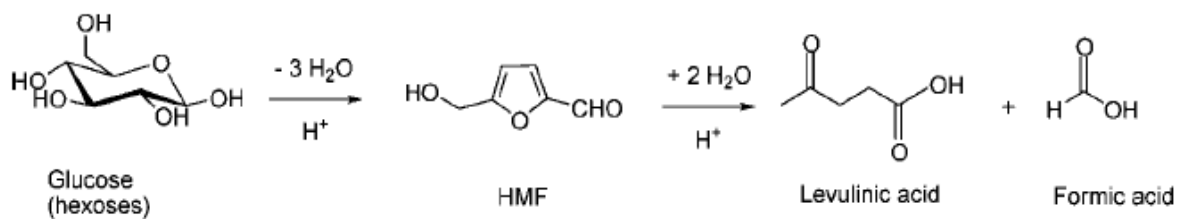
Figure 1.4. Acid catalyzed dehydration of Glucose.[14]
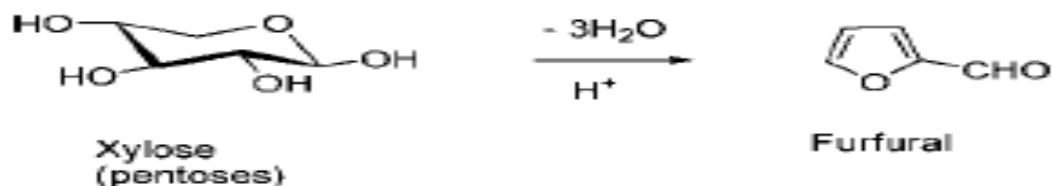
Figure 1.5. Acid catalyzed dehydration of Xylose (pentoses).[14]

Pyrolysis Gas Chromatography Mass Spectrometry (Py/GC/MS):

Pyrolysis gas chromatography mass spectrometry is a method which enables a

reproducible characterization of the intractable macromolecular complexes of the

materials found in the natural environment.[19-22] It is an excellent technique for various

qualitative analyses. The volatile compounds obtained from the pyrolysis of wood can be

extracted by using Solid Phase Micro Extraction (SPME) method and then injected into

the analytical column of a GC proceeded by MS. SPME was first developed by

Pawliszyn and coworkers and it has been marketed by Supelco in order to eliminate the

limitations inherent in Solid phase extraction (SPE) and Liquid liquid extraction (LLE).[23]

SPME is well known for rapid sampling and sample preparation. SPME method can

integrate sampling, extraction, concentration and sample introduction into a single step

and provides a simple, solvent-free alternative to traditional methods of sample

preparation. SPME is known for its simplicity, low cost, rapidity, selectivity and sensitivity.[23, 24] Headspace-SPME is a modified SPME in which fused silica fibers coated with a thin polymer is used to trap and concentrate the analytes from the head space of the sample.[25] The most important point to consider for an SPME method is the choice of an appropriate SPME fiber coating. The sensitivity of a fiber differs depending on the polarity and molecular mass of the analytes that are to be extracted.[23] Hence, HS-SPME method is commonly being used by the researchers in this field to extract the volatile compounds obtained from the pyrolysis of wood.

II. EXPERIMENTAL

A. Chemicals and Materials:

      All chemicals used were of ACS reagent grade. All solutions were prepared using distilled water. Nitrogen gas was purchased from the Modern Supply. The yellow pine wood used in the experiment was purchased from the Lowes home improvement store.

A.1. Sulfuric acid was purchased from Sigma-Aldrich chemicals.

A.2. Solid Phase Micro-Extraction Holder (manual) 57330-U was purchased from Supelco, Bellefonte, PA, USA.

A.3. Solid Phase Micro-Extraction Fiber Assemblies were purchased from Supelco, Bellefonte, PA, USA.

B. Instrumentation:

B.1. Weighing balance: Denver Instrument M-220D

B.2. Vacuum Tube Furnace: GSL 1100X MTI Corporation

B.3. Gas Chromatograph: Hewlett Packard 5890 series II

B.4. Gas Chromatograph-Mass Spectrometer: Agilent 5973

B.4. Oven : Vulcan 3-1750

B.5. Thermo gravimetric analyzer (TGA): TA instruments Q-5000-I

C. Design of the Experiment:

The design of this experimental work mainly consists of – (i) Tube Furnace (ii) Collection of the condensed vapors of the by-products in the 'U' shaped tube (iii) Solid Phase Micro Extraction (SPME) and (iv) Gas Chromatography-Mass Spectrometry.

The wood species selected for this work was Yellow Pine. It was cut into small pieces, depending on the nature of the experiment, and thermally treated in a furnace. Depending on the heating rates, pyrolysis of wood was categorized into three different types- (i) Fast (ii) Slow and (iii) Flash. The heating rate for fast pyrolysis was 5°C/min and slow pyrolysis was 0.83°C/min. In fast and slow pyrolysis, pieces of wood were placed in the tube furnace and heated with a specific heating rate, whereas in flash pyrolysis, the tube furnace was first pre-heated to a specific temperature and then pieces of wood were placed in the center of the tube for five minutes. The preliminary goals of this work were to collect the condensed vapors of pyrolyzed wood for analysis and to produce pieces of carbonized wood to characterize the charcoal. Analysis of the resulting condensate was done by sampling it through solid phase micro extraction (SPME) technique and injecting it into Gas Chromatography - Mass Spectrometry instrument. Characterization of the resulting carbonized wood was done by measuring the changes in its - dimensions and mass. Thermal analysis by TGA was also performed.

D. Pyrolysis of yellow pine wood:

D.1. Tube Furnace:

The furnace used in this experimental work was a vacuum tube furnace, model number GSL 1100X, manufactured by MTI Corporation. It was equipped with heating elements embedded in ceramic fiber insulation providing rapid chamber heat-up and cool-down. This chamber includes two interchangeable end pieces to accommodate process tubes with 2'' O.D. Two vacuum flanges were installed at the two ends of the tube. The operating temperature range of the furnace was $100 \sim 1100°C$ but it was only used up to 600°C. It was also equipped with a programmable temperature controller, allowing temperature ramp. A nitrogen cylinder equipped with a pressure regulator served as the gas supply and was metered by a calibrated rotameter. Figure 2.1 shows a photograph of the set up.
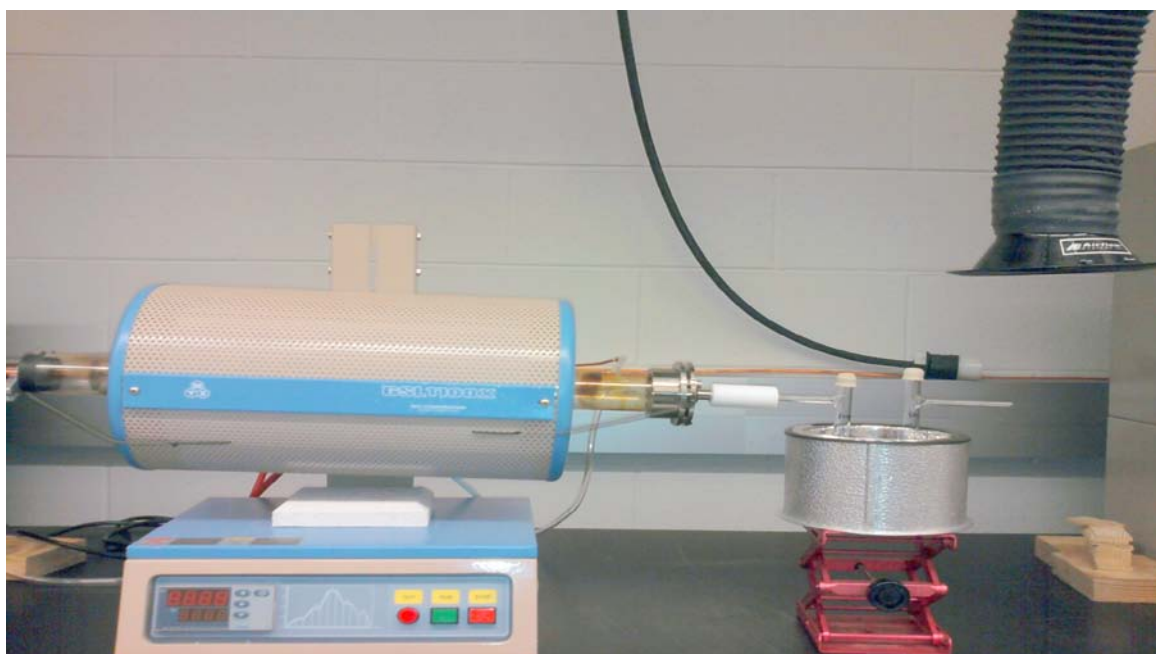
Figure 2.1. Experimental set-up of a vacuum tube furnace

As shown in Figure 2.1, a 'U' shaped tube was connected to the tube of the furnace by using a teflon connector between the vacuum flange and the 'U' shaped tube. This 'U' shaped tube was immersed in an ice bath, which condensed the vapors coming out of the tube furnace. The other end of the 'U' shaped tube was left open, so that the off gases coming out of the furnace were vented through a lab exhaust.

Pyrolysis of wood using fast and slow rates was done by placing the wood samples in the center of the tube and setting the temperature program accordingly, using the temperature controller. During the pyrolysis, the vapors coming out of the tube furnace condense and gets collected in the 'U' shaped tube placed in an ice bath. Once the pyrolysis was done, the 'U' shaped tube was sealed on both the sides and then the liquid collected in this tube was used for further analysis. But for flash pyrolysis, the set up of the tube furnace was slightly different. In flash pyrolysis, the inlet of the tube furnace, which was sealed with a vacuum flange in fast and slow pyrolysis, was replaced with a sealed rubber stopper with through holes for copper tubing allowing the gas flow and for a push rod to push the sample inside the tube furnace. The stopper was held in place with springs. A ceramic felt was placed just inside the tube to prevent the rubber from overheating. This insulation was porous so that gas flow could be maintained. Here in flash pyrolysis, the tube furnace was first pre-heated to required temperature and then the sample was pushed into the center (hottest zone) of the tube using the push rod and left in that zone for about five minutes and again pulled back to its original position. The vapors collected in the 'U' shaped tube during this five minutes of pyrolysis were used for further analysis.

After collection of vapors in the 'U' shaped tube, the tube furnace was allowed to cool down and then the carbonized wood was removed from the tube furnace. This carbonized wood was further analyzed to calculate its charcoal yield.

E. Solid-Phase Micro Extraction (SPME):

The Solid-Phase Micro Extraction (SPME) fiber itself is a thin fused-silica optical fiber. This fiber is coated with a thin polymer film which serves as a coating material in chromatography.

E.1. Choosing a Fiber:

The most important feature in determining the analytical performance of SPME fiber is the type and thickness of the coating material on the fiber. Supelco has provided users with different fiber coatings. The list of most common commercially available polymer coatings is given in Figure 2.2.

Fiber Coating	Film Thickness	Polarity	Coating Method	Technique	Compounds to be analyzed
PDMS	100 µm	Non-polar	Non-bonded	GC/HPLC	Volatiles
PDMS	30 µm	Non-polar	Non-bonded	GC/HPLC	Non-polar semi volatiles
PDMS	7 µm	Non-polar	Bonded	GC/HPLC	Medium to nonpolar semi volatiles
PDMS-DVB	65 µm	Bipolar	Cross-linked	GC	Polar volatiles
PDMS-DVB	60 µm	Bipolar	Cross-linked	HPLC	General purpose
PDMS- DVB	65 µm	Bipolar	Cross-linked	GC	Polar volatiles
PA	85 µm	Polar	Cross-linked	GC/HPLC	Polar-semi-volatiles
Carboxen-PDMS	75 µm	Bipolar	Cross-linked	GC	Gases and volatiles

Carboxen-PDMS	85 µm	Bipolar	Cross-linked	GC	Gases and volatiles
Carbowax-DVB	65 µm	Polar	Cross-linked	GC	Polar analytes
Carbowax-DVB	70 µm	Polar	Cross-linked	GC	Polar analytes

Figure 2.2. List of commercially available SPME fibers

PDMS- Poly dimethyl siloxane, DVB- Divinyl benzene, PA- Poly acrylate

The fibers used in this experimental work were 1cm long and were coated with PDMS or Carboxen-PDMS. These two types of coatings were suitable for extracting gases and volatiles through head-space sampling.

E.2. Extraction Procedure:

Solid-Phase Micro Extraction technique can be used in two principle modes : (i) Head Space Extraction and (ii) Direct Extraction. In head space mode, the vapor present above the sample matrix is sampled, where as in the direct mode, the fiber is completely immersed in the sample matrix to extract the analytes onto the extraction phase of the fiber.

In this experimental work, head space sampling was used because direct sampling may damage the fiber or change the properties through adsorption as the samples obtained from pyrolysis of the wood were dirty. In head space sampling, the volatile analytes are transported from the sample matrix to the head space and then when the fiber is inserted into the head space of the sample matrix, the volatiles get adsorbed onto the fiber coating. This fiber adsorbed with different volatiles is used for further analysis using gas chromatography- mass spectrometry. The SPME needles used for the extraction of

different volatile substances from the samples obtained from pyrolysis of the wood are

shown in Figure 2.3.

 Figure 2.3. Supelco Solid Phase Micro Extraction needles

F. SPME Determination:

A typical SPME determination was carried out, mainly involving three steps as

follows :

- Fiber cleaning

- Adsorption

- Desorption and Chromatography

F.1. Fiber Cleaning:

The SPME fibers used for sampling the analytes were cleaned before each

analysis in order to remove any contaminants present on the fiber. A gas chromatograph

was used for cleaning the SPME fibers. The injection port temperature of the gas

chromatograph was set to 250°C and then the SPME fiber was injected into the gas

chromatograph, followed by heating up to one hour at 250°C as shown in Figure 2.4. In

this process, any contaminants on the fiber get desorbed onto the capillary column of the

gas chromatograph. After one hour, the cleaned fiber was retracted into the needle and the needle was removed slowly from the hot injection port.

F.2. Adsorption:

The cleaned SPME fiber was then immersed into the head space of the 'U' shaped tubes which contained the condensate of the vapors of pyrolysis of wood. The fiber was left in the head space of the 'U' shaped tube for about 30 minutes as shown in Figure 2.5. After 30 minutes, the fiber was retracted into the needle and the needle was slowly removed from the tube.

In this process, the volatile substances in the head space of the 'U' shaped tube get adsorbed onto the SPME fiber. This SPME fiber adsorbed with the volatile substances was then used for the further analysis by using gas chromatography- mass spectrometry.

Figure 2.4. SPME Fiber cleaning by using gas chromatograph

Figure 2.5. Adsorption of the volatile substances by SPME fiber

F.3. Desorption and Chromatography:

Once the fiber was adsorbed with the volatile substances, it was injected into the hot injection port of the gas chromatograph- mass spectrometer, GC-MS Agilent 5973, equipped with a mass selective detector as shown in Figure 2.6. The fiber was left in the injection port for about one minute in order to ensure that most of the volatile substances get desorbed thermally into the separation column for analysis. After one minute, the fiber was retracted into the needle and the needle was removed from the injection port. The sample injection was done in split less mode in order to ensure that a larger portion of the analytes transferred directly into the analytical column without any exhaustion of the analytes through the split vent.

Figure 2.6. Gas chromatograph- Mass spectrometer GC-MS Agilent 5973

G. Sulfuric acid pre-treatment of wood:

Sulfuric acid, an inexpensive and nonvolatile dehydrating agent was chosen to examine the influence of its addition on the pyrolysis of wood. The sample pieces of yellow pine wood were weighed and immersed in sulfuric acid (7%, 10% and 20%) for about five minutes by placing it under a vacuum. After five minutes, the wood pieces were removed from the sulfuric acid solution and placed in an oven at 90°C for about 18 hours for drying. Once the wood pieces were dried, its weight and dimensions were measured and then the as usual pyrolysis of wood was performed with these pre-treated

samples of wood. In order to perform thermo gravimetric analysis of the pre-treated wood samples, the dried wood pieces were made into a fine powder.

H. Thermo gravimetric analysis (TGA):

Thermal analysis was performed on the original yellow pine wood samples (fine powder) and the sulfuric acid pre-treated and dried wood samples (fine powder). A TGA instrument (TGA: TA instruments Q-5000-I) as shown in Figure 2.7, coupled with a mass spectrometer was used with inert gas flow in absence of oxygen. Sample cups used in TGA were made up of platinum. The temperature ramp rate chosen for the TGA analysis in this experimental work was 10°C/min.

Figure 2.7. Thermo gravimetric analyzer (TA instruments TGA-5000-I)

The powdered wood samples were placed in the platinum holders of thermo gravimetric analyzer and pyrolyzed up to 1000° C at a heating rate of 10°C/min under nitrogen flow of 200ml/min. Then the results obtained from thermo gravimetric analyzer and from the coupled mass spectrometer were compared and analyzed.

III. RESULTS AND DISCUSSION

A. Objectives:

The main objectives of this study were:

i) To evaluate the influence of heating rates on pyrolysis products obtained from wood pyrolysis.

ii) To evaluate the influence of acid pre-treatment on pyrolysis products obtained from pre-treated wood pyrolysis.

B. Analysis of original yellow pine wood:

The volatile products obtained from the Flash, Fast, and Slow pyrolysis of yellow pine wood in a tube furnace were extracted by using a SPME fiber and analyzed by using gas chromatograph- mass spectrometer (GC-MS). The results obtained from Flash, Fast, and Slow pyrolysis of original yellow pine wood at different temperature ranges are presented in the form of tables on the following pages. The analysis of the volatile products obtained by using GC-MS was qualitative, investigating the type of compounds produced from the pyrolysis. The library used to find the peaks from GC-MS was created by NIST. The volatile products obtained from all rates of pyrolysis, were mostly phenols with fewer number of other compounds. As per the literature, methanol, acetic acid, and water are the other major compounds which are expected to be seen in the byproducts obtained from wood pyrolysis. But we could not see any peaks for methanol, acetic acid, and water from GC-MS, which was mainly because of the use of SPME technique. In order to check for the presence of methanol, acetic acid , and water in the byproducts obtained from wood pyrolysis, thermogravimetric analysis was coupled with mass spectrometry, which will be explained in the later parts of this section.

From the results presented in the following tables, we can determine the influence of heating rates on the release of the volatile products from pyrolysis of wood.

Likely Substance	Fast 500°C	Slow 500°C
Phenol, 2– methyl	✔	✕
Phenol, 3–methyl	✔	✕
Phenol, 2,4–dimethyl	✔	✔
Phenol, 3–ethyl	✔	✔
Phenol, 2–methoxy–4–methyl	✔	✔
Phenol, 4–ethyl–2–methoxy	✔	✔
Phenol, 2–methoxy–4–(1–propenyl)	✔	✔
n–Hexadecanoic acid	✔	✔
Phenol, 2 –methoxy	✔	✕
2–hydroxy–4–methyl benzaldehyde	✔	✔
Naphthalene–1–methyl	✔	✕

Table 3.1. Volatile products obtained from pyrolysis of yellow pine when temperature is maintained constantly at only 500°C using fast and slow heating rates

The volatile products obtained from pyrolysis of yellow pine using fast and slow heating rates, when temperature is maintained constantly at only 500°C are listed in Table 3.1.

The list of compounds given in Table 3.1 were the outcome of only qualitative analysis of the volatile products obtained by using GC-MS, investigating the type of compound produced. The cross marks against some of the substances indicate that particular compound produced by using the specified heating rate is below the detection limit of the instrument. The compounds, which are below the detection limit by using slow heating rate at 500°C, were detected in lower temperature ranges. This can be

observed by finding the name of the same compounds in other tables, which list the

compounds produced at lower temperature ranges by using slow heating rates.

Likely Substance	Flash Rt-500°C	Fast 400°C-500°C	Slow 400°C-500°C
Phenol, 2-methyl	✔	✔	✔
Phenol, 2-methoxy	✔	✔	✔
Phenol, 2,3-dimethyl	✔	✔	✔
Phenol, 2-methoxy-4-methyl	✔	✔	✔
Phenol, 4-ethyl-2-methoxy	✔	✔	✔
Phenol, 2-methoxy-4-(1-propenyl)	✕	✔	✕
n-Hexadecanoic acid	✕	✔	✕
3- hydroxy-4-methyl benzaldehyde	✔	✕	✕
3,4-dimethoxy toluene	✔	✔	✔
Naphthalene-1-methyl	✔	✔	✔
Naphthalene 2,3-dimethyl	✔	✔	✔
Eugenol	✔	✔	✔
Phenol, 2-methoxy, 4-propyl	✔	✔	✔

Table 3.2. Volatile products obtained from pyrolysis of yellow pine when temperature is maintained in the range of 400°C - 500°C using flash (Rt-500°C) , fast and slow heating rates.

The volatile products obtained from pyrolysis of yellow pine using flash (Rt-500°C), fast and slow heating rates, when temperature is maintained in the range of 400°C - 500°C are listed in Table3.2.

The list of compounds given in Table 3.2 were the outcome of only qualitative analysis of the volatile products obtained by using GC-MS, investigating the type of compound produced. The cross marks against some of the substances indicate that particular compound produced by using the specified heating rate is below the detection

limit of the instrument. The compounds, which are below the detection limit by using flash heating rate in this particular temperature range were detected in a lower temperature range. The compounds, which are below the detection limit by using slow and fast heating rates in this particular range of temperature were also detected in lower temperature ranges. All this can be observed by finding the name of the same compounds in other tables, which list the compounds produced at lower temperature ranges.

Likely Substance	Flash Rt–400°C	Fast 300°C–400°C	Slow 300°C–400°C
Phenol, 2– methoxy	✓	✓	✓
Phenol, 2–methoxy–4–methyl	✓	✓	✓
Phenol, 4–ethyl–2–methoxy	✓	✓	✓
Phenol, 2–methoxy–6–(2–propenyl)	✗	✓	✓
Eicosane	✗	✓	✓
Heptadecane	✗	✓	✓
Tridecanoic acid	✗	✓	✗
Eugenol	✓	✓	✓
Phenol, 2–methoxy–4–propyl	✓	✓	✓
3–allyl–6–methoxy phenol	✗	✓	✓
Phenol, 2–methoxy–4–(1–propenyl)	✓	✓	✗
2,3–dimethoxytoluene	✓	✓	✓
Hexatriacontane	✗	✓	✓
Nonadecane	✗	✓	✓
Naphthalene 2,7–dimethyl	✓	✓	✓

Table 3.3. Volatile products obtained from pyrolysis of yellow pine when temperature is maintained in the range of 300°C - 400°C using flash (Rt-400°C) , fast and slow heating rates.

The volatile products obtained from pyrolysis of yellow pine using flash (Rt-400°C), fast and slow heating rates, when temperature is maintained in the range of 300°C - 400°C are listed in Table 3.3.

The list of compounds given in Table 3.3 were the outcome of only qualitative analysis of the volatile products obtained by using GC-MS, investigating the type of compound produced. The cross marks against some of the substances indicate that particular compound produced by using the specified heating rate is below the detection limit of the instrument. The compounds, which are below the detection limit by using flash heating rate at this particular temperature range were detected in a higher temperature range. But the compounds, which are below the detection limit by using slow heating rate at this particular range of temperature were detected in a lower temperature range. All this can be observed by finding the name of the same compounds in other tables, which list the compounds produced at temperature ranges higher and lower than this particular range of temperature.

Likely Substance	Flash (Rt-300°C)	Fast (Rt-300°C)	Slow (Rt-300°C)
Butylated hydroxytoluene	✓	✓	✓
Eicosane	✓	✓	✓
n-Hexadecanoic acid	✓	✓	✓
Hexadecane	✗	✓	✗
Phenol, 2-methoxy-4-(1-propenyl)	✓	✓	✓
3-allyl-6-methoxy phenol	✓	✓	✓
Eugenol	✓	✓	✓
Phenol, 2- methoxy / Phenol, 4-ethyl-2-methoxy	✓	✓	✓
Phenol, 2-methoxy-4-methyl	✓	✓	✓
Benzofuran, 2-methyl	✓	✓	✗
Phenol, 4-ethyl-2methoxy	✓	✓	✓
Phenol, 2-methoxy-4-propyl	✓	✓	✓
1H-Indene, 3-methyl	✓	✓	✗
Benzene, 1-methoxy-4-(2-propenyl)	✓	✓	✓
Nonaoic acid, methyl ester	✓	✓	✓
Benzene Hexyl	✓	✗	✗
2-methoxy-4-vinyl phenol	✓	✓	✓
Pentadecene	✓	✗	✓

Table 3.4. Volatile products obtained from pyrolysis of yellow pine when temperature is maintained in the range of Rt - 300°C using flash, fast and slow heating rates.

The volatile products obtained from pyrolysis of yellow pine using flash (Rt-500°C), fast and slow heating rates, when temperature is maintained in the range of Rt - 300°C are listed in Table 3.4.

The list of compounds given in Table 3.4 were the outcome of only qualitative analysis of the volatile products obtained by using GC-MS, investigating the type of compound produced. The cross marks against some of the substances indicate that particular compound produced by using the specified heating rate is below the detection limit of the instrument. The compounds, which are below the detection limit by using flash, fast , and slow heating rates at this particular temperature range were detected in a higher temperature range. This can be observed by finding the name of the same

compounds in other tables, which list the compounds produced at higher temperature ranges.

From the above four tables 3.1, 3.2, 3.3, and 3.4, it was observed that most of the volatile products obtained from the pyrolysis of untreated wood were phenols with fewer number of other compounds. The overall volatile products obtained from wood pyrolysis by using Flash, Fast and Slow heating rates were the same, but the volatile products obtained at different temperature ranges like Room temperature-300°C, 300°C - 400°C, and 400°C -500°C in Flash, Fast, and Slow pyrolysis were different. From this it can be deduced that by using slow heating rates, compounds were produced at lower apparent temperatures, when compared to that of flash and fast heating rates.

C. Analysis of sulfuric acid pre-treated yellow pine wood:

The samples of yellow pine wood, which was pre-treated with sulfuric acid and dried   were subjected to pyrolysis by using fast and slow heating rates. The sulfuric acid used for the pre-treatment was of different concentrations, like 7%, 10%, and 20%. The changes in the dimensions and mass of the resulting carbonized wood pieces were measured to calculate the charcoal yield. The resulting mass percent decrease in charcoal yields obtained from the wood pyrolysis using different concentrations of sulfuric acid are presented in Table 3.5.

The volatile products obtained from the fast and slow pyrolysis of sulfuric acid (7%, 10%, and 20%) pre-treated and dried wood pieces of yellow pine were extracted through SPME fiber and analyzed by using gas chromatograph- mass spectrometer, GC-MS. The analysis in this part of experimental work by using GC-MS was qualitative

and semi-quantitative, investigating the type of compounds produced and determining the increase or decrease in the amount of compounds produced. The semi-quantitative analysis was a comparison of the amount of compounds produced from using different concentrations of sulfuric acid for pre-treatment and a comparison of the amount of compounds produced by using different heating rates. The library used to find the peaks from GC-MS was created by NIST. For the semi-quantitative comparison, the peak areas of particular compounds were taken into account.

From the data to be presented in the following tables and graphs, we can investigate the influence of sulfuric acid pretreated wood pyrolysis on the charcoal yield and the production of volatile products.
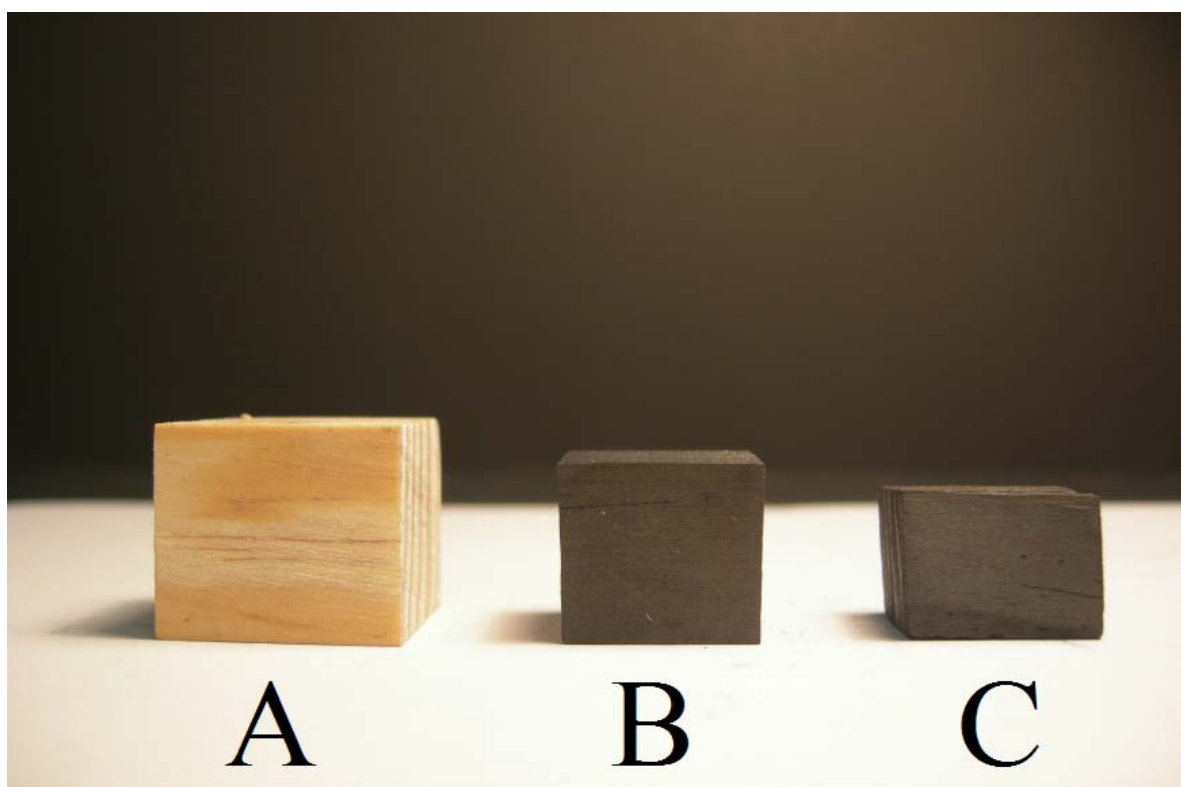

Figure 3.1. Shrinkage of wood block by 600°C treatment for Yellow Pine
(A) Original (B) treated with sulfuric acid (C) without sulfuric acid

The appearance of original and 600°C pyrolyzed wood blocks of Yellow Pine, with and without sulfuric acid pre-treatment are shown in Figure 3.1.

From Figure 3.1, it can be observed that the shrinkage of the pyrolyzed wood block, which is pre-treated with sulfuric acid, is less when compared to that of the untreated pyrolyzed wood block. It implies that the volume of charcoal can be increased by pre-treating the wood block with sulfuric acid before subjecting it to pyrolysis. This also suggests that pre-treatment of wood with sulfuric acid alters the decomposition pathways during pyrolysis.

Sno	Wood Type	Sulfuric acid Treatment	Heating Rate	Axial % decrease	Tangential %decrease	Radial % decrease	Mass % decrease
1	Yellow Pine	No	Fast	23.076	35.391	29.385	75.338
2	Yellow Pine	Yes 20%	Fast	23.076	28	23.076	62.1106
3	Yellow Pine	No	Slow	18.336	36	30.952	75.3185
4	Yellow Pine	Yes 20%	Slow	25.462	23.913	25.462	62.521
5	Yellow Pine	Yes 10%	Slow	20.417	22.417	21.905	**58.234**
6	Yellow Pine	Yes 7%	Slow	20	24	20	60.843

Table 3.5. Percent decrease of dimensions in three directions and percent decrease of mass of the pyrolyzed wood blocks using different conditions.

The percent decrease of dimensions in axial, tangential and radial directions and

the percent decrease in the mass of the pyrolyzed wood blocks by using different heating rates and with or without sulfuric acid (different concentrations) pretreatment are shown in Table 3.5.

From the data in Table 3.5, it was observed that **10 %** sulfuric acid pretreatment of wood followed by slow pyrolysis produced *maximum* mass yield of charcoal. This suggests that pre-treatmet of wood with sulfuric acid alters the decomposition pathways during pyrolysis, resulting in the production of different byproducts, which can be observed in the following parts of this section.

	Furfural	**Phenol**	**Phenol- 2-methyl**	**Benzofuran -2-methyl**	**Naphthalene**	**Dibenzo furan**
YP Fast Treated Vs Untreated	0 : 1	0.634 : 1	0.316 : 1	1: 0.965	1 : 0.281	1 : 0
YP Slow Treated Vs Untreated	0 : 1	0.394 : 1	0.541: 1	1 : 0.455	1 : 0.873	1 : 0.358
YP Treated Fast Vs Slow	0:0	0.708 : 1	0.593 : 1	1 : 0.637	1 : 0.671	0.549 : 1
YP Treated Slow 20% Vs 10% Vs 7%	0:0:0	0.545 : 0.826 : 1	0.613: 0.178: 1	1: 0.267: 0.319	1: 0.154: 0.381	1: 0.252: 0.195

Table 3.6. Ratios of normalized peak areas of particular compounds from SPME-GC-MS of the volatile products obtained from different pyrolysis experiments using different conditions.

The ratios of the normalized peak areas of particular compounds which show significant difference in their production from SPME-GC-MS of the volatile products obtained from different pyrolysis experiments by using different conditions are shown in Table 3.6. The conditions of the pyrolysis experiment include different heating rates, with and without sulfuric acid pre-treatment, and different concentrations of sulfuric acid used for the pre-treatment.

In order to compare the above data more clearly, each comparison has been plotted into separate bar graphs as shown in the following Figures 3.2 - 3.5.
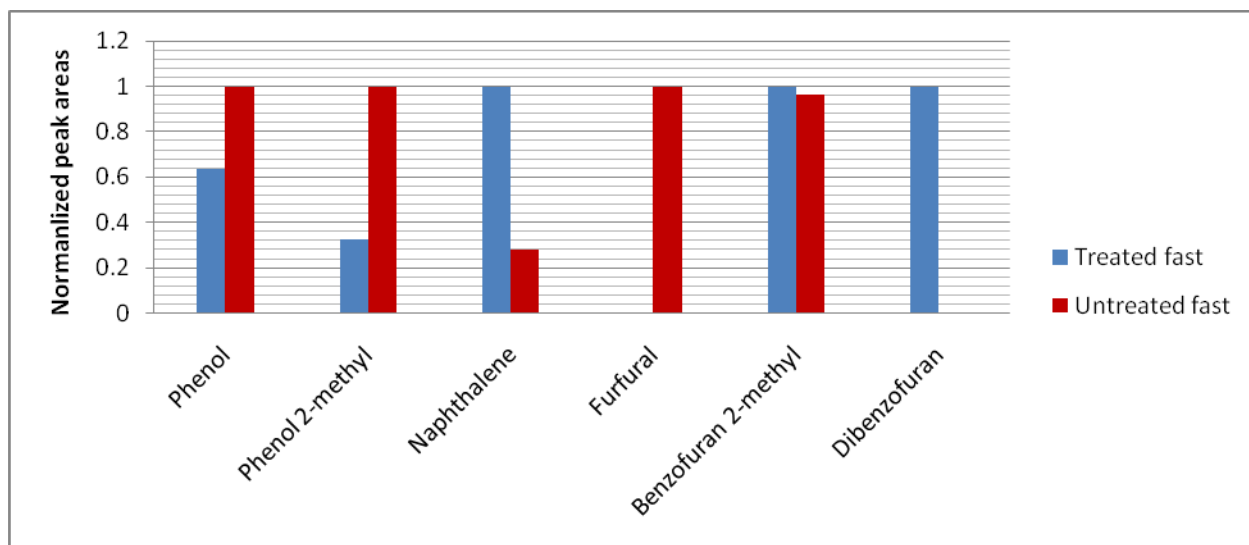

Figure 3.2. Graph showing differences in the peak areas of particular compounds from the experiments *Yellow Pine - Fast - Treated Vs Untreated*

The peak areas of particular compounds produced from the pyrolysis of sulfuric acid pre-treated yellow pine wood and untreated yellow pine wood by using fast heating rate are compared in the form of bar graphs in the above Figure 3.2.

From the above graph, it can be observed that by using fast heating rate the amount of *phenols* produced from the pyrolysis of sulfuric acid pre-treated yellow pine

wood is *less* when compared to that of untreated yellow pine wood, and the amount of *furan derivatives* produced from the pyrolysis of sulfuric acid pre-treated yellow pine wood is *more* when compared to that of untreated yellow pine wood. The untreated yellow pine wood produced furfural on pyrolysis but when the wood was treated with sulfuric acid, furfural was no longer produced.

The increase in the production of furan derivatives is a very significant result, because furan derivatives are the compounds which have higher energy density than that of ethanol. Since ethanol is the major component of the first generation biofuels, many of the researchers are trying to replace ethanol with furan derivatives (higher efficiency than ethanol) in the second generation biofuels.
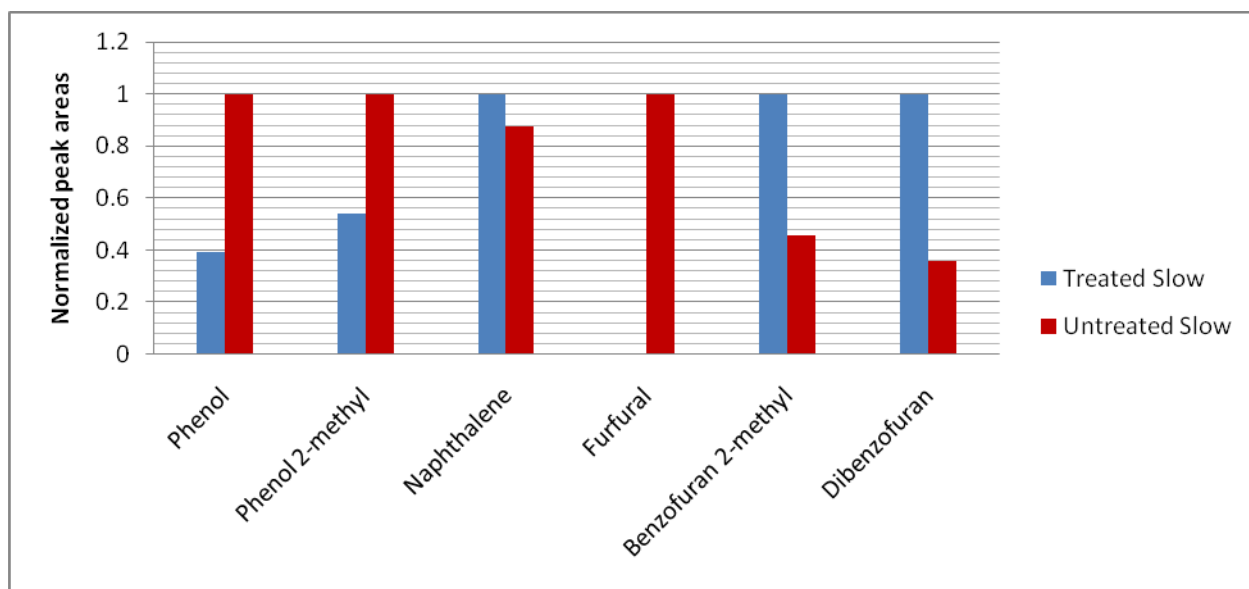

Figure 3.3. Graph showing differences in the peak areas of particular compounds from the experiments *Yellow Pine - Slow- Treated Vs Untreated*

The peak areas of particular compounds produced from the pyrolysis of sulfuric acid pre-treated yellow pine wood and untreated yellow pine wood by using slow heating rate are compared in the form of bar graphs in the above Figure 3.3.

From the above graph, it can be observed that even by using slow heating rate the amount of *phenols* produced from the pyrolysis of sulfuric acid pre-treated yellow pine wood is *less* when compared to that of untreated yellow pine wood, and the amount of *furan derivatives* produced from the pyrolysis of sulfuric acid pre-treated yellow pine wood is *more* when compared to that of untreated yellow pine wood. The untreated yellow pine wood produced furfural on pyrolysis but when the wood was treated with sulfuric acid, furfural was no longer produced.

When treated and untreated wood pyrolysis were compared using slow heating rate and fast heating rate, slow heating rates produced the same results as that of fast heating rates, that is the sulfuric acid pre-treatment increased the abundance of furan derivatives and decreased the abundance of phenols. But when treated wood pyrolysis using slow and fast heating rates were compared, the results are as shown in Figure 3.4.
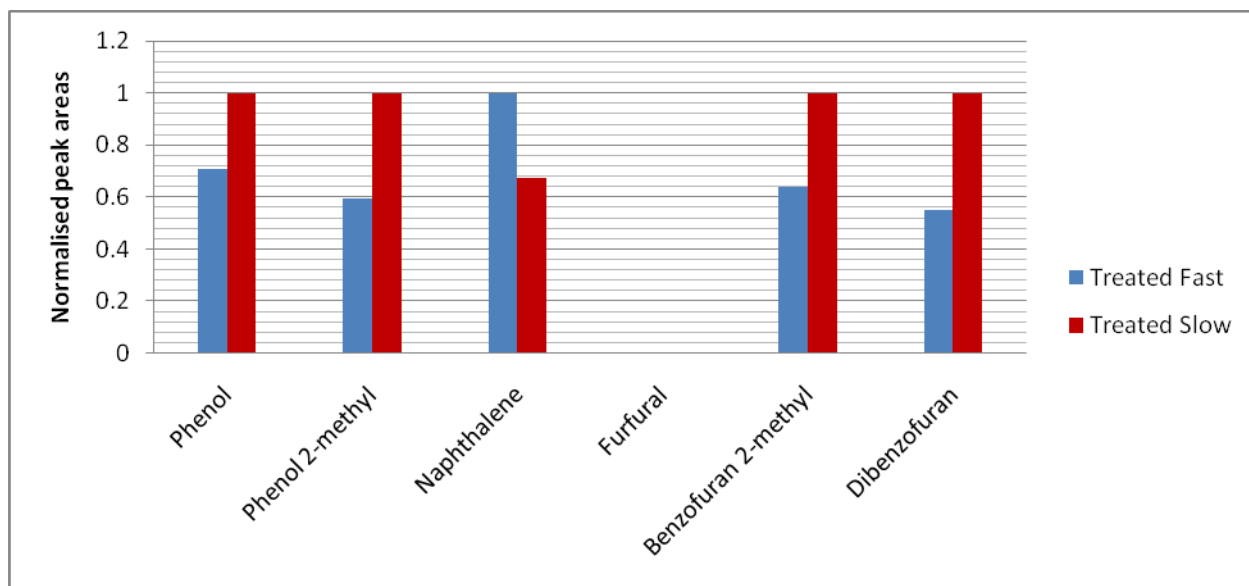
Figure 3.4. Graph showing differences in the peak areas of particular compounds from the experiments *Yellow Pine - Treated- Fast Vs Slow*

The peak areas of particular compounds produced from the pyrolysis of sulfuric acid pre-treated yellow pine wood by using fast and slow heating rates are compared in the form of bar graphs in the above Figure 3.4.

From the above graph, it can be observed that from the pyrolysis of sulfuric acid pre-treated wood the amount of *phenols* obtained by using slow heating rate is *more* when compared to that obtained by using fast heating rate, and the amount of *furan derivatives* obtained by using slow heating rate is *more* when compared to that obtained by using fast heating rate. This implies that the abundance of the volatile products is more by using slow heating rate when compared to that fast heating rate. Since slow heating rate produced more amounts of volatile products, slow heating rate was chosen in specific to carry out the next set of experiments using different concentrations of sulfuric acid pre-treatment for wood pyrolysis.
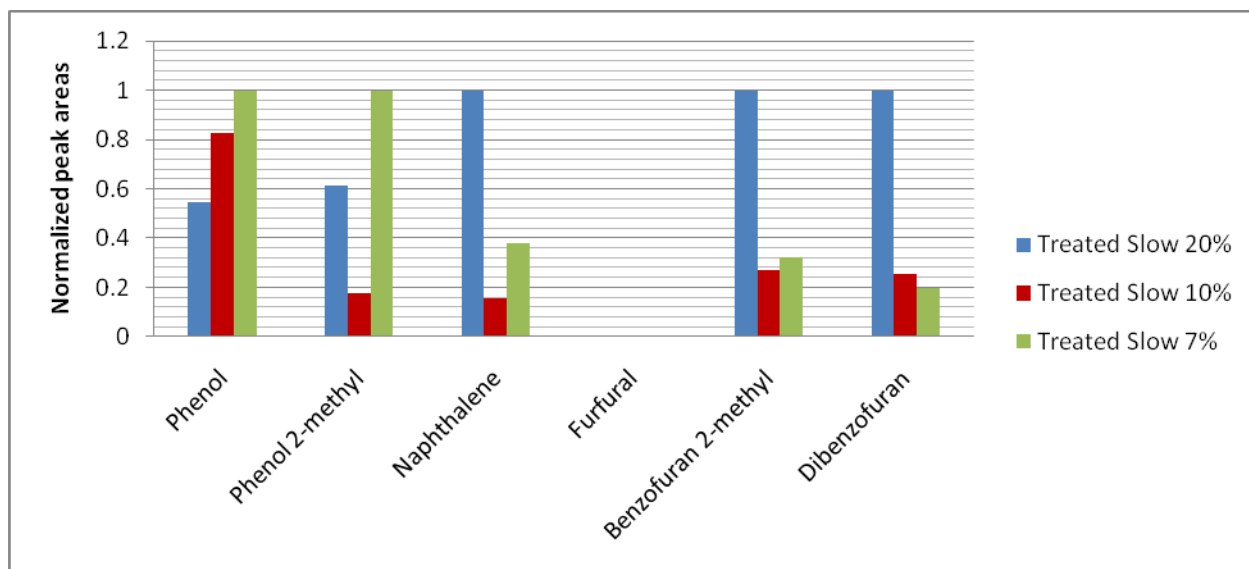
Figure 3.5. Graph showing differences in the peak areas of particular compounds from the experiments *Yellow Pine –Slow- Treated – 20% Vs 10% Vs 7%*

The peak areas of particular compounds produced by using slow heating rate for the pyrolysis of sulfuric acid pre-treated yellow pine wood using different concentrations of sulfuric acid like 20%, 10%, 7% for pre-treatment are compared in the form of bar graphs in the above Figure 3.5.

From the above graph, it can be observed that by using slow heating rate for the pyrolysis of sulfuric acid pre-treated wood the amount of *phenols* obtained is higher when 7% of sulfuric acid is used for the pretreatment, and the amount of *furan derivatives* obtained is higher when 20% of sulfuric acid is used for the pretreatment. The untreated yellow pine wood produced furfural on pyrolysis but when the wood was treated with sulfuric acid, furfural was no longer produced.

This data implied that using higher concentrations of sulfuric acid (20%) produced maximum amounts of furan derivatives, which are of major research interest. These furan derivatives have higher energy density than that of ethanol. Since ethanol is

the major component of the first generation biofuels, many of the researchers are trying to replace ethanol with furan derivatives (higher efficiency than ethanol) in the second generation biofuels.

D. Thermo gravimetric analysis:

The thermo gravimetric analysis of original yellow pine wood and the sulfuric acid pre-treated yellow pine wood was performed using a thermogravimetric analyzer (TGA) which was coupled with a mass spectrometer. The mass spectrometer used in this part of the experimental work was different from the GC-MS which have been used before for the other set of experiments . The thermo gravimetric analysis (TGA) curves and its derivative curves for treated and untreated samples of yellow pine are shown in the Figures 3.6, 3.7, 3.11, 3.12, 3.16, and 3.17. The thermo gravimetric analysis and mass spectrometry coupled data of the treated and untreated samples of yellow pine wood are shown in the Figures 3.8, 3.9, 3.10, 3.13, 3.14, and 3.15. When the derivative of thermo gravimetric analysis curve was coupled with the mass spectrometry peaks obtained, the release of water, methanol and acetic acid during decomposition was identified. Apart from methanol, acetic acid, and water, many other compounds were also seen but it was hard to make conclusions about other compounds as they were seen all over the temperature range. The TGA curves obtained from the thermal analysis of treated and untreated samples of yellow pine wood were overlapped as shown in Figures 3.16 and 3.17 to compare the different temperature ranges of decomposition.
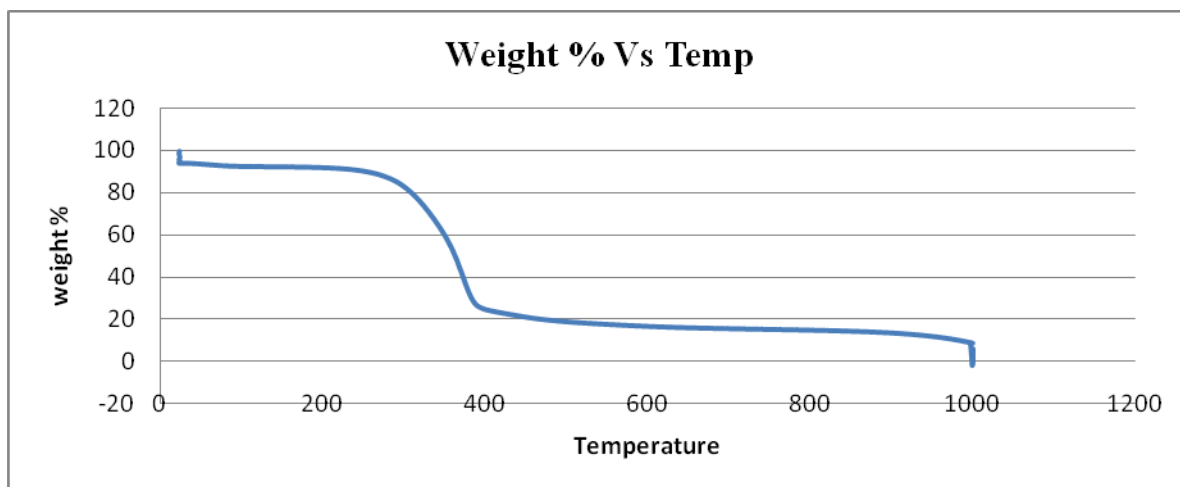
Figure 3.6. TGA of original yellow pine

The thermo gravimetric curve of original yellow pine is shown in the above Figure 3.6.
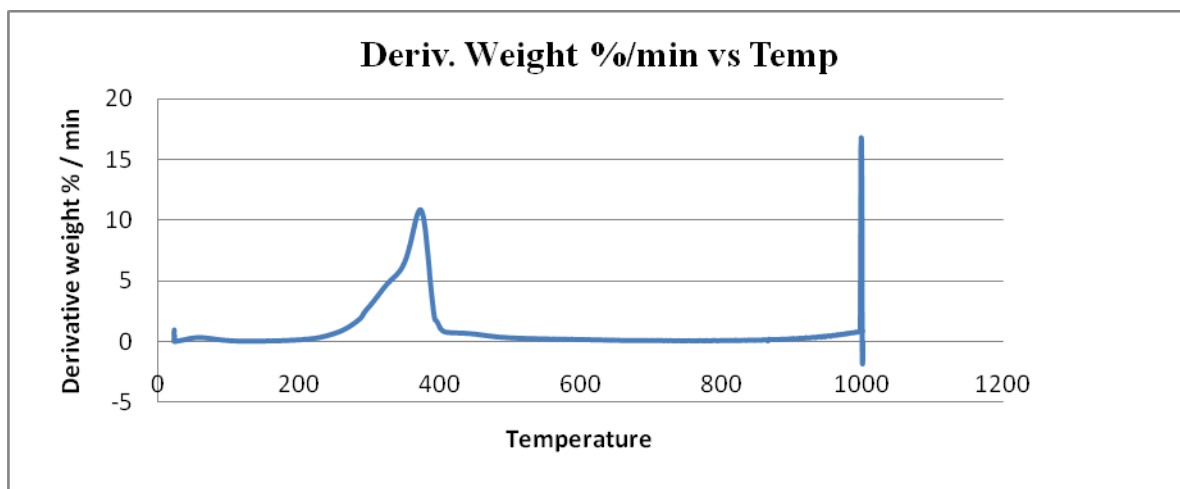

Figure3.7. DTG of yellow pine

The derivative of thermo gravimetric analysis of original yellow pine is shown in the above Figure 3.7.

From the Figures 3.6 and 3.7, it can be observed that yellow pine showed rapid decomposition in a temperature range of 250°C - 400°C. The starting weight loss before

100°C is mainly due to the loss of moisture from the sample. The peak seen at 1000°C in

the DTG of yellow pine is because of the oxidation, which is done at the end of the
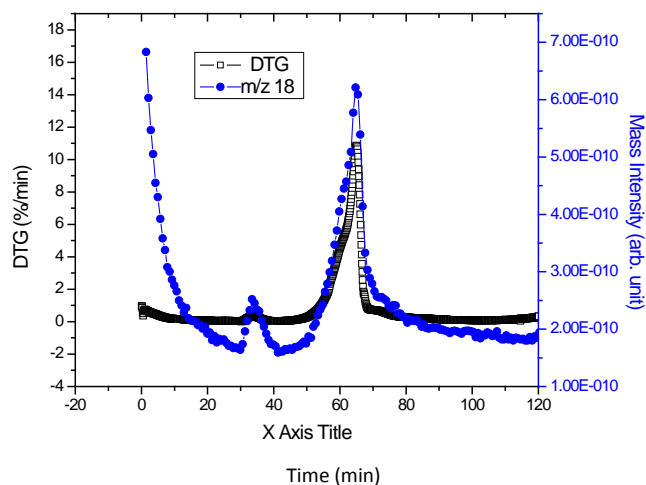
process to clean up the TGA.

Figure 3.8. TGA of yellow pine, indicating the release of water (m/z 18)

The thermo gravimetric curve and the mass spectrometric peak of water (m/z 18)

are shown in the above Figure 3.8, indicating the release of water during the

decomposition of original yellow pine sample, whose TGA is shown in Figure 3.6. For

this graph and all the subsequent graphs, every 10 minute increment indicates 100°C rise

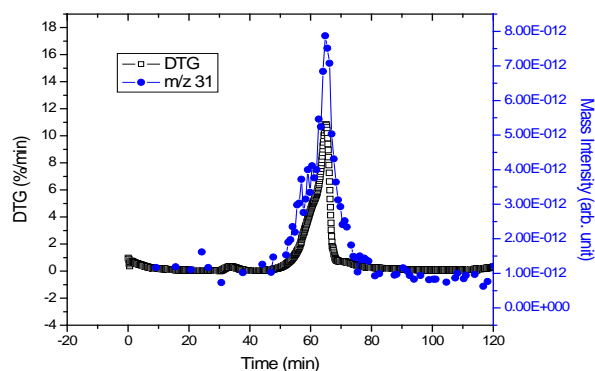in temperature starting from room temperature.

Figure 3.9. TGA of yellow pine, indicating the release of methanol (m/z 31)

The thermo gravimetric curve and the mass spectrometric peak of methanol (m/z 31) are shown in Figure 3.9, indicating the release of methanol during the decomposition of original yellow pine sample, whose TGA is shown in Figure 3.6.
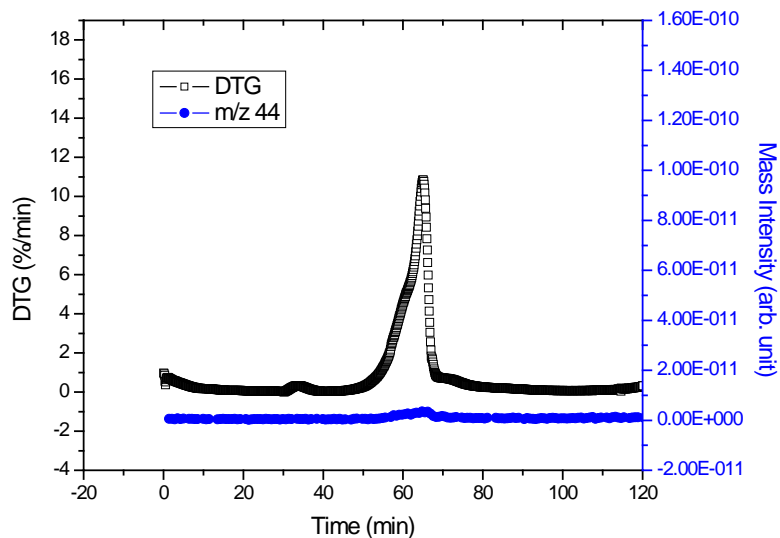

Figure 3.10. TGA of yellow pine, indicating the release of acetic acid (m/z 44)

The thermo gravimetric curve and the mass spectrometric peak of acetic acid (m/z 44) are shown in the above Figure 3.10, indicating the release of acetic acid during the decomposition of original yellow pine sample, whose TGA is shown in Figure 3.6. The peak observed in this Figure 3.10 is very small which can be observed by looking at the base line of the mass spectrum.
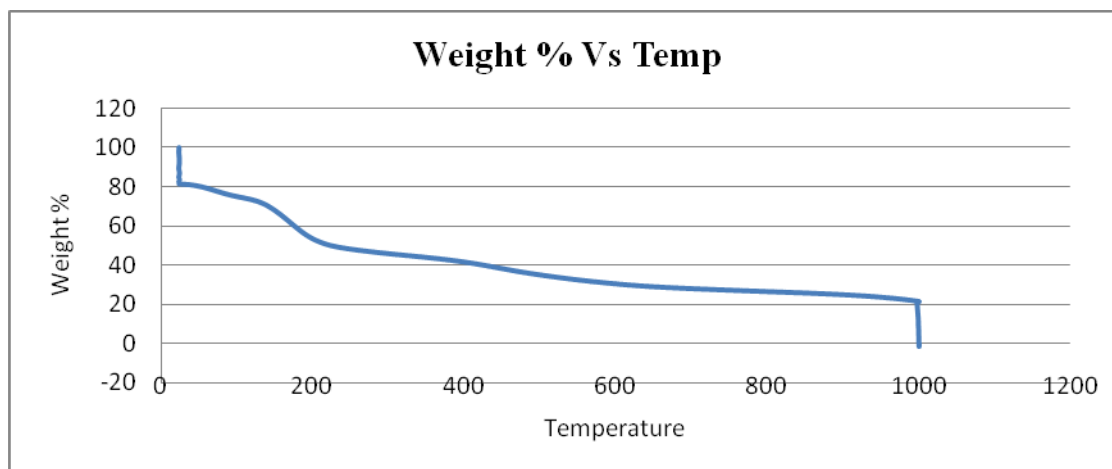
Figure 3.11. TGA of sulfuric acid pre-treated yellow pine wood

The thermo gravimetric analysis of sulfuric acid pre-treated yellow pine is shown in the above Figure 3.11.
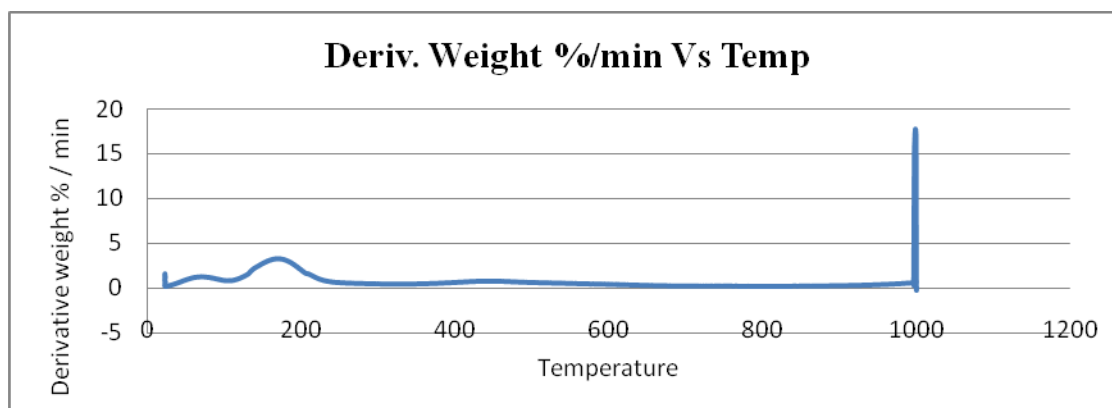

Figure 3.12. DTG of sulfuric acid pre-tretaed yellow pine wood

The derivative of thermo gravimetric analysis of sulfuric acid pre-treated yellow pine is shown in the above Figure 3.12.

From the above figure, it can be observed that sulfuric acid pre-treated yellow pine showed rapid decomposition in a narrow temperature range of 150°C - 250°C. It can also be observed that the temperature range of decomposition has broadened when compared to that of the TGA of original yellow pine. The starting weight loss before 100°C is mainly due to the loss of moisture from the sample. The peak seen at 1000°C in

the DTG of yellow pine is because of the oxidation, which is done at the end of the process to clean up the TGA.
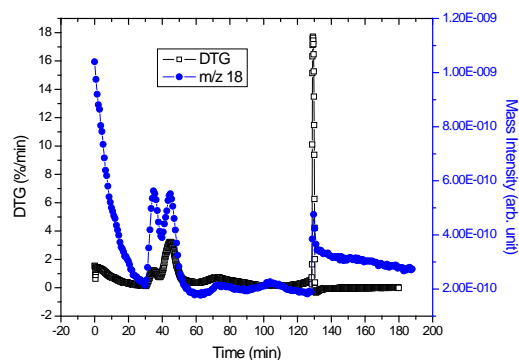

Figure 3.13. TGA of sulfuric acid pre treated yellow pine, indicating the release of water (m/z 18)

The thermo gravimetric curve and the mass spectrometric peak of water (m/z 18) are shown in the above Figure 3.13, indicating the release of water during the decomposition of sulfuric acid pre-treated yellow pine wood sample, whose TGA is shown in Figure 3.11. For the treated wood samples, the release of water was seen at lower temperatures when compared to that of untreated wood samples. This indicates that pre-treatment of wood altered the decomposition pathway during the pyrolysis.
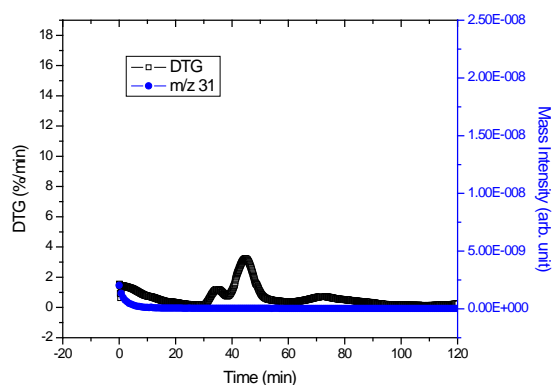

Figure 3.14.TGA of sulfuric acid pre treated yellow pine, indicating that methanol (m/z 31) is not released

In Figure 3.14, by looking at the base line of the mass spectrum, it can be observed that no peak is obtained for the mass to charge ratio (m/z 31).The thermo gravimetric curve and the mass spectrum of methanol (m/z 18) are shown in the above Figure 3.14, indicating that methanol is not released during the decomposition of sulfuric acid pre-treated yellow pine wood sample, whose TGA is shown in Figure 3.11. This implied that methanol was not produced from the treated wood but it was produced from the untreated wood.
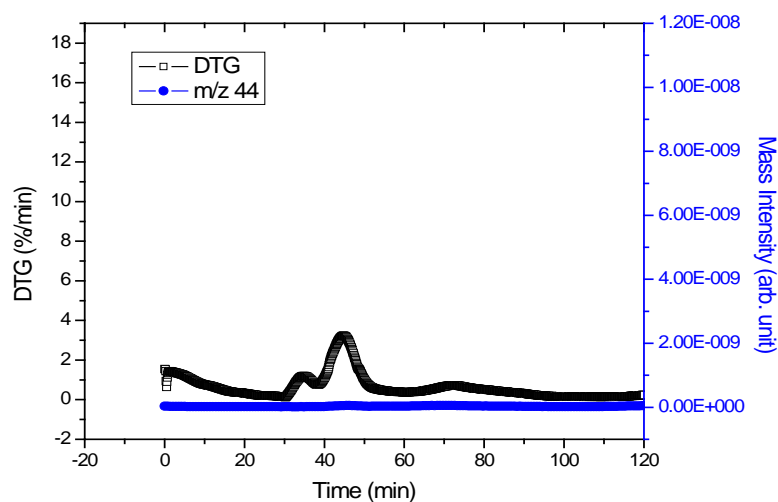

Figure 3.15. TGA of sulfuric acid pre treated yellow pine, indicating release of very small amounts of acetic acid (m/z 44)

In Figure 3.15, by looking at the uneven base line of the mass spectrum just below the peaks shown in derivative of thermogravimetric curve (DTG), it can be observed that a very small peak is obtained, which almost looks like a straight line for the mass to charge ratio (m/z 44). In order to compare all the graphs, same scale was chosen for all the graphs, but when the same data is plotted on a different scale, a good peak was obtained. The thermo gravimetric curve and the mass spectrometric peak of water

(m/z 44) are shown in the above Figure 3.15, indicating release of very small amounts of acetic acid during the decomposition of sulfuric acid pre-treated yellow pine wood sample, whose TGA is shown in Figure 3.11. For the treated wood samples, the release of acetic acid was observed at lower temperatures when compared to that of untreated wood samples.
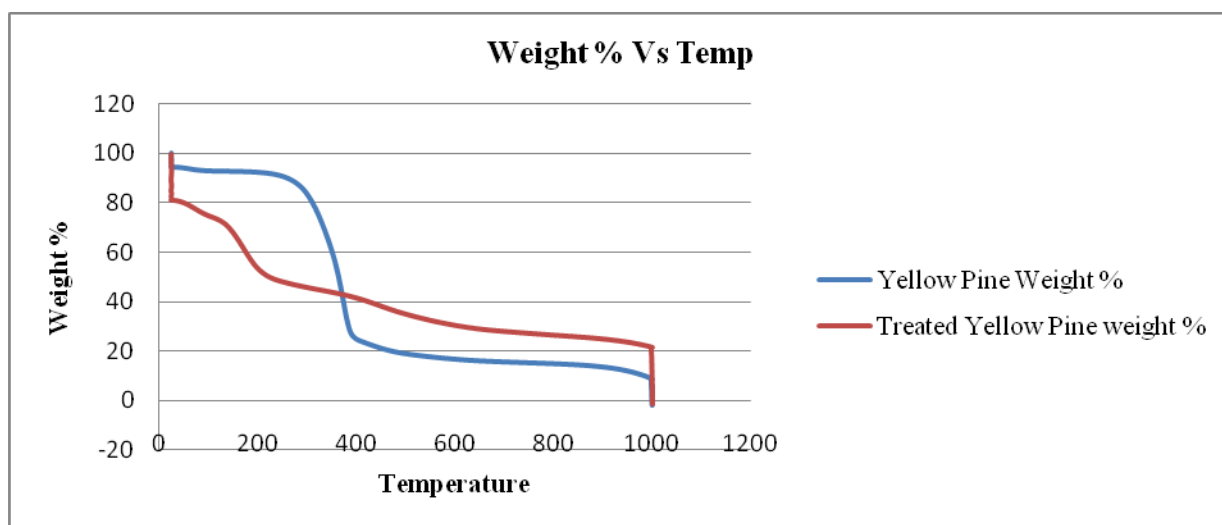

Figure 3.16. Comparison of TGA of original yellow pine and sulfuric acid pre-treated yellow pine
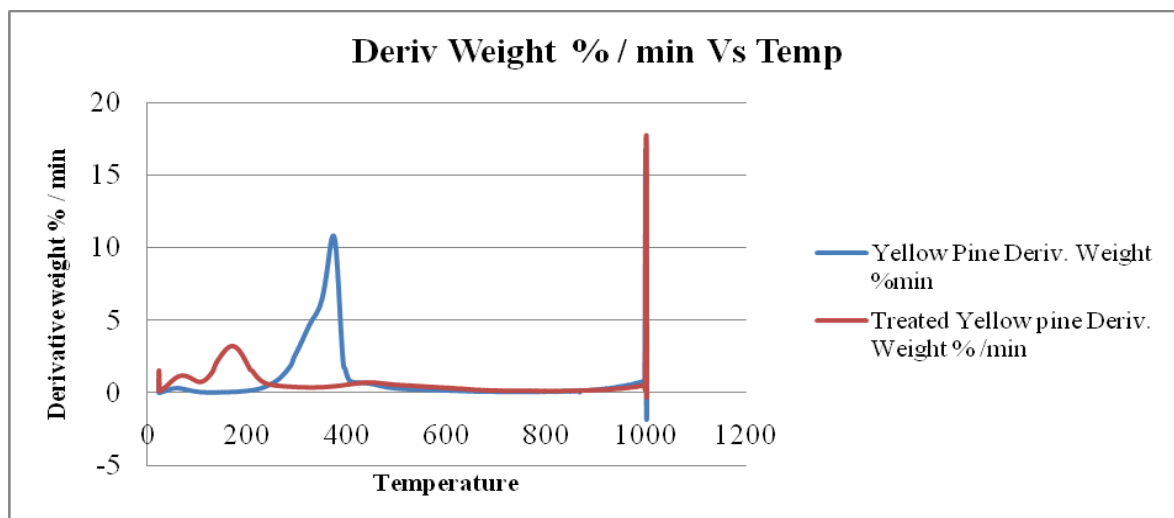

Figure 3.17. Comparison of DTG of original yellow pine and sulfuric acid pre-treated yellow pine

From the above Figures 3.16 and 3.17, it can be observed that sulfuric acid pre-treatment lowered the onset temperature and also broadened the temperature range of decomposition. This implies that when yellow pine is pre-treated with sulfuric acid, the decomposition takes place at much lower temperatures. It can also be observed that the mass yield obtained from treated wood is more than 20% and the mass yield obtained from untreated wood is less than 20%. The peak seen at 1000°C in the DTG of treated and untreated yellow pine is because of the oxidation, which is done at the end of the process to clean up the TGA.

IV. CONCLUSIONS

As stated in the Results and Discussion section, the main objectives of this study were: (i) to evaluate the influence of heating rates on pyrolysis products obtained from wood pyrolysis, and (ii) to evaluate the influence of acid pre-treatment on pyrolysis products obtained from pre-treated wood pyrolysis.

i) Influence of heating rates:

By using the Flash, Fast, and Slow heating rates, most of the volatile products obtained from the pyrolysis of untreated wood were phenols. The volatile products obtained at different temperature ranges like Room temperature-300°C, 300°C - 400°C, and 400°C -500°C in Flash, Fast, and Slow pyrolysis were different. However, the overall volatile products obtained from wood pyrolysis (i.e. the overall list of all the compounds obtained from different temperature ranges in wood pyrolysis by using different heating rates) were the same. It has been deduced that by using slow heating rates, compounds were produced at lower apparent temperatures , when compared to that of flash and fast heating rates.

ii) Influence of sulfuric acid pre-treatment:

a) *Charcoal yield*: It was observed that the shrinkage of the pyrolyzed wood block, which is pre-treated with sulfuric acid is less when compared to that of the untreated pyrolyzed wood block. It was observed that 10 % (compared to that of 7% and

20%) sulfuric acid pretreatment of wood followed by slow pyrolysis produced maximum mass yield of charcoal. This implied that the mass yield of charcoal can be increased by pre-treating the wood block with 10% sulfuric acid before subjecting it to pyrolysis.

b) *Volatile products*: It was observed that by using slow heating rate for the pyrolysis of sulfuric acid pre-treated yellow pine wood, the amount of phenols obtained was lower and the amount of furan derivatives obtained was higher. This increase in production of furan derivatives by using sulfuric acid pre-treatment is a good improvement for the production of Furanics, the furan based biofuels, which are of increasing research interest because of their significant advantages over the first generation biofuels.

c) *Thermo gravimetric analysis*: It was observed that sulfuric acid pre-treatment of yellow pine wood lowered the onset temperature and also broadened the temperature range of decomposition. When the thermo gravimetric analysis and the mass spectrometry results were coupled, it was observed that during the decomposition of untreated yellow pine wood, water, methanol, and acetic acid were released. But during the decomposition of treated yellow pine wood, only water and

acetic acid were released and there was no production of methanol.

V. FUTURE WORK

1. To find out the exact mechanism for the production of furan derivatives from the sulfuric acid pre treated wood pyrolysis.

2. To determine the charcoal yield by using concentrations higher than 10% and less than 20% of sulfuric acid.

3. To do an additional study on charcoal properties like surface area.

4. To try with other types of wood.

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