Bio-oil Production through Fast Pyrolysis and Upgrading to "Green" Transportation Fuels

by

Suchithra Thangalazhy Gopakumar

A dissertation submitted to the Graduate Faculty of
Auburn University
in partial fulfillment of the
requirements for the Degree of
Doctor of Philosophy

Auburn, Alabama
May 7, 2012

Keywords: Fast pyrolysis, bio-oil, catalytic pyrolysis, aromatic hydrocarbons,
hydrogen pressure, algae-bio-oil

Approved by

Sushil Adhikari, Co-chair, Assistant Professor of Biosystems Engineering
Ram B. Gupta, Co-chair, Professor of Chemical Engineering
Christopher B. Roberts, Professor of Chemical Engineering
Susanne Striegler, Associate Professor of Chemistry and Biochemistry

Abstract

Utilization of renewable energy sources is one of the finest resolutions to solve issues related to environment and energy demands. In this regard, biomass is an intriguing candidate to substitute fossil based liquid fuels. Fast pyrolysis of biomass produces bio-oil as major product, which is an intermediate in biofuel production. There are some challenges for the utilization of bio-oil because of its some negative attributes.

The current research is focused on understanding the effect of fast pyrolysis process parameters on the bio-oil quality and upgrading to “drop-in”, non-ethanol, “green” hydrocarbon fuels. A detailed research plan was discussed in Chapter 1 and Chapter 2 reviews fast pyrolysis process, reactors, bio-oil properties and upgrading, and economical analysis of pyrolysis.

In this study, bio-oil was produced in a laboratory scale auger reactor and its physical and chemical properties were investigated in Chapter 3. The bio-oil produced at four different temperatures (425-500^{o}C) met the specifications listed in ASTM D7544-09. Changes in pyrolysis process parameters, such as temperature, heating rate and feedstock were carried out to study their effect on the yield of individual component in the bio-oil (Chapter 4) and a statistical analysis was performed to know significance of the effects. The effect of pyrolysis temperature on each group of compounds also depends on feedstock characteristics.

Catalytic pyrolysis of biomass was carried out in two different methods and the effect of different gases for catalytic pyrolysis was observed (Chapter 5). The catalytic pyrolysis after making a homogeneous mixture of biomass and catalyst (ZSM-5) gave high yield for aromatic hydrocarbons. Catalytic pyrolysis was carried out under different hydrogen pressures in order to investigate the effect of pressure (Chapter 6). The presence of metals on ZSM-5 catalyst provided high yield for aromatic hydrocarbons. Fixed-bed pyrolysis of microalgae, another type of biomass, provided high yield for bio-oil with a high H/C ratio (Chapter 7). Aromatic hydrocarbons were produced from the catalytic pyrolysis of algae over ZSM-5 catalyst.

Catalytic pyrolysis under hydrogen pressure is a promising method to produce biofuel directly from biomass. However, more detailed study is required for further development of this system (Chapter 8).

Acknowledgments

I profoundly thank my major advisors Dr. Sushil Adhikari and Dr. Ram B Gupta for their constant guidance, motivation and cooperation given throughout my dissertation work. Without their encouragement and help, this thesis could have never achieved its current form. I am grateful to Dr. Sushil Adhikari for mentoring me in this project and his personal and moral support at all stages of my work. I would like to express my gratitude to my advisory committee members Dr. Christopher Roberts and Dr. Susanne Striegler for their valuable comments and suggestions. I express special thank to Dr. Oladiran Fasina for letting me use his analytical instruments and for his valuable suggestions. I would like to express my gratitude to Dr. Steven Taylor for his inspiration and comments on my work. I am thankful to Dr. Maobing Tu for serving as university reader for my dissertation.

Special thanks to my friends and colleagues Harideepan Ravindran, Gopal Gautam, Chad Carter, Shyamsundar Ayalur Chattanathan, Nourrrdine Abdoulmoumine, Avanti Kulkarni, and Vaishnavi Srinivasan for their joyful and memorable company and help during my graduate research. I also thank the faculty and staff of Biosystems Engineering and Chemical Engineering departments for their constant inspiration. Ms. Linda Newton, Mr. Russel Davis, Mr. Bobby Epling and Mr. Dawayne Doc Flynn deserve special thanks for helping me in administrative and technical matters. I would like to express my gratitude to all staff in USDA Forest Service and Research Station, Auburn for giving access to their instruments and facilities.

I owe all my success to my husband Nishanth, my parents Gopakumar and Ragini, and my sweet sisters Sumithra and Sunithra who withstood by me all the time. I also express my gratitude to my parents-in-laws Gopalakrishnan and Vijayakumari for their support and encouragement. Thanks to my sweet baby "Arnav" for his patience and cooperation even when I could not spend time with him during the early months of his life. Special thanks to my dear friends in Auburn for their constant encouragement and emotional support. It is really a moment of great pleasure for me while expressing my hearty gratitude to those who have helped me in this successful completion of my dissertation.

I sincerely thank and acknowledge to Alabama Agricultural Experiment Station and Center for Bioenergy and Bioproducts at Auburn University for funding me in this project.

Table of Contents

List of Tables

List of Figures

1. Introduction

Nowadays, the research in different types of alternative energy resources has increased in order to meet the world demand for energy and fuel. Biomass, a renewable energy resource, can provide a variety of carbon based energy forms including liquid fuel. Biomass can be converted to biofuels through thermal and biological methods. The fast pytolysis is one of the thermal methods which provide liquid yield up to 75 wt.%. Eventhough biomass pyrolysis has a history of more than thousand years, it has been only thirty years since this method has been used for liquid fuel production. In fast pyrolysis, biomass is heated at high heating rate in the absence of oxygen and the resulting vapors are condensed rapidly to produce a dark colored liquid called bio-oil. The two co-products from fast pyrolysis are bio-char and gas; both have potential applications in energy production. Bio-oil is a mixture of more than 300 compounds and can be used for a variety of applications such as an energy carrier, as a source for many commodity chemicals, and can be upgraded to transportation fuel. The conversion of biomass to bio-oil can reduce some of the issues related to the biomass logistics. However, bio-oil has some negative attributes which make difficult to use it as it is.

There are different techniques to upgrade bio-oil which include catalytic cracking, hydrotreatment, solvent addition, emulsification, and esterification. Catalytic cracking and hydrodeoxygenation are the two major methods to produce hydrocarbon fuel from bio-oil. The upgrading of bio-oil as diesel and gasoline range compounds can reduce the demand for petroleum reserves for transportation fuels. In catalytic cracking, shape selective catalysts are used to crack bio-oil components to produce hydrocarbons whereas in hydrodeoxygention, hydrogen reacts with bio-oil components under high pressure to produce hydrocarbons and water. In catalytic pyrolysis, the catalyst is introduced during the pyrolysis so that the cracking of bio-oil components would occur simultaneously as they produced. This process can reduce a number of upgrading steps and can provide less oxygenated bio-oil. Therefore, the studies on biomass fast pyrolysis and the bio-oil upgrading to transportation fuels are getting more importance in the area of energy and fuels.

A background literature of biomass fast pyrolysis and upgrading methods to hydrocarbon fuels has given in Chapter 2.

1.1. Research Plan

Biomass fast pyrolysis and bio-oil upgrading, which are in the initial stages of development, have some unique challenges which have to be solved before making it as an industrial process for the technical and economical development of the nation. Technical improvement of fast pyrolysis requires detailed study on each of the process parameters like pyrolysis temperature, heating rate, pressure, feedstock, and pyrolysis environment. The distinctive properties of bio-oil such as acidity, high char content and instability have not made the upgrading process economically yet. Therefore, new catalytic routes have to be investigated for economical upgrading of bio-oil to “green” transport fuels. In addition, catalytic pyrolysis makes an impact for production of “green” transportation fuels by eliminating a series of upgrading techniques. Herein, this research study focuses on a systematic study of fast pyrolysis process and bio-oil upgrading for drop-in fungible transportation fuel. This study will try to find an economical and alternative solution for the production of green transportation fuel from fast pyrolysis process.

This study is divided into five specific objectives and discussed briefly below:

1.1.1. Bio-oil Production and Study of Physicochemical Properties

This study is proposed to explore the effect of temperature on the yield and physical and chemical properties of bio-oil. An auger reactor, which is simple in operation and requires no carrier gas, has been selected for the production of bio-oil. Physical properties of bio-oil such as pH, water content, higher heating value, solid content, and ash will be analyzed and compared with ASTM standard (D 7544 - 09). Chemical composition of bio-oil will be investigated by GC-MS analysis.

1.1.2. Influence of Pyrolysis Operating Conditions on Bio-oil Components

The technical improvement of fast pyrolysis requires an optimization of process parameters, such as feedstock, temperature and heating rate. This study is projected a detailed investigation of change in the yield of individual component of bio-oil for the changes in these pyrolysis parameters. Moreover, this study will explore how significant the effect of pyrolysis temperature, heating rate and biomass on the yield of individual component in bio-oil by performing statistical analysis.

1.1.3. Catalytic Pyrolysis under Different Environments

This study is focused on hydrocarbons production through changing carrier gas, and using zeolite catalysts during pyrolysis. Two different gases (hydrogen and helium) will be used for pyrolysis to understand their influence on the composition of bio-oil. Catalytic pyrolysis of biomass in presence of zeolite (H^+ZSM-5) catalyst will be studied in different methods and in different ratios of biomass to catalyst under different gases, such as hydrogen and helium.

1.1.4. Catalytic Pyrolysis under Hydrogen Pressure

This study is proposed to know the effect of hydrogen pressure on catalytic pyrolysis using acid catalyst (H^+ZSM-5) and acid-metal catalyst (Mo/ZSM-5). It is hypothesized that catalytic pyrolysis in presence of metal impregnated ZSM-5 catalyst under hydrogen pressure would require lower pressure than a typical hydrodeoxygenation process of bio-oil to produce hydrocarbon fuel. Metals such as Ni, Co, Mo, and Pt will be prepared on ZSM-5 support and in-catalytic pyrolysis will be performed at higher hydrogen pressure.

1.1.5. Catalytic Pyrolysis of Algae

In this study, a chlorella species (representing algae residue after trans-esterification) is selected for catalytic and non-catalytic pyrolysis in order to utilize a waste product for value added products. The bio-oil yield and the properties of bio-oil will be investigated in fixed bed reactor. In addition, the catalytic pyrolysis of whole algae biomass will be conducted to find the yield of hydrocarbon from algae residue.

2. Literature Review

2.1. Introduction

National energy security, energy sustainability and climate changes are the primary reasons to find alternative, renewable and reliable resources to fulfill energy demand. Currently, the world energy demand increases at an annual growth rate of 1.6% up to 45% by 2030 [1]. Figure 2.1 depicts the world consumption of marketed energy from different fuel sources [2] and most of our energy demand depends on conventional fossil fuels. However, fossil fuels are non-renewable energy sources, and will be exhausted in near future. In addition, the consumption of fossil fuels produces different pollutants and causes environmental issues. These issues and depletion of fossil fuel resources have led a rapid expansion of renewable resources. At present, there are different renewable resources, namely wind, tide, hydropower and biomass. These renewable resources can satisfy energy demand in power sector, but transportation sector mainly depends on liquid fuels, which cannot be produced from other renewable sources except biomass. The world energy outlook projected to meet 5% of world demand for transportation fuel by biofuels in 2030 [1].

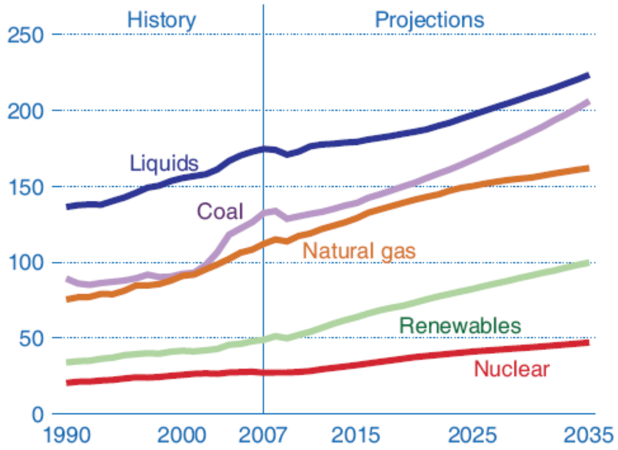


Figure 2.1: World marketed energy use by fuel type, 1990-2035 (quadrillion Btu) [2]

It is projected that the primary energy consumption in the U.S. increases by 0.5% per year from 2008 to 2035, which include 0.6% per year growth in the transportation sector [3]. The U.S is a net importer of liquid fuels and it is projected to reduce the net import share of petroleum from 57% in 2008 to 49%in 2035 [3]. In order to reduce the consumption of petroleum fuels in the U. S., the Energy Independence and Security Act (EISA) 2007 mandated to replace 36 billion gallons of transportation fuel by biofuels by 2022. Among 36 billion gallons of biofuels, 15 billion gallons will come from 1st generation biofuels, primarily corn ethanol and soybean based biodiesel and 16 billion gallons will come from 2nd generation biofuels using lignocellulosic biomass [4]. Other 5 billion gallons will come from either biomass thermochemical or biochemical conversion technologies, which are being developed.

2.2. Biomass and Biofuels

Biomass is widely accepted as a sustainable source for transportation fuel. The term biomass includes plant and animal derived materials, agricultural wastes and biobased segments of industrial and municipal wastes [5]. Carbon dioxide produced during the biofuel production and application is considered to be utilized for the growth of the plant. Therefore, biomass is a carbon neutral renewable source for energy production. Moreover, the greenhouse gas and NO_x and SO_x emissions are negligible compared to fossil fuels. Since biomass is available mostly in rural areas, the concept of biorefinery can bring more opportunities for rural developments.

Major research on biofuel is focused on lignocellulosic biomass, such as woody and herbaceous plants because it is renewable and abundant. Major feedstocks for lignocellulosic biomass are energy crops, agriculture crops, municipal waste, agriculture wastes and forest residues. Currently, corn and sugar cane are the two major agriculture crops used for biofuel production. Agriculture crops are expensive feedstocks because of the requirement for input nutrition and low annual productivity [6]. Energy crops have some advantages as a feedstock for energy production. Advantages are high yield, low requirement of fertilizer, and low water consumption, can grow on low grade soils and different climates. Bermuda grass, miscanthus, sorghum and switchgrass are some energy crops used for energy production. Municipal waste is a low cost feedstock for biofuel production. In 2008, the U. S. generated 250 million tons of municipal solid wastes, of which 50.8% constitute lignocellulosic biomass (paper, yard trimmings and wood) which can be utilized for energy production [7]. Corn stover, wheat straw, baggase, peanut hulls and rice husk are some agriculture residues widely used for biofuel production. Annually 368 million dry tons of woody biomass could be sustainably removed from forestlands in the U. S. [8] and wood residues account for 39% of total biomass available [9].

The structural and chemical composition of biomass is highly variable. Major constituents of biomass are cellulose (35 – 50%), hemicelluloses (20 – 35%) and lignin (15 – 30%) and minor amounts of other compounds such as proteins, minerals (5 – 10%). Cellulose is the most common organic compound on earth and has a generic formula $(C_6H_{10}O_5)_n$ consists of a linear chain of glucose polymer linked by β – 1, 4 glycosidic bonds. Properties of cellulose depend on its degree of polymerization which ranges from 100 to 10,000 in biomass. Cellulose fiber is constituted by microfibrils (which are formed by elemental fibrils) which covered by lignin and hemicellulose [10]. Cellulose has both crystalline and amorphous forms and literature say cellulose has six structural forms (I, II, III_1, $\mathrm{III}_{\mathrm{II}}$, IV_{I}, and $\mathrm{IV}_{\mathrm{II}}$) which are interconvertable [11]. Second major constituent of biomass is hemicelluloses which is a branched polymer of sugar units. Hemicellulose consists of D-xylose, D-mannose, D-galactose, D-glucose, L-arabinose, 4-O-methyl-glucuronic, D-galacturonic and D-glucuronic acids [10]. Unlike cellulose, hemicellulose has a lower degree of polymerization (50 – 300) and mainly consists of five carbon sugars. Lignin, second most abundant organic compound on earth, is a complex polymer of phenyl propane units linked by ether bond. Lignin is not soluble in water and it is optically inactive. Three monomers of lignin are p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. The chemical structures of these constituents are shown in Figure 2.2 [6].

Biomass can be converted to energy via thermochemical and biochemical pathways. In biochemical conversion method, biomass is treated with microorganisms or enzymes to produce biomethanol, bioethanol or biobutanol. Biochemical process requires more time to convert biomass as biofuel than thermochemical methods. Moreover, only holocellulose part of lignocellulosic biomass can be utilized for biochemical methods and it also requires pretreatment of biomass before conversion.

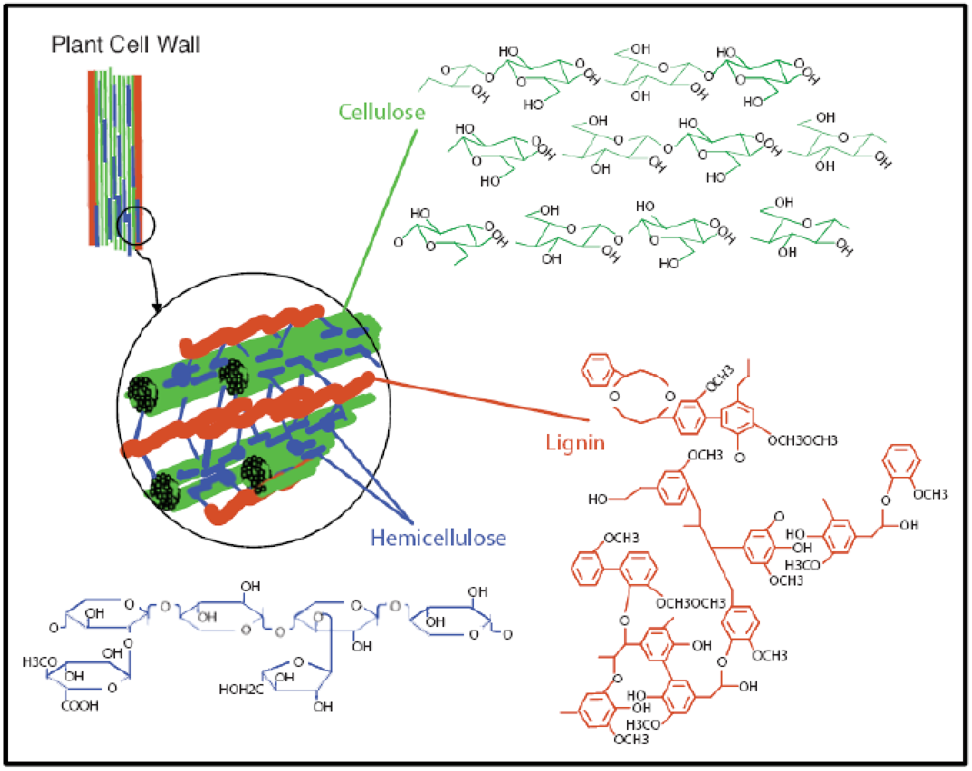


Figure 2.2: Structure of biomass constituents [6]

There are different thermochemical conversion methods to produce biofuel from biomass. Gasification is a well developed method to produce syngas which can be further processed via Fischer-Tropsch method to produce liquid fuels. In addition, syngas from gasification can be utilized for the production of power and electricity. In combustion method, biomass is mainly utilized for the production of heat or power. Another two major conversion methods to produce liquid fuels are hydrothermal liquefaction and pyrolysis. In hydrothermal liquefaction, biomass is treated at moderate temperature and high pressure to produce bio-crude oil which is an intermediate for the production fuels and chemicals [12]. Biochar and noncondensable gases are the major by-products from hydrothermal liquefaction. Pyrolysis of biomass is another method which is described in the following section. A fast pyrolysis of biomass produces bio-oil as major product and char and gas are the minor products. Elliott and

Schiefelbein compared the properties of oil produced by both the hydrothermal liquefaction and fast pyrolysis [13]. The fast pyrolysis process requires lower capital cost than hydrothermal liquefaction process [14]. One of the major advantages of the fast pyrolysis over other thermochemical conversion methods is the flexibility over biomass. The fast pyrolysis technique has been utilized for a wide variety of biomass types including high ash content chicken litter [15], waste biomass like oil cakes [16], agriculture residues [17-18], energy crops [19], forest residues [20] and plastic wastes [21-24]. Bio-oil from plastic wastes contained high amount of aromatics and this is a promising method for handling waste plastics.

2.3. Fast Pyrolysis

The history of pyrolysis started in ancient Egyptian times. However, research on pyrolysis for the production of liquid began in the 1980s [25]. Pyrolysis is a thermal degradation process that occurs in the absence of oxygen. The rate of thermal decomposition depends on biomass particle size and type, as well as, the heating rate, final temperature, reactor configuration and presence of impurities. Major products of pyrolysis are char, liquid, and gas. The relative yield of these products can be changed by selecting appropriate heating rates and pyrolysis temperatures. Pyrolysis is broadly classified as slow pyrolysis and fast pyrolysis. Slow pyrolysis is a conventional method in which biomass is heated slowly to produce char as a major product. In fast pyrolysis, biomass is heated rapidly in the absence of oxygen, and it decomposes as vapors, aerosols, gases and char. The vapors and aerosols are quickly condensed to liquid called bio-oil. The criteria for fast pyrolysis are: (i) moderate temperature (400 – 600^{o}C), (ii) high heating rate and heat transfer rate, and (iii) short residence time (< 2 s) for vapors.

The rate of pyrolysis reaction is limited by the rate of heat transfer and mass transfer. Finely ground and dried biomass is required to attain a high heating rate. In contrast to slow pyrolysis, fast pyrolysis requires careful control over the temperature in order to get maximum liquid yield. Rapid cooling is another requirement for fast pyrolysis to prevent further cracking of vapors as gases. As the residence time decreases, the liquid yield increases, and the yields of gas and char decrease. Since the major product from fast pyrolysis is in liquid form (bio-oil), it can be readily stored and transported. A mobile fast pyrolysis plant near the source of biomass and subsequent transportation of bio-oil to a biorefinery can reduce the cost of biomass harvesting and handling [26].

Pyrolysis is an endothermic reaction. In order to gain the temperature gradient for heat transfer, the reactor temperature should be higher than the temperature of the reaction [27]. In fast pyrolysis, mainly conductive and convective modes of heat transfer occur, and their contribution towards complete heat transfer changes with the reactor configuration. In a fast pyrolysis process, all the steps occur in a small time scale. The major events that occur during the pyrolysis are described below [28-29]:

- heat transfer to increase the temperature of biomass;
- initiation of pyrolysis at higher temperatures which release volatiles and form char;
- heat flow from hot volatiles to cooler, unpyrolyzed biomass;
- condensation of some part of volatiles followed by secondary reactions to produce tar;
- autocatalytic secondary pyrolysis in competition with simultaneous primary pyrolysis; and

- further decomposition, reforming, water-gas shift reaction, radical combination and dehydration can also occur. The degree of these reactions depends on process parameters such as residence time and temperature.

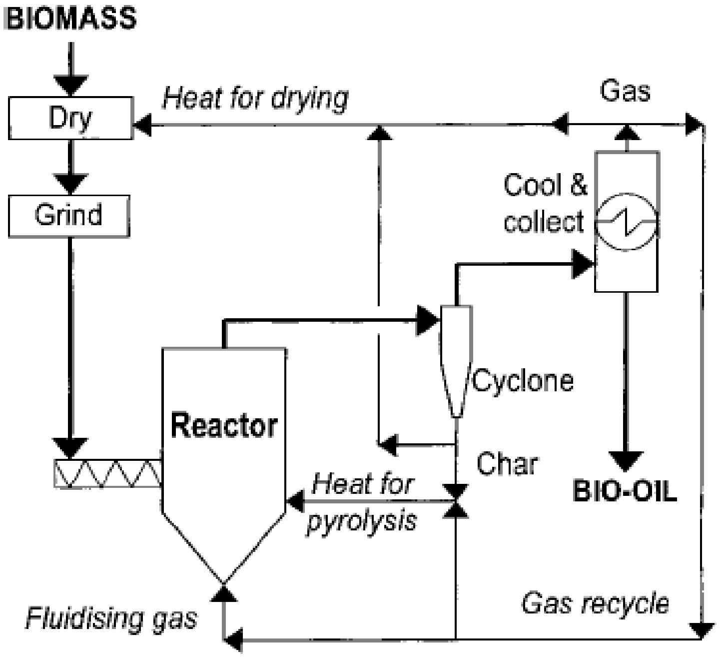


Figure 2.3: A conceptual fast pyrolysis reactor system adapted from Bridgwater and Peacocke [27, 30]

A conceptual fast pyrolysis system where by-products have been utilized is shown in Figure 2.3. Bridgwater and Peacocke have reviewed about the design features of a fast pyrolysis technology [30]. The key features are summarized below:

Biomass Pretreatment-- In order to achieve high heat and mass transfer requirements for fast pyrolysis, biomass pretreatment is required before pyrolysis. The biomass needs to be dried below a moisture content of 10 wt.%, which can be done by utilizing the process heat of the gas produced during pyrolysis. A detailed review of drying technologies for an integrated gasification, bio-energy plant is presented elsewhere with these technologies being applicable to fast pyrolysis also [31]. Most of the reactor configurations for fast pyrolysis require very fine particles of biomass (approximately 2 mm or less) which makes the process expensive. Klass reviewed a variety of size reduction equipment for biomass applications [32]. Mani et al. discussed the energy required for grinding feedstocks of different size and moisture content [33]. For example, the energy required for grinding switchgrass (moisture content 8 wt.%) through a hammer mill (screen opening 1.6 mm) is 58.47 $kWh_e\ t^{-1}$ (210.5 kJ_e/kg), which accounts for 1% of the energy content of the switchgrass.

Fast Pyrolysis – The fast pyrolysis reactor is the heart of the plant, and it requires only 10 – 15% of the capital cost of the plant [34-35]. Different types of reactor configurations for fast pyrolysis are discussed in Section 2.4.

Char and Ash Separation – Ash in the biomass is retained with char, and successful char removal from bio-oil removes ash as well [30]. Char also contains different metals present in the biomass, and it acts as the catalyst for polymerization to increase the viscosity. Char, therefore, has to be removed from bio-oil before storing or further processing. A cyclone separator followed by a pyrolysis reactor is usually employed for char removal, but cyclones are not effective in removing char particles that are smaller than 3 μm. Another unit is required for removing fine particles of char, which are carried over from a cyclone separator. Hot-vapor filters are being developed for the removal of fine char [36]. The char collected can be burned to produce heat necessary for biomass drying.

Condensation and Liquid Collection – Pyrolytic vapors will be cracked continuously as they stay at a high temperature. Therefore, vapors have to be condensed quickly in order to prevent further cracking and loss in organic yield. A few milliseconds of vapor phase residence time is necessary to optimize the yield of some chemicals; whereas a maximum vapor residence time of two seconds can be used for pyrolytic vapors if the bio-oil is being used as a fuel [30, 37]. Collection of liquid is one of the most difficult operations in fast pyrolysis, and it needs careful design and control. Quenching and electrostatic precipitation used for liquid collection have been found to be effective.

2.4. Pyrolysis Reactor Configurations

Some basic, desirable criteria for designing a pyrolysis reactor are a simple design, ease of operation, scale-up potential, high thermal efficiency, and a compact design suitable for rural environments [38]. A wide variety of reactor configurations have been used for fast pyrolysis of biomass. Reactor configurations and the mode of heat transfer significantly influence the distribution of compounds in bio-oil. Major reactor configurations are bubbling and circulating fluidized bed, ablative, vacuum, rotating cone and auger [28]. All of these reactors have some advantages and some drawbacks, with the latter acting as barriers for their commercial application to fast pyrolysis [38].

2.4.1. Bubbling-Fluidized Bed

A bubbling-fluidized bed reactor (Figure 2.4 (a)) is a very popular configuration for fast pyrolysis, as it features good temperature control, an efficient heat transfer rate, and short residence time [34]. This reactor configuration is simple in construction and operation and can, therefore, be scaled-up for large scale pyrolysis. In addition, bubbling-fluidized bed pyrolysis yields bio-oil up to 80 wt.% of dry biomass [30]. This configuration requires a carrier gas to fluidize the bed. Biomass needs more residence time to complete conversion where vapors require lees residence time. The residence time of solids and vapors can be efficiently controlled by using a shallow bed and or by changing the flow rate of carrier gas in the bubbling-fluidized reactor. Major heat transfer limitations are within the biomass particle, therefore small particle size of biomass give high yield conversion [30]. Effective separation of char is required in order to prevent its catalytic effect for bio-oil polymerization. High quality bio-oil can be produced from this reactor.

2.4.2. Circulating-Fluidized Bed

Circulating-fluidized bed reactor (Figure 2.4 (b)) has many features similar to a bubbling-fluidized bed reactor where the bed material from product vapors and gases are circulated back to the reactor by passing through a cyclone separator and a combustion chamber (to remove char from the bed material). If a catalyst is used in the fluidizing bed, the coke and char formed during pyrolysis can be burned out during recirculation [39]. In addition, the product gas can be circulated back to the bed as a carrier gas. Therefore, presence of carbon monoxide and hydrogen gases (reducing gases) in the product (when used as carrier gas) can reduce the oxygen content of vapors during pyrolysis. Here, the residence time of vapors and char is almost same. This configuration is suitable for higher throughputs. Circulating fluidized bed reactor is as not efficient as bubbling fluidized bed reactor for temperature control and heat transfer. Post-treatment of bio-oil is required for removing char because of high char attrition and carryover with the vapors [38]. Accumulation of ash content in the circulating-bed acts as a catalyst for cracking bio-oil components, which creates a loss of volatiles and improves some of the bio-oil properties.

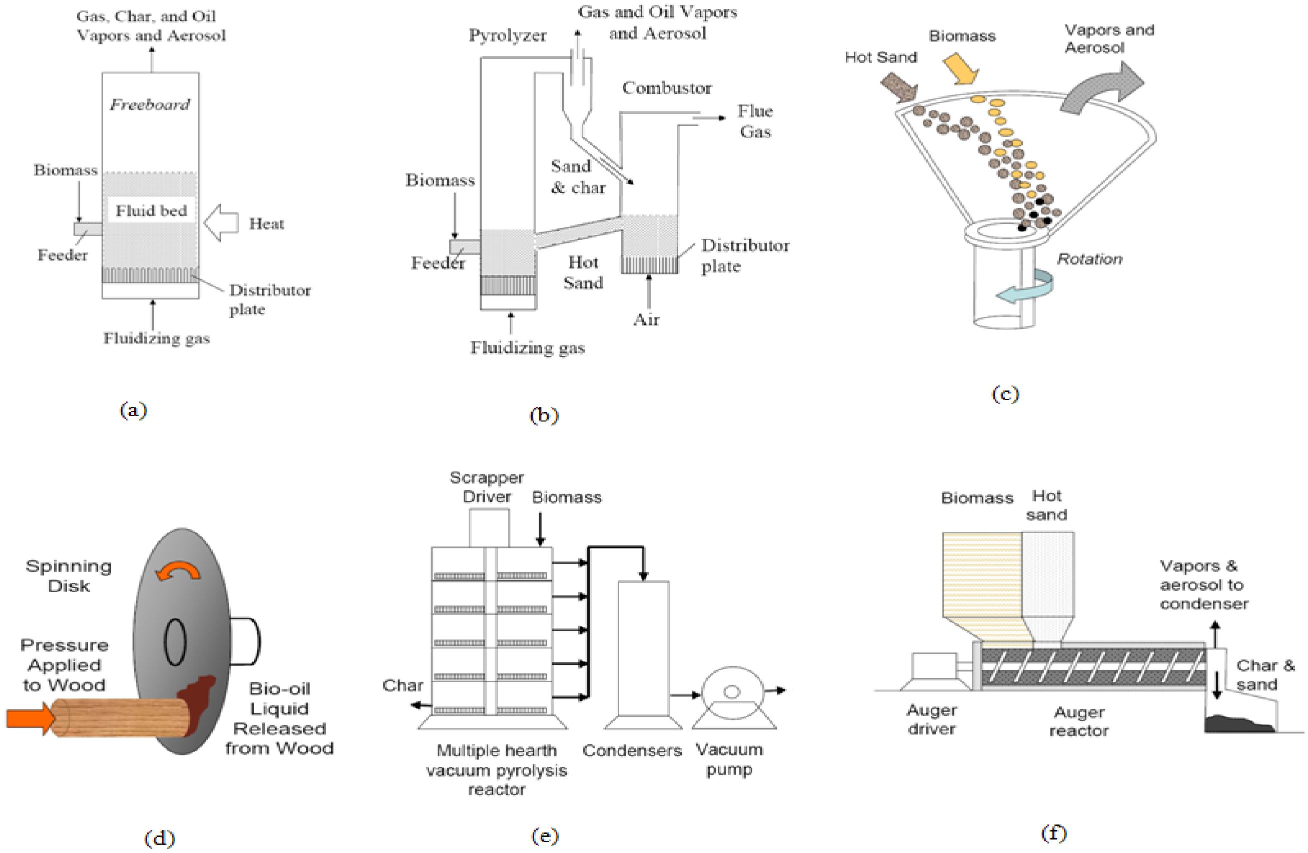


Figure 2.4: Major reactor configurations for biomass pyrolysis (a) bubbling fluidized bed, (b) Circulating fluidized bed (c) Rotating cone (d) Ablative pyrolysis (e) Vacuum pyrolysis (f) Auger reactor [43]

2.4.3. Rotating Cone Pyrolyzer

Twinte University invented a new reactor design for fast pyrolysis called a rotating cone pyrolyzer (Figure 2.4 (c)) which was further developed by the Biomass Technology Group (BTG) in the Netherlands. Rotating cone pyrolyzer (Figure) is similar to circulating fluidized bed reactor in process where sand and biomass are transported by centrifugal forces. Sand is added to avoid fouling the cone wall and to enhance heat transfer. Biomass and sand are fed to the bottom of a rotating cone, and the biomass is pyrolyzed while transporting upward through a spiral motion along the hot side wall of the cone. Very small particle size is required for this configuration. These reactors are very compact in design and can be used for high throughput. BTG and its daughter company, BTG BioLiquids (Trade name BTG-BTL), have optimized the design and developed a 200 kg/h rotating cone pilot plant [40-41]. Lede et al., described about a cyclone reactor for fast pyrolysis which is similar to rotating cone pyrolyzer, however, not mentioned about the sand bed [42].

2.4.4. Ablative Pyrolysis

When large particles of wood are mechanically pressed against a rapidly moving hot surface, they melt, evaporate or sublimate to produce vapors which are condensed as bio-oil. The residual oil on the hot surface provides lubrication and helps to enhance the evaporation of the successive biomass particles. The rate of reaction is influenced by the applied pressure and the relative velocity between biomass and the hot surface. Since the rate of reaction is not limited by the rate of heat transfer, an ablative reactor can utilize large wood pieces for pyrolysis. However, a high heat loss occurs since the hot surface stays at a higher temperature than the reaction temperature [38]. The reactor (Figure 2.4 (d)) has hot moving parts, which make the operation mechanically complex. A compact and complex design is also required for this reactor. In addition, this process is controlled by surface area [29]. Therefore, the scaling up of an ablative reactor could be very costly.

2.4.5. Vacuum Pyrolysis

Short residence time for vapors can be easily achieved by applying vacuum in the reactor (Figure 2.4 (e)). Here, secondary reactions are normally avoided by the rapid withdrawal of pyrolytic vapors from the pyrolysis zone. In this configuration, biomass is fed to the top of the reactor, which contains stacked hot circular plates. Biomass will be pyrolyzed when it contacts with hot plates while dropping from the top to bottom plate. The process occurs normally at a pressure of 15kPa [29]. Since the pyrolysis occurs in vacuum, the convective heat transfer is minimum in this reactor configuration. Although vapors have a very small residence time, the long residence time of biomass can be independently achieved. However, the reactor has poor heat and mass transfer rates, and it occupies a large amount of space [38]. In addition, the process is very expensive because of the need for a vacuum. Liquid yield will be typically lower than for previous configurations discussed.

2.4.6. Auger Reactor

An auger reactor (Figure 2.4 (f)) is simple in operation and can be used for continuous processing. It does not require a carrier gas, and the mode of heat transfer is mainly due to conduction. Biomass particles are moved by an auger inside an externally heated, cylinder tube. In some designs, hot sand is used as a medium for heat transfer. Residence time of vapors can be controlled by the auger speed and the heated zone in the tube. The energy cost for the operation is very low compared to other designs [44]. Studies have reported the production of bio-oil using laboratory scale auger reactors [20, 45]. The major weakness of this configuration is the mechanical wear due to moving parts.

Another configuration, entrained flow reactors have been tested for fast pyrolysis. Since it is difficult to attain the high heat transfer rate from hot carrier gas to biomass, this configurations has not been developed further [25]. Some studies have reported about fast pyrolysis in fixed bed reactors [16, 46]. Fixed bed reactors operate normally in batch mode and a sweep gas is applied for the removal of gas and vapors from the reactor [47]. The major drawback of this configuration is the high residence time of vapors and therefore high char yield. Free fall reactors comprise another class of reactors; they are simple in design and easy to operate. Moving parts and carrier gas are not required in this design [48].

Ensyn, DynaMotive, BTG-BTL, KiOR, and Renewable Oil International are the major companies involved in bio-oil production through fast pyrolysis [25]. Ensyn Technologies Inc.'s fast pyrolysis process is patented as Rapid Thermal Processing (RTP). The reactor configuration for this technique is analogous to that of the circulating-fluidized bed reactor. Their first commercial plant was built in 1984 and seven plants have been operated since then [25, 49]. UOP, a Honeywell company, was awarded $25 million in 2010 by the U.S. Department of Energy (DOE) to build a demonstration unit in Hawaii to convert cellulosic biomass into green transportation fuels using fast pyrolysis technology. The plant will employ Ensyn's RTP process to produce bio-oil from biomass, and the plant is expected to be running in 2014 at the Tesoro Corp. refinery in Kapolei, Hawaii [50]. Ensyn Technologies Inc. and Tolko Industries Ltd. also announced in June 2010 that they have formed a partnership to build the world's largest, commercial, fast pyrolysis plant in High Level, Alberta, Canada. The plant will process 400 dry tons of biomass per day and will produce about 22.5 million gallons of bio-oil per year [51]. In 2008, Ensyn and UOP (a Honeywell company) joined to create Envergent Technologies LLC in order to upgrade the Ensyn RTP liquid to "drop-in" transportation fuels [52]. Dynamotive Technologies Corporation, another major company which conducts fast pyrolysis of biomass, was incorporated in 1991 [53]. Dynamotive's Fast Pyrolysis process was developed by Dr. Desmond Radlein at Resource Transfroms International (RTI) of Waterloo, Ontario Canada which is based on fluidized bed pyrolysis. First commercial pilot plant (10 Tonne Per Day) for

Dynamotive was constructed at the BC Research Facility in Vancouver, Canada which was later upgraded to 15TPD and commissioned in 2001. In 2005, the first commercial plant (100TPD) was launched in West Lorne, Ontario with Erie Flooring Inc. and the Orenda Division of Magellan Aerospace. Another 200 TPD plant at Guelph, Ontario was completed in 2007. Dynamotive in agreement with FP Energies nouvelles (public-sector for research and innovation in the field of energy, transportation and environment) and Axens (an international provider of advanced technologies, catalysts) developing the process of scale-up and commercialization of the Dynamotive's pyrolysis oil upgrading to produce second generation biofuels [53]. BTG-BTL, another major company for fast pyrolysis of biomass utilizes the rotating cone reactor for bio-oil production. In 2005 they started the demonstration plant in Malaysia for processing 2 t/hr of Empty Fruit Bunch (EFB). Currently, they are a designing 5 t/hr plant. The bio-oil from BTG-BTL is currently utilizing for boiler applications [41]. Pytec's (another industry for fast pyrolysis) BTO (biomass to oil) process utilizes ablative pyrolysis to produce bio-oil from wood. Pytec was founded in 2002 and the first pilot plant was built in 2005 to produce 4 tons of bio-oil per day. Bio-oil will be utilized in CHP (combined heat and power) plant [54]. Another industry, Pyrovac in Province of Québec, Canada had utilized vacuum pyrolysis for the conversion of biomass to bio-oil. Pyrovac's demonstration plant had a capacity of 3.5t/hour [55]. Renewable Oil International (ROI) developed auger reactor for bio-oil production. ROI has designed and constructed a pilot plant of capacity 5 dry ton per day in Russellville, Alabama to convert poultry litter as bio-oil [56].

KiOR, another fast pyrolysis company, has demonstrated a catalytic pyrolysis plant, which is located just outside of Houston, Texas. The company has produced up to 15 barrels of bio-oil (named as renewable crude) per day from wood chips [57]. KiOR has a plan to build several plants in Mississippi and has already secured a loan from the Mississippi State Governor's Office. A spin-off company associated with the University of Massachusetts is named Anellotech. The goal of this company is to produce aromatic hydrocarbons from biomass using fast pyrolysis. The company has projected to produce about 50 gallons of chemicals per metric ton of biomass (wood), with a yield of 40 percent [58].

2.5. Pyrolysis Mechanism and Pathways

When biomass is heated, its constituents thermally degrade and vaporize. The thermal decomposition rates of biomass constituents differ. All three components (cellulose, hemicellulose and lignin) of biomass are chemically stable until 150^{o}C. Numerous studies have been published on cellulose pyrolysis, and a number of reaction pathways and kinetic models have been proposed for cellulose decomposition [59-66]. One of the earlier works by Kilzer and Broido proposed a pathway for pyrolysis of cellulose which includes three distinct processes – dehydration, depolymerization and decomposition [59]. Another major study on the cellulose pyrolysis mechanism has shown the formation of 'active cellulose', which is further decomposed to volatiles, char, and gas [65]. The proposed Broido-Shafizadeh model was accepted for many years but has been subjected to further evaluation [67]. As the temperature and heating rate increased (fast pyrolysis), the complexity of pyrolysis increased and a variety of products were created [61-62, 68].One vital mechanism of fast pyrolysis of cellulose, proposed by Piskorz et al., is known as Waterloo model (Figure 2.5) [62]. The Waterloo model suggested two parallel pathways leading to a variety of products from fast pyrolysis of cellulose. A major intermediate product in cellulose pyrolysis is levoglucosan. However, these pyrolysis mechanisms will change with the change in heating rate, temperature and presence of impurities. A later study on mechanisms of cellulose pyrolysis suggested that the anhydro monosaccharide can be repolymerized to anhydro oligomers or undergo further reactions like fragmentation or retroaldol condensation, dehydration, decarbonylation, or decarboxylation to transform other volatile compounds. They proposed that the majority of char is formed not by the parallel pathway from ‘active cellulose’ but due to the repolymerization of volatile anhydro sugars and fragmented species [69]. Another study involving the Broido-Shafizadeh model showed that the char formation is exothermic, while its competing reaction (formation of anhydro sugars) is endothermic. Since char formation has lower activation energy than the anhydro sugars formation, char yield decreases with the increase in temperature [70].

Hemicellulose degrades at a lower temperature (150 – 300^{o}C) than cellulose. The degradation behavior of hemicellulose has been less studied because of the lower abundance and variety in structures [71-74]. Most of the thermal behavior studies of hemicellulose are limited to xylan (major component in plant hemicellulose). Unlike the levoglucosan intermediate in cellulose pyrolysis, xylan produces furan derivatives as intermediate compounds before complete decomposition [75]. Antal Jr. *et al.* proposed a mechanism for the degradation of xylan to furfural [76]. Lignin is, thermally, the most stable component in biomass and is hydrophobic and aromatic in nature. There are three major monomers for lignin: p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. The two major techniques which can utilize lignin for biofuel production are gasification and high temperature fast pyrolysis. Even though there are some studies reported for lignin pyrolysis [64, 77-81], a well-defined reaction pathway for lignin has not been developed.

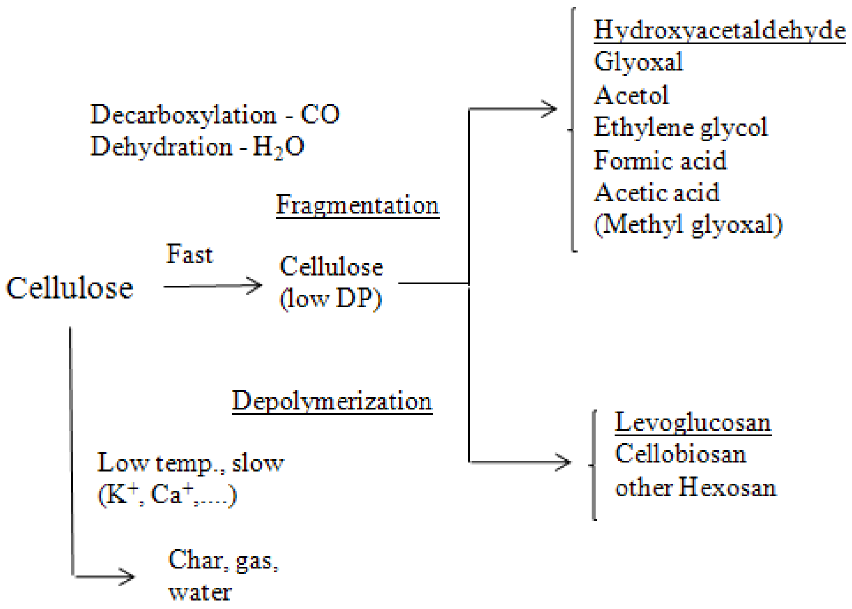
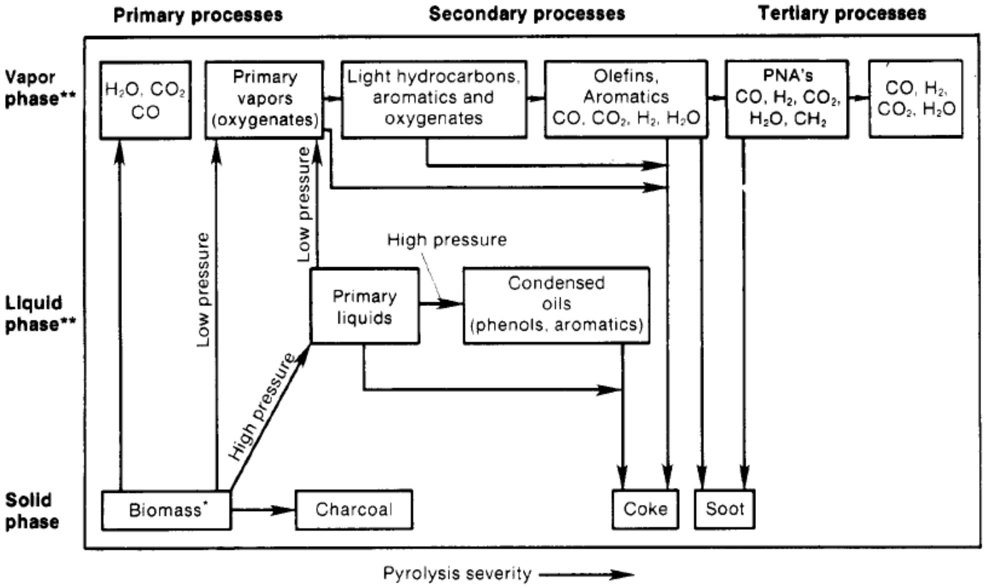


Figure 2.5: Waterloo model for cellulose pyrolysis [62]



*This box is meant to include solid biomass, but also its plastic or rubbery forms prior to major rupture of covalent bonds to produce low molecular weight vapors or liquids.

**Only first-formed products are shown. All of these products could be condensed to liquids and solids.

Figure 2.6: Pyrolysis reaction pathway for whole biomass [75]

When holocellulose and lignin combine to form whole biomass, their pyrolytic behavior is influenced by other components. Therefore, it is difficult to propose a single reaction pathway for different types of lignocellulosic biomass. However, Evans and Milne have proposed a reaction pathway for the thermal degradation of whole biomass (Figure 2.6) [75]. A detailed description of pyrolysis reaction mechanisms of biomass and its components can be found elsewhere [82].

2.6. Bio-oil Properties

Bio-oil is a dark brown liquid having a distinct odor. It has a higher heating value of around 17 MJ/kg and a water content of 25 wt. %. Compared to traditional biomass fuels such as black liquor or hog fuel, bio-oil has a higher energy density which presents a much better opportunity for high-efficiency energy production. Typical properties of bio-oil in comparison with other conventional fuels are listed in Table 2.1 [83]. Bio-oil is a complex mixture of more than 300 compounds containing alcohols, acids, aldehydes, ketones, esters, sugars, furans, phenols, guaiacols and other aromatics [84-85]. This complex nature of bio-oil provides potential and challenges for its applications. Since bio-oil is formed by rapid heating and cooling, the compounds in bio-oil are not in thermal equilibrium. Properties of bio-oil depend on the type of biomass and pyrolysis operating parameters such as temperature, heating rate, and residence time.

Recently ASTM standard (ASTM D 7544 – 09) has been published for the commercial purpose of bio-oil [86]. The required physical properties of bio-oil, according to this ASTM standard, are listed in Table 2.2. Some ions such as potassium, calcium which are inherently contained in biomass act as catalyst for the depolymerization reactions occur during pyrolysis

[29]. The presence of these ions will affect the bio-oil properties. A detailed discussion of the physical properties of bio-oil and measuring methods were described elsewhere [37].

Table 2.1: Comparison of bio-oil and conventional fuel oil characteristics adapted from [83]

Properties		Bio-oil	Diesel	Heavy fuel oil
Density	kg/m^3 at 15°C	1220	854	963
Typical composition	% C	48.5	86.3	86.1
	% H	6.4	12.8	11.8
	% O	42.5	-	-
	% S	-	0.9	2.1
Viscosity	cSt at 50°C	13	2.5	351
Flash point	°C	66	70	100
Pour point	°C	27	20	21
Ash	% wt	0.13	0.01	0.03
Sulfur	% wt	0	0.15	2.5
Water	% wt	20.5	0.1	0.1
LHV	MJ/kg	17.5	42.9	40.7
Acidity	pH	3	-	-

2.6.1. Density

Density of bio-oil is around 1100 – 1300 kg/m^3. This is because of the presence of some high molecular weight compounds such as guaiacols, syringols and sugar compounds.

2.6.2. pH

Pyrolysis of holocellulose gives some acids such as formic acid, acetic acid which lower the bio-oil pH. Usually pH of bio-oil varies from 2 to 3. Therefore storage vessels of bio-oil have to be made up of acid proof materials. In some cases, acidity has to be retained in order to prevent polymerization of polyphenols [30].

Table 2.2: ASTM standard for bio-oil [86]

Properties	Specifications
Gross Heat of Combustion (MJ/kg)	15 min.
Water content (mass %)	30 max.
Solid content (mass %)	2.5 max.
Kinematic viscosity at 40^oC (mm2/s)	125 max.
Density at 20^oC (kg/dm^3)	1.1 - 1.3
Sulfur content (mass %)	0.05 max.
Ash content (mass %)	0.25 max.
pH	Report
Flash point (^oC)	45 min.
Pour point (^oC)	-9 max.

2.6.3. Water Content

Water is the most abundant compound in bio-oil and normally varies from 15 – 30 wt. %. Water in bio-oil is either from the moisture content of biomass or from the dehydration of compounds during the pyrolysis [87]. In addition, the water content in bio-oil depends on process parameters and extends of secondary cracking of pyrolytic vapor [30]. ASTM recommended the water content of bio-oil below 30 wt. % for the use in industrial burners or for the guidance of consumers [86]. Water in bio-oil gives both positive and negative effects for its applications. Most of the compounds are soluble in water and therefore it serves as a good solvent to reduce the viscosity and enhances the transportation of bio-oil if the water content is in the range of 15 – 25 wt. % [38]. Simultaneously, the presence of water reduces the heating value of bio-oil and thus negatively affects its fuel properties [88].

2.6.4. Oxygen Content

Oxygen content of biomass is normally 35 – 40 wt. %. More than 200 oxygenated compounds are present in bio-oil. Since of these compounds are not in thermal equilibrium, some polymerization reactions occur if bio-oil is at higher temperature. Therefore complete evaporation is not possible for bio-oil. Due to high oxygen content, bio-oil is not miscible with petroleum products.

2.6.5. Higher Heating Value (HHV)

Higher heating value is an important parameter for bio-oil if the application of bio-oil is in energy production. The HHV of bio-oil is normally about 17 MJ/kg which is half the HHV of other conventional fuels used for stationary applications. However the energy density of bio-oil is six times higher than that of biomass, therefore bio-oil can be transported effectively. The energy content in bio-oil is about 40 % by weight and 60 % by volume of the energy content of fossil fuels.

2.6.6. Viscosity

Viscosity is an important parameter for the design and selection of handling, processing and transportation equipment for liquid fuels. Bio-oil viscosity varies in a wide range with the properties such as water content, oxygen content and the storage conditions. Therefore, in ambient conditions or at higher temperature, these compounds reacts each other to make stable compounds which increase the viscosity of bio-oil. Viscosity is an indicator for the stability and age of bio-oil. Additives like ethyl acetate, methyl isobutyl ketone and methanol, acetone, methanol, acetone and methanol, and ethanol will reduce the initial viscosity of bio-oil and aging rate [89].

2.6.7. Solid Content

Bio-oil contains uniformly suspended char which are escaped from cyclones and other filters. Increase in solid content increases the ash content of bio-oil and act as catalyst for the reactions between the unstablilzed compounds which affect the viscosity and stability of bio-oil. In addition, the presence of chars in bio-oil interfere its final applications such as injection through the nozzles, atomization. Two types of filtration methods are employed to remove solids – hot vapor filtration and liquid filtration. However complete removal of solid is hard to achieve.

2.6.8. Flash Point and Pour Point

Since bio-oil has a wide variety of compounds, the flash point varies from 40 to 100^{o}C. The flash point is the maximum temperature at which the oil can be handled without serious fire hazards. This property does not have any information about the performance of oil in engines. Pour point of bio-oil is prescribed along with the conditions of storage. Pour point of bio-oil varies from -12 to -36^{o}C depend on the biomass [37]. Low viscosity of bio-oil is an indication of low pour point. Therefore minor equipment modifications are needed for the direct applications of bio-oil in engines, turbines and boilers.

2.7. Bio-oil Applications

Bio-oil is a potential source for fuel and energy applications. In addition, many commodity chemicals can be extracted or produced from bio-oil. From the literature, final applications of bio-oil are summarized in Figure 2.7 [27, 30]. Piskorz and Radlein conducted a biodegradability study of bio-oil by means of respirometry. The study showed that bio-oils degraded aerobically at a higher rate than hydrocarbon fuels, and this biodegradability rate was enhanced when bio-oil was neutralized for pH [90].

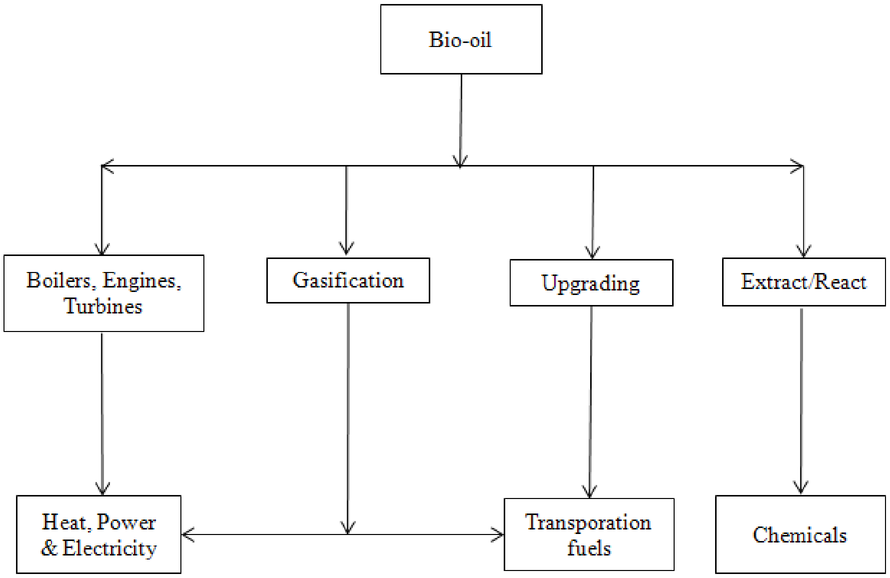


Figure 2.7: Applications of bio-oil

2.7.1. Combustion

Even though bio-oil has a high water content and low heating value, the combustion property of bio-oil has been tested for heat and power generations in engines, turbines, furnaces and boilers. One advantage of bio-oil is the easiness of handling liquid fuels, as opposed to solid or gas fuels, for combustion applications. Bio-oil is not easily combustible, and therefore the engine should be run first with conventional fuels before switching it over to bio-oil. One major problem of handling bio-oil is its high viscosity. Therefore, either the bio-oil delivery line has to be preheated before pumping it or the viscosity has to be reduced by using some additives. Either way, bio-oil requires basic modifications to existing instruments and a supporting fuel for start up in combustion applications [88]. Emissions of particulates are higher in bio-oil combustion than heavy fuel oil combustion; however, the emission of NOx can be lowered in bio-oil combustion by increasing water content [88]. Even though CO emission from bio-oil combustion is high, it is acceptable (30 – 50 ppm) [91]. Bio-oil has been tested for co-firing with coal at Manitowoc Public Utilities in Red Arrow, Wisconsin [25]. Ensyn claims that their bio-oil can replace number 2 and 6 heating fuels for co-firing with natural gas and coal in a vast array of boiler applications. In addition, Orenda, a division of Magellan Aerospace, has developed a turbine with an efficiency range of 29 % to 41 % to generate 1 to 25 MW power from Ensyn bio-oil [49]. Magellan’s Orenda turbine can generate 2.5 MW power with Dynamotive’s bio-oil [53]. The ‘silo’ type combustion chamber in Orenda gas turbines can be easily modified and optimized to any fuel [88]. The major issues for bio-oil in turbines are acid corrosion and deposition on the combustion chamber and blades. Shihadeh and Hochgreb investigated fuel properties of bio-oil from two different sources and compared it with No.2 diesel fuel in direct injection diesel engines [92]. Thermal efficiencies of bio-oils were similar to those of the diesel fuel; however, bio-oils required greater ignition activation energies and had longer ignition delays. The longer ignition delay resulted from slow fuel – air mixing [92]. Chiaramonti et al. conducted bioemulsions (bio-oil – diesel emulsions) for testing in diesel engines. These emulsions were more stable than normal bio-oil; however, they damaged the injectors and fuel pumps. Therefore, their study recommended special considerations in the design of injectors and fuel pumps[93-94].

2.7.2. Transportation Fuels

Bio-oil can be upgraded to a transportation fuel by removing its oxygen content. Gasoline range liquid fuels are technically feasible from bio-oil. However, economic feasibility of these techniques is under research [95]. The upgrading techniques are described in section 2.8

2.7.3. Chemicals

Since bio-oil is a mixture of more than 300 chemicals, many commodity and specialty chemicals such as pharmaceuticals and synthons, fertilizers, environmental chemicals and resins can be prepared from bio-oil. Currently commercial use bio-oil reported is in the production of food flavors such as liquid smoke in the Red Arrows Products Co., Inc. [96]. Ensyn commissioned six commercial RTP plants for food applications in Red Arrow Products Company [49]. Chemicals that have been reported as recovered from bio-oil are phenol formaldehyde, calcium and/or magnesium acetate for biodegradable de-icers, fertilizers, levoglucosan, levoglucosenone, hydroxyacetaldehyde (glycolaldehyde), and a range of flavorings and essences for the food industry [27, 88].

Nonetheless, concentrations of all these compounds are fairly low, which makes economically unfeasible. Bio-oil can be used as an insecticide or fungicide because of the presence of some phenolic compounds. Calcium salts produced by a reaction with carboxylic acids in the aqueous phase of bio-oil can be used as an environmentally friendly road de-icer [88, 97]. Bio-oil can be converted to a nitrogen slow-release fertilizer by a reaction with nitrogen sources like ammonia, urea and proteinaceous materials like manure [98]. The carbonyl group in bio-oil reacts with any $–NH_2$ source and nitrogen will be converted to a stable, biodegradable organic form, which can be used as a slow, nitrogen-releasing fertilizer. An economical analysis of a plant using fertilizer (containing 10% N) produced from bio-oil showed that the capital cost for the plant of capacity 20,000 t/yr was $3.36 million [99]. The carboxylic acids and phenols in bio-oil can react with lime to form calcium salts and phenates (themolabilealkane earth compounds), which is called ‘BioLime’. When this compound is introduced into flue gas, it decomposes at flue gas temperature and reacts with SO_2 in the flue gas, neutralizing the gas [100]. BioLime can remove more than 90% of sulfur dioxide from flue gas [88].

Hydrogen, the primary energy carrier for future, can be produced from bio-oil. As per density, bio-oil can be separated into two phases by simply adding water. Top aqueous phase mainly contains anhydrosugars, carboxylic acids, aldehydes and ketones while bottom tar phase contains mainly lignin derived oligomers. Several studies have been conducted to produce hydrogen from the aqueous phase of bio-oil [101-102]. Hydrogen can be produced from bio-oil by steam reforming, partial oxidation, autothermal, and aqueous phase and supercritical water reforming. Most of the studies were based on steam reforming of the aqueous phase of bio-oil. The amount of hydrogen that can be produced from bio-oil depends on its hydrogen content. However, on an average, two moles of hydrogen can be produced from one mole of carbon in bio-oil if water-gas shift reaction is also considered. Previous studies have shown the hydrogen yield was more than 80% of its theoretical yield [103-105]. The major challenge in hydrogen production from bio-oil is the catalyst deactivation due to coking. Therefore, most of these studies were focused on developing new catalysts for continuous reforming of hydrogen from an aqueous fraction of bio-oil [103-107].

Table 2.3: Chemicals recovered from bio-oil [82]

Chemical Recovered from biomass pyrolysis liquid	
Chemical	**Organization**
Acetol	University of Waterloo
Adhesives	NREL*
Alkanes and Alkenes	University of Toronto
Anhydrosugars	University of Montana, University of Waterloo
Anisole	CPERI**
Aromatics	NREL
Aryl ethers	CPERI
Calcium acetate	BC Research***
Carboxylic acids	University of Laval
Cresols	DuPont
Fatty acids	University of Tubingen
Food flavorings	Red Arrow
Glyoxal	BC Research
Hydroxyacetaldehyde	BC Research, University of Waterloo
Levoglucosan	BC Research, University of Waterloo, University of Montana
Olefins and Gasoline	China Lake, NREL
Oxychemicals	Texas A&M, University of Hamburg
Phenols	CPERI, DuPont, NREL, University of Laval
Polyphenols	NREL
Reformulated Gasoline	NREL

* National Renewable Energy Laboratory, Golden, CO, USA; ** Centre for Process Engineering Research Institute, University of Thessalonika, Greece; *** British Columbia Research Corporation, Vancouver, Canada;

In addition to the above applications, bio-oil has the potential for other end-use markets. The sticky, resin-like quality of bio-oil means it can be utilized as an asphalt binder. Therefore, bio-oil can substitute for some petroleum products in asphalt emulsions for concrete paving [25]. Another potential application of bio-oil is in coal dust suppression. The environmental and physical requirements of bio-oil such as biodegradability, water immiscibility and the strength of its polymerization reactions have to be analyzed in order to coat the coal piles [25]. Ensyn has produced a commercial resin called “MNRP” to replace 50% phenol in the manufacture of phenol formaldehyde and V-additive (plasticizer and emulsifier) from bio-oil [49]. Bridgwater listed some of the organizations where chemicals from bio-oil were being investigated (Table 2.3) [82].

2.8. Bio-oil Upgrading

Certain properties of bio-oil such as high density, high viscosity, high acidity, high water content and oxygen content and low heating value negatively affect the fuel properties of bio-oil. In order to improve the fuel quality, bio-oil has to be completely deoxygenated. There are basically two different techniques to upgrade bio-oil as an end-use fuel – hydrotreating to produce alkane fuels characterized as CH_2, and zeolite-cracking to produce aromatic fuels characterized as $CH_{1.2}$ [82]. Both hydrotreating and catalysts-cracking were performed for pyrolytic vapors also. A new approach has been published for the production of commodity chemicals by upgrading bio-oil which involves the hydroprocessing of bio-oils over metal catalysts, followed by zeolite-cracking [95]. Another technique which is being studied is catalytic pyrolysis where gasoline range, hydrocarbon fuels can be recovered directly from biomass by introducing a catalyst during pyrolysis [108]. In catalytic pyrolysis, either the biomass is fed to a catalyst bed reactor for simultaneous pyrolysis and cracking, or a catalyst bed is inserted above the inert bed so that the vapor passes through the catalyst bed just after pyrolysis on the inert bed [17, 109]. A detailed review of the catalytic hydroprocessing of bio-oil can be seen elsewhere [34, 110].

2.8.1. Hydrotreating

In hydrodeoxygenation (HDO), hydrogen reacts with oxygenated compounds in bio-oil under high pressure and moderate temperature (350-500^oC) in the presence of a heterogeneous catalyst to produce water and hydrocarbon. Normally this process is carried out in two steps. In the first step, bio-oil is treated at around 250^oC followed by conventional hydrodeoxygenation at a higher temperature and high pressure. The initial step is for stabilization in order to avoid polymerization reactions and coke formation. This step consumes a lower amount of hydrogen than the second step [82]. The second step involves HDO at higher temperature and complete deoxygenation. The catalysts normally used for the HDO process is sulfided NiMo or CoMo supported on Al_2O_3. The HDO process for a bio-oil of chemical formula $C_xH_yO_z$ can be simplified as in equation 2.1.

$C_xH_yO_z + (x+z-y/2)\ H_2 \rightarrow x\ CH_2 + z\ H_2O$ ……………………. (Equation 2.1)

Hydrodeoxygenation of bio-oil has been proved technically but not economically feasible. The conventional HDO catalysts are very expensive, and the high char content in bio-oil and coke formation shorten the life of these catalysts. Thermally unstable compounds in bio-oil lead to the coking of catalysts. Therefore, the regeneration of catalysts has to be done more frequently but makes a process expensive. Another challenge with using conventional catalysts is the chance of stripping sulfur from the catalysts, increasing the sulfur content in the bio-oil. Nowadays, the research on hydrotreating of bio-oil has concentrated on the utilization of heterogeneous, noble metal catalysts and transition metal catalysts [111-112]. Another approach in HDO is the utilization of hydrogen donor solvents which also helps to decrease the viscosity of bio-oil. An upgrading of hemicellulose-derived compounds to produce jet and diesel fuels was also reported elsewhere [113-114]. Establishment of new catalytic systems and optimization of process parameters are required for the economical development of HDO of bio-oil. Many studies have been carried out utilizing different or modified catalysts for hydrodeoxygenation of bio-oil or its model compounds [115-116]. However, none of this work has been successful in controlling the coke deposition to make the process a continuous operation. In order to minimize the cost of hydrogen supply; hydrogen can be produced by reforming the water produced during the production of hydrocarbon in the HDO process. A combined HDO and reforming process can reduce the operating cost of HDO.

2.8.2. Catalytic Cracking

In catalytic cracking, bio-oil compounds are deoxygenated in the presence of some shape- selective catalysts such as zeolites. Zeolite, ZSM-5, catalysts are acidic, shape-selective and highly active, converting oxygenated compounds to C1 – C10 hydrocarbons [117]. Deoxygenation with zeolite catalysts can be done in atmospheric pressure and does not require the supply of hydrogen. In zeolite cracking, the oxygen is removed as carbon dioxide and water. Cracking reactions involve the rupture of C-C bonds associated with dehydration, decarboxylation, and decarbonylation; where dehydration is the main reaction. The reaction can be simplified as shown in equation 2.2.

$C_xH_yO_z \rightarrow a.\ CH_{1.2} + b.\ H_2O + c.\ CO_2$ ………………………….. (Equation 2.2)

Here a, b, c depends on x, y and z. The aromatic yield is limited by the hydrogen available in the bio-oil. Bridgwater suggested the use of a multifunctional catalyst which can operate in a carbon- limited environment for cracking of bio-oil [82]. In carbon limited environment, the water gas shift reaction is possible for the production of hydrogen which can be utilized during cracking.

In some studies, catalytic cracking of bio-oil components has been carried out for pyrolytic vapors before condensing as bio-oil. When the catalysts introduced, a high reduction in the oil yield was noticed, however, the upgraded bio-oil contained less oxygen [17]. There was no significant reduction in coke formation even after coprocessing methanol for vapor cracking method [109].

2.8.3. Catalytic Pyrolysis

Catalytic pyrolysis is another promising route to produce deoxygenated liquid fuel directly from biomass within a single step pyrolysis process. There are some advantages for catalytic pyrolysis over bio-oil upgrading. Since the deoxygenation occurs in the vapor phase in simultaneous with pyrolysis, the polymerization of condensed molecules while reheating can be prevented. In addition, some compounds like anhydrosugars are relatively stable in vapor phase; therefore, they don't produce coke[118]. Most of the catalytic pyrolysis studies were conducted with zeolite catalysts [119-123]; in addition, some mesoporous catalysts such as Al-MCM-41, Al-MSU-F [124-127] were utilized. Catalytic pyrolysis can produce bio-oil with very low oxygen content. However, a high reduction in liquid yield was noticed because oxygen (40 – 50 % in the elemental composition of biomass) was being removed. Both fluidized-bed and fixed-bed reactors can be utilized with catalyst particles as bed material. Currently, catalytic pyrolysis studies are mainly focused on modifying existing catalysts or introducing new catalytic systems to reduce coke, water, and gas formation, and increase aromatic yield.

A study conducted by Lappas et al. utilized different catalysts such as a fluid-catalytic cracking (FCC) catalyst and a ZSM-5 additive as bed materials for fluidization in a circulating-fluidized bed reactor (CFB) where catalysts were regenerated and circulated continuously.

Catalytic biomass pyrolysis led to the production of additional water, coke and gases compared to conventional pyrolysis; however, the liquid was more stable in catalytic pyrolysis [39]. A detailed description of catalytic pyrolysis in a pilot plant is provided elsewhere [128] and that pilot plant study provided similar results as that in the study of Lappas et.al. In most of the catalytic pyrolysis studies, catalysts particles are used as bed material instead of sand. However, in some cases, the catalyst particles and inert particles have been kept side-by-side so that biomass entered into the inert bed also passed through the catalyst bed [124-126]. Iliopoulou et al. achieved a similar yield of bio-oil for both catalytic and non-catalytic (Al-MCM-41 catalyst) pyrolysis, and the aromatic yield was very high in the catalytic pyrolysis [124]. Conical spouted bed reactor can be considered as a good alternative for fluidized bed reactor for catalytic pyrolysis of biomass which gives good gas-solid contact and reduce segregation. A high liquid yield (~60 wt.%) was observed for the catalytic pyrolysis of saw dust with ZSM-5 catalyst in conical spouted bed reactor; however, the aromatic yield was only 6.3 wt.% [129].

Nowadays high catalyst to feed ratio is getting more attention for producing high quality fuel directly from solid biomass [108, 120]. French and Czernik studied catalytic pyrolysis with different types of zeolite catalysts and metal impregnated zeolite catalysts; ZSM-5 group catalysts performed better than other zeolite catalysts [120]. Other studies also reported better aromatic yield with ZSM-5 catalyst than other molecular sieve catalysts [44, 121, 126, 130]. In bio-oil cracking, even though ZSM-5 catalysts produced more hydrocarbons, H-Y catalyst provided better yield for aliphatic hydrocarbons than ZSM-5 [44, 130]. Microcatalytic pyrolysis studies by Carlson et al. reported aromatics yield of 30% (on carbon basis) from glucose using ZSM-5 [108, 121, 131]. Study on different types of catalysts (zeolite ZSM-5, aluminosilicate mesoporous Al-MCM-41 and Al-MSU-F, and a proprietary commercial catalyst alumina-stabilized ceria MI-575) showed that all the catalysts produced aromatic hydrocarbons and reduced oxygenated lignin derived compounds. However ceria MI-575 increased the yield of acetic acid [126]. Agblevor et al. have patented for fractional catalytic pyrolysis where catalyst used as in-bed material to convert lignin fraction of biomass into high yields of phenols and cresols while carbohydrate part selectively converted as gaseous products [132].

2.9. Zeolite ZSM-5 Catalyst

The molecular sieve effects determine the catalytic selectivity of zeolite catalysts. The high concentration of ionic hydrogen atoms (H^+) attached to oxygen atom framework is another key feature for zeolite catalyst [133]. Among the zeolite catalysts, ZSM-5 has some unique features for its catalyst activity towards cracking and aromatization. These features are strong acid sites, the easiness for their availability (acid sites are lie on the intercrystalline surface), high silica-alumina ratio, a well defined three dimensional intersecting channel system, medium pore size, and high diffusivity for hydrocarbons. That means the catalytic activity of ZSM-5 mainly depends on its pore structure and acidity.

2.9.1. Pore Structure

Zeolite ZSM-5 catalysts has unique channel structures which gives its special catalytic properties and high thermal stability. The building unit of ZSM-5 framework is a linked tetrahedral having eight five membered rings (Figure 2.8(a). These units joined through edges to form chains (Figure 2.8(b), chained connected to form sheets (Figure 2.8(c), and sheets linked to form three dimensional framework structure. The framework consists of two intersecting channel systems (Figure 2.8(d), straight channel having diameters of about 5.4 X 5.6 A^o free diameter and the sinusoidal channel having diameters of about 5.1 X 5.5 A^o free diameter[133-134].

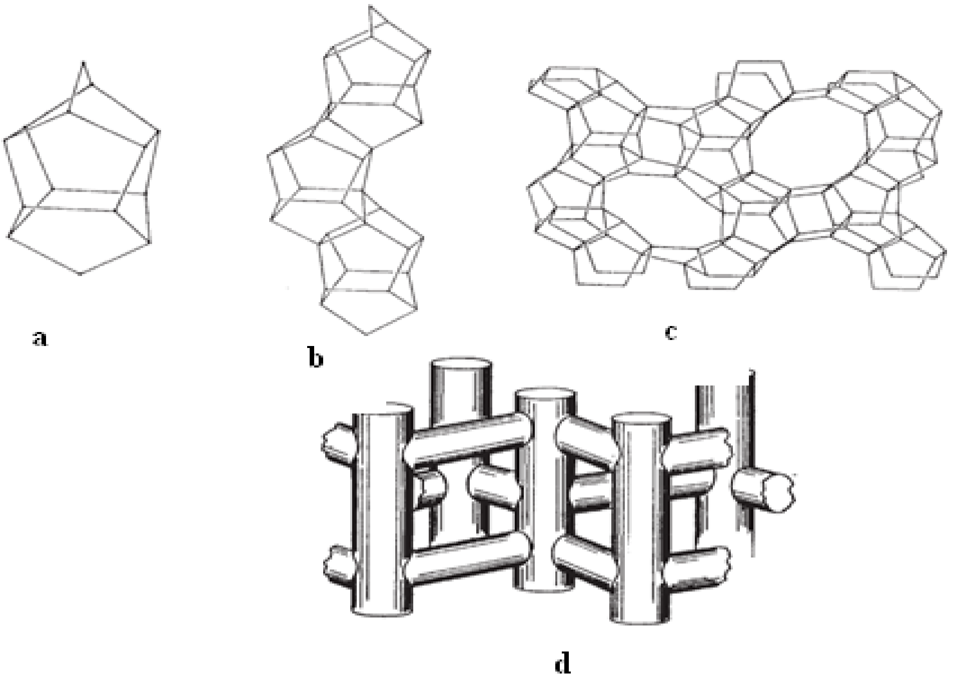


Figure 2.8: Crystal structure of zeolite ZSM-5 (a) building unit, (b) chain, (c) sheets, (d) three dimensional channel structure

ZSM-5 is in crystal in nature. The catalyst activity of porous crystalline zeolite also depends on the diffusion within the crystals. Olson et al. have shown the zeolitic crystal diffusivity of ZSM-5 and silicalite for various hydrocarbons such as hexane, benzene, p/m/o-xylene, ethyl benzene, cycloheane, and 1,3,5-trimethylbenzne. They found that the diffusivity of ZSM-5 is one or two order magnitude higher than that of silicalite [133, 135-136].

The shape selectivity properties of zeolite catalysts for aromatic hydrocarbon were compared with silica-alumina catalyst. The absence of a defined pore sizes caused low selectivity for aromatic production from bio-oil cracking in presence of silica-alumina [44, 130].

2.9.2. Acidity

The primary requirement for catalytic activity for cracking reaction is acid nature. An acid site on zeolite catalyst can be Brønsted type which gives proton to an unsaturated hydrocarbon (gives proton from surface to absorbed molecule) or Lewis type which acts as an electron acceptor by removing hydride ion from absorbed molecule. The acidic properties of zeolites depend on the method of preparation and Si/Al ratio present. Si/Al ratio in ZSM-5 can be varied from 10 to 100[133]. Change in Si/Al ratio will not affect the structure; however it cause in the acidity of catalyst. As the ratio increases, the acidity of catalyst increases. Therefore, as Si/Al increase the quality of bio-oil produced also increase. The protonated form of ZSM-5 (H-ZSM-5) can be obtained by thermal decomposition of ammoniated form of ZSM-5. The conditions applied for deammoniation (temperature, heating rate, and period) will affect the acidity of ZSM-5.

The acidity ZSM-5 catalyst for cracking bio-oil components were studied by comparing with silicalite. Silicalite is a molecular sieve catalyst having similar pore structure as that of ZSM-5. However, silicalite don’t have any acid sites, therefore any ion-exchange property. In all cases, ZSM-5 provided more aromatics whereas the silicalite produced primarily coke. The results confirm the presence of Brønsted acid sites in ZSM-5 produces more aromatic yield [44, 121]. The acidity of ZSM-5 catalyst responsible for cracking the high molecular weight compounds to smaller molecular compounds, as a result these compounds passed through the pores in the catalyst for further reaction. In the case of silicalite catalyst, the high molecular weight components are prevented from the access of pores, therefore they polymerize over the catalyst [44].

2.9.3. Reaction Mechanism

Catalytic activity of ZSM-5 for bio-oil cracking at lower temperatures (upto 330 ^{o}C) produced ketones, phenols, ethers, and esters in addition to the production of aromatic hydrocarbons. However, as temperature increased mostly aromatic hydrocarbons and a few phenols were produced [44]. Adjaye and Bakhshi had proposed reaction mechanisms for bio-oil upgrading in the presence of zeolite catalysts [130]. They proposed the reaction mechanisms for acidic zeolite catalysts (ZSM-5, H-modernite, and H-Y), non-acidic zeolite catalyst (silicalite), and amorphous silica-alumina catalyst (shown in Figures 2.9, 2.10, & 2.11). In all mechanisms, the initial reaction occurs because of high temperature (thermal effect) followed by thermo-catalytic effect. In thermo effect, bio-oil components are either polymerized to char or separated into heavy organics and light organics. In thermo-catalytic effect, heavy organics are either polymerized to coke and tar or cracked to light organics which is also common for all catalysts. The reactions through which light organics undergo depend on the nature of catalyst.

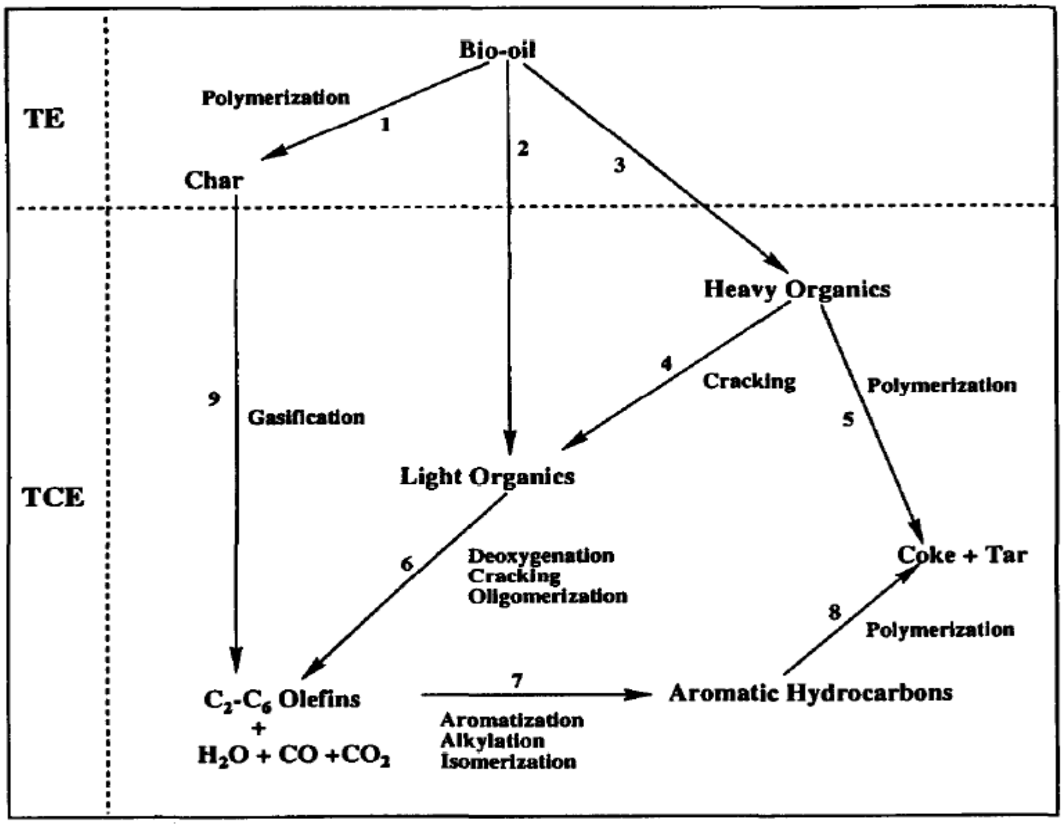


Figure 2.9: Reaction pathway proposed by Adjaye and Bakhshi for the conversion of bio-oil over acidic zeolite catalysts (i.e. HZSM-5, H-mordenite and H-Y) [130]. TE: thermal effect; TCE: thermocatalytic effect

In presence of acid zeolites, some of light organics are deoxygenated and cracked. Deoxygenation of light organics (esters, ketones, alcohols, ethers, and phenols) on acid catalysts involve decarbonylation, decarboxylation and dehydration which produce hydrocarbons, water, and carbon oxides. Cracking will give various carbon fragments which undergo oligomerization to produce mixture of C_2-C_6 olefins. These olefins undergo a series of aromatization reactions to produce benzene followed by alkylation and isomerization to produce varios aromatic hydrocarbons. Aromatization involes cyclization and hydrogen or hydride transfer. Some aromatics are polymerized to tar eventually to coke.

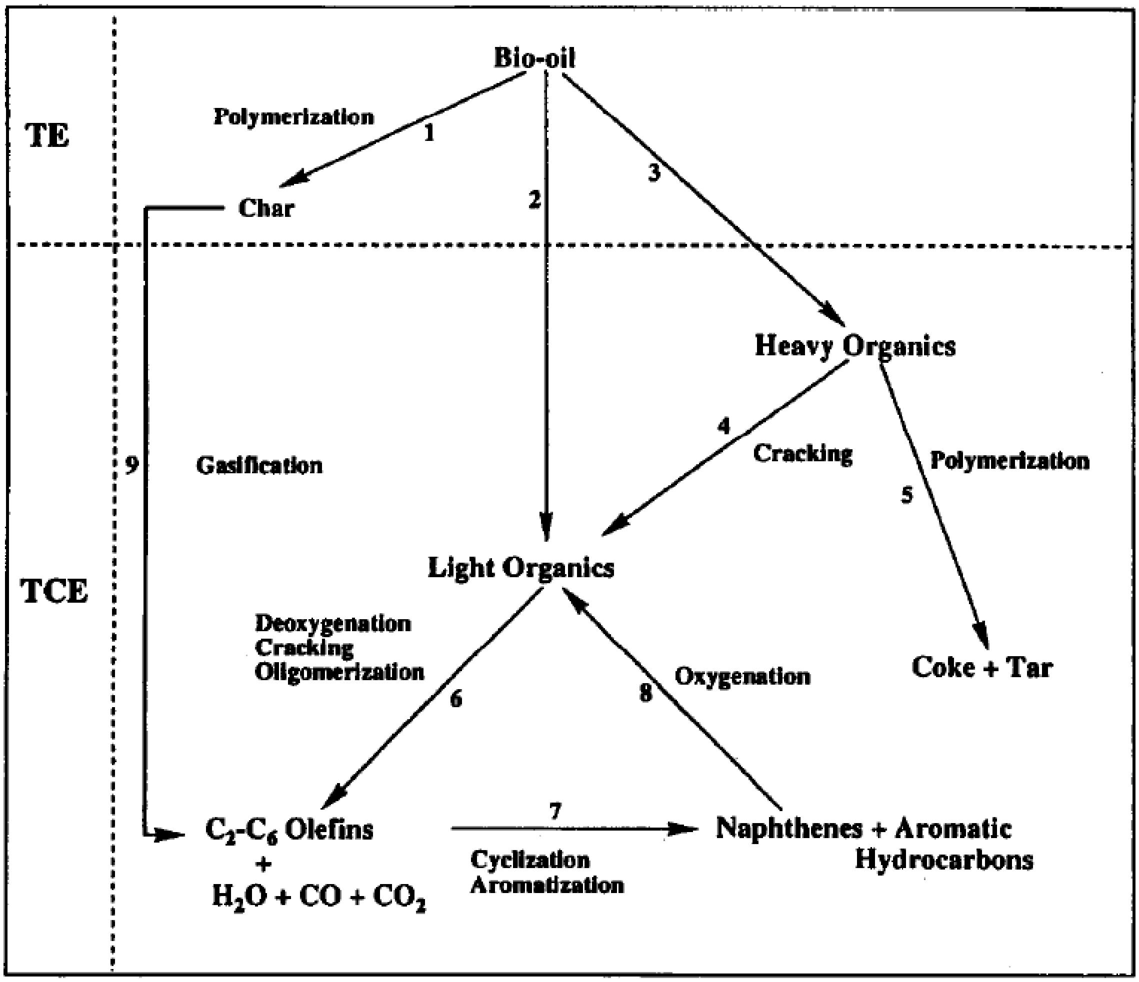


Figure 2.10: Reaction pathway proposed by Adjaye and Bakhshi for the conversion of bio-oil over non-acidic silicalite catalyst [130]. TE: thermal effect; TCE: thermocatalytic effect

The activity of non-acidic zeolite catalysts are similar upto the reactions of light organics as that of acidic zeolite catalysts. In the absence of acidity, some of the olefins produce naphtehnes by cyclization while remaining under aromatization. Some of these naphthenes are oxygenated to form cyclic ketones.

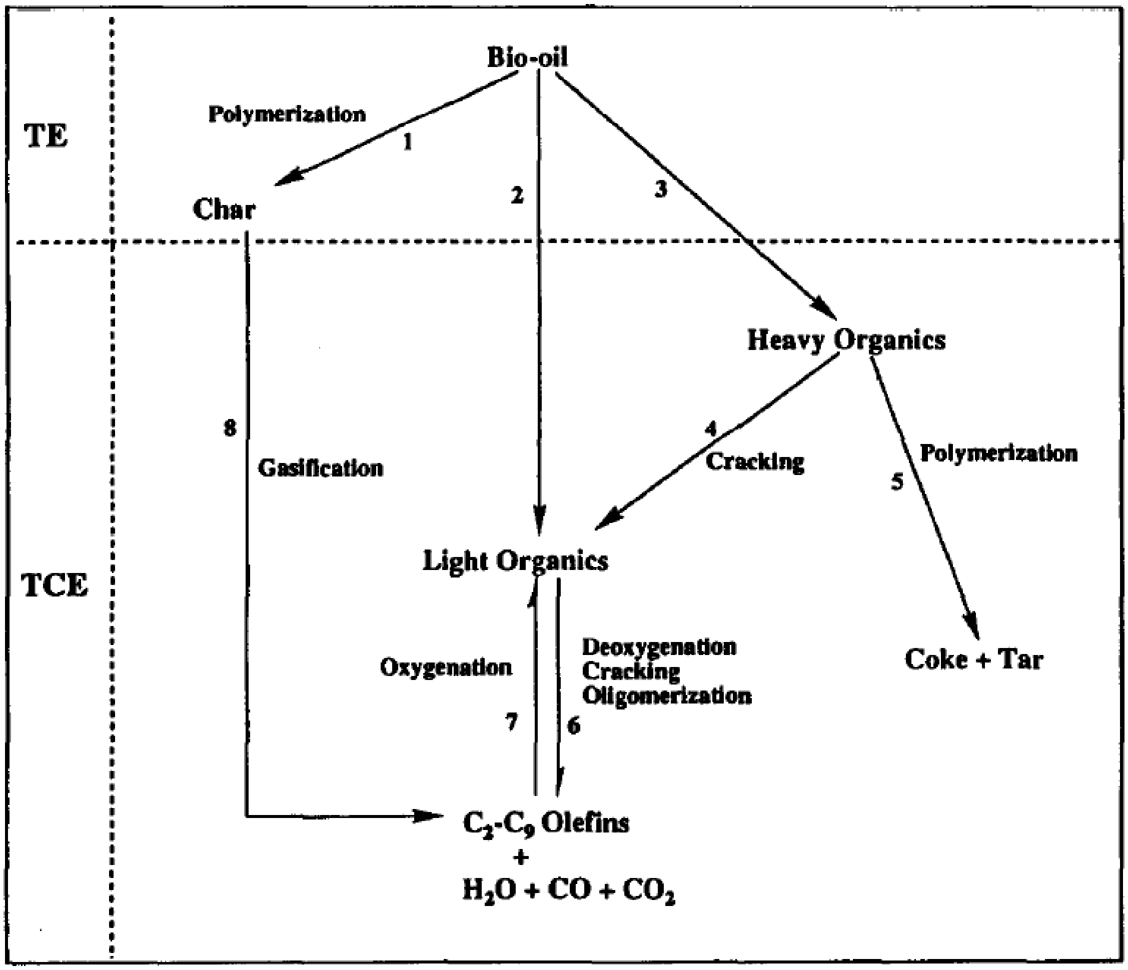


Figure 2.11: Reaction pathway proposed by Adjaye and Bakhshi for the conversion of bio-oil over silica-alumina catalyst [130]. TE: thermal effect; TCE: thermocatalytic effect

The reactions until the production of olefins are similar for amorphous catalysts also. Unlike zeolite catalysts, these olefins are not aromatized to hydrocarbons. Some of them are re-oxygenated. Therefore, amorphous silica predominantly produces non-cyclic aliphatic hydrocarbons.

These reaction mechanisms can be applied to catalytic pyrolysis where thermal effects cause biomass to pyrolize to char, light and heavy organics in simultaneous with their separation. Recently, Carlson et al. proposed the glucose catalytic pyrolysis reaction mechanism over ZSM-

5 catalyst (Figure 2.12) [131]. Glucose is thermally decomposed to intermediate oxygenates which diffuse to ZSM-5 pores and undergo a series of decarbonylation, decarboxylation, dehydration, and oligomerization reactions to produce aromatic hydrocarbons. The aromatization is the slow step which determines the kinetic of this reaction mechanism.

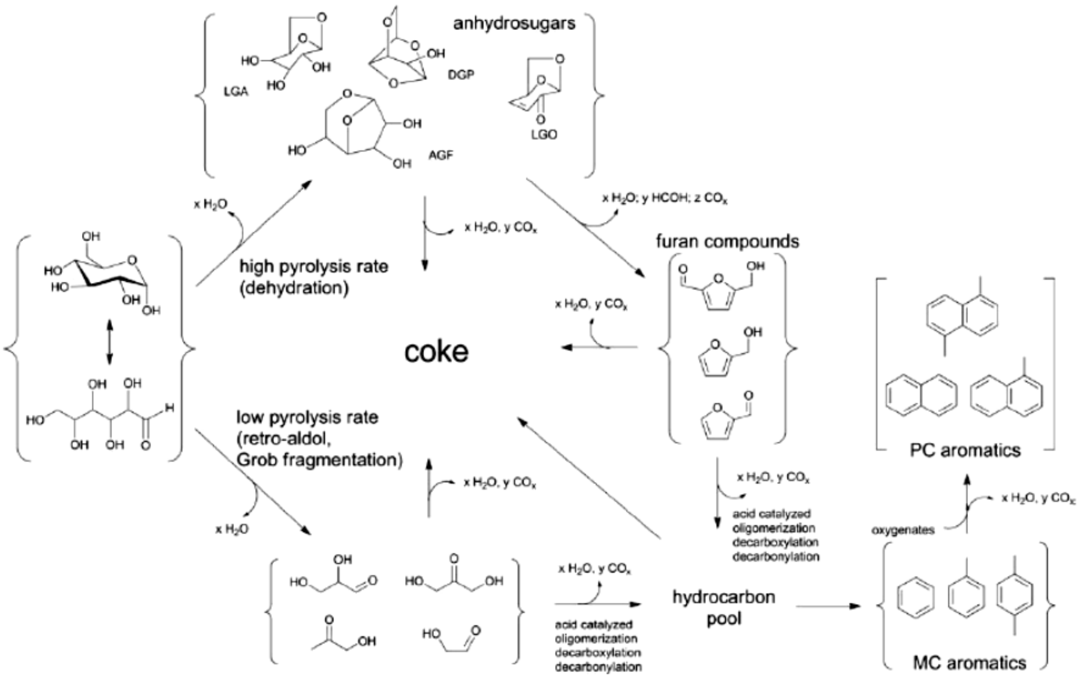


Fig. 21. Reaction chemistry for the catalytic fast pyrolysis of glucose with ZSM-5.

Figure 2.12: Reaction mechanism for the catalytic pyrolysis of glucose over ZSM-5 catalyst proposed by Carlson et al. [131]

They have discussed about similar reaction mechanism of catalytic pyrolysis of cellulose (Figure 2.13) [118] where the initial step in catalytic pyrolysis is the pyrolysis of cellulose to anhydrosugar and oxygenated products. The competitive reaction for this step is the formation of coke, water and carbon oxides. The thermal decomposition of cellulose to anhydrosugars requires high activation energy; therefore high heating rate and temperature prefer this reaction.

These anhydrosugars undergo dehydration and re-arrangement to produce furans, aldehydes and other oxygenates which diffuse into the catalyst pores for aromatization.

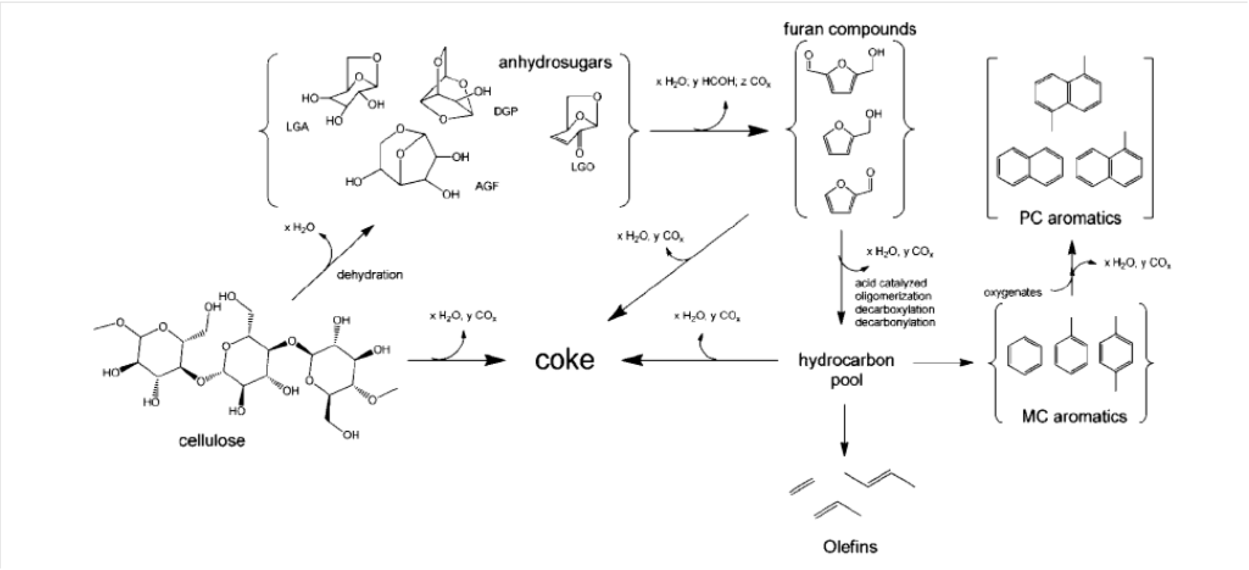


Figure 2.13: Reaction mechanism for the catalytic pyrolysis of cellulose over ZSM-5 catalyst proposed by Carlson et al. [118].

2.9.4. Catalyst deactivation

The major competing reaction for the aromatization of oxygenated compounds is the polymerization of oxygenated compounds which eventually lead to the formation of coke. Coke deposition will decrease the activity of catalyst, finally catalysts are deactivated. Coke formation can be due to two mechanisms; one is due to the macromolecules (polyaromatic hydrocarbons) formed inside the catalyst pore which block the other species entering inside the catalyst and another is due to the formation of coke near the acid sites which covers the aperture of catalyst pores.

Generally, the rate and extent of coke formation increased with increase in acid strength and concentration and coke yield decrease with the decrease in pore size [137]. Coke formation is mainly due to the extensive dehydrogenation of fused aromatic rings which leads to the formation of polynuclear aromatics which is rather complex and involve a series of reactions. The major reactions are oligomerization of olefins on the acids sites followed by their cyclization reactions to form aromatic compounds and finally chain reactions to form polynuclear aromatic hydrocarbons. PAHs are relatively stable and condense as coke. Therefore the precursors for coke formation are olefins and aromatics [137-138].

Carlson et al. discussed about the deactivation of ZSM-5 catalyst (medium pore size) is mainly due to the unsaturated coke on the external surface of catalyst whereas in large pore sized zeolite catalysts (H-Y, β-zeolites) the deactivation is due to the formation of polyaromatic species within the pore system [131]. However, another study on coke precursor on ZSM-5 catalyst during bio-oil upgrading showed that the major coke precursors were inside of catalyst which were mainly aromatic compounds (dicyclic arenes and PAHs) and the other precursors were mainly saturated hydrocarbons on the outer surface of catalyst [139].

High temperature pyrolysis minimizes the coke formation; however, above 600 ^{o}C, aromatic yield decrease [131]. As the reaction time increases, mono-aromatics reacts with oxygenated compounds and polymerized to poly-aromatics (such as naphthalenes) which deactivate the catalyst by blocking the pores. Therefore, the reaction time has to be minimized by rapid heating rate and cooling of vapors. Co-feeding hydrogen slightly reduced the catalyst deactivation during the conversion of anisole over HZSM-5 catalysts; however, a significant improvement in catalyst stability was not observed [140]. In the deoxygenation of benzaldehyde, co-feeding hydrogen over Ga-ZSM-5 catalyst showed a shift in product selectivity because of the presence of hydrogenation/hydrogenolysis reactions [141]. No significant decrease in the coke yield was noticed even during the co-processing of methanol for upgrading bio-oil over ZSM-5[109]. Another method to minimize the coke formation by diluting oxygenates which reacts with catalyst. Recently, high catalyst to biomass ratio for catalytic pyrolysis is getting attention [108]. Zeolites catalysts can be regenerated by heating at high temperature in presence of oxygen [142]. However, the regeneration of catalysts decrease the number of acid sites available and therefore, an increase in oxygen content was noticed in the presence of regenerated catalyst instead of fresh catalyst [139].

2.10. Economical Analysis

Some economic studies are available for bio-oil production and its upgrading as a surrogate of transportation fuels [35, 143-147]. Ringer et al. conducted a detailed economic analysis of a pyrolysis plant with a capacity of 550 tons per day [35]. In their economical analysis, pyrolysis plant was divided as five major processing areas: feed handling and drying, pyrolysis, char combustion, product recovery, and steam generation. The economical assessment was done for a plant of capacity 550 tons/day biomass (wood chips, 50% by mass water content, 20MJ/kg HHV) feed to get a bio-oil yield of 59.9 wt. % of dry biomass (17.9 MJ/kg, 4.55kg/gallon density).The total project investment was calculated as $ 48.29 million and a total operating cost was $ 9.6 million. About 65 % of total capital investment ($43.9 million) was dedicated to equipments and their installed costs. The selling price of the bio-oil was projected to be $7.62/GJ, LHV [35].

Bricka has distributed the operation costs for a bio-oil plant of 100 / 200 / 400 tons/day, which is given in Figure 2.8 [148].

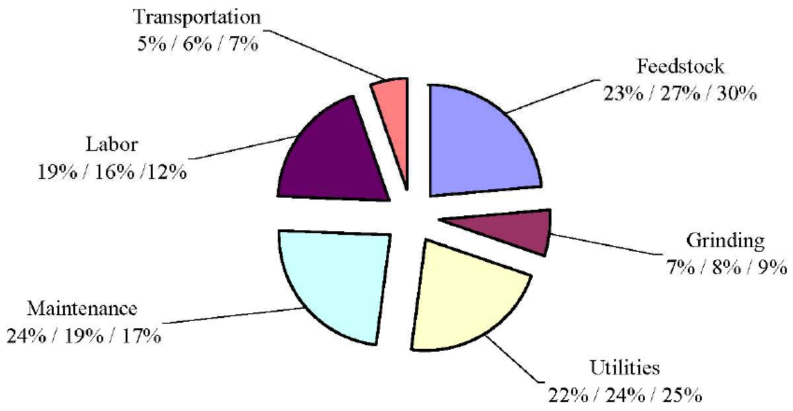


Figure 2.14: An operation cost of typical fast pyrolysis plant [148]

Another economic study was conducted by the Pacific Northwest National Laboratory (PNNL) for the production of 76 million gallons/year of gasoline and diesel through fast pyrolysis [143]. This economical assessment has considered the upgrading bio-oil to gasoline and diesel. In this study, the size of the plant was taken as 2000 dry metric tons/day of hybrid poplar wood chips. The process included six major steps, which were feed drying and size reduction, fast pyrolysis, hydro-treating bio-oil to get hydrocarbon oil with <2% oxygen liquid, hydro-cracking of a heavy portion of the hydrocarbon oil, distillation of hydrotreated and hydrocracked oil to diesel and gasoline blends, and steam reforming of off-gas to produce hydrogen. This report used the data from Ringer et al. (2006), scaled up to 2000 dry metric tons/day and represented as single pyrolysis process which constituted 30 % of total project investment. The cost distribution for total capital investment in this study is represented in Figure 2.9. The minimum selling price for the fuels from this study was $ 2.04/ gallon. The total capital cost of this process can be reduced by coupling with an existing refinery for separation and finishing of upgraded bio-oil to motor fuels and steam reforming of off-gas. Therefore, the selling price of fuels could be reduce to $ 1.74/ gallon gasoline equivalent [143].

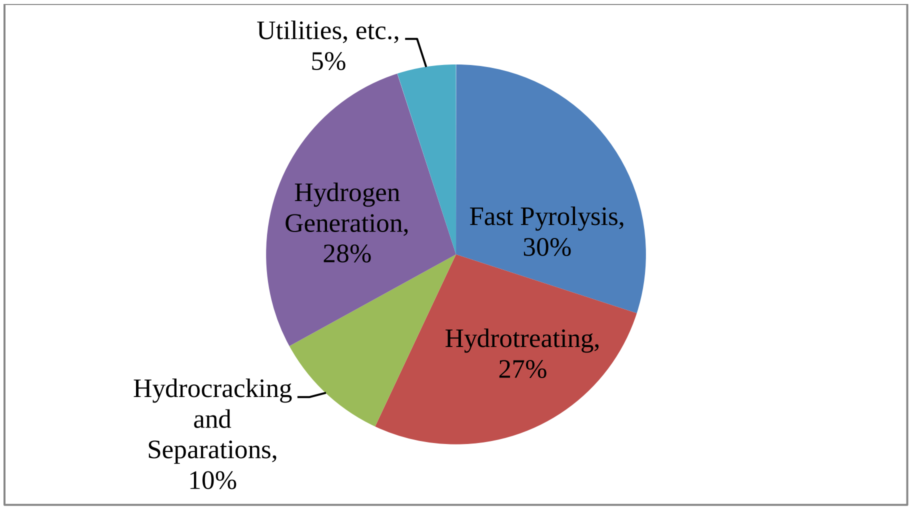


Figure 2.15: Total capital investment for production of diesel and gasoline blends through fast pyrolysis [143]

Recently, the National Renewable Energy Laboratory (NREL) conducted an economic analysis of the production of transportation fuels (naphtha range and diesel range) from corn stover biomass through fast pyrolysis [144]. In this study, two scenarios were used for bio-oil upgrading. One was a hydrogen production scenario where the hydrogen required for bio-oil upgrading would be produced from reforming a portion of the aqueous phase of bio-oil. The second scenario involved purchasing the hydrogen required for bio-oil upgrading. The study proposed to process 2000 MT/day of corn stover (25 wt. % moisture content and 10 to 25 mm in size). In the first scenario, the estimated production of fuel was 35.4 million gallons/yr. The capital expenditure for the combined pyrolysis and upgrading plant was estimated as $287 million, and the competitive product value was $3.09/gallon of gasoline equivalent. In the second scenario, the estimated production of fuel was 58.2 million gallons/yr. The capital expenditure for the combined pyrolysis and upgrading plant was estimated as $200 million, and the competitive product value was $ 2.11/gallon [144-145]. The cost of feedstock was estimated to be $ 83/MT, the cost of electricity was projected as $0.054/kWh, and the catalyst replacement cost as $1.77 million/year.

2.11. References

1. IEA, *World Energy Outlook 2008.* International Energy Agency, 2008.

2. EIA, U.S. (2010) *Intenrational Energy Outlook*. www.eia.gov/oiaf/ieo/index.html **DOE/EIA-0484(2010)**.

3. EIA (2010) *Annual Energy Outlook*. www.eia.doe.gov/oiaf/aeo/ **DOE/EIA-0383(2010)**.

4. EISA (2007) *Energy Independence and Security Act of 2007*. http://frwebgate.access.gpo.gov/cgi-bin/getdoc.cgi?dbname=110_cong_bills&docid=f:h6enr.txt.pdf

5. ANSI/ASABES593, *Terminology and Definitions for Biomass Production, Harvesting and Collection, Storage, Processing Conversion and Utilization*. 2006, American Society of Agricultural and Biological Engineers: St. Joseph, MI, USA.

6. Sierra, R., et al., *Producing Fuels and Chemicals from Lignocellulosic Biomass* Chemical Engineering Progress, 2008. **SBE Special Section - Biofuels**: p. 10 - 18.

7. EPA, U.S., *Municipal Solid Waste Generation, Recycling, and Disposal in the United States: Facts and Figures for 2008*, in *United States Environmental Protection Agency, Solid Waste and Emergency Response (5306P)*. 2009: Washington, DC.

8. Perlack, R.D., et al., *Biomass as a Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-Ton Annual Supply*. 2005, USDA/DOE.

9. Milbrandt, A., *A Geographic Perspective on the Current Biomass Resource Availability in the United States*, in *NREL*. 2005.

10. Perez, J., et al., *Biodegradation and Biological Treatments of Cellulose, Hemicellulose and Lignin: an Overview*. International Microbiology, 2002. **5**: p. 53 - 63.

11. O'sullivan, A.C., *Cellulose: the Structure Slowly Unravels.* Cellulose, 1997. **4**(3): p. 173 - 207.

12. Kumar, S. and R.B. Gupta, *Biocrude Production from Switchgrass using Subcritical Water.* Enegry & Fuels, 2009. **23**(10): p. 5151 -5159.

13. Elliott, D.C. and G.F. Schiefelbein. *Liquid Hydrocarbon Fuels from Biomass*. in *Division of Fuel Chemistry Annual Meeting Preprints*. 1989: American Chemical Society.

14. Peterson, A.A., et al., *Thermochemical Biofuel Production in Hydrothermal Media: A Review of Sub- and Supercritical Water Technologies.* Energy & Environmental Science, 2008. **1**: p. 32 - 65.

15. Kim, S.-S., F.A. Agblevor, and J. Lim, *Fast Pyrolysis of Chicken Litter and Turkey Litter in a Fluidized Bed Reactor.* Journal of Industrial and Engineering Chemistry, 2009. **15**(2): p. 247 - 252.

16. Ozbay, N., et al., *Biocrude from Biomass: Pyrolysis of Cottonseed Cake.* Renewable Energy, 2004. **24**: p. 615 - 625.

17. Williams, P.T. and N. Nugranad, *Comparison of Products from the Pyrolysis and Catalytic Pyrolysis of Rice Husks.* Energy, 2000. **25**: p. 493 - 513.

18. Jung, S.-H., B.-S. Kang, and J.-S. Kim, *Production of Bio-Oil from Rice Straw and Bamboo Sawdust under Various Reaction Conditions in a Fast Pyrolysis Plant Equipped with a Fluidized Bed and a Char Separation System.* Journal of Analytical and Applied Pyrolysis, 2008. **82**(2): p. 240 - 247

19. He, R., et al., *Influence of Pyrolysis Condition on Switchgrass Bio-Oil Yield and Physicochemical Properties.* Bioresource Technology, 2009. **100**(21): p. 5305-5311.

20. Ingram, L., et al., *Pyrolysis of Wood and Bark in an Auger Reactor: Physical Properties and Chemical Analysis of the Produced Bio-oils.* Enegry & Fuels, 2008. **22**(1): p. 614-625.

21. Rutkowski, P. and A. Kubacki, *Influence of Polystyrene Addition to Cellulose on Chemical Structure and Properties of Bio-Oil Obtained During Pyrolysis.* Energy Conversion & Management, 2006. **47**: p. 716 - 731.

22. Scott, D.S., et al., *Fast Pyrolysis of Plastic Wastes.* Enegry & Fuels, 1990. **4**(4): p. 407 - 411.

23. Karaduman, A., et al., *Flash Pyrolysis of Polystyrene Wastes in a Free-Fall Reactor under Vacuum.* Journal of Analytical and Applied Pyrolysis, 2001. **60**: p. 179 - 186.

24. Bhattacharya, P., et al., *Wood/Plastic Copyrolysis in an Auger Reactor: Chemical and Physical Analysis of the Products.* Fuel, 2009. **88**(7): p. 1251-1260.

25. Farag, I.H., C.E. LaClair, and C.J. Barrett, *Technical, Environmental and Economic Feasibility of Bio-Oil in New Hampshire's North Country*. 2002, New Hampshire Industrial Research Center (NHIRC): Durham, NH. p. 1 - 95.

26. Badger, P.C. and P. Fransham, *Use of Mobile Fast Pyrolysis Plants to Densify Biomass and Reduce Biomass Handling Costs—A Preliminary Assessment.* Biomass and Bioenergy, 2006. **30**: p. 321 - 325.

27. Bridgwater, A., D. Meier, and D. Radlein, *An Overview of Fast Pyrolysis of Biomass.* Organic Geochemistry, 1999. **30**: p. 1479 - 1493.

28. Mohan, D., C.U.P. Jr., and P.H. Steele, *Pyrolysis of Wood/Biomass for Bio-Oil: A Critical Review*. Energy & Fuels, 2006. **20**: p. 848-889.

29. Gupta, R.B. and A. Demirbas, *Gasoline, Diesel and Ethanol Biofuels from Grasses and Plants*. 2010, Cambridge University Press: New York, USA. p. 140 - 157.

30. Bridgwater, A.V. and G.V.C. Peacocke, *Fast Pyrolysis Processes for Biomass.* Renewable and Sustainable Energy Reviews, 2000. **4**: p. 1-73.

31. Brammer, J.G. and A.V. Bridgwater, *Drying Technologies for an Integrated Gasification Bio-Energy Plant.* Renewable and Sustainable Energy Reviews, 1999. **3**: p. 243 - 289.

32. Klass, D.L., *Biomass for Renewable Energy, Fuels and Chemicals*. 1998, Academic Press: San Diego, USA. p. 230 - 231.

33. Mani, S., L.G. Tabil, and S. Sokhansanj, *Grinding Performance and Physical Properties of Wheat and Barley Straws,Corn Stover and Switchgrass.* Biomass and Bioenergy, 2004. **27**: p. 339 - 352.

34. Huber, G.W., S. Iborra, and A. Corma, *Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering.* Chemical Reviews, 2006. **106**(9): p. 4044 - 4098.

35. Ringer, M., V. Putsche, and J. Scahill, *Large-Scale Pyrolysis Oil Production: A Technology Assessment and Economic Analysis*. 2006, National Renewable Energy Laboratory.

36. Bridgwater, A.V., et al., *Fast pyrolysis of biomass: a handbook.* 2008, Newbury: CPL Press. 34.

37. Oasmaa, A. and C. Peacocke, *A Guide to Physical Property Characterisation of Biomass - Derived fast pyrolysis liquids*, in *VTT Publications 450*. 2001, Technical Research Centre of Finland.

38. Scott, D.S., et al., *A Second Look at Fast Pyrolysis of Biomass—the RTI Process.* Journal of Analytical and Applied Pyrolysis, 1999. **51**: p. 23 - 37.

39. Lappas, A.A., et al., *Biomass Pyrolysis in a Circulating Fluid Bed Reactor for the Production of Fuels and Chemicals.* Fuel, 2002. **81**: p. 2087 - 2095.

40. BTG. *www.btgworld.com*. 2011 - 01 - 12].

41. BTL. *www.btg-btl.com*. 2011 - 01 - 12].

42. Lede, J., et al., *Properties of Bio-oils Produced by Biomass Fast Pyrolysis in a Cyclone Reactor*. Fuel, 2007. **86**(12-13): p. 1800 - 1810.

43. Brown, R.C. and J. Holmgren *Fast Pyrolysis and Bio-Oil Upgrading*. www.ars.usda.gov/.../biomasstoDiesel/RobertBrown&JenniferHolmgrenpresentationslides.pdf.

44. Adjaye, J.D. and N.N. Bakhshi, *Production of Hydrocarbons by Catalytic Upgrading of a Fast pyrolysis Bio-Oil. Part I: Conversion Over Various Catalysts.* Fuel Processing Technology, 1995. **45**: p. 161-183.

45. Garcia-Perez, M., et al., *Production and Fuel Properties of Pine Chip Bio-oil/Biodiesel Blends.* Enegry & Fuels, 2007. **21**(4): p. 2363-2372.

46. Asadullah, M., et al., *Production of Bio-Oil from Fixed Bed Pyrolysis of Bagasse.* Fuel, 2007. **86**(16): p. 2514-2520.

47. Basu, P., *Pyrolysis* in *Biomass Gasification and Pyrolysis* 2010, Academic Press: Burlington, MA, USA. p. 65 - 92.

48. Onay, O. and O.M. Kockar, *Pyrolysis of Rapeseed in a Free Fall Reactor for Production of Bio-Oil.* Fuel, 2006. **85**: p. 1921 - 1928.

49. Ensyn. *http://www.ensyn.com*. 2010 - 08 - 18].

50. UOP. *http://www.ensyn.com/news/DOEBiomassToGreenFuelsGrant.pdf*. 2010 2010 - 09 - 18].

51. Ensyn. *http://www.ensyn.com/news/Ensyn-Press%20Release-HighNorth.pdf*. 2010 2010 - 09 - 18].

52. Evergrent-Technologies. *http://www.envergenttech.com/*. 2012-04-13].

53. Dynamotive. *http://www.dynamotive.com*. 2010 - 08 - 18].

54. Pytec. *http://www.pytecsite.de/pytec_eng/index.htm*. 2012-04-17].

55. Windt, M. *Bio Crude Oil*. in *Biofuel conference*. 2009. dbb-forum, Berlin.

56. ROI, *"Demonstrating BioOil Technology for Poultry Litter Nutrient Management" Final Report*. 2006: Florence, Alabama.

57. KiOR. *http://www.kior.com/index.shtml* 2010-09-18].

58. Anellotech. *http://anellotech.com/index.html*. 2010 - 09 - 18].

59. Kilzer, F.J. and A. Broido, *Speculations on the Nature of Cellulose Pyrolysis.* Pyrodynamics, 1965. **2**: p. 151-163.

60. Shafizadeh, F., *Introduction to Pyrolysis of Biomass.* Journal of Analytical and Applied Pyrolysis, 1982. **3**: p. 283-305.

61. Radlein, D., J. Piskorz, and D.S. Scott, *Fast Pyrolysis of Natural Polysaccharides as a Potential Industrial Process.* Journal of Analytical and Applied Pyrolysis, 1991. **19**: p. 41-63.

62. Piskorz, J., et al., *Pretreatment of Wood and Cellulose for Production of Sugars by Fast Pyrolysis.* Journal of Analytical and Applied Pyrolysis, 1989. **16**: p. 127-142.

63. Shafizadeh, F., *Industrial Pyrolysis of Cellulosic Materials.* Applied Polymer Symposia, 1975. **28**: p. 153-174.

64. Demirbas, A., *Mechanisms of Liquefaction and Pyrolysis Reactions of Biomass.* Energy Conversion & Management, 2000. **41**: p. 633-646.

65. Bradbury, A.G., Y. Sakai, and F. Shafizadeh, *A Kinetic Model for Pyrolysis of Cellulose.* Journal of Applied Polymer Science, 1979. **23**: p. 3271-3280.

66. Varhegyi, G., et al., *Kinetic Modeling of Biomass Pyrolysis.* Journal of Analytical and Applied Pyrolysis, 1997. **42**: p. 73-87.

67. Varhegyi, G., et al., *Application of Complex Reaction Kinetic Models in Thermal Analysis.* Journal of Thermal Analysis, 1996. **47**: p. 535 - 542.

68. Diebold, J.P., *A Unified, Global Model for the Pyrolysis of Cellulose.* Biomass and Bioenergy, 1994. **7**(1-6): p. 75-85.

69. Lin, Y.-C., et al., *Kinetics and Mechanism of Cellulose Pyrolysis.* The Journal of Physical Chemistry C, 2009. **113**: p. 20097-20107.

70. Cho, J., J.M. Davis, and G.W. Huber, *The Intrinsic Kinetics and Heats of Reactions for Cellulose Pyrolysis and Char Formation.* ChemSusChem, 2010. **3**: p. 1162 - 1165.

71. Hosoya, T., H. Kawamoto, and S. Saka, *Pyrolysis Behaviors of Wood and Its Constituent Polymers at Gasification Temperature.* Journal of Analytical and Applied Pyrolysis, 2007. **78**(2): p. 328-336.

72. Ponder, G.R. and G.N. Richards, *Thermal Synthesis and Pyrolysis of a Xylan.* Carbohydrate Research, 1991. **218**: p. 143-155.

73. Pouwels, A.D., et al., *Characterization of Beech Wood and Its Holocellulose and Xylan Fractions by Pyrolysis-Gas Chromatography-Mass Spectroscopy.* Journal of Analytical and Applied Pyrolysis, 1987. **11**: p. 417 - 436.

74. Shafizadeh, F., G.D. Mcginnis, and C.W. Philpot, *Thermal Degradation of Xylan and Related Model Compounds.* Carbohydrate Research, 1972. **25**: p. 23 - 33.

75. Evans, R.J. and T.A. Milne, *Molecular Characterization of the Pyrolysis of Biomass. 1.Fundamentals.* Enegry & Fuels, 1987. **1**(2): p. 123 - 137.

76. Antal Jr., M.J., T. Leesomboon, and W.S. Mok, *Mechanism of Formation of 2-Furaldehyde from D-Xylose.* Carbohydrate Research, 1991. **217**: p. 71 - 85.

77. Britt, P.F., A.C. BuchananIII, and D.R. Matineau, *Flash Vacuum Pyrolysis of Lignin Model Compounds: Reaction Pathways of Aromatic Methoxy Groups*, in *ORNL/CP - 101275*. 1999.

78. Windt, M., et al., *Micro-Pyrolysis of Technical Lignins in A New Modular Rig And Product Analysis by GC–MS/FID And GCxGC–TOFMS/FID.* Journal of Analytical and Applied Pyrolysis, 2009. **85**: p. 38-46.

79. Petrocelli, F.P. and M.T. Klein, *Model Reaction Pathways in Kraft Lignin Pyrolysis.* Macromolecules, 1984. **17**(2): p. 161-169.

80. Kuroda, K.-I. and Y. Inoue, *Analysis of Lignin by Pyrolysis-Gas Chromatography I Effect of Inorganic Substances on Guaiacol-Derivative Yield from Softwoods and Twir Lignins.* Journal of Analytical and Applied Pyrolysis, 1990. **18**: p. 59-69.

81. Nowakowski, D.J., et al., *Lignin Fast Pyrolysis: Results from an International Collaboration.* Journal of Analytical and Applied Pyrolysis, 2010. **88**: p. 53 - 72.

82. Bridgwater, A., *Thermal Biomass Conversion and Utilization - Biomass Information System*, in *European Commission - Science, Research and Development*. 1996: Luxembourg.

83. Bridgwater, A.V., A.J. Toft, and J.G. Brammer, *A Techno-Economic Comparison of Power Production by Biomass Fast Pyrolysis with Gasification and Combustion.* Renewable and Sustainable Energy Reviews, 2002. **6**: p. 181 - 248.

84. Diebold, J.P., *A Review of the Chemical and Physical Mechanisms of the Storage Stability of Fast Pyrolysis Bio-Oils* 2000.

85. Milne, T.A., et al., eds. *A Review of the Chemical Composition of Fast Pyrolysis Oils*. Developments in Thermal Biomass Conversion, ed. A.V. Bridgwater and D.G.B. Boocock. 1997, Blackie Academic & Professional: London, New York.

86. ASTMD7544, *Standard Specification for Pyrolysis Liquid Biofuel*, in *Petroleum Standards (D02.E0), Book of Standards Volume: 05.04*. 2009, ASTM International: West Conshohocken, PA, USA.

87. Elliot, D.C., *Water, Alkali and Char in Flash Pyrolysis of Oils.* Biomass and Bioenergy, 1994. **7**(1-6): p. 179 - 185.

88. Czernik, S. and A.V. Bridgwater, *Overview of Applications of Biomass Fast Pyrolysis Oil.* Enegry & Fuels, 2004. **18**(2): p. 590-598.

89. Diebold, J.P. and S. Czernik, *Additives To Lower and Stabilize the Viscosity of Pyrolysis Oils during Storage.* Enegry & Fuels, 1997. **11**: p. 1081-1091.

90. Piskorz, J. and D. Radlein, eds. *Determination of Biodegradation Rates of Bio-oil by Respirometry*. Fast Pyrolysis of Biomass: A Handbook, ed. A. Bridgwater, et al. 2008, Cpl Press: Newbury, HW. 119 - 134.

91. Shaddix, C.R. and D.R. Hardesty, *Combustion Properties of Biomass Flash Pyrolysis Oils: Final Project Report*. 1999, Sandia National Laboratories.

92. Shihadeh, A. and S. Hochgreb, *Diesel Engine Combustion of Biomass Pyrolysis Oils.* Enegry & Fuels, 2000. **14**: p. 260 - 274.

93. Chiaramonti, D., et al., *Development of Emulsions from Biomass Pyrolysis Liquid and Diesel and Their Use in Engines—Part 1: Emulsion Production.* Biomass and Bioenergy, 2003. **25**: p. 85-99.

94. Chiaramonti, D., et al., *Development of Emulsions from Biomass Pyrolysis Liquid and Diesel and Their Use in Engines—Part 2: Tests in Diesel Engines.* Biomass and Bioenergy, 2003. **25**: p. 101 - 111.

95. Vispute, T.P., et al., *Renewable Chemical Commodity Feedstocks from Integrated Catalytic Processing of Pyrolysis Oils.* Science, 2010. **330**: p. 1222 - 1227.

96. RedArrows. *http://www.redarrowusa.com*. 2010 - 08 - 17].

97. Oehr, K.H., D.S. Scott, and S. Czernik, *Method of Producing Calcium Salts from Biomass*, U.S. Patent, Editor. 1993, Energy Mines and Resources Canada.

98. Radlein, D., J. Piskorz, and P. Majerski, *Method of Producing Slow-Release Nitrogenous Organic Fertilizer from Biomass*. 1997: United States.

99. Beckman, D. and D. Radlein, *Slow Release Fertilizer Production Plant from Bio-Oil Technical-Economic Assessment*, in *IEA Bioenergy Task 22: Techno-Economic Assessment for Bioenergy Applications 1998–1999*, Y. Solantausta, et al., Editors. 2000, VTT TECHNICAL RESEARCH CENTRE OF FINLAND.

100. Oehr, K., *Acid Emission Reduction*, U.S. Patent, Editor. 1995, Dynamotive Corporation.

101. Galdmez, J.R., L. Garca, and R. Bilbao, *Hydrogen Production by Steam Reforming of Bio-Oil Using Coprecipitated Ni-Al Catalysts. Acetic Acid as a Model Compound.* Enegry & Fuels, 2005. **19**(3): p. 1133 - 1142.

102. Czernik, S. and R.J. French, *Production of Hydrogen from Plastics by Pyrolysis and Catalytic Steam Reform.* Enegry & Fuels, 2006. **20**(2): p. 754 - 758.

103. Czernik, S., R. Evans, and R. French, *Hydrogen from Biomass-Production by Steam Reforming of Biomass Pyrolysis Oil.* Catalysis Today, 2007. **129**: p. 265–268.

104. Czernik, S., et al., *Hydrogen by Catalytic Steam Reforming of Liquid Byproducts from Biomass Thermoconversion Processes.* Industrial and Engineering Chemistry Research, 2002. **41**(17): p. 4209-4215.

105. Wang, D., S. Czernik, and E. Chornet, *Production of Hydrogen from Biomass by Catalytic Steam Reforming of Fast Pyrolysis Oils.* Energy & Fuels, 1998. **12**(1): p. 19-24.

106. Basagiannis, A.C. and X.E. Verykios, *Steam Reforming of the Aqueous Fraction of Bio-Oil over Structured Ru/MgO/Al_2O_3 Catalysts.* Catalysis Today, 2007. **127**: p. 256 - 264.

107. Garcia, L., et al., *Catalytic Steam Reforming of Bio-Oils for the Production of Hydrogen: Effects of Catalyst Composition.* Applied Catalysis A: General, 2000. **201**: p. 225–239.

108. Carlson, T.R., T.P. Vispute, and G.W. Huber, *Green Gasoline by Catalytic Fast Pyrolysis of Solid Biomass Derived Compounds.* ChemSusChem, 2008. **1**: p. 397-400.

109. Horne, P.A., N. Nugranad, and P.T. Williams, *Catalytic Coprocessing of Biomass-Derived Pyrolysis Vapours and Methanol.* Journal of Analytical and Applied Pyrolysis, 1995. **34**: p. 87 - 108.

110. Elliott, D.C., *Historical Developments in Hydroprocessing Bio-oils.* Enegry & Fuels, 2007. **21**: p. 1792 - 1815.

111. Ramanathan, S. and S.T. Oyama, *New Catalysts for Hydroprocessing: Transition Metal Carbides and Nitrides.* Journal of Physical Chemistry, 1995. **99**: p. 16365 - 16372.

112. Wildschut, J., et al., *Hydrotreatment of Fast Pyrolysis Oil Using Heterogeneous Noble-Metal Catalysts.* Industrial and Engineering Chemistry Research, 2009. **48**: p. 10324 - 10334.

113. Xing, R., et al., *Production of Jet And Diesel Fuel Range Alkanes From Waste Hemicellulose-Derived Aqueous Solutions.* Green Chemistry, 2010. **12**: p. 1933 - 1946.

114. Subrahmanyam, A.V., S. Thayumanavan, and G.W. Huber, *C-C Bond Formation Reactions for Biomass-Derived Molecules.* ChemSusChem, 2010. **3**: p. 1158 - 1161.

115. Centeno, A., E. Laurent, and B. Delmon, *Influence of the Support of CoMo Sulfided Catalysts and of the Addition of Potassium and Platinum on the Catalytic Performances for the Hydrodeoxygenation of carbonyl, Carboxyl, and Guaiacol - Type Molecules.* Journal of Catalysis, 1995. **154**: p. 288 - 298.

116. Senol, O.I., et al., *Effect of Hydrogen Sulphide on the Hydrodeoxygenation of Aromatic and Aliphatic Oxygenates on Sulphided Catalysts.* Journal of Molecular Catalysis A: Chemical, 2007. **277**: p. 107 - 112.

117. Costa, E., et al., *Conversion of n -Butanol-Acetone Mixtures to C1-Cl0 Hydrocarbons on HZSM-5 Type Zeolites.* Industrial and Engineering Chemistry Research, 1992. **31**(4): p. 1021 - 1025.

118. Carlson, T.R., et al., *Production of Green Aromatics and Olefins by Catalytic Fast Pyrolysis of Wood Sawdust.* Energy and Environmental Science, 2011. **4**(1): p. 145 - 161.

119. Aho, A., et al., *Catalytic Pyrolysis of Biomass in a Fluidized Bed Reactor: Influence of The Acidity of H-Beta Zeolite.* Trans IChemE, Process Safety and Environmental Protection, 2007. **85** (B5): p. 473 - 480.

120. French, R. and S. Czernik, *Catalytic Pyrolysis of Biomass for Biofuels Production.* Fuel Processing Technology, 2010. **91**: p. 25 - 32.

121. Carlson, T.R., et al., *Aromatic Production from Catalytic Fast Pyrolysis of Biomass-Derived Feedstocks.* Topics in Catalysis, 2009. **52**: p. 241 - 252.

122. Aho, A., et al., *Catalytic Pyrolysis of Woody Biomass in a Fluidized Bed Reactor: Influence of the Zeolite Structure.* Fuel, 2008. **87**: p. 2493 - 2501.

123. Boateng, A.A., et al., *Guayule (Parthenium argentatum) Pyrolysis and Analysis by PY–GC/MS.* Journal of Analytical and Applied Pyrolysis, 2010. **87**: p. 14 - 23.

124. Iliopoulou, E.F., et al., *Catalytic Conversion of Biomass Pyrolysis Products by Mesoporous Materials: Effect of Steam Stability and Acidity of Al-MCM-41 Catalysts.* Chemical Engineering Journal, 2007. **134**: p. 51 - 57.

125. Pattiya, A., J.O. Titiloye, and A.V. Bridgwater, *Evaluation of Catalytic Pyrolysis of Cassava Rhizome by Principal Component Analysis.* Fuel, 2010. **89**: p. 244 - 253.

126. Pattiya, A., J.O. Titiloye, and A.V. Bridgwater, *Fast pyrolysis of cassava rhizome in the presence of catalysts.* Journal of Analytical and Applied Pyrolysis, 2008. **81**(72 - 79).

127. Adam, J., et al., *In Situ Catalytic Upgrading of Biomass Derived Fast Pyrolysis Vapours in a Fixed Bed Reactor Using Mesoporous Materials.* Microporous and Mesoporous Materials, 2006. **96**: p. 93 - 101.

128. Antonakou, E.V., V.S. Dimitropoulos, and A.A. Lappas, *Production and Characterisation of Bio-Oil from Catalytic Biomass Pyrolysis.* Thermal Science, 2006. **10**(3): p. 151 - 160.

129. Olazar, M., et al., *Pyrolysis of Sawdust in a Conical Spouted-Bed Reactor with a HZSM-5 Catalyst.* AIChE Journal, 2000. **46**(5): p. 1025-1033.

130. Adjaye, J.D. and N.N. Bakhshi, *Production of Hydrocarbons by Catalytic Upgrading of a Fast Pyrolysis Bio-Oil. Part II: Comparative Catalyst Performance and Reaction Pathways.* Fuel Processing Technology, 1995. **45**(3): p. 185-202.

131. Carlson, T.R., et al., *Catalytic Fast Pyrolysis of Glucose With HZSM-5: The Combined Homogeneous and Heterogeneous Reactions.* Journal of Catalysis, 2010. **270**: p. 110 - 124.

132. Agblevor, F.A., et al., *Fractional Catalytic Pyrolysis of Hybrid Poplar Wood.* Industrial & Engineering Chemistry Research, 2010. **49**(8): p. 3533-3538.

133. bhatia, S., *Zeolite Catalysts: Principles and Applications*. 1990, CRC Press: Florida.

134. Kokotailo, G.T., et al., *Structure of Synthetic Zeolite ZSM-5.* Nature, 1978. **272**: p. 437 - 438.

135. Olson, D.H., W.O. Haag, and R.M. Lago, *Chemical and Physical Properties of the ZSM-5 Substitutional Series.* Journal of Catalysis, 1980. **61**(2): p. 390-396.

136. Olson, D.H., et al., *Crystal Structure and Structure-related Properties of ZSM-5.* The Journal of Physical Chemistry, 1981. **85**(15): p. 2238-2243.

137. Calvin H, B., *Mechanisms of Catalyst Deactivation.* Applied Catalysis A: General, 2001. **212**(1–2): p. 17-60.

138. Naccache, C., ed. *Deactivation of Acid Catalysts*. Deactivation and Poisoning of Catalysts, ed. J. Oudar and H. Wise. 1985, Marcel Dekker: New York, USA. Chapter 5.

139. Guo, X., et al., *Analysis of Coke Precursor on Catalyst and Study on Regeneration of Catalyst in Upgrading of Bio-Oil.* Biomass and Bioenergy, 2009. **33**(10): p. 1469-1473.

140. Zhu, X., R.G. Mallinson, and D.E. Resasco, *Role of Transalkylation Reactions in the Conversion of Anisole over HZSM-5.* Applied Catalysis A: General, 2010. **379**(1–2): p. 172-181.

141. Ausavasukhi, A., T. Sooknoi, and D.E. Resasco, *Catalytic Deoxygenation of Benzaldehyde over Gallium-Modified ZSM-5 Zeolite.* Journal of Catalysis, 2009. **268**(1): p. 68-78.

142. Corma, A., et al., *Processing biomass-derived oxygenates in the oil refinery: Catalytic cracking (FCC) reaction pathways and role of catalyst.* Journal of Catalysis, 2007. **247**(2).

143. Jones, S.B., et al., *Production of Gasoline and Diesel from Biomass via Fast Pyrolysis, Hydrotreating and Hydrocracking: A Design Case.* DE-AC05-76RL01830, 2009. **PNNL-18284 Rev. 1**.

144. Wright, M.M., et al., *Techno-Economic Analysis of Biomass Fast Pyrolysis to Transportation Fuels*. 2010, National Renewable Energy Laboratory: Golden, Colorado, USA.

145. Wright, M.M., et al., *Techno-Economic Analysis of Biomass Fast Pyrolysis to Transportation Fuels.* Fuel, 2010. **89**: p. S2-S10.

146. Islam, M.N. and F.N. Ani, *Techno-Economics of Rice Husk Pyrolysis, Conversion with Catalytic Treatment to Produce Liquid Fuel.* Bioresource Technology, 2000. **73**: p. 67 75.

147. Mullaney, H., *Technical, Environmental and Economic Feasibility of Bio-Oil in New Hampshire's North Country*. 2002, New Hampshire Industrial Research Center (NHIRC): Durham, NH.

148. Bricka, M.R. *Bio-Oil the Good, Bad and the Ugly*. in *Bio Fuels Conference*. 2007. ChemE-Mississippi State University.

3. Physicochemical Properties of Bio-Oil Produced at Various Temperatures from Pine Wood using an Auger Reactor

3.1. Abstract

A fast pyrolysis process produces a high yield of liquid (a.k.a. bio-oil) and has gained a lot of interest among various stakeholders. Nonetheless, some of the properties inherent by the bio-oil create significant challenges for its wider applications. Quality of the bio-oil and its yield are highly dependent on process parameters, such as temperature, feedstock, moisture content and residence time. In this study, the effect of temperature on bio-oil quality and its yield were examined using pine wood, an abundant biomass source in the southeastern part of the United States. Physical properties of bio-oil such as pH, water content, higher heating value, solid content and ash were analyzed and compared with a recently published ASTM standard. Bio-oil produced from pine wood using an auger reactor met specifications suggested by the ASTM standard. Thirty-two chemical compounds were analyzed. The study found that the concentration of phenol and its derivatives increased with the increase in pyrolysis temperature whereas the concentration of guaiacol and its derivatives decreased as the temperature increased. Concentration of acetic and other acids remained almost constant or increased with the increase in temperature although the pH value of the bio-oil increased with the increase in temperature.

3.2. Introduction

Over the last few years, interest in using biomass derived energy/fuels has increased because of diminishing fossil fuel supply and growing concerns about its environmental issues. The Billion-Ton study showed that approximately 1.3 billion dry tons of biomass is available annually in the US, which potentially can be used to replace about 60 billion gallons of the country's annual petroleum consumption [1]. Many efforts have been made to convert biomass to liquid fuels via thermochemical and biochemical platforms. Among the various options within the thermochemical platform, a fast pyrolysis process has gained a lot of interest from academia and industries due to a high liquid yield. The fast pyrolysis process is preferred over a slow pyrolysis because of the high liquid yield and low solid yield [2]. Since the major product of fast pyrolysis is in the liquid form, it can be readily stored and transported. Further, there is a growing interest in utilizing bio-char (solid left from the pyrolysis process) as a soil amendment.

In the fast pyrolysis process, biomass is rapidly heated in the absence of oxygen [3]. As a result, biomass is decomposed to char, vapors/aerosols and gas. The vapors/aerosols are quickly condensed to a liquid called bio-oil. It is a complex mixture of more than 200 compounds containing water, sugars, acids, esters, aldehydes, ketones, furans, phenols, cresols, and guaiacols [4-5]. Bio-oil has many applications in the field of energy and fuels and can be used as a feedstock for many commodity chemicals. Bio-oil has been tested for static applications such as in boilers, furnaces, turbines and diesel engines for heat, power or electricity generations [6]. Moreover, it can be upgraded as transportation fuels by improving its negative attributes, such as high acidity, high oxygen content, high viscosity, low heating value and instability. A detailed review of bio-oil production techniques, its applications and properties is documented elsewhere

[7]. Some of these negative properties can be removed by upgrading the bio-oil through simple physical treatments while others need chemical treatments [8-13]. An extensive review of bio-oil upgrading techniques is discussed in published documents elsewhere [14-15].

A variety of reactor configurations has been developed for the fast pyrolysis of biomass [16]. An auger reactor does not require a carrier gas and easy for handling and operation. These advantages make an auger reactor one of the promising reactor configurations for the fast pyrolysis process. An auger reactor was designed and operated to produce bio-oil in this study. Many studies have reported an influence of pyrolysis parameters such as pyrolysis temperature, heating rate, feedstock composition, particle size and moisture content on the yield of bio-oil [17-20]. However, a handful of studies [21-23] reported an influence of these parameters on the physiochemical properties of bio-oil but those studies did not examine how each parameter would be influenced if the bio-oil is produced at different temperatures. In this paper, the physical and chemical properties of bio-oil produced at different temperatures were investigated to understand the influence of pyrolysis temperature in order to make the downstream process (upgrading) easier. Major physical properties such as density, pH, water content, heating value, ash and solid contents were measured and compared with the ASTM standard (D 7544-09) published recently [24]. Chemical compounds were analyzed to quantify the effect of temperature during the fast pyrolysis process.

The biomass used for bio-oil production in this study was pine wood, and the justification for using woody biomass for bio-oil production is as follows. Wood residues are widely available biomass in the US and about 368 million dry tons/year of biomass could be sustainably removed from forestlands [1]. Another study conducted by Milbrandt showed that wood residues account for 39% of total biomass available in the US [25]. Further, the state of Alabama's potential for annual wood residue was listed as 2.81 million dry tons of forest residues, 6.45 million dry tons of primary mill residues, 63 thousand dry tons of secondary mill residues, and 532 thousand dry tons of urban wood residues. Pine wood is widely available biomass in the southern part of the US. The South's market for forest products has weakened in recent years due to increasing global competition in the pulp and paper industry and mill closures due to aging facilities. Landowners are looking for new markets for their timber, and it is anticipated that a new bioenergy sector could make up for previous setbacks.

3.3. Material and Methods

3.3.1. Biomass Preparation and Characterization

Pine wood chips used in this study were obtained from a local wood chipping plant in Opelika, Alabama. Wood chips were dried in an oven at 75°C for 12 h and ground in a hammer mill (New Holland Grinder Model 358) fitted with a 1.58 mm(1/16 in.) screen size. The ground biomass sample was then fractionated using screens with sieve numbers 20 (0.84 mm opening) and 30 (0.60 mm opening). The sample that was retained on the 0.60 mm screen but passed through the 0.84 mm screen was used for bio-oil production. Moisture content of the biomass (wet basis) was determined by calculating weight loss of a sample by heating it in an oven at 103°C for 16 h according to the ASTM E 871 standard [26]. Ash content in the biomass sample was measured using the ASTM E 1755 standard. Higher heating value (HHV) of the biomass sample was measured using an oxygen bomb calorimeter (IKA, model C200).

3.3.2. Bio-oil Production using Auger Reactor

An auger reactor was used for bio-oil production and four different temperatures (425, 450, 475 and 500°C) were selected in order to obtain the highest bio-oil yield. The temperature range of 425–500°C was based on trial studies that were carried out prior to conducting this experiment. A schematic diagram of the reactor configuration is given in Figure 3.1. Two condensers were used for bio-oil collection. The second condenser, maintained at 0°C, was used to condense the vapors which escaped from the first condenser. In each experiment, about 500 g of biomass was fed into the reactor using a screw feeder. An inert atmosphere in the reactor was maintained by purging nitrogen gas before the pyrolysis process. Liquid products from the first and second condensers were collected and mixed together to determine the total yield of liquid. For each temperature, experiments were run in triplicate and the average of three values is reported in this paper. Bio-oil and char yields were calculated by measuring their weights at the end of each experiment whereas the gas yield was determined from the difference (100 minus the sum of the weight of bio-oil and char).

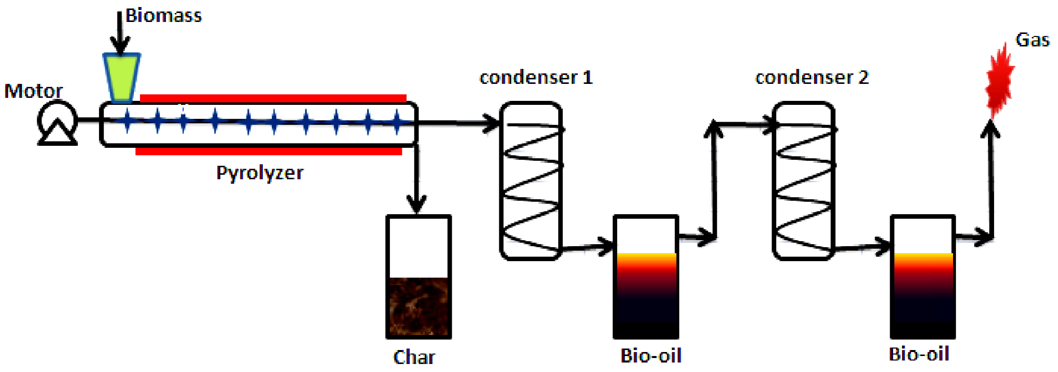


Figure 3.1: An auger reactor configuration for pyrolysis of pinewood

3.3.3. Bio-oil Analysis

Physical and chemical properties of bio-oil produced at various temperatures were measured. Physical analysis of the bio-oil includes density, pH, viscosity, water, ash, and solid content, and heating value measurements while chemical composition was determined with a gas chromatograph/mass spectrometer (GC/MS). To measure density of bio-oil, a 2 mL, calibrated density bottle (Cole-Parmer Model EW-34580-40) was filled with a known mass of bio-oil. The pH measurements were performed with a digital pH meter (Oakton, Model PC 510). Water content of bio-oil samples was calculated by Karl–Fischer (KF) analysis using a Barnstead aquametry II apparatus (Cole-Parmer Model EW-25800-10). In the volumetric KF titration, the known amount of sample was dissolved in methanol and titrated against the KF reagent (purchased from Sigma–Aldrich). The water equivalence of the KF reagent (mg of H2O/mL of KF reagent) was calculated, and the water content of the bio-oil was measured. Viscosity measurements were conducted using a rheometer (Bohlin, Model CVO 100) at 40^{o}C. Dynamic viscosity (Pa s) data were obtained as a function of shear rate (0.1–100 s^{-1}). The solids content in the bio-oil was measured as the ethanol insoluble portion. Briefly, about 1 g of bio-oil was added into a beaker containing 100 mL ethanol and mixed well. The solution was then filtered through a dried and pre-weighed filter paper (1 lm pore size) followed by drying in an oven at 105^{o}C for 30 min. The insoluble portion remaining on the dried filter paper was weighed. HHV and ash content were also determined as discussed in Section 3.3.1. Each measurement was repeated thrice and the average values are reported in the paper.

Chemical composition of bio-oil was analyzed with an Agilent 7890 GC/5975MS using a DB-1701 column (30 m; 0.25 mm i.d.; 0.25 mm film thickness). Five data points were generated for calibration in such a way that the concentration of bio-oil compounds fell within those five points. A representative bio-oil sample (~150 mg) was weighed and mixed with 3 mL of methanol and diluted to 10 mL with dichloromethane. A dilute sample was injected into the column and each sample was injected twice. The initial temperature of the column, 40°C, was maintained for 2 min, and the temperature was subsequently increased to 250 °C at 5°C/min, and the final temperature was held for 8 min. Helium of ultra high purity (99.99%) supplied from Airgas Inc. (Charlotte, NC) was used as a carrier gas and flowed at 1.25 mL/min. The injector and the GC/MS interface were kept at constant temperature of 280 and 250°C, respectively. Compounds were ionized at 69.9 eV electron impact conditions and analyzed over a mass per change (m/z) range of 50–550. Bio-oil compounds were identified by comparing the mass spectra with the NIST (National Institute of Standards and Technology) mass spectral library. Thirty-two compounds were selected for quantification.

3.3.4. Bio-char Analysis

The physical properties of bio-char, such as moisture content, ash content and heating value were, measured as described in Section 3.3.1.

3.4. Results and Discussion

3.4.1. Biomass Characterization

The physical properties of a feedstock play a major role in bio-oil yield and its properties. The moisture content of biomass used for the pyrolysis was found to be as 5.79 ± 0.34 wt%. Pine wood used in this study had a higher heating value of 18.14 ± 0.20 MJ/ kg. The ash content of the pine wood biomass sample was found as 0.7 ± 0.09 wt%.

3.4.2. Product Yield

Pyrolysis of pine wood was performed at four different temperatures from 425 to 500°C to find a temperature for maximum bio-oil yield. Yields of pyrolysis products as a function of temperature are given in Figure 3.2. Pyrolysis of pine wood at 425°C gave 45 wt% bio-oil and 35 wt% char. As the pyrolysis temperature increased to 450°C, the yield of bio-oil increased to 50 wt% and a further increase in pyrolysis temperature resulted in a net decrease of bio-oil yield. These numbers are comparable with previous studies [27-29] of bio-oil production from pine wood in continuous auger reactors. As the pyrolysis temperature increased from 425 to 500°C, the yield of char decreased continuously and the yield of gas increased monotonically. Similar trends in product yields have been noticed for the pyrolysis of different types of biomass types [17, 23, 30]. This is because the primary decomposition of biomass will take place at a lower pyrolysis temperature and, as the temperature increases, the pyrolytic vapors will be further cracked into low molecular weight organic compounds and gaseous products.

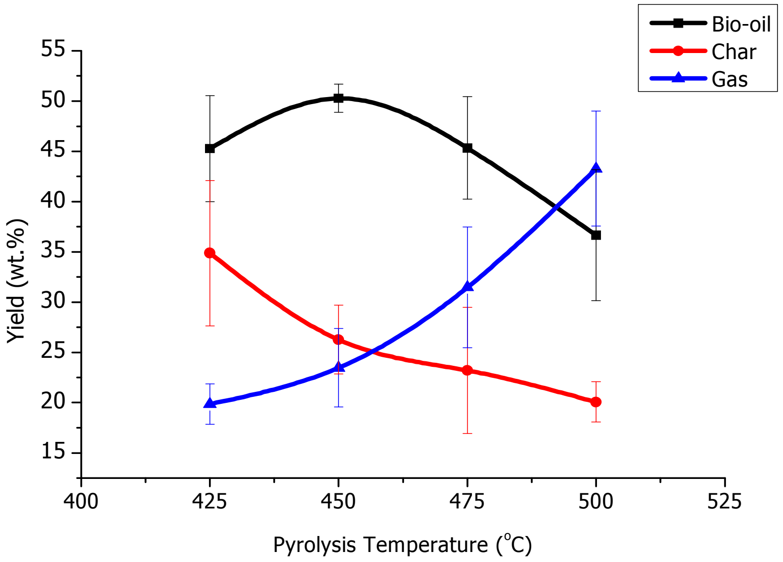


Figure 3.2: Product yield of pine wood pyrolysis at selected temperature

ANOVA analysis (95% confidence interval) was performed for the data collected on the yields of bio-oil, char and gas during the pyrolysis. The smaller p-values (<0.05) indicate the significant effect of pyrolysis temperature on the yield. The p-value for the yield data of bio-oil was 0.0549. Since bio-oil had optimum yield at 450°C, the statistical analysis could not give conclusive evidence for the effect of pyrolysis temperature on the yield of bio-oil and therefore, the Tukey–Kramer procedure was also used. The Tukey–Kramer procedure for multiple comparison sorted bio-oil yields at 425, 450, and 475°C as one group and bio-oil yields at 425, 475, and 500°C as another. That means, there was a significant change (decrease) in the yield of bio-oil when the final pyrolysis temperature changed from 450 to 500°C. The p-value for char yield data (0.0392) provided moderate evidence for the decrease in the yield of char when the pyrolysis temperature increased from 425 to 500°C whereas there was a significant increase in the gas yield with the increase in pyrolysis temperature (p-value = 0.0013).

3.4.3. Physical Analysis of Bio-oil

There were some physical differences between bio-oils collected from the first and second condensers. Bio-oil collected from the second condenser had lower amounts of tar components than that of the first condenser's bio-oil. It was noticed that heavier compounds in the bio-oil tend to settle when stored for several days without any disturbance. However, in this study, bio-oils from both condensers were mixed well to avoid any physical separation of phases prior to physical and chemical analyses. Physical properties, such as density, pH, calorific value, water content, solid content and ash content were measured to characterize the bio-oil produced at different temperatures, and the results are summarized in Table 3.1. Average and standard deviation of the experiments were calculated and ANOVA test (95% confidence interval) was used to determine the p-value for null hypothesis. The null hypothesis was that the average of each property at four different temperatures would be same. If the p-value > 0.05, the null hypothesis is true whereas the p-value < 0.05 indicates that the given data failed to prove the null hypothesis and, therefore, there is a change in the property with the temperature. In addition, the properties of bio-oil were compared with the ASTM standard D 7544-09.

Table 3.1: Physical properties of bio-oil produced at selected temperature[†]

Bio-oil properties	Pyrolysis Temperature, °C				p-value from ANOVA test	ASTM Standard D 7544-09
	425	450	475	500		
Density, kg/m^3	1174±40	1156±17	1142±26	1138±31	0.0594	1100-1300
pH	2.1±0.09	2.2±0.08	2.3±0.07	2.4±0.07	<0.0001	Report
Water, wt%	20.8±3.9	21.0±4.6	20.3±2.8	20.6±3.9	0.9773	30 max.
HHV, MJ/kg	18.6±0.8	19.1±1.3	18.4±0.5	19.7±1.2	0.1452	15 min.
Ash, wt%	0.12±0.09	0.10±0.06	0.12±0.05	0.11±0.03	0.9511	0.25
Solid, wt%	0.3±0.17	0.4±0.13	0.5±0.21	0.7±0.36	0.005	2.5 max.

[†] values are means of repeated analyses and numbers after ± are standard deviations.

Bio-oils produced at four temperatures met the specifications listed in ASTM D 7544-09. The p-value from the ANOVA test indicated that there was a small decrease in the density of the bio-oil for the increase in pyrolysis temperature; however, it was not a significant change. Concurrently, statistical analysis showed that pH and solid content of the bio-oil were significantly affected ($p < 0.05$) by pyrolysis temperature. The pH and solid content of the bio-oil increased with pyrolysis temperature. A similar change in pH of the bio-oil with the increase in pyrolysis temperature was also documented elsewhere [21]. On the other hand, water content, HHV and ash content of bio-oil were almost constant with the increase in pyrolysis temperature and therefore not significantly affected by pyrolysis temperatures. Since the ash content was constant at four temperatures, the increase in solid content might be due to the presence of char particles. More char particles escaped into the vapor phase at higher pyrolysis temperatures. Use of a cyclone or electrostatic precipitator before condensation may solve this problem.

3.4.4. Viscosity Analysis

Viscosity is a significant physical property of fuels that should be considered when attempting to design and select handling, processing and transportation equipment. In general, viscosity of bio-oil is relatively higher than that of other liquid fuels (0.011 Pa s for diesel and 0.006 Pa s for gasoline). Viscosity analysis of the bio-oil was carried out at 40^{o}C. Figure 3.3 shows the variation in viscosity as the shear rate increased from 0.1 to 100 s^{-1}. Bio-oil had a higher viscosity at low shear rate but the viscosity decreased exponentially as the shear rate increased up to 10 s^{-1}. At a higher shear rate (shear rate > 20 s^{-1}), bio-oil behaved as a Newtonian fluid (constant viscosity). Further analysis of bio-oil (produced at 450^{o}C) showed that its viscosity decreased as the measurement temperature increased. For example, Figure 3.4 shows that the viscosity of the bio-oil at 30^{o}C was 6–7 times greater than it was at 80^{o}C. The effect of temperature on viscosity was described by the Arrhenius relation (Eq. 2.1). Viscosity of bio-oil (produced at 450^{o}C) was measured at different temperatures between 10 and 80^{o}C to determine activation energy for flow.

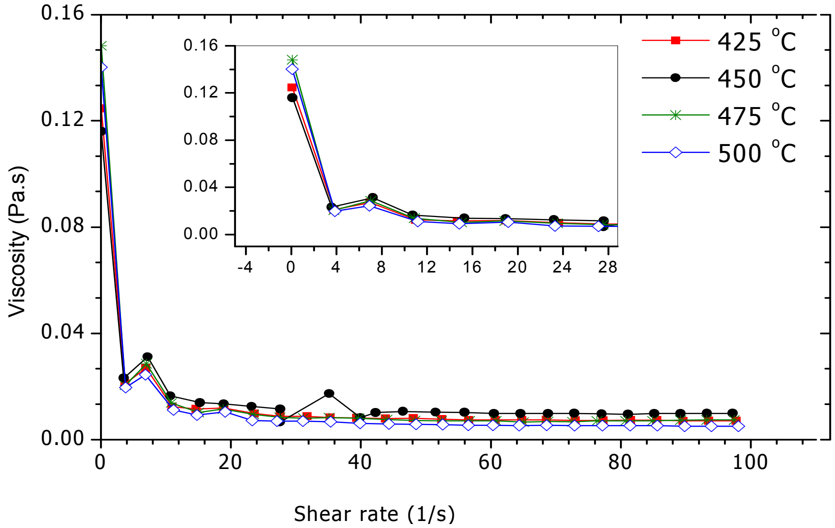


Figure 3.3: Viscosity of bio-oils at selected shear rates

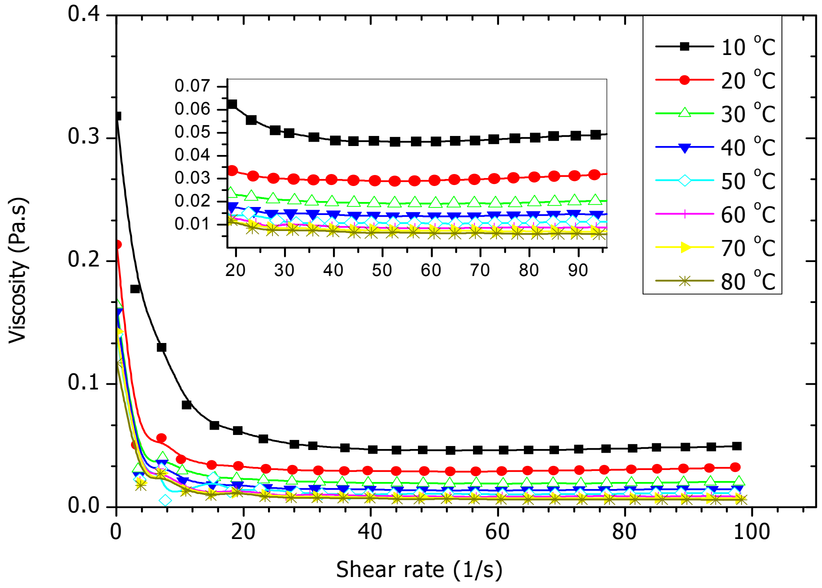


Figure 3.4: Variation of bio-oil viscosity with temperature and shear rate

The Arrhenius relation for viscosity with an effect of temperature, T, can be expressed as follows:

$$\mu = Ae^{E/RT} \text{……………………………………… (Equation 3.1)}$$

where μ represents the viscosity of bio-oil, A is a constant (unit is similar to viscosity unit), E is the flow activation energy and R is the universal gas constant.

Equation 3.1 can be expressed as follows:

$$ln\,\mu = ln\,A + E/RT \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(Equation 3.2)}$$

A plot for ln μ vs. 1/T is illustrated in Figure 3.5. Here, the viscosity was measured only in the Newtonian range (shear rate > 20 s^{-1}). The p-value for parameters (intercept and slope) was < 0.0001 with a confidence interval of 95% which indicates the strength of these values. The values of A and E were calculated for the data presented in Figure 3.5, which are given as A = 3.623 x 10^{-9} Pa.s and E = 41.04 kJ/mol. Leroy et al. reported similar values of A and E for 16 pyrolytic wood derived oils [31].

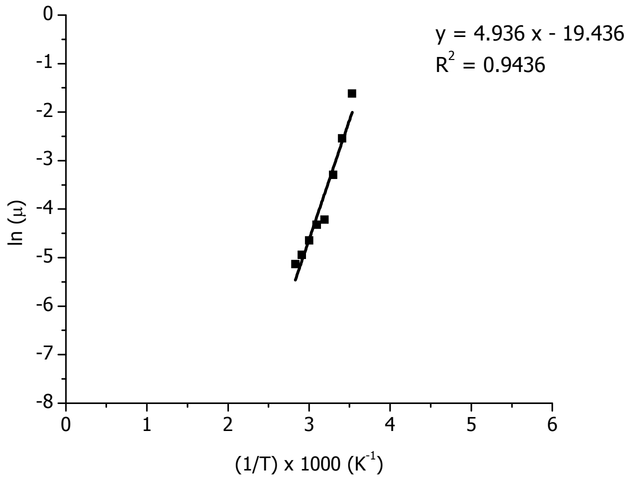


Figure 3.5: Variation of bio-oil viscosity (in logarithmic scale) with the inverse of temperature

3.4.5. Chemical Analysis of Bio-oil

Thirty-two compounds from pine wood bio-oil were quantified and those compounds were grouped as carbohydrates, aromatics, furans, phenols and cresols and guaiacols (Table 3.2).

Similar classification was seen in another document also [32]. The group named carbohydrates included all straight chain compounds with carbon, hydrogen and oxygen molecules. Branca et al. subdivided the carbohydrates group in to major and minor carbohydrates [32]. Table 3.2 depicts an average concentration (six measurements from three samples) of each compound from bio-oil produced at 425°C and the relative yield of each compound at different pyrolysis temperatures.

The concentration of acetic acid was almost steady with the change in pyrolysis temperature while the concentration of propionic and crotonoic acid increased with pyrolysis temperatures. Based on the compounds identified, chemical analysis contradicted to the physical analysis where the acidity decreased with the increase in temperature. It is a general conception that the high acidity of bio-oil is due to the presence of organic acids in which acetic acid is a major compound. However, this study showed that the concentration of acetic acid did not decrease with the increase in temperature. Based on the chemical analysis, a conclusion cannot be drawn as to why the pH value of bio-oil increased with the increase in temperature. Furthermore, there was a sudden increase in the concentration of 2-cyclopenten-1-one, 3-methyl when the temperature increased from 450 to 475°C while 1,2-cyclopentanedione, 3-methyl had a higher concentration at 450 and 475°C. Maximum yield of levoglucosan was found at 475°C.

Table 3.2: Concentration of bio-oil compounds and their relative yield at selected temperature

Compounds	**Concentration, wt.%**		**Relative Yield**			
			Pyrolysis Temp, ^{o}C			
	average	std. dev.	425	450	475	500
Carbohydrates						
Acetic acid	0.21	0.028	1	1.11	0.94	1.05
Propoinic acid	0.01	0.001	1	1.42	1.87	2.27
Crotonic acid	0.19	0.075	1	1.71	2.71	3.02
2-Cyclopenten-1-one, 3-methyl-	0.07	0.017	1	1.41	2.25	2.26
1,2-Cyclopentanedione, 3-methyl-	0.67	0.082	1	1.22	1.19	0.98
1,6-Anhydro-.beta.-D-glucopyranose (levoglucosan) and other anhydrosugars‡	6.37	0.146	1	1.60	1.74	1.43
BTX						
Toluene	0.04	0.016	1	1.37	0.77	0.34
Furans						
Furfural	0.75	0.080	1	1.11	1.14	0.95
2-Furancarboxaldehyde, 5-methyl-	0.02	0.006	1	1.19	1.27	1.01
2(5H)-Furanone	0.74	0.076	1	0.89	0.57	0.36
2-Furancarboxaldehyde, 5-(hydroxymethyl)-	0.38	0.018	1	1.11	0.98	0.87
Phenols , Cresols and Catechols						
Phenol	0.05	0.007	1	1.50	2.95	3.48
Phenol, 2-methyl-; (o-Cresol)	0.05	0.011	1	1.53	2.80	2.79
Phenol, 2,6-dimethyl; (2,6-Xylenol)	0.05	0.001	1	1.23	1.47	1.55
2-Hydroxy-5-methylbenzaldehyde	0.03	0.004	1	1.20	1.66	1.17
Phenol, 4-methyl-; (p-Cresol)	0.09	0.025	1	1.53	2.99	3.04
Phenol, 2-ethyl-	0.00	0.000	1	1.18	2.15	1.93
Phenol, 2,4-dimethyl-; (m-Xylenol)	0.08	0.008	1	1.59	3.11	2.76
Phenol, 2,3-dimethyl-; (o-Xylenol)	0.01	0.002	1	1.37	2.66	2.22
phenol, 4 ethyl	0.01	0.003	1	1.60	3.31	3.24
1,2-Benzenediol; (pyrocatechol)	0.23	0.036	1	1.65	2.81	3.29
1,2-Benzenediol, 4-methyl-; (Homocatechol)	0.11	0.033	1	1.79	3.36	3.37
1,4-Benzenediol, 2-methyl-; (p-Toluhydroquinone)	0.02	0.002	1	1.27	1.44	1.36
1,3-Benzenediol, 4-ethyl-; (4-Ethylcatechol)	0.20	0.091	1	2.34	6.06	5.79
Guaiacols						
Phenol, 2-methoxy (Guaiacol)	0.35	0.056	1	0.87	0.50	0.29
Phenol, 2-methoxy-4-methyl- (Homoguaiacol)	0.34	0.082	1	0.88	0.44	0.24
Phenol, 4-ethyl-2-methoxy- (p-ethyl guaiacol)	0.10	0.029	1	0.96	0.57	0.39
2-Methoxy-4-vinylphenol (p-vinyl guaiacol)	0.08	0.024	1	0.74	0.43	0.15
Eugenol; (Phenol, 2-methoxy-4-(2-propenyl))	0.13	0.033	1	0.86	0.46	0.21
cis & trans Isoeugenol	0.29	0.113	1	0.93	0.64	0.36
Vanillin (Benzaldehyde, 4-hydroxy-3-methoxy)	0.17	0.027	1	0.99	0.60	0.38
Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-; (Acetoguaiacone)	0.11	0.016	1	0.92	0.45	0.26
Total	**11.95**					

‡Other anhydrosugar peaks were identified closer to the levoglucosan peak. Entire area of anhydrosugar peaks was taken and the concentration was calculated by using levoglucosan.

Most of the phenol and its derivatives (cresols and catechols) behaved similarly in terms of the change in pyrolysis temperature. There was a rapid increase in the concentration of phenol derivatives when the pyrolysis temperature increased from 450 to 475°C. Simultaneously, the concentration of guaiacol and its derivatives decreased as the pyrolysis temperature increased from 425 to 500°C. Similar behavior was noticed for bio-oils produced from beech wood, spruce wood, olive husk and hazelnut shell [33]. This is because, as the temperature increases, the guaiacol compounds are further cracked down in to phenols, cresols and catechols. Phenol derivatives are easier to hydrogenate than guaiacol derivatives.

3.4.6. Bio-char analysis

The physical properties of bio-char also were measured as a function of pyrolysis temperature and depicted in Table 3.3. Statistical analysis was performed to determine the effect of temperature on different properties. The low p-value from the ANOVA test for the higher heating value of bio-char indicated that the HHV of bio-char increased with the increase in pyrolysis temperature.

The high heating value of bio-char makes it an attractive feed for energy production. In addition, McHenry (2009) listed the importance and application of bio-char in agricultural sustainability and greenhouse gas emission reduction. Based on the statistical analysis, it can be found that the moisture content of bio-char was not affected with the change in pyrolysis temperature while the ash content was increased with the increase in pyrolysis temperature.

Table 3.3: Physical properties of bio-char obtained from pine wood[‡]

Bio-char Properties	Pyrolysis temperature, °C				p-value from ANOVA test
	425	450	475	500	
HHV, MJ/kg	24.39±1.06	26.50±0.40	26.79±2.21	28.13±1.52	0.0025
Moisture content, wt%	2.97±0.15	2.82±0.17	2.71±0.10	2.87±0.33	0.2037
Ash content, wt%	0.88±0.15	1.20±0.29	1. 39±0.29	1.59±0.23	0.0005

[‡] values are means of repeated analyses and numbers after ± are standard deviations

3.5. Conclusions

Pyrolysis of pine wood was performed at selected temperatures from 425 to 500°C in an auger reactor and the maximum yield of bio-oil was obtained at 450°C. The physical properties of bio-oil produced at four temperatures were measured and compared with the ASTM standard. The bio-oil produced from pine wood met the specifications for the measured properties. Viscosity analysis showed Newtonian behavior of bio-oil at higher shear rates (shear rate $>20\ s^{-1}$) and Newtonian viscosity of bio-oil was measured at various temperatures (10–80°C) with the flow activation energy of pine wood bio-oil found to be 41.0 kJ/mol. Based on the chemical analysis, some of the carbohydrate compounds and most of the furan compounds had a higher concentration either at 450 or at 475°C. The concentration of phenol and its derivatives was increased whereas the concentration of guaiacol and its derivatives was decreased with the increase in pyrolysis temperature. A modest compromise in the yield (5 wt %) could provide bio-oil with better composition which would make the downstream process easier. Therefore, fast pyrolysis of pine wood at 475°C would be an appropriate temperature for the production of bio-oil.

3.6. Acknowledgement

The authors would like to acknowledge the Alabama Agricultural Experiment Station (AAES) and the Center for Bioenergy and Bioproducts of Auburn University for funding this study. Also, the authors would like to express sincere thanks to Mr. Russell Davis and Ms. Anshu Shrestha for their assistance in collecting data. However, only the authors are responsible for the opinions expressed in this paper and for any remaining errors.

3.7. References

1. Perlack, R.D., et al., *Biomass as a Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-Ton Annual Supply*. 2005, USDA/DOE.

2. Bridgwater, A.V., *Principles and Practice of Biomass Fast Pyrolysis Processes for Liquids.* Journal of Analytical and Applied Pyrolysis, 1999. **51**: p. 3-22.

3. Gupta, R.B. and A. Demirbas, *Gasoline, Diesel and Ethanol Biofuels from Grasses and Plants*. 2010, Cambridge University Press: New York, USA. p. 140 - 157.

4. Diebold, J.P., *A Review of the Chemical and Physical Mechanisms of the Storage Stability of Fast Pyrolysis Bio-Oils* 2000.

5. Milne, T.A., et al., eds. *A Review of the Chemical Composition of Fast Pyrolysis Oils*. Developments in Thermal Biomass Conversion, ed. A.V. Bridgwater and D.G.B. Boocock. 1997, Blackie Academic & Professional: London, New York.

6. Czernik, S. and A.V. Bridgwater, *Overview of Applications of Biomass Fast Pyrolysis Oil.* Enegry & Fuels, 2004. **18**(2): p. 590-598.

7. Mohan, D., C.U.P. Jr., and P.H. Steele, *Pyrolysis of Wood/Biomass for Bio-Oil: A Critical Review.* Energy & Fuels, 2006. **20**: p. 848-889.

8. Adjaye, J.D. and N.N. Bakhshi, *Production of Hydrocarbons by Catalytic Upgrading of a Fast pyrolysis Bio-Oil. Part I: Conversion Over Various Catalysts.* Fuel Processing Technology, 1995. **45**: p. 161-183.

9. Chiaramonti, D., et al., *Development of Emulsions from Biomass Pyrolysis Liquid and Diesel and Their Use in Engines—Part 1: Emulsion Production.* Biomass and Bioenergy, 2003. **25**: p. 85-99.

10. Diebold, J.P. and S. Czernik, *Additives To Lower and Stabilize the Viscosity of Pyrolysis Oils during Storage.* Enegry & Fuels, 1997. **11**: p. 1081-1091.

11. Qi, Z., et al., *Review of Biomass Pyrolysis Oil Properties and Upgrading Research.* Energy Conversion and Management, 2007. **48**: p. 87-92.

12. Senol, O.I., T.R. Viljava, and A.O.I. Krause, *Hydrodeoxygenation of Methyl Esters on Sulphided NiMo/c-Al2O3 and CoMo/c-Al2O3 Catalysts.* Catalysis Today, 2005. **100**: p. 331-335.

13. Zhang, Q., et al., *Upgrading Bio-oil over Different Solid Catalysts.* Enegry & Fuels, 2006. **20**: p. 2717-2720.

14. Elliott, D.C., *Historical Developments in Hydroprocessing Bio-oils.* Enegry & Fuels, 2007. **21**: p. 1792 - 1815.

15. Furimsky, E., *Catalytic Hydrodeoxygenation.* Applied Catalysis A: General, 2000. **199**: p. 147-190.

16. Bridgwater, A.V. and G.V.C. Peacocke, *Fast Pyrolysis Processes for Biomass.* Renewable and Sustainable Energy Reviews, 2000. **4**: p. 1-73.

17. Asadullah, M., et al., *Production of Bio-Oil from Fixed Bed Pyrolysis of Bagasse.* Fuel, 2007. **86**(16): p. 2514-2520.

18. Demirbas, A., *Kinetics for Non-Isothermal Flash Pyrolysis of Hazelnut Shell.* Bioresource Technology, 1998. **66**(3): p. 247-252.

19. Park, H.J., Y.-K. Park, and J.S. Kim, *Influence of Reaction Conditions and the Char Separation System on the Production of Bio-Oil from Radiata Pine Sawdust by Fast Pyrolysis.* Fuel Processing Technology, 2008. **89**(8): p. 797 - 802.

20. Sensoz, S., I. Demiral, and H.F. Gercel, *Olive Bagasse (Olea europea L.) Pyrolysis.* Bioresource Technology, 2006. **97**(3): p. 429-436.

21. He, R., et al., *Influence of Pyrolysis Condition on Switchgrass Bio-Oil Yield and Physicochemical Properties.* Bioresource Technology, 2009. **100**(21): p. 5305-5311.

22. Horne, P.A. and P.T. Williams, *Influence of Temperature on the Products from the Flash Pyrolysis of Biomass.* Fuel, 1996. **75**(9): p. 1051-1059.

23. Lee, S.-H., et al., *The Yields and Composition of Bio-Oil Produced from Quercus Acutissima in a Bubbling Fluidized Bed Pyrolyzer.* Journal of Analytical and Applied Pyrolysis, 2008. **83**(1): p. 110-114.

24. ASTMD7544, *Standard Specification for Pyrolysis Liquid Biofuel*, in *Petroleum Standards (D02.E0), Book of Standards Volume: 05.04*. 2009, ASTM International: West Conshohocken, PA, USA.

25. Milbrandt, A., *A Geographic Perspective on the Current Biomass Resource Availability in the United States*, in *NREL*. 2005.

26. ASTME871-82, *Standard Test Method for Moisture Analysis of Particulate Wood Fuels*. 2006, American Society for Testing and Materials.

27. Bhattacharya, P., et al., *Wood/Plastic Copyrolysis in an Auger Reactor: Chemical and Physical Analysis of the Products.* Fuel, 2009. **88**(7): p. 1251-1260.

28. Garcia-Perez, M., et al., *Production and Fuel Properties of Pine Chip Bio-oil/Biodiesel Blends.* Enegry & Fuels, 2007. **21**(4): p. 2363-2372.

29. Ingram, L., et al., *Pyrolysis of Wood and Bark in an Auger Reactor: Physical Properties and Chemical Analysis of the Produced Bio-oils.* Enegry & Fuels, 2008. **22**(1): p. 614-625.

30. Ji-lu, Z., *Bio-oil from Fast Pyrolysis of Rice Husk: Yields and Related Properties and Improvement of the Pyrolysis System.* Journal of Analytical and Applied Pyrolysis, 2007. **80**(1): p. 30-35.

31. Leroy, J., L. Choplin, and S. Kaliaguine, *Rheological Characterization of Pyrolytic Wood Derived Oils: Existence of a Compensation Effect.* Chemical Engineering Communications, 1988. **71**: p. 157-176.

32. Branca, C., P. Giudicianni, and C.D. Blasi, *GC/MS Characterization of Liquids Generated from Low-Temperature Pyrolysis of Wood.* Industrial and Engineering Chemistry Research, 2003. **42**(14): p. 3190-3202.

33. 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): p. 591-597.

4. Influence of Pyrolysis Operating Conditions on Bio-Oil Components

4.1. Abstract

A fast pyrolysis process has emerged as one of the techniques to produce transportation fuels using various biomass types that are regionally important. It is well understood that high heating rates, very small particles with low mass transfer limitations, and moderate operating temperatures are essential for obtaining high yield of liquid from the fast pyrolysis process. However, how the heating rates and operating temperatures would influence individual compounds in the liquid obtained from the fast pyrolysis process has not been studied in detail. Therefore, a microscale pyrolysis study was performed by changing different parameters (biomass type, filament heating rate, and final pyrolysis temperature) to understand the influence of these operating parameters on each compound formed during the process. Two biomass types (pine wood and switchgrass) were selected for this study: (i) pine wood was selected because of its availability in the southeastern region of the United States, and (ii) switchgrass was chosen because it has been identified as one of the bioenergy crops in the United States. Pyrolysis temperatures were changed from 450 to 750 ^{o}C in increments of 50 ^{o}C, whereas the heating rates selected were 50, 100, 500, 1000, and 2000 ^{o}C/s. Twenty-eight bio-oil compounds were quantified in each experimental condition.

This study found that phenols and toluene concentrations increased with the increase in pyrolysis temperature irrespective to the biomass type. On the other hand, the change in the yield of ketones, furans, and guaiacols with the change in pyrolysis temperature depended on the type of biomass. The effect of filament heating rate on bio-oil yield was not statistically significant because the biomass heating rate was almost constant irrespective of different filament heating rates.

4.2. Introduction

Biomass is considered to be one of the alternative resources to meet future energy demand. As a result, interest in converting biomass to valuable energy forms has been increased over several years. The "Energy Independence and Security Act of 2007" has mandated 36 billion gallons per year of biofuels by 2022 as transportation fuel. Among the biofuels, advanced biofuels (other than corn bioethanol and soybean biodiesel) account for 20 billion gallons [1]. In order to achieve 20 billion gallons/year of biofuel by 2022, both biochemical and thermochemical processes have to be utilized. A fast pyrolysis (residence time of up to 2 s), a thermochemical process, can attain a high liquid yield from lignocellulosic biomass [2]. The uniqueness of the fast pyrolysis process is the flexibility of feedstock and the high liquid yield, up to 70% of dry biomass [3-5]. In the fast pyrolysis process, biomass is rapidly heated in the absence of oxygen [6]. As a result, biomass is decomposed to char, vapors and aerosols, and gas. The vapors and aerosols are quickly condensed to a liquid called bio-oil which is a mixture of more than 300 compounds and has many applications. The major applications of bio-oil are as a feedstock for commodity chemicals and as an intermediate for fuel production. In addition, bio-oil has been tested for static applications such as boilers, furnaces, turbines, and diesel engines for heat, power, or electricity generation [7]. However, the final applications of bio-oil are limited because of some of the negative attributes, such as high density, viscosity, acidity, water, oxygen, and low heating value. Some of these negative attributes can be removed partially through physiochemical treatments [8-10]. Although there are different techniques to upgrade bio-oil as transportation fuel, none of the processes have been demonstrated commercially [11]. Current studies are being focused on optimizing pyrolysis conditions, upgrading bio-oil, and finding more applications for bio-oil [12].

A detailed analysis of chemical composition in bio-oil is required to optimize the pyrolysis process for its final applications. Composition of bio-oil varies with the properties of biomass, pyrolysis temperature, heating rate, and the pyrolytic environment. Although a number of studies reported the influence of these parameters on bio-oil yield [13-18], only a handful of studies [19-23] have analyzed bio-oil's chemical composition. However, previous studies did not evaluate the significance of changing each pyrolysis process parameter on an individual species yield [24-25]. To fill the knowledge gap in the field, this study systematically investigated the change in the yield of individual components of bio-oil by changing process parameters such as biomass type, pyrolysis temperature, and heating rate. Biomass types used in this study were pine wood and switchgrass. Pine wood is the primary forest woody biomass available in the southeastern region [26]. Furthermore, the South's market for forest products has weakened in recent years due to increasing global competition in the pulp and paper industry and mill closures due to aging facilities [27], and it is expected that biorefineries will rejuvenate this industry. Switchgrass can be grown on marginal lands that are not well suited for food crops and it has a tolerance for cold temperatures [28-29]. Also, it has been designated as an energy crop by the

U.S. Department of Energy because of its high yield, excellent conservation attributes, and good compatibility with conventional farming practices [30-31].

4.3. Materials and Methods

4.3.1. Biomass Characterization

Pine wood chips were obtained from a local wood chipping plant in Opelika, Alabama, and a switchgrass (Alamo cultivar) sample was obtained from the E.V. Smith Research Center of Auburn University in Shorter, Alabama. Pine wood chips were dried in a furnace at 75 ^{o}C for 12 h prior to size reduction; whereas switchgrass was ground without drying (it was stored in a room for more than two years). A hammer mill (New Holland grinder model 358, New Holland, PA.) with 1.58-mm (1/16 in.) sieve size was used for particle size reduction. These biomass samples were further ground in a coffee grinder to make them fine powder (particle size <420 μm). Particle size distribution of these biomass samples was measured. Moisture content of the biomass samples (wet basis) was determined by calculating weight loss after heating the samples in an oven at 103 ^{o}C for 16 h according to ASTM E 871 standard, and the ash content was measured using ASTM E 1755 standard. Chemical constituents of biomass samples were analyzed in the Bioenergy Laboratory at the Center for Bioenergy and Bioproducts, Auburn University, according to “Standard Biomass Analytical Methods” developed by the National Renewable Energy Laboratory [32].

4.3.2. Pyrolysis GC/MS

Pyrolysis studies were carried out using a commercial pyrolyzer (Pyroprobe model 5200, CDS Analytical Inc., Oxford, PA), which was interfaced with a gas chromatograph/mass spectrometer (GC/MS). The pyrolyzer had a probe that contained a computer-controlled heating element, and the heating element held the finely ground biomass in the middle of a quartz tube (25 mm long, 1.9 mm i.d.). The final filament temperature was maintained for 30 s to minimize temperature gradient in the quartz tube. The actual temperature inside the quartz tube should be approximately 100 ^oC lower than the filament temperature (according to the manufacturer's manual) but the test runs using a thin thermocouple (K-type, probe diameter 0.5 mm, time constant 0.85 s) showed that the temperature gradient between filament and biomass was not always constant and varied between 50 and 125 ^oC depending up on the final filament temperature. Therefore, the pyrolysis temperature reported in this study is the filament temperature that heats biomass inside the quartz tube for consistency. Pine wood and switchgrass were pyrolyzed at seven different filament temperatures at a constant heating rate (100 ^oC /s) and four different filament heating rates, 50, 100, 1000, and 2000 ^oC /s, to a filament temperature of 550 ^oC. About 100 μg of biomass sample was taken for pyrolysis and the sample was pyrolyzed at selected filament temperatures and heating rates under inert conditions using helium gas. Biomass was converted into vapors and the helium gas carried the pyrolysis vapors from the probe to a trap (adsorbent), which was resting at 40 ^oC. The trap adsorbed the condensed bio-oil components and the noncondensed vapors were purged with helium gas. Noncondensable gases were not analyzed in this study. The adsorbed bio-oil was desorbed by heating a trap to 300 ^oC, and the vapors were carried out using helium gas for GC analysis; a similar method has been used in earlier works [33-35]. Also, there could be a possibility of poly condensation reactions leading to the formation of solid residues in a trap but it was not investigated. All the pyrolysis experiments were repeated five times.

The bio-oil components were analyzed with an Agilent 7890 GC/5975MS using a DB-1701 column (30 m; 0.25 mm i.d.; 0.25 mm film thickness). Twenty-eight compounds were selected for quantification, and pure forms of these chemicals were purchased from Sigma-Aldrich. Stock solutions were made by weighing about 100 mg of these chemicals, and dissolving each chemical in 2 mL of methanol then made to 100 mL by adding dichloromethane. Aliquots of solution were diluted with dichloromethane to different concentrations in such a way that the concentration of bio-oil compounds fell within the range. The diluted solutions were injected into a GC/MS for analysis. Each solution was injected twice, and the average area of the two injections was determined. The area was plotted against the quantity injected and five data points were generated. The slope of the calibration line was taken as the quantification factor. A split ratio of 125:1 was selected for injection. The injector and the GC/MS interface were kept at constant temperatures of 280 and 250 ^{o}C, respectively. The initial temperature of the column, 40 ^{o}C, was maintained for 2 min and was subsequently increased to 250 at 5 ^{o}C /min. The final temperature was maintained for 8min.Heliumof ultra high purity (99.999%) supplied fromAirgas Inc. (Charlotte, NC) was used as a carrier gas and flowed at 1.25 mL/min.Compounds were ionized at 69.9 eV electron impact conditions and analyzed over a mass per charge (m/z) range of 50-550. Bio-oil compounds were identified by comparing the mass spectra with the NIST (National Institute of Standards and Technology) mass spectral library.

4.3.3. Quantification

All anhydrosugar compounds were quantified according to levoglucosan quantification and their combined yield was reported. The same quantification factor was used for similarly structured compounds (if pure chemical was not available) [33]. Twenty-eight compounds from pine wood pyrolysis were identified and quantified. Quantified compounds include ketone, anhydrosugars, furans, aromatics, phenols, and guaiacols. The other anhydro sugars were 1,4:3,6-dianhydro-RD- glucopyranose, and 2,3-anhydro-D-mannosan. Toluene was the only compound to represent the aromatics group. The quantified elements in each group are listed in Table 4.1. The yield of each compound was calculated as the weight of the compound/weight of the biomass used for pyrolysis. Therefore, all wt % reported in this study were based on the weight of biomass. The average yield and its standard deviation for all compounds produced under each pyrolysis condition were reported. An ANOVA analysis (95% confidence interval) was performed for the data collected on the yields of all compounds. The ANOVA test was used to determine the p-value for null hypothesis. The null hypothesis was that the average yield of a compound with a change in one of the operating parameters (temperature, heating rate, or biomass) would be the same. The p-value <0.05 indicates that there is a significant effect of pyrolysis parameters on the yield with 95% confidence interval (CI) and all the statistical tests were done at 95% CI unless it is mentioned otherwise [36].

4.4. Results and Discussion

4.4.1. Biomass Characterization

Particle size distribution of biomass samples is given in Figure 4.1. For both the biomass samples, about 65-70% of particles were less than 250 μm. Physical properties and chemical constituents of biomass samples are listed in Table 4.2. Types of sugar available in pine wood and switchgrass vary, and, as expected, xylan (C_5) is significantly lower in the case of pine wood as compared to switchgrass. Also, ash content in switchgrass is higher than in pine wood.

Table 4.1: Quantified bio-oil compounds from pine wood and switchgrass

Ketones	**Guaiacols**
2-Cyclopenten-1-one, 2-methyl-	Phenol, 2-methoxy; (Guaiacol)
2-Cyclopenten-1-one, 3-methyl-	Phenol, 2-methoxy-4-methyl-; (Homoguaiacol)
1,2-Cyclopentanedione, 3-methyl-	Phenol, 4-ethyl-2-methoxy-; (p-ethyl guaiacol)
levoglucosan and other sugar compounds	2-Methoxy-4-vinylphenol; (p-vinyl guaiacol)
Furans	Eugenol; (Phenol, 2-methoxy-4-(2-propenyl))
Furfural	(cis & trans) Isoeugenol
2-Furancarboxaldehyde, 5-methyl-	Vanillin; (Benzaldehyde, 4-hydroxy-3-methoxy)
2(5H)-Furanone	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-; (Acetoguaiacone)
2-Furancarboxaldehyde, 5-(hydroxymethyl)-	**Syringols**
Phenols	Phenol, 2,6-dimethoxy-; (Syringol)
Phenol	4-Hydroxy,3,5-dimethoxy benzaldehyde; (Syringaldehyde)
Phenol, 2-methyl-; (o-Cresol)	**Aromatics**
Phenol, 4-methyl; (p-Cresol)	Toluene
Phenol, 2,4-dimethyl-; (m-Xylenol)	
phenol, 4 ethyl	
1,2-Benzenediol; (pyrocatechol)	
1,2-Benzenediol, 4-methyl-; (Homocatechol)	
1, 4 benzene diol; (Hydroquinone)	
1,4-Benzenediol, 2-methyl-; (Toluhydroquinone)	

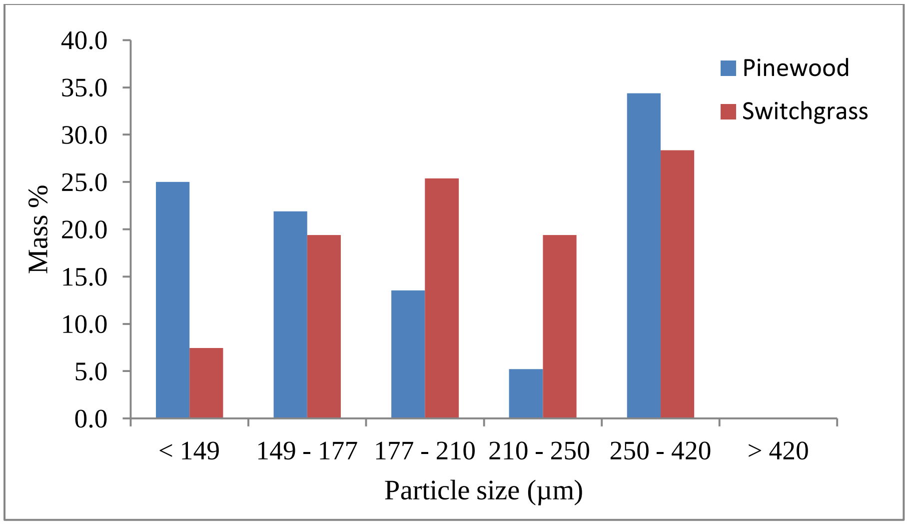


Figure 4.1: Particle size distribution of biomass samples used in the study

Table 4.2: Selected properties of biomass used for pyrolysis[†]

Properties	**Pine wood**	**Switchgrass**
Moisture Content, wt.%	5.6±0.2	5.6±0.02
Cellulose, wt.%		
Glucan	43.8±0.5	37.4±0.0
Hemicellulose, wt.%		
Xylan	6.9±0.2	22.8±0.1
Galactan	2.3±0.1	2.6±0.0
Arabinan	1.4±0.0	3.3±0.5
Mannan	9.2±0.0	nd
Extractives , wt.%	1.8±0.0	1.5±0.1
Lignin, wt.%		
Acid Insoluble	23.5±2.1	17.3±0.4
Acid Soluble	0.8±0.0	3.1±0.1
Ash, wt.%	0.9±0.01	4.4±0.05

[†] values are means of repeated analyses and numbers after ± are standard deviations.

4.4.2. Pine Wood Pyrolysis

The total yield of each group at each temperature is given in Table 4.3. Pyrolysis temperature did not have a significant effect on the yield of total ketones. However, it had a significant effect on the yield of compounds having one ketone group. Since 3-methyl-1,2-cyclopentanedione was the major compound in the ketones group, the total concentration of the ketone group had behavior similar to that of methyl-cyclopentanedione. One issue with a pyroprobe study is that the standard deviation for some compounds is very large, and it can be observed in the case of levoglucosan. Since, these experiments were performed with a very small amount of biomass sample (100-300 μg), the basic constituents in biomass (cellulose, hemicellulose, and lignin) could vary in large proportion, and the amount of sample used in the pyroprobe might therefore not be a representative sample. Levoglucosan is the major product of cellulose pyrolysis. Therefore, a significant change in the cellulose content in biomass could result in a very different yield of levoglucosan for the repeated pyrolysis under the same experimental condition. A small amount of biomass could be one of the reasons for the high standard deviation and, as a result, the yield of levoglucosan was not significantly affected when the filament temperature was increased from 450 to 750 ^{o}C in this study. However, some of the previous studies on biomass fast pyrolysis showed that the levoglucosan had a maximum yield around 350-500 ^{o}C [18-22]. Pine wood pyrolysis in an auger reactor showed a maximum yield (11 wt % of bio-oil) of levoglucosan at 475 ^{o}C [18]. The reported maximum yield accounted for only 5 wt % of pine wood; whereas the current study reported as high as 11.4 wt % of pine wood. Another study on pine wood pyrolysis reported the yield for levoglucosan approximately 7 wt % of biomass (14% of bio-oil) at 450 ^{o}C [37]. A decrease in levoglucosan yields for four different types of biomass was reported as the pyrolysis temperature increased from 350 to 600

°C [21]. Demirbas reported the highest yield of levoglucosan in bio-oil as 2.6 wt % from beech wood, 2.4 wt % from spruce wood, 2.1 wt % from olive husk, and 2.3 wt % from hazelnut shell (all on dryweight basis) at 350 °C. Garcia-Perez et al. reported the highest yield of levoglucosan as 6.5 wt % of bio-oil (approximately 4 wt % of biomass) at 500 °C from Mallee wood [22]. Lee et al. reported the highest yield of levoglucosan as 4 wt%of bio-oil (approximately 1.4 wt%of biomass) from Quercus acutissima saw dust [19]. Among the four furan-based compounds, only 2(5H)-furanone had a significant change with pyrolysis temperature. The 2(5H)-furanone had the maximum concentration at 500 and 550 °C (yields at 500 and 550 °C were not significantly different) and decreased thereafter. However, there was a high yield of four furan-based compounds in total from 500 to 600 °C (no significant difference was observed in temperatures between 500 to 600 °C. In the case of toluene, ANOVA analysis (p-value <0.0001) showed that an increase in pyrolysis temperature increased the concentration. All the compounds in the phenol group except hydroquinone showed a significant increase with the increase in pyrolysis temperature. The total concentration of the phenol group increased as the pyrolysis temperature increased from 450 to 750 °C, and a significant increase was noticed in the temperature range of 500-650 °C. The increase in the yield of hydroquinone was not as significant as that of the other phenol compounds. Furthermore, ANOVA analysis (p-value <0.05) confirmed that the pyrolysis temperature had a significant effect on the yield of most of the guaiacol compounds and also for their total concentration. However, vanillin (p-value >0.1) showed no change with the increase in pyrolysis temperature, and the effect of pyrolysis temperature on eugenol and acetoguaiacone was not significant. Tukey's HSD (Honestly Significant Difference) test indicated that there was a significant decrease in the total yield when the pyrolysis temperature increased from 550 to 700 °C. The maximum concentration for most of the compounds was in the range of 500-650 °C.

Table 4.3: Change in the yield of pine wood bio-oil components with the change in pyrolysis temperature[†]

Pine wood bio-oil compounds	Pyrolysis temperature, ^{o}C						
	450	500	550	600	650	700	750
	wt. % of biomass						
Ketones	0.3±0.1	0. 7±0.4	0.8±0.3	0.7±0.3	0.8±0.1	0.7±0.3	0.7±0.3
Levoglucosan and other anhydro sugars	9.5±7.5	8.2±4.9	11.4±6.3	9.5±6.4	8.1±4.6	10.2±3.7	10.0±5.3
Furans	3.6±0.9	5.3±1.3	5.8±1.9	4.4±1.5	4.1±0.6	3.7±1.0	3.9±0.9
*Toluene	0.01±0.01	0.03±0.01	0.05±0.03	0.05±0.02	0.05±0.03	0.09±0.04	0.13±0.05
*Phenols	0.4±0.1	0.8±0.6	1.2±0.5	1.8±1.0	2.9±1.0	3.3±1.1	3.1±1.3
*Guaiacols	3.3±0.8	5.3±1.3	5.7±1.6	4.4±1.7	3.4±0.9	2.8±0.9	2.5±1.2
Total	17.2±9.0	20.3±4.7	24.9±9.7	20.9±7.78	19.4±4.0	20.7±6.2	20.2±8.9

*Yield is significant with the increase in pyrolysis temperature at 95% confidence level. [†]values are means of repeated analyses and numbers after ± are standard deviations.

The filament heating rate did not have any effect on the concentration of all the groups (Table 4.4). The final pyrolysis temperature was kept constant at 550 ^{o}C for all the runs. Even though the filament was heated at different heating rates, biomass heating rates did not change with the change in filament heating rates in our selected runs using a thin thermocouple as discussed in Section 4.3.2. The biomass heating rate was approximately 50 ^{o}C/s even when the filament heating rate was changed from 100 to 2000 ^{o}C/s, and the final filament temperature was set at 550 ^{o}C.

Table 4.4: Change in the yield of pine wood bio-oil components with the change in pyrolysis heating rate to final pyrolysis temperature*†

Pine wood bio-oil compounds	Heating rate for pyrolysis °C/s				
	50	100	500	1000	2000
	wt. % of biomass				
Ketones	0.5±0.2	0.8±0.3	1.0±0.6	1.4±0.6	1.4±0.8
Levoglucosan and other anhydro sugars	8.8±5.4	11.4±6.3	11.0±12.2‡	20.7±13.4	11.2±6.3
Furans	4.3±1.5	5.8±1.9	4.5±1.3	5.4±0.8	6.6±2.0
Toluene	0.03±0.01	0.05±0.03	0.06±0.04	0.08±0.04	0.08±0.05
Phenols	0.8±0.5	1.2±0.5	1.1±0.6	1.7±0.5	1.5±0.6
Guaiacols	4.3±1.8	5.7±1.6	4.9±1.9	6.7±1.6	7.3±2.3
Total	18.8±9.4	24.9±9.7	22.5±15.8	35.9±15.7	28.1±10.0

*In some cases, the standard deviation was higher than the average value and the numbers could be negative based on statistical analysis but that is not possible practically. †values are means of repeated analyses and numbers after ± are standard deviations.

4.4.3. Switchgrass Pyrolysis

An additional syringol compound was listed for switchgrass pyrolysis. Syringol compounds confirmed the presence of a synapyl alcohol (common to these types of biomass) monomer in switchgrass lignin. The concentration of different compounds and the influence of pyrolysis temperature on these concentrations are presented in Table 4.5. In switchgrass pyrolysis, all ketone compounds showed significant increase in their yield as the pyrolysis temperature increased from 450 to 750 °C as did the total concentration of ketones. Unlike pine wood pyrolysis, 3-methyl-1,2-cyclopentanedione showed an increase in yield when the pyrolysis temperature was raised from 450 to 600 °C but it was almost constant thereafter. The yield of levoglucosan was almost constant with the pyrolysis temperature and, similar to pine wood pyrolysis, a high standard deviation was observed for some temperatures. Previous study for switchgrass in a fluidized bed reactor reported pyrolysis at 450 °C always favored the high yield of levoglucosan from biomass with different moisture contents [25]. The highest yield of levoglucosan reported in that work was 0.7 wt % of switchgrass (1.61 wt % of bio-oil) [25] for a feedstock of moisture content of 10 wt %. A current study reported about 7.7 wt % of switchgrass as the yield of levoglucosan whereas the intervals of confidence was as high as ±45%.

Table 4.5: Change in the yield of switchgrass bio-oil components with the change in pyrolysis temperature‡†

Switchgrass bio-oil compounds	Pyrolysis temperature, °C						
	450	500	550	600	650	700	750
	wt. % of biomass						
*Ketones	0.4±0.2	0.7±0.2	0.7±0.3	1.0±0.2	0.9±0.3	1.0±0.1	1.2±0.5
Levoglucosan and other anhydro sugars	2.4±1.6	6.5±4.3	6.6±5.6	6.05±2.9	6.5±3.0	6.1±1.8	7.7±3.5
Furans	2.4±0.9	3.5±1.3	3.4±0.8	3.7±1.2	3.6±1.4	3.9±0.2	4.6±1.9
*Toluene	0.02±0.01	0.03±0.01	0.04±0.01	0.09±0.02	0.1±0.06	0.2±0.07	0.2±0.07
*Phenols	0.7±0.3	1.1±0.4	1.1±0.1	1.9±0.5	1.9±0.7	2.2±0.5	2.7±1.0
Guaiacols	3.3±1.6	4.0±1.7	3.3±1.2	3.4±0.9	3.7±1.5	4.1±0.5	4.5±2.6
Syringols	0.3±0.1	0.4±0.1	0.3±0.1	0.4±0.1	0.4±0.2	0.4±0.03	0.5±0.2
Total	9.5±3.5	16.3±7.6	15.3±7.9	16.6±5.1	17.0±2.8	17.8±2.3	18.4±1.8

‡ In some cases, the standard deviation was higher than the average value and the numbers could be negative based on statistical analysis but that is not possible practically. * Yield is significant with the increase in pyrolysis temperature at 95% confidence level. †values are means of repeated analyses and numbers after ± are standard deviations.

An increase in the average yield of all furan compounds was observed with the increase in pyrolysis temperature. However, there was no effect on concentration with the change in pyrolysis temperature based on the ANOVA analysis. 2(5H)- Furanone showed a significant change with pyrolysis temperature in pine wood pyrolysis which was not observed in switchgrass pyrolysis. A large increase in pyrolysis temperature (p value <0.0001) for the concentration of toluene was observed for both pine wood and switchgrass pyrolysis. All phenol compounds except pyrocatechol showed a significant increase with pyrolysis temperatures in the range of 450-750 ^{o}C. Therefore, the total yield of phenol also had a similar trend with pyrolysis temperature. In the case of pyrocatechol, the increase in its yield was not statistically significant. Similar behavior was noticed for hydroquinone in pine wood pyrolysis; however, pyrocatechol showed a significant increase in pine wood pyrolysis.

Table 4.6: Change in the yield of switchgrass bio-oil components with the change in pyrolysis heating rate to final pyrolysis temperature[†]

Switchgrass bio-oil compounds	Heating rate for pyrolysis ^{o}C/s				
	500	100	500	1000	2000
	wt. % of biomass				
Ketones	0.7±0.3	0.7±0.3	1.1±0.6	1.0±0.3	1.4±0.9
Levoglucosan and other anhydro sugars	4.4±3.5	6.6±5.6	5.5±0.5	4.9±1.4	6.1±2.9
Furans	3.2±1.8	3.5±0.8	4.1±1.0	4.4±1.0	4.6±1.3
Toluene	0.03±0.01	0.04±0.01	0.07±0.04	0.13±0.12	0.16±0.14
Phenols	1.1±0.6	1.1±0.1	1.4±0.6	1.3±0.2	1.7±0.9
Guaiacols	3.5±2.4	3.3±1.2	4.4±1.1	4.9±1.0	5.0±1.5
Syringols	0.3±0.2	0.3±0.1	0.5±0.2	0.5±0.01	0.6±0.2
Total	13.2±8.5	15.3±7.9	17.1±3.4	17.1±1.7	19.6±6.5

[†] values are means of repeated analyses and numbers after ± are standard deviations.

Even though an increase in the average yield was noticed for all guaiacol and syringol compounds, the statistical analysis (p value >0.1) showed that there was no effect of pyrolysis temperature on their yield at this temperature range. The current study reported a higher yield for phenol and furfural than the yield reported for same compounds from similar biomass in previous studies [23, 25]. Pyrolysis of pine wood at 550 ^{o}C gave a total average yield of 5.7 wt % for guaiacols whereas switchgrass produced only an average yield of 4.5 wt %. Similar to pine wood, the heating rate did not have any effect on the bio-oil compounds and the data are presented Table 4.6.

The major difference between pine wood and switchgrass pyrolysis was the presence of syringol compound in the switchgrass pyrolysis. This is because of the difference in the lignin structure in the feedstocks. The three major monomers for lignin are p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, and the sinapyl alcohol monomer is found in grassy crops such as in switchgrass but not in pine wood. As expected, pine wood pyrolysis did not show any syringol compounds. The change in the behavior of ketones group between biomass types was due to 3-methyl-1,2-cyclopentanedione. Since this was the major compound and it did not have a significant change with the final temperature in pinewood pyrolysis. On the other hand, a significant change was noticed for the yield of 3-methyl-1,2- cyclopentanedione with the change in the final temperature for switchgrass pyrolysis. Cellulose content in pine wood was higher than that in switchgrass. A similar change was noticed in the yield of levoglucosan and other anhydrosugar compounds. However, it was difficult to explain the difference because of the large variation. The yields of most of the groups were comparable for both pinewood and switchgrass pyrolysis. However, the total yield of all groups was higher for pine wood pyrolysis than for switchgrass pyrolysis. Another major difference involved the guaiacols compounds, where most of these compounds in pine wood pyrolysis had a significant change with final pyrolysis temperature and in Tukey’s HSD test showed the significant change occurred with temperatures from 450 to 550 ^oC and from 550 to 700 ^oC. That means the pine wood pyrolysis at 500-650 ^oC gave maximum yield for guaiacol compounds but similar behavior was not observed with switchgrass pyrolysis. Isoeugenol concentration had a significant increase as the filament heating rate increased from 50 to 2000 $^oC/s$, irrespective to the type of biomass.

Compounds identified during the pyrolysis of pine wood and switchgrass resulted from cellulose, hemicellulose, and lignin, which are the major constituents of biomass. Numerous studies have been published on cellulose pyrolysis, and a number of reaction pathways and kinetic models have been proposed for cellulose decomposition [38-45]. One of the earlier works done by Kilzer and Broido proposed a pathway for pyrolysis of cellulose that includes three distinct processes: dehydration, depolymerization, and decomposition [38]. They also showed possible reactions in these distinct processes. Dehydration of cellulose occurred at lower temperatures (200-280 ^oC) and these “dehydrocellulose” further decomposed as gaseous products and char. Decomposition of “dehydrocellulose” also provided 5-hydroxymethylfurfural. Depolymerization of cellulose, which occurred at higher temperature (280-340 ^oC), gave tar products in which levoglucosan was the main product (>50%) [38]. However, as the temperature and heating rate increased (fast pyrolysis), the complexity of pyrolysis increased and a variety of products were produced [40-41, 46]. Although a high yield of anhydrosugar (40%) was reported from the fast pyrolysis of cellulose obtained from pretreated wood at 300-500 ^oC [41], the presence of hemicelluloses and lignin in biomass could interfere with the high yield of levoglucosan and other anhydrosugars. Another major pathway, suggested by Shafizadeh [39], showed that at higher temperature (300-500 ^oC) the cellulose rapidly depolymerized to anhydrosugars, mainly levoglucosan and other tar products such as furan and pyran derivatives. With further heating, anhydrosugars decomposed to gaseous and volatile compounds. There are handfuls of other studies on the pyrolytic pathway for cellulose [33, 47-48] and also on the decomposition of levoglucosan [42, 49-50]. Nonetheless, all these pyrolysis pathways change with pyrolytic parameters such as heating rate and temperature and the presence of impurities.

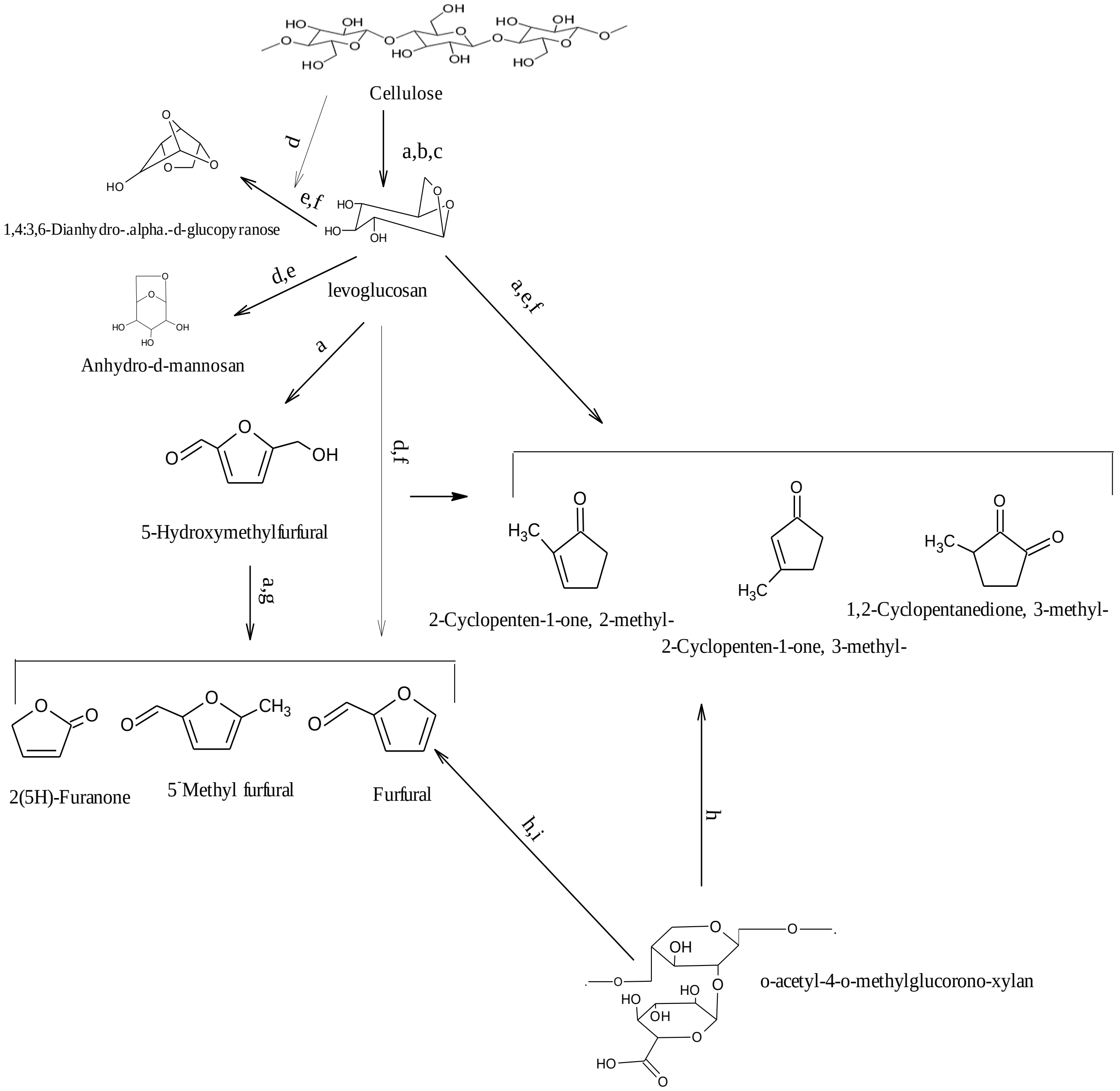


Figure 4.2: Existence of quantified compounds from cellulose and hemicellulose (primarily xylan) pyrolysis from literature. a: ref 42; b: ref 38; c: ref 41; d: ref 48; e: ref 49; f: ref 33; g: ref 63; h: ref 56; i: ref 55.

Identifying the exact reaction pathway is, perhaps, the most daunting task because the reaction pathways could be influenced by how basic biomass constituents are interacting.

On the other hand, limited numbers of studies have been reported for the thermal decomposition and pathway products of hemicelluloses [51-54]. Major studies of hemicelluloses were done by using xylan (a major component in plant hemicelluloses) as a model compound. The major product from hemicellulose decomposition was 2-furaldehyde, and Antal et al. proposed a mechanism for the degradation of xylan to furfural [55]. Another study by Shen et al. suggested different pathways for thermal decomposition of o-acetyl-4-o-methylglucorono-xylan to furfural, acetone, and other low molecular weight compounds [56]. Currently, interest in utilizing lignin for biofuel production has increased. The two major techniques that can utilize lignin for biofuel production are gasification and “high temperature” fast pyrolysis. Even though there are some studies reported for lignin pyrolysis [43, 57-62], a well-defined reaction pathway for lignin is difficult to develop because of the diversity in its structure. Phenol compounds could be formed either from lignin monomers or thermal cracking of guaiacol compounds. Therefore, the concentration of phenol increased as the pyrolysis temperature increased. Further increase in the pyrolysis would lead to the formation of an aromatic like toluene. The thermal cracking of guaiacols was dominant after 550 ^{o}C, and it caused the decrease in guaiacol derivatives and an increase in phenol derivatives in pine wood pyrolysis. In the case of switchgrass pyrolysis, the cracking of lignin and cracking of guaiacol compounds were at almost similar rates; therefore, the average yield of guaiacols was almost constant. Figures 4.2 and 4.3 show the reaction pathways of sugars and lignin, respectively, and delineate how the compounds listed in Tables 4.3 - 4.6 can be formed during the pyrolysis of biomass.

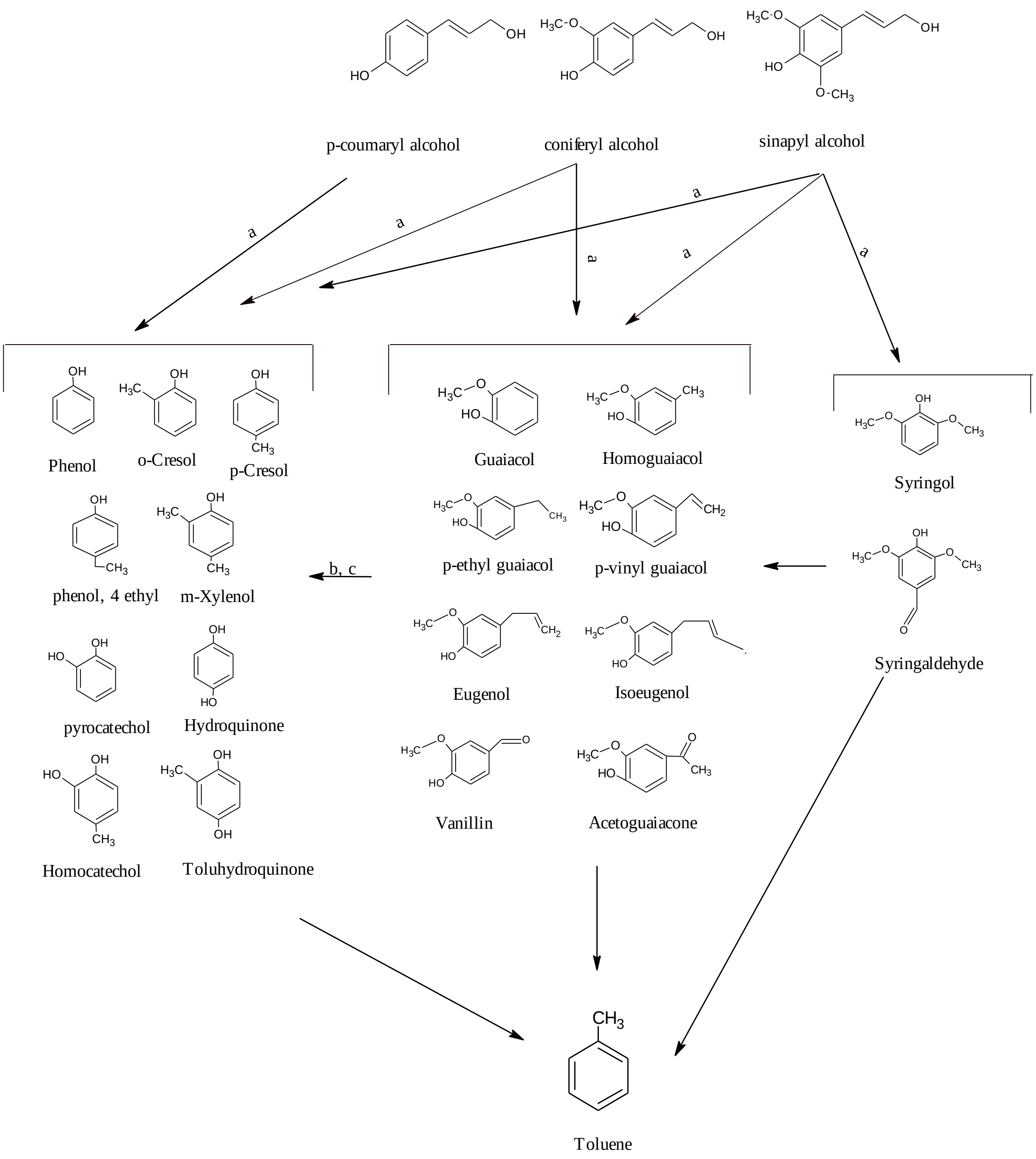


Figure 4.3: Existence of quantified compounds from the pyrolysis of lignin monomers from literature. a: ref 57; b: ref 62; c: ref 43

4.5. Conclusions

Two feedstocks, pine wood and switchgrass, were pyrolyzed at seven temperatures from 450 to 750 ^{o}C at a constant heating rate and at five heating rates (50, 100, 500, 1000, and 2000 ^{o}C/s) with a final temperature of 550 ^{o}C. Yields of 28 compounds were calculated in each case and analyzed statistically. It was difficult to conclude the yield of levoglucosan because it had high standard deviation. Most of the groups, except furans and guaiacols, behaved similarly to the change in the pyrolysis temperature. In pine wood pyrolysis, there was a maximum concentration for these compounds in the range of 500-550 ^{o}C; whereas in switchgrass pyrolysis there was no significant change with pyrolysis temperature. However, guaiacols yield was almost constant within the filament temperature of 600-750 ^{o}C. There was no significant increase in the yield of compounds when the filament heating rate was increased from 50 to 2000 ^{o}C/s in both biomass types. Comparative yield of each compound was different for two biomass types under the same pyrolysis conditions, and the yield of each group of compounds could be tuned by changing temperature and biomass based on the final application of the bio-oil.

4.6. References

1. EISA (2007) *Energy Independence and Security Act of 2007.* http://frwebgate.access.gpo.gov/cgi-bin/getdoc.cgi?dbname=110_cong_bills&docid=f:h6enr.txt.pdf

2. Bridgwater, A.V. and G.V.C. Peacocke, *Fast Pyrolysis Processes for Biomass.* Renewable and Sustainable Energy Reviews, 2000. 4: p. 1-73.

3. Luo, Z., et al., *Research on Biomass Fast Pyrolysis for Liquid Fuel.* Biomass and Bioenergy, 2004. 26: p. 455 - 462.

4. Onay, O., S.H. Beis, and O.M. Kockar, *Fast Pyrolysis of Rape Seed in a Well-Swept Fixed-Bed Reactor.* Journal of Analytical and Applied Pyrolysis, 2001. 58 - 59: p. 995 - 1007.

5. Onay, O. and O.M. Kockar, *Technical Note on Slow, Fast and Flash Pyrolysis of Rapeseed.* Renewable Energy, 2003. 28: p. 2417 - 2433.

6. Gupta, R.B. and A. Demirbas, *Gasoline, Diesel and Ethanol Biofuels from Grasses and Plants*. 2010, Cambridge University Press: New York, USA. p. 140 - 157.

7. Czernik, S. and A.V. Bridgwater, *Overview of Applications of Biomass Fast Pyrolysis Oil.* Enegry & Fuels, 2004. 18(2): p. 590-598.

8. Chiaramonti, D., et al., *Development of Emulsions from Biomass Pyrolysis Liquid and Diesel and Their Use in Engines—Part 1: Emulsion Production.* Biomass and Bioenergy, 2003. 25: p. 85-99.

9. Qi, Z., et al., *Review of Biomass Pyrolysis Oil Properties and Upgrading Research.* Energy Conversion and Management, 2007. 48: p. 87-92.

10. Zhang, Q., et al., *Upgrading Bio-oil over Different Solid Catalysts.* Enegry & Fuels, 2006. 20: p. 2717-2720.

11. Vispute, T.P., et al., *Renewable Chemical Commodity Feedstocks from Integrated Catalytic Processing of Pyrolysis Oils.* Science, 2010. 330: p. 1222 - 1227.

12. Bridgwater, A.V., et al., *Fast pyrolysis of biomass: a handbook*. 2008, Newbury: CPL Press. 34.

13. Asadullah, M., et al., *Production of Bio-Oil from Fixed Bed Pyrolysis of Bagasse.* Fuel, 2007. 86(16): p. 2514-2520.

14. Demirbas, A., *Kinetics for Non-Isothermal Flash Pyrolysis of Hazelnut Shell.* Bioresource Technology, 1998. 66(3): p. 247-252.

15. Sipila, K., et al., *Characterization of Biomass-Based Flash Pyrolysis Oils.* Biomass and Bioenergy, 1998. 14(2): p. 103 - 113.

16. Park, H.J., Y.-K. Park, and J.S. Kim, *Influence of Reaction Conditions and the Char Separation System on the Production of Bio-Oil from Radiata Pine Sawdust by Fast Pyrolysis.* Fuel Processing Technology, 2008. 89(8): p. 797 - 802.

17. Oasmaa, A., E. Kuoppala, and Y. Solantausta, *Fast Pyrolysis of Forestry Residue. 2. Physicochemical Composition of Product Liquid.* Enegry & Fuels, 2003. 17: p. 433 - 443.

18. Thangalazhy-Gopakumar, S., et al., *Physiochemical properties of bio-oil produced at various temperatures from pine wood using an auger reactor.* Bioresource Technology, 2010. 101(21): p. 8389 - 8395.

19. Lee, S.-H., et al., *The Yields and Composition of Bio-Oil Produced from Quercus Acutissima in a Bubbling Fluidized Bed Pyrolyzer.* Journal of Analytical and Applied Pyrolysis, 2008. 83(1): p. 110-114.

20. He, R., et al., *Influence of Pyrolysis Condition on Switchgrass Bio-Oil Yield and Physicochemical Properties.* Bioresource Technology, 2009. 100(21): p. 5305-5311.

21. 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): p. 591-597.

22. Garcia-Perez, M., et al., *Effects of Temperature on the Formation of Lignin-Derived Oligomers during the Fast Pyrolysis of Mallee Woody Biomass.* enegry & Fuels, 2008. 22: p. 2022-2032.

23. Horne, P.A. and P.T. Williams, *Influence of Temperature on the Products from the Flash Pyrolysis of Biomass.* Fuel, 1996. 75(9): p. 1051-1059.

24. Branca, C., P. Giudicianni, and C.D. Blasi, *GC/MS Characterization of Liquids Generated from Low-Temperature Pyrolysis of Wood.* Industrial and Engineering Chemistry Research, 2003. 42(14): p. 3190-3202.

25. Wojtowicz, M.A., et al., *Modeling the Evolution of Volatile Species during Tobacco Pyrolysis.* Journal of Analytical and Applied Pyrolysis, 2003. 66: p. 235 - 261.

26. Wear, D.N. and J.G. Greis, *Southern forest resource assessment*, in *Gen. Tech. Rep. SRS-53*. 2002, U.S. Department of Agriculture, Forest Service, Southern Research Station: Asheville, NC.

27. Wear, D.N., D.R. Carter, and J. Prestemon, *The U.S. South's timber sector in 2005: a prospective analysis of recent change*, in *Gen. Tech. Rep. SRS-99*. 2007, Southern Forest Resource Assessment, U.S. Department of Agriculture, Forest Service, Southern Research Station: Asheville, NC.

28. Khanna, M., B. Dhunganaa, and J. Clifton-Brown, *Costs of Producing Miscanthus and Switchgrass for Bioenergy in Illinois* Biomass and Bioenergy, 2008. 32(6): p. 482-493.

29. Wright, L., *Historical Perspective on How and Why Switchgrass was Selected as a "Model" High-Potential Energy Crop.* Report ORNL/TM-2007/109, 2007. Oak Ridge National Laboratory, U.S. Department of Energy under contract DE-AC05-00OR22725.

30. McLaughlin, S.B. and L.A. Kszos, *Development of Switchgrass (Panicum virgatum) as a Bioenergy Feedstockin the United States.* Biomass and Bioenergy, 2005. 28: p. 515-535.

31. Missaoui, A.M., V.A. Fasoula, and J.H. Bouton, *The Effect of Low Plant Density on Response to Selection for Biomass Production in Switchgrass.* Euphytica, 2005. 142: p. 1-12.

32. NREL, *Determination of Structural Carbohydrates and Lignin in Biomass*, in *via http://www.nrel.gov/biomass/analytical_procedures.html Accessed on July 9, 2009*. 2008, Available from National Renewable Energy Laboratory: Colorado, USA.

33. Lin, Y.-C., et al., *Kinetics and Mechanism of Cellulose Pyrolysis.* The Journal of Physical Chemistry C, 2009. 113: p. 20097-20107.

34. Carlson, T.R., T.P. Vispute, and G.W. Huber, *Green Gasoline by Catalytic Fast Pyrolysis of Solid Biomass Derived Compounds.* ChemSusChem, 2008. 1: p. 397-400.

35. Pattiya, A., J.O. Titiloye, and A.V. Bridgwater, *Fast pyrolysis of cassava rhizome in the presence of catalysts.* Journal of Analytical and Applied Pyrolysis, 2008. 81(72 - 79).

36. Ramsey, F.L. and D.W. Schafer, *The statistical sleuth: a course in methods of data analysis*. 2002: Duxbury/Thomson Learning.

37. Ingram, L., et al., *Pyrolysis of Wood and Bark in an Auger Reactor: Physical Properties and Chemical Analysis of the Produced Bio-oils.* Enegry & Fuels, 2008. 22(1): p. 614-625.

38. Kilzer, F.J. and A. Broido, *Speculations on the Nature of Cellulose Pyrolysis.* Pyrodynamics, 1965. 2: p. 151-163.

39. Shafizadeh, F., *Introduction to Pyrolysis of Biomass.* Journal of Analytical and Applied Pyrolysis, 1982. 3: p. 283-305.

40. Radlein, D., J. Piskorz, and D.S. Scott, *Fast Pyrolysis of Natural Polysaccharides as a Potential Industrial Process.* Journal of Analytical and Applied Pyrolysis, 1991. 19: p. 41-63.

41. Piskorz, J., et al., *Pretreatment of Wood and Cellulose for Production of Sugars by Fast Pyrolysis.* Journal of Analytical and Applied Pyrolysis, 1989. 16: p. 127-142.

42. Shafizadeh, F., *Industrial Pyrolysis of Cellulosic Materials.* Applied Polymer Symposia, 1975. 28: p. 153-174.

43. Demirbas, A., *Mechanisms of Liquefaction and Pyrolysis Reactions of Biomass.* Energy Conversion & Management, 2000. 41: p. 633-646.

44. Bradbury, A.G., Y. Sakai, and F. Shafizadeh, *A Kinetic Model for Pyrolysis of Cellulose.* Journal of Applied Polymer Science, 1979. 23: p. 3271-3280.

45. Varhegyi, G., et al., *Kinetic Modeling of Biomass Pyrolysis.* Journal of Analytical and Applied Pyrolysis, 1997. 42: p. 73-87.

46. Diebold, J.P., *A Unified, Global Model for the Pyrolysis of Cellulose.* Biomass and Bioenergy, 1994. 7(1-6): p. 75-85.

47. Liao, Y.-f., S.-r. Wang, and X.-q. Ma, *Study of Reaction Mechanisms in Cellulose Pyrolysis.* Pap.-Am. Chem. Soc., Div. Fuel Chem., 2004. 49(1): p. 407-411.

48. Nowakowski, D.J. and J.M. Jones, *Uncatalysed and Potassium-Catalysed Pyrolysis of the Cell-Wall Constituents of Biomass and Their Model Compounds.* Journal of Analytical and Applied Pyrolysis, 2008. 83: p. 12 - 25.

49. Bahng, M.-K., et al., *Thermal Degradation Pathways of Levoglucosan as an Intermediate in Cellulose Pyrolysis* Pap.-Am. Chem. Soc., Div. Fuel Chem., 2009. 54(1): p. 367-368.

50. Nimlos, M.R. and R.J. Evans, *Levoglucosan Pyrolysis.* Fuel Chemistry Division Preprints, 2002. 47(1): p. 393-394.

51. Hosoya, T., H. Kawamoto, and S. Saka, *Pyrolysis Behaviors of Wood and Its Constituent Polymers at Gasification Temperature.* Journal of Analytical and Applied Pyrolysis, 2007. 78(2): p. 328-336.

52. Ponder, G.R. and G.N. Richards, *Thermal Synthesis and Pyrolysis of a Xylan.* Carbohydrate Research, 1991. 218: p. 143-155.

53. Pouwels, A.D., et al., *Characterization of Beech Wood and Its Holocellulose and Xylan Fractions by Pyrolysis-Gas Chromatography-Mass Spectroscopy.* Journal of Analytical and Applied Pyrolysis, 1987. 11: p. 417 - 436.

54. Shafizadeh, F., G.D. Mcginnis, and C.W. Philpot, *Thermal Degradation of Xylan and Related Model Compounds.* Carbohydrate Research, 1972. 25: p. 23 - 33.

55. Antal Jr., M.J., T. Leesomboon, and W.S. Mok, *Mechanism of Formation of 2-Furaldehyde from D-Xylose.* Carbohydrate Research, 1991. 217: p. 71 - 85.

56. Shen, D.K., S. Gua, and A.V. Bridgwater, *Study on the Pyrolytic Behaviour of Xylan-Based Hemicellulose Using TG–FTIR and Py–GC–FTIR.* Journal of Analytical and Applied Pyrolysis, 2010. 87: p. 199 - 206.

57. Britt, P.F., A.C. BuchananIII, and D.R. Matineau, *Flash Vacuum Pyrolysis of Lignin Model Compounds: Reaction Pathways of Aromatic Methoxy Groups*, in *ORNL/CP - 101275*. 1999.

58. Windt, M., et al., *Micro-Pyrolysis of Technical Lignins in A New Modular Rig And Product Analysis by GC–MS/FID And GCxGC–TOFMS/FID*. Journal of Analytical and Applied Pyrolysis, 2009. 85: p. 38-46.

59. Petrocelli, F.P. and M.T. Klein, *Model Reaction Pathways in Kraft Lignin Pyrolysis.* Macromolecules, 1984. 17(2): p. 161-169.

60. Kuroda, K.-I. and Y. Inoue, *Analysis of Lignin by Pyrolysis-Gas Chromatography I Effect of Inorganic Substances on Guaiacol-Derivative Yield from Softwoods and Twir Lignins*. Journal of Analytical and Applied Pyrolysis, 1990. 18: p. 59-69.

61. Nowakowski, D.J., et al., *Lignin Fast Pyrolysis: Results from an International Collaboration.* Journal of Analytical and Applied Pyrolysis, 2010. 88: p. 53 - 72.

62. Hwang, B.-h. and J.R. Obst, *Basic Studies on the Pyrolysis of Lignin Compounds.* The Korean Society of Wood Science and Technology, International Association of Wood Products Societies, 2003. Proceedings of the International Conference on Forest products Better Utilization of Wood for Human, Earth and Future, Daejeon, KOREA.

5. Production of Hydrocarbon Fuels from Biomass using Catalytic Pyrolysis under Helium and Hydrogen Environments

5.1. Abstract

This study is focused on hydrocarbons production through changing carrier gas, and using zeolite catalysts during pyrolysis. A large reduction in high molecular weight oxygenated compounds was noticed when the carrier gas was changed from helium to hydrogen during pyrolysis. A catalytic pyrolysis was conducted using two different methods based on how the biomass and catalysts were contacted together. For both methods, there was no significant change in the carbon yield with the change in pyrolysis environment. However, the mixing-method produced higher aromatic hydrocarbons than the bed method. In addition, two methods were also tested using two ratios of biomass to catalyst. Nonetheless, there was no significant increase in hydrocarbon yield as the catalyst loading was increased from two to five times of biomass in the catalyst-bed method. In contrast to this, a significant increase was noticed for the catalytic-mixing method when the biomass to catalyst loading was increased from 1:4 to 1:9.

5.2. Introduction

National energy security, energy sustainability, and climatic issues are the major driving forces in accepting alternative energy resources in our daily life. In this regard, biomass, an intriguing candidate for future energy demand, is being studied widely for effective conversion to fuels. Biomass is the only renewable source for carbon-based liquid fuel which can help to alleviate dependence on foreign oils, and mitigate global warming and other environmental issues associated with the use of fossil fuels [1]. The southeastern part of the United States is blessed with woody biomass and the logging residues from forest cleaning operations. This could be a major source of biomass for biofuel production in the Southeast. The Energy Independent and Security Act (EISA) 2007 has mandated to replace 36 billion gallons/year of petroleum based transportation fuel with biofuels by 2022 [2]. In order to meet this requirement, both biochemical and thermochemical pathways have been tested to utilize lignocellulosic biomass for liquid fuels production. Carbon dioxide produced during the biofuel production and utilization is used for plant growth, and therefore, biomass is a carbon neutral renewable source for energy production. Moreover, greenhouse gas, and NOx and SOx emissions are negligible compared to those of fossil fuels. Also, biomass is available mostly in rural areas and biorefineries can bring more opportunities to these areas. A fast pyrolysis is one of the emerging thermochemical conversion methods which can convert up to 80 wt.% (dry weight basis) of biomass into liquid. The liquid product (bio-oil) is easier to handle during transportation than high bulk density solid biomass. Therefore, a pyrolysis plant can be installed near the source of biomass, and the bio-oil can be transported to a refinery for further processing. Any biomass such as agricultural residues, forest residues, leachate, municipal solid waste, and animal manure can be used as a feedstock for fast pyrolysis [3-6]. A fast pyrolysis is feedstock agnostic, which is a major advantage compared to some other biomass to biofuel conversion processes.

Bio-oil, the major product of biomass fast pyrolysis, has many applications in the area of energy and fuels [7]. In addition, bio-oil can be used as a resource for many chemicals such as biodegradable de-icers, fertilizers, levoglucosan, levoglucosenone, hydroxyacetaldehyde (glycolaldehyde), phthalate esters and a range of flavorings and essences for the food industry [3, 7]. However, the final applications of bio-oil are limited because of some negative properties such as high acidity, high water content, instability, and low heating value. Since the bio-oil is formed by the rapid heating and cooling of pyrolytic vapors, the oxygenated compounds in bio-oil are not in a thermal equilibrium, and this can cause further reaction of these compounds during storage. In order to prevent these reactions, bio-oil has to be either deoxygenated or stored at a low temperature [8]. A series of upgrading steps make biofuel production through pyrolysis an expensive process and, therefore, economical upgrading techniques have to be developed to fully utilize the potential of fast pyrolysis process.

There are two major techniques used to produce hydrocarbon fuels from bio-oil: one is catalytic cracking, and another is hydrodeoxygenation [9-13]. In catalytic cracking, bio-oil compounds are deoxygenated in the presence of some shape selective catalysts such as zeolites, whereas in hydrodeoxygenation, hydrogen (H_2) reacts with oxygenated compounds at high pressures and moderate temperatures to form hydrocarbons and water. Both the techniques have some advantages and disadvantages. Even though, both of these techniques are technically feasible, they have not been economically developed on a large scale [14]. Deoxygenation with zeolite catalysts can be done in atmospheric pressure, and it does not require the supply for H_2. Cracking reactions involve the rupture of C-C bonds associated with dehydration, decarboxylation, and decarbonylation. Synthetic zeolite (ZSM-5) catalysts have been successfully used for deoxygenation of organic compounds to produce aromatic hydrocarbons. Since the SiO_2/Al_2O_3 ratio can be varied by many orders of magnitude, ZSM-5 has been used for cracking a variety of compounds by varying the acidity and catalytic properties. Many studies have reported upgrading pyrolysis oil (bio-oil) or pyrolytic vapors with the ZSM-5 catalyst [15-17]. There is a growing interest in producing hydrocarbon fuels using catalytic pyrolysis (catalyst is being used during pyrolysis) [18-20]. Catalytic pyrolysis produces better quality bio-oil and makes downstream upgrading processes less expensive. Most of the studies utilized zeolite catalysts for catalytic cracking. Earlier studies reported stable bio-oil from catalytic pyrolysis; however, a high reduction in the yield was observed [21]. In addition, there are two major issues with zeolite cracking, which are high coke formation and catalyst deactivation. Currently, a few studies had reported catalytic pyrolysis in micro-scale [22-29] and presented encouraging results with zeolite catalysts

Zeolite cracking of biomass to produce gasoline and diesel range compounds alleviates the need of H_2 gas which provides a major advantage over hydrodeoxygenation process. Hydrogen is a reducing gas and the cracking of biomass in the presence of hydrogen can reduce the oxygen content in bio-oil. Therefore, the first goal of this study was to compare the effects of pyrolysis environment on the products formed during pyrolysis. If indeed there is any effect of reducing environment in biomass pyrolysis, an integrated system can be developed in which synthesis gas from biomass gasification can be used. Hence, the current paper involves a comparative study of hydrogen and helium (inert) as a carrier gas. Here, helium was used as the inert gas in order to minimize the difference in the effect of thermal conductivity of gases, which will influence on heating rates. The second objective was to find the best approach to use a catalyst-biomass mixture. In previous studies, either biomass was thoroughly mixed with catalysts prior to use or biomass and catalysts were placed in two sections as explained in Section 5.3.4.

5.3. Materials and Methods

5.3.1. Biomass Preparation and Characterization

Pine wood chips were collected from a local wood chipping plant in Opelika, Alabama, dried in an oven at 75 °C for 12 h, and ground in a hammer mill (New Holland Grinder Model 358) fitted with a 1.58 mm(1/16 in.) sized screen. Dried and ground pine wood biomass sample (particle size < 420 μm) was utilized for this study. Moisture content of the biomass sample (wet basis) was determined by calculating weight loss after the sample was heated in an oven at 103 ^{o}C for 16 h according to ASTM E 871 standard, and the ash content was measured using ASTM E 1755 standard. Chemical constituents of the biomass sample was analyzed in the Bioenergy Laboratory at the Center for Bioenergy and Bioproducts, Auburn University, according to "Standard Biomass Analytical Methods" developed by the National Renewable Energy Laboratory [30]. Ultimate analysis of the biomass sample was done in a CHNS/O analyzer (Perkin Elmer model 2400).

5.3.2. Catalyst

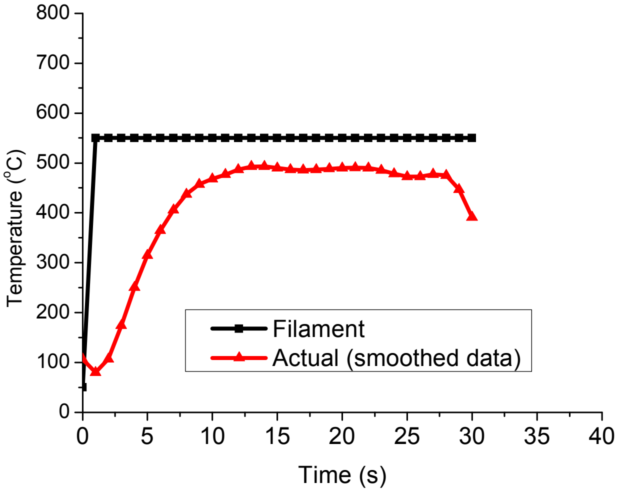
The ZSM-5 zeolite catalyst (SiO_2/Al_2O_3 = 50 and surface area equal to 425 m^2/g) used in this study purchased from Zeolyst International (Conshohocken, PA, USA). ZSM-5 powder was received in ammonium cation form. In order to obtain in HZSM-5 form, the catalyst was calcined in air at 550 ^{o}C for 2 h prior to use.

5.3.3. Thermogravimetric Analysis

Pyrolytic behaviors of biomass-inert and biomass-catalyst mixtures (1:9) were studied in a Pyris 1 TGA (PerkinElmer). Hydrogen gas was not used for the TGA studies because of technical and safety reasons. About 5 mg of mixtures were taken for analysis and heated from 30 to 600 ^{o}C at a heating rate of 50 ^{o}C/min. A gas flow rate of 20 mL/min was maintained during pyrolysis. All experiments were run in duplicates.

5.3.4. Pyrolysis – GC/MS

Pyrolysis studies were carried out using a commercial pyrolyzer which was interfaced with a gas chromatograph/mass spectrometer (GC/MS). The pyrolyzer (Pyroprobe model 5200, CDS Analytical Inc.) had a probe that contained a computer controlled heating element, and the heating element held the finely ground biomass in a quartz tube (25 mm long with 1.9 mm internal diameter). The actual temperature inside the quartz tube (biomass temperature) was approximately 75 ^{o}C lower than the filament temperature (see Figure 5.1), but the pyrolysis temperature reported in this study is the filament temperature that heats biomass inside the quartz tube (not the biomass temperature). The actual (biomass) temperature and the heating rate of the biomass inside the quartz tube were measured with the help of a K-type thermocouple (Omega HH147U). A typical biomass temperature profile is given in Figure 5.1. The biomass heating rate was almost 50 ^{o}C/s, irrespective to the heating rates (100, 500, 1000 and 2000 ^{o}C/s) of filament. About 200- 400 µg of biomass sample was taken for pyrolysis and the sample was pyrolyzed at 550 ^{o}C with a filament heating rate of 2000 ^{o}C/s in presence of different gases (He and H_2).



(c)

Figure 5.1: Comparison between the filament and actual temperature and heating rate; filament final temperature 550 °C, heating rate 2000 °C/s. Final filament temperature was maintained for 30 s.

The pressure inside the pyroprobe was equal to the cylinder output pressure (80 psia) for all the gases. The gas carried pyrolysis vapors from the probe to a trap (adsorbent) which was resting at 40 °C. The trap adsorbed the condensed bio-oil components and the non-condensed vapors were purged with the same gas (Figure 5.2). Noncondensable gases were not analyzed in this study. The adsorbed bio-oil components were desorbed by heating a trap at 300 °C and the vapors were carried out using He gas for GC analysis. All the pyrolysis experiments were repeated five times.

Catalytic pyrolysis was performed in two ways or what we call catalyst-bed and catalyst-mixing methods here. With the catalyst-bed method, the biomass and catalysts were inserted in stages and quartz wool was kept in between. In this case, pyrolytic vapors could pass through the catalyst-bed which was held at the pyrolysis temperature. The catalyst-bed method was performed using two different ratios of biomass to catalyst, and they were 1:2 and 1:5. With the catalyst-mixing method, biomass and catalyst were mixed physically in defined proportions prior to the pyrolysis. In order to investigate the effect of catalyst loading, two different biomass: catalyst ratios (1:4 and 1:9) were selected. The biomass-catalyst mixture was inserted between the quartz wool in a quartz tube for pyrolysis. The catalyst mixing method is also described elsewhere [22, 26]. Typically, the amount of char formed with the use of a pyrolyzer is higher than the bench-scale reactors [31], and, therefore, char and coke formation were not quantified in this study.

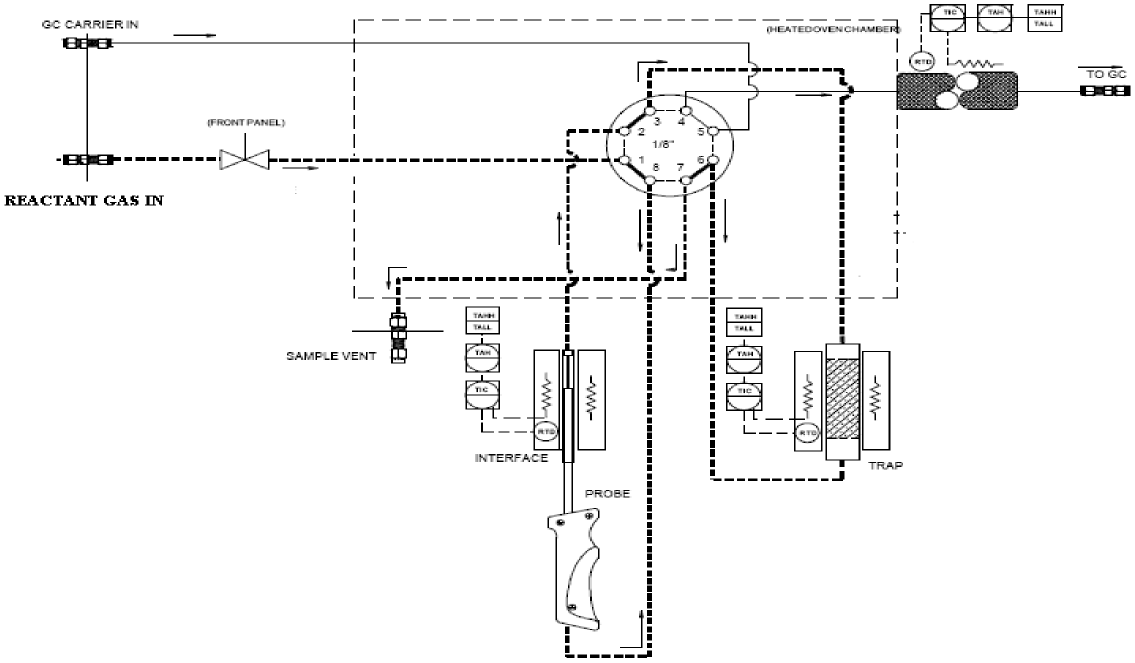


Figure 5.2: Flow diagram of reactant gas and GC carrier gas during pyrolysis (Adopted from the CDS pyroprobe 5200 manual)

The bio-oil components were analyzed with an Agilent 7890 GC/5975MS using a DB-1701 column (30 m; 0.25 mm i.d.; 0.25 mm film thickness). The selected compounds (which appear in all runs and show high probability with MS library) were quantified. For quantification, five data points were generated in such a way that concentration of bio-oil compounds fell within those five points. A split ratio of 125:1 was selected for injection. The injector and the GC/MS interface were kept at constant temperatures of 280 °C and 250 °C, respectively. The initial temperature of the column, 40 °C, was maintained for 2 min with the temperature being subsequently increased to 250 °C at 5 °C/min, with the final temperature being held for 8 min. Helium of ultra high purity (99.999%) supplied from Airgas Inc. (Charlotte, NC) was used as a carrier gas and flowed at 1.25 mL/min. Compounds were ionized at 70 eV electron impact conditions and analyzed over a mass per change (m/z) range of 50 – 550. Bio-oil compounds were identified by comparing the mass spectra with the NIST (National Institute of Standards and Technology) mass spectral library. The quantification of bio-oil compounds were calculated using their pure forms obtained from Sigma-Aldrich. The quantification factor for each compound was determined from the slope of concentration vs. area (integration area for compound peak in chromatogram). The carbon yield was calculated using Equation 5.1.

$$\%\ \text{carbon yield} = \frac{\text{wt.of compound} \times \text{mass fraction of carbon in each compound}}{\text{wt.of biomass} \times \text{mass fraction of carbon in biomass}} \text{x}100 \ldots\ldots \text{(Equation 5.1)}$$

Mass fraction of carbon in each compound was calculated using chemical formula, whereas the mass fraction of carbon in biomass was calculated from ultimate analysis.

5.4. Results and Discussion

5.4.1. Biomass Characterization

The pine wood sample taken for this study had 5.6±0.2 wt.% (wet basis) moisture content and 0.9±0.1 wt. % ash content. Cellulose, hemicelluloses and lignin contents (by mass) were 43.8±0.5%, 19.8±0.3%, and 24.3±2.1% respectively. The carbon, hydrogen, oxygen, and nitrogen contents of pine wood sample were found to be 45.7±0.1%, 6.5±0.1%, 45.5±0.1%, and 0.1% respectively and are based on "as received". The sulfur content was below the detection limit of the instrument. From the ultimate analysis of pine wood, the chemical formula found is $(C_{3.8}H_{6.5}O_{2.8})_n$.

5.4.2. Thermogravimetric Analysis

Figure 5.3 shows the thermal behavior of pine wood-sand (1:9) and pine wood-catalyst mixtures (1:9) under a helium environment. The initial weight loss until 150 ^{o}C can be contributed to the loss of moisture in the sample [32] under inert conditions. Nonetheless, the thermal degradation rate before 150 ^{o}C was more significant for the pine wood-catalyst mixture than for the pine wood-sand mixture. The reason may be that some level of dehydration occurred or some volatile compounds might have been produced in the presence of the catalyst. A rapid thermal degradation was noticed for biomass in the temperature range of 250 - 400 ^{o}C, peaking at around 370 ^{o}C. This shows that the catalyst had some influence in devolatization at a lower temperature although there might be no influence at a higher temperature, which suggests that it is temperature - driven process.

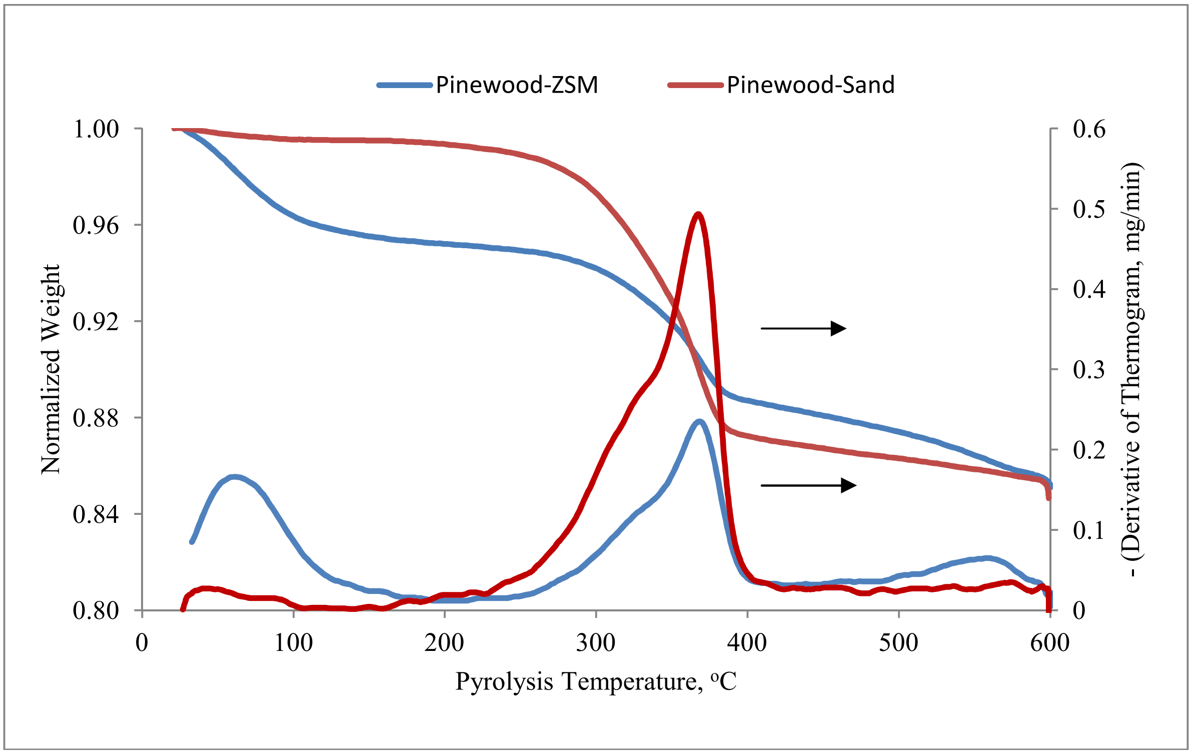


Figure 5.3: Thermo gravimetric behavior of pine wood-sand and pine wood-catalyst mixtures under helium gas

5.4.3. Pyrolysis under Different Gases

Pine wood was pyrolyzed under the presence of He and H_2 gases. Fifteen compounds were identified and quantified. One issue with a pyroprobe study is that the standard deviation for some compounds was very large, and it was particularly observed in the case of levoglucosan. These experiments were performed with a very small amount of biomass sample (200 – 400 µg); the basic constituents in biomass (cellulose, hemicellulose and lignin) could vary in large proportions. Therefore, even though levoglucosan was a major compound identified, it was not included in this study. Carbon yields of the selected compounds under the presence of two different gases are presented in Table 5.1.

Table 5.1: Carbon yield of bio-oil compounds from the pyrolysis of pine wood under different gases[†]

Bio-oil compounds	MW	Helium	Hydrogen
		Carbon yield, wt%	
1,2-Cyclopentanedione, 3-methyl-	112	1.5±0.5	0.4±0.0
1,4:3,6-Dianhydro-.alpha.-d-glucopyranose	144	0.5±0.2	0.1±0.0
Furfural	96	2.4±0.5	0.6±0.1
2(5H)-Furanone	84	3.3±1.0	0.8±0.1
2-Furancarboxaldehyde, 5-(hydroxymethyl)-	126	2.6±1.4	0.9±0.1
Toluene	92	0.1±0.1	0.1±0.0
Phenol	94	0.4±0.2	0.1±0.0
Phenol, 4-methyl; (p-Cresol)	108	0.3±0.1	0.2±0.0
1,2-Benzenediol; (pyrocatechol)	110	0.6±0.4	0.1±0.0
Phenol, 2-methoxy; (Guaiacol)	124	1.5±0.5	0.4±0.0
Phenol, 2-methoxy-4-methyl-; (Homoguaiacol)	138	1.5±0.6	0.6±0.1
2-Methoxy-4-vinylphenol; (p-vinyl guaiacol)	150	4.8±1.0	1.5±0.1
(cis & trans) Isoeugenol	164	1.8±0.4	0.6±0.1
Vanillin; (Benzaldehyde, 4-hydroxy-3-methoxy)	152	0.5±0.2	0.2±0.0
Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-; (Acetoguaiacone)	166	0.4±0.1	0.2±0.1
Total		22.3±6.2	6.7±0.5

† number after ± is the standard deviation; MW is molecular weight

In the presence of inert gas (He), the total quantified compounds accounted for about 22 wt.% of carbon in the biomass. However, when a reducing environment (H_2) was introduced during the pyrolysis, only about 6 wt.% of carbon was recovered from these compounds. Most of the compounds included in this study were of higher molecular weight. A reduction in the yield of all compounds was noticed when the pyrolysis environment was changed from He to H_2. The reduction was more than 50% for the ketone, furan and guaiacol derived compounds. However, the reduction in the yield of toluene and phenol derived compounds were not significant. It is expected that under the presence of H_2 lower molecular weight compounds might have been produced or higher coke formed but it was not confirmed in this study.

5.4.4. Catalytic Pyrolysis

5.4.4.1. Catalyst-Bed Method

Table 5.1 depicts the carbon yield from some major compounds identified during the non-catalytic pyrolysis of pine wood in the presence of He and H_2 gas. When a ZSM-5 catalyst was introduced in to the path of pyrolytic vapors, aromatic hydrocarbons were also formed (Table 5.2). Two ratios of biomass to catalyst (1:2 and 1:5) were selected for the catalyst-bed method. Table 5.2 also shows the carbon yield of catalytic pyrolysis under hydrogen gas.

The only aromatic quantified in the non-catalytic pyrolysis was toluene, which represented maximum 0.1% of biomass pyrolyzed. In this method of catalytic pyrolysis, the aromatic compounds quantified constituted carbon yields of 8.3 ± 1.3 % and 9.8 ± 2.8 % for biomass:catalyst ratios of 1:2, and 1:5, respectively under an inert environment, and 7.4 ± 2.8% at the biomass to catalyst ratio of 1:5 under a reducing environment. Table 5.2 shows there was no significant increase in the production of aromatic compounds when increasing the catalyst loading. In addition, the tail end of the catalyst-bed was not utilized for cracking when the biomass to catalysts mixture was increased from 1:2 to 1:5. Therefore, further experiments were not performed by increasing the catalyst amount in the path of pyrolytic vapors.

Table 5.2: Major compounds and their carbon yield for different ratios of biomass-catalyst ratios and different environments from the catalytic pyrolysis of pine wood in catalyst-bed method †

Bio-oil compounds for bed method of catalytic pyrolysis	yield, % carbon		
	Helium		Hydrogen
	Ratio of biomass to catalyst		
	1:2	1:5	1:5
Benzene	0.6±0.2	0.9±0.3	0.6±0.3
Toluene	1.1±0.2	1.5±0.5	1.0±0.5
Ethylbenzene	0.3±0.0	0.2±0.1	0.2±0.0
p-Xylene; (Benzene, 1,4-dimethyl-)	2.9±0.5	3.5±1.0	2.7±1.0
m-Xylene; (Benzene, 1,3-dimethyl-)	0.5±0.1	0.8±0.3	0.6±0.3
o-Ethyltoluene; (Benzene, 1-ethyl-2-methyl-)	0.3±0.0	0.3±0.1	0.2±0.1
Benzene, 1,3,5-trimethyl-	0.6±0.1	0.6±0.1	0.5±0.1
Indane; (1H-Indene, 2,3-dihydro-)	0.3±0.0	0.3±0.1	0.2±0.1
Indene; (1H-Indene)	0.2±0.0	0.2±0.1	0.1±0.1
Naphthalene	0.3±0.1	0.4±0.1	0.3±0.2
Naphthalene, 2-methyl-	0.8±0.1	0.9±0.2	0.7±0.3
Naphthalene, 2,6-dimethyl-	0.5±0.1	0.4±0.1	0.3±0.1
Furfural	0.7±0.1	0.7±0.2	0.5±0.1
2(5H)-Furanone	1.1±0.1	1.0±0.2	0.5±0.3
2-Furancarboxaldehyde, 5-(hydroxymethyl)-	0.9±0.2	0.7±0.2	0.6±0.3
Phenol	0.2±0.0	0.2±0.0	0.2±0.1
Phenol, 4-methyl-	0.1±0.0	0.1±0.0	0.1±0.0
Phenol, 2,4-dimethyl-	0.2±0.0	0.1±0.0	0.1±0.0
Phenol, 2-methoxy-	0.6±0.1	0.6±0.1	0.4±0.1
Phenol, 2-methoxy-4-methyl-	0.6±0.0	0.5±0.0	0.4±0.2
2-Methoxy-4-vinylphenol	1.4±0.1	1.3±0.1	1.1±0.4
(cis & trans) Isoeugenol	0.6±0.1	0.5±0.1	0.5±0.2
Vanillin	0.2±0.0	0.2±0.0	0.1±0.1
Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	0.2±0.0	0.2±0.0	0.1±0.0
1,2-Cyclopentanedione, 3-methyl-	0.5±0.1	0.4±0.1	0.3±0.1
Total	15.4±2.0	16.3±3.3	12.3±4.4

† number after ± is the standard deviation

In the case of non-catalytic pyrolysis, a large reduction in the higher molecular weight oxygenated was noticed when a reducing environment was introduced, whereas such reduction was not observed in the bed-method of catalytic pyrolysis. This shows that there was no significant reduction for the input to catalyst bed in the presence of hydrogen gas, and the reduction in high molecular weight oxygenated compound was compromised by some other unidentified compounds.

5.4.4.2. Catalytic-Mixing Method

Table 5.3 shows the major compounds quantified in the mixing method of catalytic pyrolysis under the He environment. Here, two ratios of biomass to catalyst were selected as 1:4 and 1:9. As the catalyst loading increased, the total yield of quantified compounds increased significantly.

Most of the compounds identified in non-catalytic pyrolysis were phenol, guaiacol compounds which have a boiling point above 180 ^{o}C whereas in catalyst-mixing pyrolysis compounds contained a range of different boiling points; low aromatic hydrocarbons like benzene, toluene, xylene have a boiling point below 150 ^{o}C, whereas naphthalenes have boiling point above 200 ^{o}C and antracenes have above 300 ^{o}C.

The major compounds in mixing method were benzene, toluene, xylene and methyl-naphthalene. In addition, there were other aromatic compounds together which constitute a carbon yield of 24.0±5.2% for biomass:catalyst = 1:4; 41.5±7.3% for biomass:catalyst = 1:9 under inert environment and 42.5± 3.8 for biomass:catalyst = 1:5 for reducing environment. Most of the compounds present in conventional pyrolysis were not present in mixing method, which indicated that these compounds were cracked and deoxygenated to aromatic hydrocarbons. Earlier catalytic pyrolysis studies [20, 24, 33-34] with lower amounts of catalysts (different types of catalysts) had reported some other oxygenated compounds that were absent in the present study.

Table 5.3: Major compounds and their carbon yield for different ratios of biomass-catalyst ratios and different environments from the catalytic pyrolysis of pine wood in catalytic-mixing method[†]

Bio-oil compounds for mixing method of catalytic pyrolysis	Yield, % carbon		
	Helium		Hydrogen
	Ratio of biomass to catalyst		
	1:4	1:9	1:9
Benzene	2.1±0.5	3.5±0.5	3.2±0.4
Toluene	3.7±0.8	5.7±0.9	5.6±0.6
Ethylbenzene	0.5±0.1	0.8±0.2	0.8±0.1
p-Xylene; (Benzene, 1,4-dimethyl-)	7.8±1.5	13.6±2.7	14.4±1.2
m-Xylene; (Benzene, 1,3-dimethyl-)	1.1±0.2	2.5±0.3	2.5±0.2
o-Ethyltoluene; (Benzene, 1-ethyl-2-methyl-)	0.7±0.1	1.2±0.5	1.5±0.1
Benzene, 1,2,3-trimethyl-	0.9±0.1	2.2±0.5	2.6±0.4
Indane; (1H-Indene, 2,3-dihydro-)	0.9±0.3	1.7±0.4	1.8±0.2
Indene; (1H-Indene)	0.7±0.2	1.0±0.2	1.0±0.2
1H-Indene, 1-methyl-	0.6±0.2	1.0±0.3	1.0±0.2
1H-Indene, 2-methyl-	0.4±0.1	0.5±0.1	0.5±0.1
Naphthalene	0.8±0.3	1.4±0.2	1.2±0.2
Naphthalene, 2-methyl-	2.4±0.7	4.0±0.5	3.8±0.5
Naphthalene, 2,6-dimethyl-	1.1±0.3	2.1±0.3	2.2±0.3
Fluorene; (2,2'-Methylenebiphenyl)	0.1±0.0	0.1±0.0	0.1±0.0
Anthracene	0.1±0.0	0.1±0.0	0.1±0.0
Anthracene, 2-methyl-	0.1±0.1	0.2±0.1	0.2±0.0
Benzofuran	0.8±0.5	0.8±0.2	0.7±0.1
Benzofuran, 7-methyl	0.2±0.0	0.2±0.0	0.2±0.1
Benzofuran, 2-methyl-	0.2±0.1	0.3±0.1	0.2±0.1
Phenol	0.5±0.2	0.6±0.2	0.6±0.2
Phenol, 2-methyl-	0.2±0.1	0.2±0.1	0.2±0.1
Phenol, 4-methyl-	0.3±0.2	0.3±0.1	0.4±0.2
Phenol, 2,4-dimethyl-	0.5±0.2	0.5±0.1	0.2±0.3
Phenol, 2-methoxy-4-methyl-	0.1±0.1	0.1±0.1	0.0±0.0
	26.8±5.7	44.5±7.7	45.8±4.7

† number after ± is the standard deviation

Pattiya et al. reported a reduction in all lignin-derived oxygenated compounds using catalysts such as ZSM-5, Criterion-534, Al-MCM-41, Al-MSU-F, copper chromite, char, and ashes while they promoted acids at the same time [24-25]. Zang et al. reported a decrease in methoxy-phenol compounds such as methoxy phenol while using catalytic pyrolysis compared to non-catalytic pyrolysis which was in-line with the present study [20]. Another study reported a small reduction in oxygenated compounds, and the presence of minor amounts of polycyclic aromatic hydrocarbons (PAH) during the catalytic pyrolysis [33, 35]. A study on two-stage catalytic pyrolysis (catalyst were present in second stage only) of refuse derived fuel (RDF) showed an increase in oxygen free aromatics, and a decrease in oxygen containing aromatics compared to two-stage non-catalytic pyrolysis [6]. In addition, the side alkane chains of furan compounds were deoxygenated to aromatic chains. A previous study [24] reported that ZSM-5 favors the production of the phenol compounds, but the total yield of the phenol group was almost similar to that of non-catalytic pyrolysis in the present study. Samolada et al. [36] reported that all carbonyl compounds were deoxygenated to aromatic compounds in the presence of HZSM-5 catalysts, and similar observations were made in this study where the ketone compound identified in non-catalytic pyrolysis was not present in catalytic-mixing. Catalytic pyrolysis studies from Carlson et al. [26-28] reported a high aromatic yield (30% carbon yield) from a ZSM-5-glucose mixture of ratio 19:1 (HZSM:glucose) and proposed reaction mechanisms for catalytic pyrolysis of glucose. Nonetheless, a similar yield cannot be expected from lignocellulosic biomass. Pattiya et al. [24-25] investigated catalytic pyrolysis of lignocellulosic biomass over a number of catalysts (ZSM-5, Al-MCM-41, Al-MSU-F, zinc oxide, zirconium (IV) oxide, cerium (IV) oxide, copper chromite, criterion-534, MI-575, slate, char and ash), and found that ZSM-5, criterion-534 and Al-MSU-F were most selective for deoxygenation of lignin derived compounds, and enhanced aromatic hydrocarbons and phenols. French and Czernik [23] reported similar studies over 40 catalysts including metal substituted ZSM-5 catalysts, and found that nickel substituted ZSM-5 gave the highest hydrocarbon yield.

If the catalyst used for the complete deoxygenation of pine wood is to give aromatic hydrocarbons ($CH_{1.2}$), the reaction can be written as Eq. 5.2 [37]. The theoretical yield of aromatics from pine wood will be 42.2 wt.% which corresponds to 81.6 wt.% of carbon yield.

$$(C_{3.8}H_{6.5}O_{2.8})_n \rightarrow n(3.1CH_{1.2}) + n(0.7CO_2) + n(1.4H_2O) \text{ ………………… (Equation 5.2)}$$

In the case of a 1:9 biomass-catalyst mixture under a helium environment corresponding to Equation 5.2, total aromatic carbon yield was 41.5%, which is about 51% of the theoretical yield from pine wood. Previous catalytic pyrolysis studies [15, 38] using ZSM-5 reported that the maximum aromatics yield was in the range of 8 – 11 wt.% when cracking either pyrolysis oil or vapors. A recent catalytic pyrolysis study reported total aromatic production of 16 wt.% from when using catalyst to biomass ratio from 1:5 to 1:10 [23]. In their study, the biomass was covered with the catalyst. In this study, biomass was mixed with the catalyst and a higher yield of aromatics was observed compared to previous studies. Therefore, the current study showed that the biomass and catalyst mixing has a higher influence in aromatics yield and the catalyst-mixing method seems to be a better option than the catalyst-bed method for aromatics production. The catalyst mixing methods were also performed in presence of H_2 gas (Table 5.3). Here also, there was no significant change as a result of changing the environment for catalytic pyrolysis. Normally, catalyst cracking of biomass occurs in a H_2 limited environment, and the H_2 in biomass has to be utilized for producing both hydrocarbons and water. In the catalyst-mixing method, it is hypothesized that the presence of an external supply of hydrogen can be utilized to produce more aromatic compounds. However, no significant increase in aromatics was noticed when the hydrogen was supplied during cracking. As can be inferred, the major reason is the absence of a hydrogenation catalyst. Perhaps, aromatic yields can be improved if the metal (hydrogenation catalyst) impregnated ZSM-5 catalyst can be used under the presence of hydrogen. There was no reduction in the total yield of carbon when the pyrolysis environment was changed from the inert gas to reducing gas.

In a study conducted by Carlson et al. [26], 7.5% carbon yield was reported from toluene when glucose was pyrolyzed at glucose to catalysts ratio of 1: 19. The present study found about 5 % carbon yield was obtained from toluene using lignocellulosic biomass, and the major compound was xylene (about 15% for biomass:catalyst = 1:9 under helium gas). It was significantly higher than the literature [28]. The absence of most of the guaiacol compounds in the catalytic-mixing method showed that the lignin derived compounds were also cracked to aromatic compounds. This is the reason that this study reported higher carbon yield for aromatics than the previous study (Carlson *et al.*, 2008) on glucose pyrolysis. Since the major compounds were aromatic hydrocarbons, a high heating value and low oxygen content can be expected from the oil phase of catalytic pyrolysis bio-oil. Here, the mixing-method holds promise for producing aromatic hydrocarbon fuel directly from biomass, and it provided better results than previously reported.

Mixing can provide good surface contact between biomass and catalyst. Therefore, in the mixing-method, all the vapors formed during the pyrolysis can be adsorbed on the catalyst surface, and have to diffuse into the pores for catalytic cracking. The catalyst-bed method can be considered as a packed-bed reactor where the bio-oil vapors were entered in to the catalyst bed for cracking. The initial vapors were adsorbed to the catalyst surface, diffused through the pores and cracked to aromatic hydrocarbons. This reaction also formed a large amount of coke, which prevented the diffusion of the vapors through the pores. It was visible in the catalyst-bed method where high coke formation was observed at the entrance of the catalyst bed, and no coke was observed in the tail portion. In addition, some bio-oil components (similar to those found in non-catalytic pyrolysis) were also observed in GC/MS while using the catalyst-bed method. The possible reason is that in the catalyst-bed method, primary tar compounds may convert into more stable secondary and tertiary compounds before reaching the catalyst-bed. It can be concluded from this study that the mixing-method provides better mass transfer for catalyst cracking of bio-oil vapors than the catalyst-bed method, and results in a high yield of aromatic hydrocarbons.

Based on the experimental conditions used in this study, it was found that a high amount of catalyst (90 wt. % of biomass) in the catalyst biomass mixture was suitable to make aromatic hydrocarbon fuel directly from biomass. While a further increase in the catalyst could result in more aromatics, this might not be feasible from a practical standpoint. However, a robust economic analysis is needed, although such is out of scope of this study. In addition, efficient methods for mixing the catalyst and biomass prior to the pyrolysis, and the recovery of catalyst have to be developed. Fluidized-bed and auger reactors (mixing the biomass with catalyst instead of sand) can provide a better solution for pyrolyzing the mixture on a large scale. A study conducted by Lappas et al. regenerated and reused different catalysts such as a fluid catalytic cracking catalyst (FCC) and a ZSM-5 additive in a circulating fluidized bed reactor (CFB) where catalysts were regenerated at 700 ^{o}C [19].

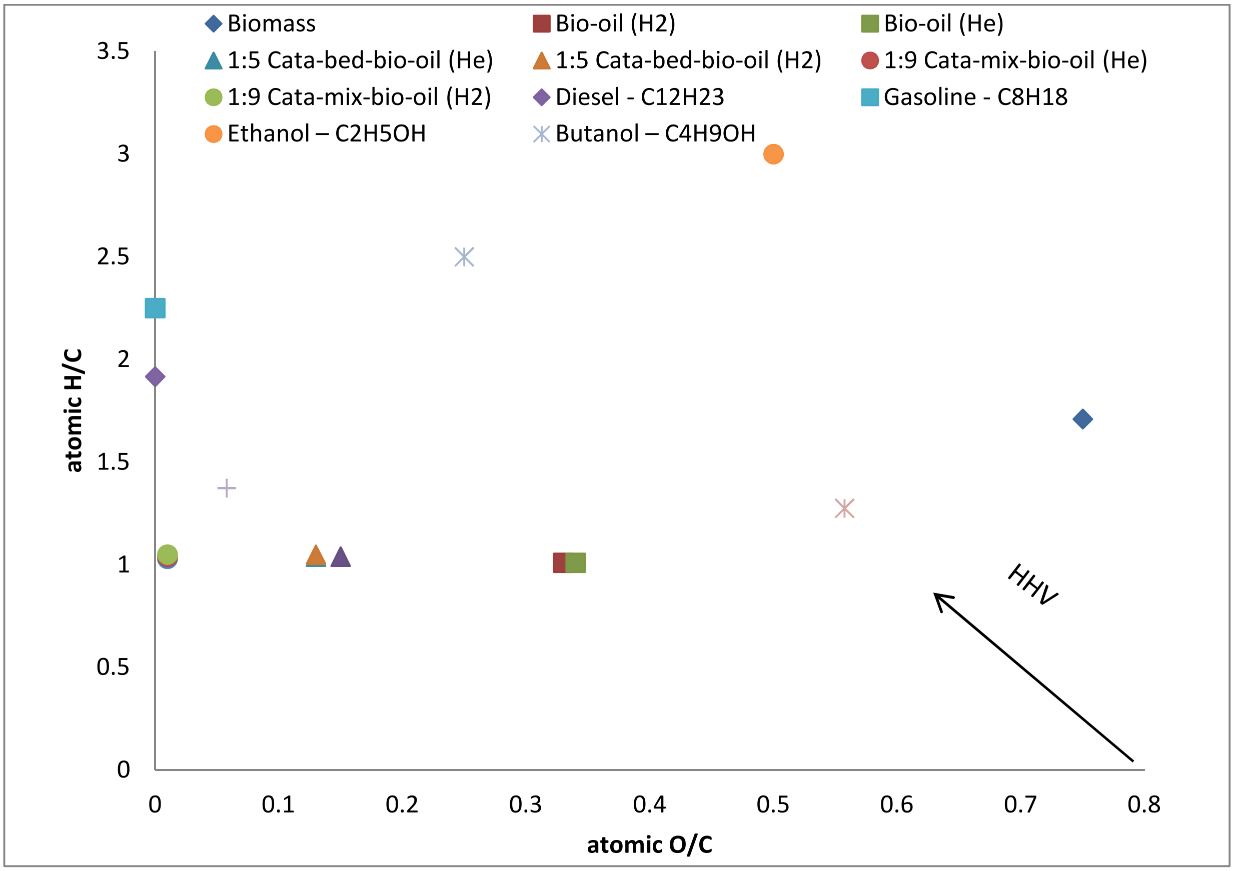


Figure 5.4 Van Krevelen diagram for catalytic and non-catalytic pyrolysis under different gases

Figure 5.4 shows the oxygen/carbon and hydrogen/carbon content of bio-oils produced under different conditions of pyrolysis. A Van Krevelen diagram was plotted for the identified compounds in bio-oils produced under different conditions of pyrolysis. Here, oxygen/carbon content was decreased in the order of biomass > non-catalytic bio-oil > catalyst-bed method bio-oil > catalyst-mixing method bio-oil. Even though biomass had the highest H/C ratio, the high O/C ratio decreased the higher heating value of biomass. Bio-oil had a lower O/C ratio than biomass. In this diagram, there was no difference between the hydrogen and helium gas for both catalytic and non-catalytic pyrolysis. Bio-oil produced in the mixing-method of catalytic pyrolysis had lower O/C ratio than the bio-oil produced from the bed-method of catalytic pyrolysis.

5.5. Conclusions

A high reduction in the yield of higher molecular weight oxygenated bio-oil compounds was observed for non-catalytic pyrolysis in the presence of H_2 as compared to pyrolysis under inert gas. However, there was no change in the catalytic pyrolysis with the change in the environment. The study also found that there was no significant increase in the yield of aromatic groups when the biomass catalyst ratio was increased from 1:2 to 1:5 using the catalyst-bed method; whereas, a significant increase in the yield of aromatic compounds was noticed when the biomass to catalyst ratio increased from 1:4 to 1:9 with the mixing-method.

5.6. Acknowledgement

The authors would like to acknowledge the Southeastern SunGrant and the United States Department of Agriculture-NIFA for funding this study. However, only the authors are responsible for the opinions expressed in this paper and for any remaining errors.

5.7. References

1. McKendry, P., *Energy production from biomass (part 1): overview of biomass.* Bioresource Technology, 2002. **83**(1): p. 37–46.

2. EISA (2007) *Energy Independence and Security Act of 2007.* http://frwebgate.access.gpo.gov/cgi-bin/getdoc.cgi?dbname=110_cong_bills&docid=f:h6enr.txt.pdf

3. Zeng, F., et al., *Separation of Phthalate Esters from Bio-oil Derived from Rice Husk by a Basification–Acidification Process and Column Chromatography.* Bioresource Technology, 2011. **102**: p. 1982 - 1987.

4. Heo, H.S., et al., *Catalytic Upgrading of Oil Fractions Separated from Food Waste Leachate.* Bioresource Technology, 2011. **102**: p. 3952 - 3957.

5. Zhang, S.-Y., et al., *Low Temperature Catalytic Gasification of Pig Compost to Produce H_2 Rich Gas.* Bioresource Technology, 2011. **102**: p. 2033 - 2039.

6. Miskolczi, N., et al., *Two Stages Catalytic Pyrolysis of Refuse Derived Fuel: Production of Biofuel via Syncrude.* Bioresource Technology, 2010. **101**: p. 8881 - 8890.

7. Czernik, S. and A.V. Bridgwater, *Overview of Applications of Biomass Fast Pyrolysis Oil.* Enegry & Fuels, 2004. **18**(2): p. 590-598.

8. Diebold, J.P., *A Review of the Chemical and Physical Mechanisms of the Storage Stability of Fast Pyrolysis Bio-Oils* 2000.

9. Bridgwater, A.V. and M.L. Cottam, *Opportunities for Biomass Pyrolysis Liquids Production and Upgrading.* Enegry & Fuels, 1992. **6**(2): p. 113-120.

10. Senol, O.I., et al., *Effect of Hydrogen Sulphide on the Hydrodeoxygenation of Aromatic and Aliphatic Oxygenates on Sulphided Catalysts.* Journal of Molecular Catalysis A: Chemical, 2007. **277**: p. 107 - 112.

11. Qi, Z., et al., *Review of Biomass Pyrolysis Oil Properties and Upgrading Research.* Energy Conversion and Management, 2007. **48**: p. 87-92.

12. Sharma, R.K. and N.N. Bakhshi, *Catalytic Upgrading of Pyrolysis Oil.* Enegry & Fuels, 1993. **7**(2): p. 306 - 314.

13. Gupta, R.B. and A. Demirbas, *Gasoline, Diesel and Ethanol Biofuels from Grasses and Plants*. 2010, Cambridge University Press: New York, USA. p. 140 - 157.

14. Vispute, T.P., et al., *Renewable Chemical Commodity Feedstocks from Integrated Catalytic Processing of Pyrolysis Oils.* Science, 2010. **330**: p. 1222 - 1227.

15. Diebold, J., et al., *Catalytic Upgrading of Biocrude Oil Vapors to Produce Hydrocarbons for Oil Refinery Applications.* A.C.S. Division of Fuel Chemistry, 1994. **39**: p. 1043 - 1047.

16. Williams, P.T. and H.M. Chishti, *Two Stage Pyrolysis of Oil Shale Using a Zeolite Catalyst.* Journal of Analytical and Applied Pyrolysis, 2000. **55**: p. 217 - 234.

17. Putun, E., B.B. Uzun, and A.E. Putun, *Rapid Pyrolysis of Olive Residue. 2. Effect of Catalytic Upgrading of Pyrolysis Vapors in a Two-Stage Fixed-Bed Reactor.* Enegry & Fuels, 2009. **23**: p. 2248 - 2258.

18. Onay, O., *Fast and Catalytic Pyrolysis of Pistacia Khinjuk Seed in a Well-Swept Fixed Bed Reactor.* Fuel, 2007. **86**: p. 1452 - 1460.

19. Lappas, A.A., et al., *Biomass Pyrolysis in a Circulating Fluid Bed Reactor for the Production of Fuels and Chemicals.* Fuel, 2002. **81**: p. 2087 - 2095.

20. Zhang, H., et al., *Catalytic Fast Pyrolysis of Biomass in a Fluidized Bed with Fresh and Spent Fluidized Catalytic Cracking (FCC) Catalysts.* Enegry & Fuels, 2009. **23**: p. 6199 - 6206.

21. Antonakou, E.V., V.S. Dimitropoulos, and A.A. Lappas, *Production and Characterisation of Bio-Oil from Catalytic Biomass Pyrolysis.* Thermal Science, 2006. **10**(3): p. 151 - 160.

22. Torri, C., I.G. Lesci, and D. Fabbri, *Analytical Study on the Pyrolytic Behaviour of Cellulose in the Presence of MCM-41 Mesoporous Materials.* Journal of Analytical and Applied Pyrolysis, 2009. **85**: p. 192 - 196.

23. French, R. and S. Czernik, *Catalytic Pyrolysis of Biomass for Biofuels Production.* Fuel Processing Technology, 2010. **91**: p. 25 - 32.

24. Pattiya, A., J.O. Titiloye, and A.V. Bridgwater, *Evaluation of Catalytic Pyrolysis of Cassava Rhizome by Principal Component Analysis.* Fuel, 2010. **89**: p. 244 - 253.

25. Pattiya, A., J.O. Titiloye, and A.V. Bridgwater, *Fast pyrolysis of cassava rhizome in the presence of catalysts.* Journal of Analytical and Applied Pyrolysis, 2008. **81**(72 - 79).

26. Carlson, T.R., T.P. Vispute, and G.W. Huber, *Green Gasoline by Catalytic Fast Pyrolysis of Solid Biomass Derived Compounds.* ChemSusChem, 2008. **1**: p. 397-400.

27. Carlson, T.R., et al., *Aromatic Production from Catalytic Fast Pyrolysis of Biomass-Derived Feedstocks.* Topics in Catalysis, 2009. **52**: p. 241 - 252.

28. Carlson, T.R., et al., *Catalytic Fast Pyrolysis of Glucose With HZSM-5: The Combined Homogeneous and Heterogeneous Reactions.* Journal of Catalysis, 2010. **270**: p. 110 - 124.

29. Lu, C., W. Song, and W. Lin, *Kinetics of Biomass Catalytic Pyrolysis.* Biotechnology Advances, 2009. **27**(5): p. 583-587.

30. NREL, *Laboratory Analytical Procedure (LAP).* National Renewable Energy Laboratory, 1998.

31. Biagini, E., F. Lippi, and L. Tognotti, *Characterization of a Lab-Scale Platinum Filament Pyrolyzer for Studying the Fast Devolatilization of Solid Fuels.* Fuel, 2006. **85**: p. 2408-2418.

32. Lee, S.-B. and O. Fasina, *TG-FTIR Analysis of Switchgrass Pyrolysis.* Journal of Analytical and Applied Pyrolysis, 2009. **86**: p. 39 - 43.

33. Aho, A., et al., *Catalytic Pyrolysis of Biomass in a Fluidized Bed Reactor: Influence of The Acidity of H-Beta Zeolite.* Trans IChemE, Process Safety and Environmental Protection, 2007. **85** (B5): p. 473 - 480.

34. Boateng, A.A., et al., *Guayule (Parthenium argentatum) Pyrolysis and Analysis by PY–GC/MS.* Journal of Analytical and Applied Pyrolysis, 2010. **87**: p. 14 - 23.

35. Aho, A., et al., *Catalytic Pyrolysis of Woody Biomass in a Fluidized Bed Reactor: Influence of the Zeolite Structure.* Fuel, 2008. **87**: p. 2493 - 2501.

36. Samolada, M.C., A. Papafotica, and I.A. Vasalos, *Catalyst Evaluation for Catalytic Biomass Pyrolysis.* Enegry & Fuels, 2000. **14**: p. 1161 - 1167.

37. Bridgwater, A., *Thermal Biomass Conversion and Utilization - Biomass Information System*, in *European Commission - Science, Research and Development*. 1996: Luxembourg.

38. Evans, R.J. and T. Milne, eds. *Molecular-Beam, Mass Spectrometric Studies of Wood Vapor and Model Compounds over an HSZM-5 Catalyst*. Pyrolysis Oils from Biomass: Producing, Analyzing and Upgrading, ed. E.J. Soltes and T.A. Milne. 1988, American Chemical Society: Washington, DC. 311 - 327.

6. Catalytic Pyrolysis of Biomass over H^+ZSM-5 Catalyst under Hydrogen Pressure

6.1. Abstract

The catalytic-pyrolysis of pine wood was carried out using H^+ZSM-5 catalysts in hydrogen environment. The first objective was to investigate the effect of hydrogen pressure on catalytic pyrolysis using H^+ZSM-5. The study found that there was no increase in the aromatic hydrocarbons as the hydrogen pressure increased. The second objective was to incorporate hydrogenation effect in addition to catalytic-cracking during the pyrolysis so that the hydrocarbon content in bio-oil can be improved. One of the metal (Mo) impregnated catalysts was chosen for pyrolysis under different hydrogen pressures. The Mo/ZSM-5 catalyst was not as active as H^+ZSM-5 in lower pressures (100 – 300 psi), however at 400 psi, Mo/ZSM-5 gave more hydrocarbons than that of H^+ZSM-5. A significant increase in aromatic hydrocarbons was found when the H^+ZSM-5 catalysts were impregnated with metals (Ni, Co, Mo, and Pt) compared to just the zeolite catalysts at 400 psi. On average, 42.5 wt.% of biomass carbon was converted into hydrocarbons. The aromatic distribution was almost similar for all the metal impregnated catalysts.

6.2. Introduction

Alternative energy resources have a major role in reducing the demand of fossil fuels, and improving nation's energy security and energy sustainability goals. In this regard, biomass is considered as a major candidate for renewable and reliable energy resource which can provide transportation liquid fuels and other forms of energy. Biochemical and thermochemical conversion processes are the two major platforms to produce biofuels from biomass. The fast pyrolysis is one of the thermochemical conversion methods to produce liquid fuel. A high liquid yield (~70 wt. %) can be directly produced from the fast pyrolysis of biomass, which makes the process attractive [1-2]. In the fast pyrolysis, biomass is heated rapidly in the absence of oxygen and the resulting vapors are quickly condensed to produce bio-oil (a dark colored liquid). Bio-oil has potential applications in the field of energy such as energy carrier, fuel for static applications and can be upgraded as transportation fuel [3-5]. In addition, bio-oil is a feedstock for many commodity chemicals and the conversion of biomass to bio-oil help to reduce some of the issues related to biomass logistics. However, there are some negative attributes of bio-oil such as high density, high oxygen content, high viscosity, high water content and instability, which limit the final applications of bio-oil as it is. Therefore, bio-oil has to undergo downstream upgrading steps before its final application.

There are two major techniques to upgrade bio-oil as hydrocarbon fuel, hydrodeoxygenation (HDO) and catalytic-cracking [3, 5]. In hydrodeoxygenation, hydrogen reacts with bio-oil compounds under high pressure to produce hydrocarbons and water. Normally, NiMo and CoMo are used as HDO catalysts. In catalytic-cracking, bio-oil compounds are deoxygenated in the presence of shape selective catalyst such as zeolite, mesoporous Al-

MCM-41. Commercial implementation of these techniques has not been achieved. Therefore, studies are focused on technical and economical production of hydrocarbon fuels from biomass. In this regard, catalytic-pyrolysis is an emerging technology to produce hydrocarbon fuels directly from biomass which eliminates a series of bio-oil upgrading steps. In catalytic-pyrolysis, catalysts are introduced during the pyrolysis; therefore, the bio-oil compounds are deoxygenated as they produced. Since deoxygenation happens in vapor phase, some of the compounds like anhydrosugars are relatively thermally stable and do not polymerize to coke [6]. Recently, many studies have focused on aromatics production using catalytic-pyrolysis [6-11]. Synthetic zeolite (H^+ZSM-5) catalysts have been successfully used for deoxygenation of organic compounds to produce aromatic hydrocarbons [12]. The H^+ZSM-5 is a shape selective catalyst with a pore size of 5.5 A^o. This intermediate pore size largely favors hydrocarbons of less than 10 carbon atoms [13]. Since bio-oil is a mixture of a variety of compounds having different molecule sizes, catalyst with intermediate pore size would be the better choice for bio-oil upgrading. In addition, SiO_2/Al_2O_3 ratio can be varied by many orders of magnitude; H^+ZSM-5 has been used for cracking a variety of compounds by varying the acidity and catalytic properties. Usually H^+ZSM-5 cracking occurs at atmospheric pressure in presence of an inert gas.

Herein, the hypothesis of this study is that if the catalytic-pyrolysis happens under slightly higher hydrogen pressure, the principles of hydrodeoxygenation and catalytic-cracking can be combined to produce hydrocarbons in a single method. The previous study [10] found that the aromatic yield for catalytic pyrolysis in presence of H^+ZSM-5 was almost similar for both hydrogen and helium environments at the catalyst to biomass ratio of 9:1, and the study was conducted at single pressure (~80 psi). Therefore, the current study investigated the effect of pressure in hydrogen environment (hydropyrolysis) using H^+ZSM-5 catalyst. In addition, the metal catalysts (Ni, Co, Mo, and Pt) were impregnated on H^+ZSM-5 catalysts to investigate their effect in utilizing hydrogen for deoxygenation during the catalytic-pyrolysis process. Normally NiMo or CoMo on γ-alumina support are used for hydrodeoxygenation of bio-oil compounds, therefore these metals (Ni, Co, and Mo) were impregnated on H^+ZSM-5 (5 wt. %) powder as the hydrogenating elements. Since noble metals are very active for hydrogenation reactions, a noble metal platinum impregnated-ZSM-5 (0.5 wt.%) were also used for catalytic pyrolysis. These metals were impregnated to see the synergic effect of metal and the carrier gas on the deoxygenation of bio-oil compounds and hydrogenation of aromatic compounds. The objective in this study was to utilize both hydrogenation and cracking reactions over metal impregnated-ZSM-5 catalysts under a lower pressure than typical hydrodeoxygenation condition.

6.3. Materials and Methods

6.3.1. Biomass characterization

Dried and ground pine wood biomass sample (particle size 149 – 177 μm) was taken for this study. Moisture content of the biomass sample (wet basis) was determined by calculating weight loss after heating in an oven at 103°C for 16 h according to ASTM E 871 standard and the ash content was measured using ASTM E 1755 standard. Techniques for determining chemical constituents and ultimate analysis of biomass sample were described elsewhere [10].

6.3.2. Catalysts

The ammonium form of ZSM-5 catalyst (silica to alumina ratio equal to 50 and surface area equal to 425 m^2/g) for this study was purchased from the Zeolyst Internatonal (Conshohocken, PA, USA). The catalyst was calcined in air at 550°C for 3 h to covert in to

H^+ZSM-5. Metals were impregnated in H^+ZSM-5 powder using the incipient wetness method. The metals were impregnated on H^+ZSM-5 using their ammonium nitrate or nitrate solutions: $(Co(NO_3)_2$. $6H_2$ (cobalt nitrate) for Co, $Ni(NO_3)_2$. $6H_2$ (nickel nitrate) for Ni, $(NH4)_6Mo_7O_{24}$. $4H_2O$ (ammonium hepta molebdate) for Mo, and $Pt(NH_3)_4(NO_3)_2$ (tetra ammine platinum nitrate) for Pt. The metal solutions were prepared in 20 mL water in the ratio so that ZSM-5 powder contain 5 wt.% of desired metals (for platinum, it was 0.5 wt.%). After stirring the solution with H^+ZSM-5 powder for 30 min, the samples were dried at 120°C, and calcined in air at 500°C for 3 h. The dried powders of metal impregnated ZSM-5 catalysts were reduced by passing 5% H_2 and balance He gas in the rate of 35 mL/min at 500°C for 2 h.

The BET (Brunauer-Emmett-Teller) surface area of metal impregnated catalysts was measured using Quantachrome Autosorb-1 automated gas sorption system using multipoints. About 0.12 – 0.15 g of sample was taken for analysis, and the sample was degassed at 140°C under vacuum and then measured at 77.3 K using nitrogen as adsorbate. To determine the metal composition, the H^+ZSM-5 and metal impregnated ZSM-5 powders were sent to Hazen Research Inc (Golden, CO).

6.3.3. Pyrolysis – GC/MS

Pyrolysis studies were carried out using a commercial pyrolyzer (Pyroprobe model 5200, CDS Analytical Inc., Oxford, PA), which was interfaced with an Agilent gas chromatograph/mass spectrometer (7890GC/5975MS). Biomass and catalysts were mixed in the ratio of 1:9 and mixture was inserted between the quartz wool in a quartz tube for the pyrolysis. A detailed description of an experimental procedure, and biomass-catalyst mixing method are available in the published document elsewhere [10]. Briefly, about 4 mg of known amount of samples were pyrolyzed at 650^{o}C and a filament ramping rate of 2000 ^{o}C/s with a holding time of 1.5 min. Pine wood - H^{+}ZSM-5 and pine wood – Mo/ZSM-5 mixtures were pyrolyzed at 100, 200, 300, and 400 psi hydrogen environment; whereas pine wood and metal (Ni, Co, and Pt) impregnated-ZSM-5 mixtures were pyrolyzed only at 400 psi of hydrogen pressure. The bio-oil components were analyzed with an Agilent 7890GC/5975MS using a DB-1701 column (30 m; 0.25 mm i.d.; 0.25 mm film thickness). The GC/MS method for compounds identification and their calibration were similar as described in the previous paper [10]. Selectivity for aromatics was measured as wt. of carbon in individual compounds*100/ total wt. of carbon for aromatics.

6.4. Results and Discussion

6.4.1. Biomass Characterization

The pine wood powder taken for this study had 5.6 ± 0.2 wt.% (wet basis) moisture content and 0.9 ± 0.1 wt.% ash content. The chemical properties of biomass used for this study is available in the published document elsewhere [10]. From the ultimate analysis of pine wood, the chemical formula found is $(C_{3.8}H_{6.5}O_{2.8})_n$.

6.4.2. Catalyst Characterization

The BET surface area analysis showed that the H^{+}ZSM-5 catalyst used for this study had 301.9m^{2}/g which was far below the specified value. The surface areas of Co-ZSM, Ni-ZSM, and Mo-ZSM were 291.6 m^{2}/g, 292.0 m^{2}/g, and 300.2 m^{2}/g respectively. The BET plot of each sample had a correlation coefficient above 0.998. There was no significant reduction in the surface area of ZSM-5 powder after adding the metals on it, which showed that these metals were impregnated on the surface of ZSM-5 powder. Metal analysis of H^{+}ZSM-5 powder showed that it had minor amounts of metals such as Co – 10 ppm, Ni – 20 ppm, Mo < 5 ppm and Pt <0.3 ppm which were negligible. The inductively coupled plasma (ICP) analysis of metal impregnated ZSM catalysts showed that Co/ZSM contained 4.25 wt.% of Co, Ni/ZSM contained 4.39 wt.% Ni, Mo/ZSM contained 3.13 wt. % of Mo, and Pt/ZSM contained 0.5 wt.% Pt.

6.4.3. Catalytic-Pyrolysis under Different Pressure

Table 6.1: Carbon yield of aromatic hydrocarbons during catalytic pyrolysis of pinewood with H^+-ZSM-5 catalyst at different hydrogen pressures[‡]

Bio-oil compounds	C yield, wt.%			
	100 psi	200 psi	300 psi	400 psi
Benzene	4.5±0.3	5.4±1.2	3.3±1.5	5.9±2.6
Toluene	6.2±0.6	6.6±1.2	6.6±1.7	9.2±1.6
Ethylbenzene	0.6±0.1	0.4±0.1	0.5±0.2	0.4±0.0
p/m - Xylene	14.3±2.2	13.1±2.3	14±0.9	9.3±2.5
Benzene, 1-ethyl-2-methyl-	0.8±0.2	0.7±0.2	0.7±0.1	0.7±0.1
Benzene, 1,3,5-trimethyl-	0.1±0.0	0.2±0.0	0.2±0.1	0.2±0.1
Indane	0.6±0.1	0.4±0.1	0.4±0.0	0.4±0.2
Indene	0.4±0.1	0.3±0.1	0.4±0.2	0.2±0.0
Methyl indene	0.5±0.1	0.2±0.1	0.4±0.1	0.2±0.1
Naphthalene	1.8±0.1	2.2±0.4	2.6±1.3	2.5±0.8
Methyl naphthalene,	3.8±0.5	4.6±0.7	4.7±0.8	4.9±0.8
Dimethyl naphthalene	1.7±0.3	2.0±0.3	2.5±0.8	2.0±0.8
Anthracene	0.1±0.1	0.1±0.1	0.1±0.1	0.1±0.1
Total	35.5±4.1	36.2±6.9	39.7±6.9	36.2±3.2
Hydrogen yield, wt.%				
Total	21.7±2.6	21.9±3.9	23.9±3.7	21.5±2.6

[‡] Number after ± is the standard deviation

Normally catalytic pyrolysis occurs in the presence of an inert gas at atmospheric pressure. One of the major issues in catalyst deactivation is the polymerization of large bio-oil components on the surface of catalyst. Here higher pressures 100, 200, 300, and 400 psi were selected for pyrolysis to see the effect of pressure in hydrocarbon formation. Table 6.1 depicts the effect of pressure in catalytic pyrolysis for aromatic hydrocarbon formation.

There was no effect of hydrogen pressure on bio-oil compounds from 100 to 400 psi. The average of selectivity of major aromatic hydrocarbons is given in Figure 6.1. The selectivity of xylene decreased whereas the selectivity of toluene increased when the pressure increased from 300 psi to 400 psi. A previous study [14] on the deoxygenation of methanol over ZSM-5 catalyst in similar instrument had shown a decrease in the selectivity of xylene as pressure increased (0 – 300 psi) whereas the toluene had maximum selectivity in intermediate pressure (200 psi). Lower aromatic hydrocarbons have lower boiling points; therefore, they are favorable as gasoline additives than higher aromatic hydrocarbons.

Adjaye and Bakhshi [15] proposed a reaction mechanism for catalyst cracking of bio-oil compounds in the presence of zeolite catalysts where the lighter organic compounds will produce olefins which undergo cyclization reaction to produce benzene. Then there will be a series of alkylation reaction to produce substituted benzene derivatives (aromatic hydrocarbons) [15]. Carlson et al. have discussed similar mechanism for catalytic pyrolysis of cellulose/glucose over ZSM-5 catalysts where the intermediates enter a ‘hydrocarbon pool’ (which is similar for conversion to methanol to aromatics) within the zeolite framework and undergo aromatization to produce monocyclic aromatics. These monocyclic aromatic hydrocarbons could either leave the reactor as products or react with oxygenated compounds to produce polycyclic hydrocarbons [6, 16]. These larger molecules prevent the entry of other oxygenated molecules into the zeolite pores which lead to the deactivation of catalyst. At high temperatures, with the intensive of pressure, polynuclear aromatics were further cracked into mononuclear ones [17]. In addition, as hydrogen pressure increased hydrogenation of free radicals or fragments (generated during the thermal cracking of biomass) occurs and therefore a series of condensation and polymerization reactions which cause coke formation would be suppressed [17].

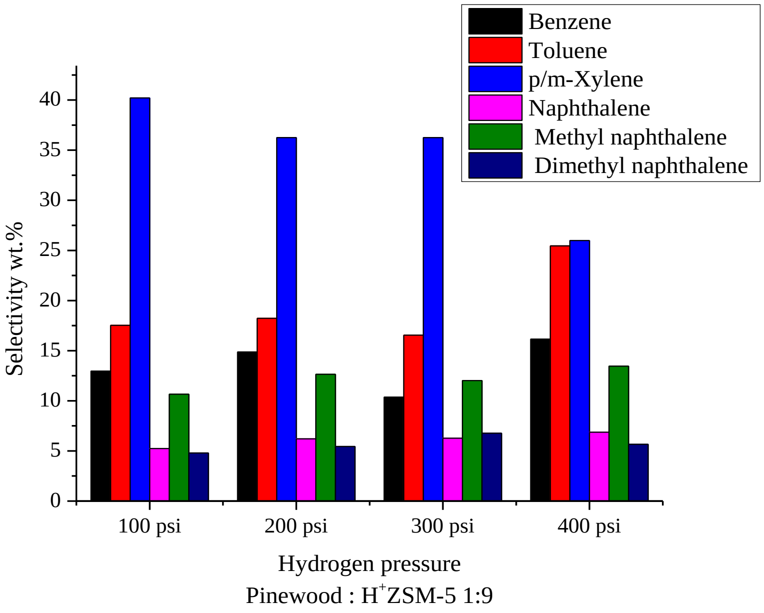


Figure 6.1: Aromatic selectivity of major hydrocarbons produced during hydrocatalytic pyrolysis of pinewood under different hydrogen pressures

Hydropyrolysis is relatively a new approach for biofuel production [18-19] whereas it has been widely used for coal pyrolysis [17, 20-21]. In hydropyrolysis of coal, as the hydrogen pressure increased the tar yield increased and gas and coke yield decreased. They stated that this was due to the effective utilization of hydrogen [17]. The reduction in gas yield was noticed only at high pressure when hydrogen pressure increased from 5 MPa (725 psi) to 10 MPa (1450 psi) which is due to the reduction in methane yield. Methane will be cracked due to high hydrogen pressure [17]. The major competing reaction for the formation of aromatics is the formation of coke due to the polymerization of reactants. In hydropyrolysis of coal, the reduction in coke as the hydrogen pressure increased was the result of hydrogenation which suppresses polymerization, condensation, and other secondary reactions that lead to coke formation [17]. In contrast to coal hydropyrolysis, a previous study [19] on biomass hydropyrolysis showed that as the pressure increased from 10 bar (145 psi) to 40 bar (580 psi) a decrease in tar yield was noticed. This study could be in contrast to current study which showed similar yield for aromatic hydrocarbons as pressure increased.

Pindoria et al. studied about the bio-oil upgrading (produced from hydropyrolysis) over H^+ZSM-5 catalyst at the same hydrogen pressures as that of hydropyrolysis (10 – 40 bar) stated that the catalyst acted only as a cracking catalyst not as an agent to promote hydrogenation [19]. Current study also showed no increase in aromatics or any other hydrogenated products. Therefore, the next objective in current study was to integrate hydrogenation with cracking.

In catalytic pyrolysis with H^+ZSM-5, the large molecules (formed by the thermal decomposition of biomass) are thermally cracked into smaller ones on the surface of catalyst and entered to the zeolite pores for subsequent reactions. Initially olefins will be formed by simple reactions such as dehydration or a series of reactions such as aldol condensation [22-23]. Olefins will be oligomerized by the formation of carbonium ions to give dienes / trienes which will undergo cyclization and dehydration to form benzene ring [24]. Benzene will react with other oxygenated compounds to form alkylated benzene or polyaromatic hydrocarbons. To facilitate the production of alkane hydrocarbons, hydrogenation of aromatics will not be desired. Therefore the oefin oligomerization has to be prevented by hydrogenation of olefins to paraffins. In order to utilize the hydrogen environment bifunctional catalysts (acid/metal) were prepared by impregnating some hydrogenating metals on zeolite . Molebdenum, the major metal element in hydrodeoxygenation catalysts (NiMo, CoMo) was impregnated on H^+ZSM-5 powders and taken for catalytic pyrolysis under different hydrogen pressures. The carbon yield of aromatic hydrocarbons during the catalytic pyrolysis of pinewood with Mo/ZSM-5 is given in Table 6.2.

Table 6.2: Carbon yield of aromatic hydrocarbons during catalytic pyrolysis of pinewood with Mo/ZSM-5 catalyst at different hydrogen pressures‡

Bio-oil compounds	C yield, wt.%			
	100 psi	200 psi	300 psi	400 psi
Benzene	3.7±0.4	5.4±1.0	6.2±1.4	6.4±1.3
Toluene	7.6±0.4	9.1±1.3	9.4±0.2	11.5±1.2
Ethylbenzene	0.5±0.1	0.6±0.1	0.5±0.1	0.7±0.1
p/m - Xylene	8.7±0.8	8.3±1.6	8.4±0.3	11.0±1.1
Benzene, 1-ethyl-2-methyl-	1.0±0.1	0.8±0.2	0.8±0.1	1.2±0.2
Benzene, 1,3,5-trimethyl-	1.5±0.4	1.2±0.4	1.4±0.1	2.2±0.6
Indane	0.5±0.1	0.5±0.1	0.4±0.1	0.6±0.1
Indene	0.4±0.1	0.5±0.1	0.4±0.1	0.5±0.1
Methyl indene	0.4±0.1	0.5±0.1	0.4±0.1	0.6±0.1
Naphthalene	1.6±0.2	2.1±0.5	2.2±0.3	2.5±0.3
Methyl naphthalene,	2.4±0.4	2.8±0.7	2.7±0.2	3.8±0.3
Dimethyl naphthalene	0.9±0.2	0.9±0.3	0.9±0.1	1.4±0.2
Anthracene	0.1±0.0	0.1±0.1	0.1±0.0	0.1±0.1
Total	29.1±2.4	32.9±5.3	33.8±1.0	42.5±3.3
Hydrogen yield, wt.%				
Total	18.0±1.5	19.9±3.2	20.5±0.5	25.9±2.0

‡ Number after ± is the standard deviation

Increases in the yields of aromatic hydrocarbons were noticed as hydrogen pressure increased from 300 to 400 psi. However, the total yield of hydrocarbons in presence of Mo/ZSM-5 was lower than that of during low pressures of hydrogen (100 – 300 psi). That shows that the presence of metal was active only after 300 psi hydrogen pressure. At lower pressures (100 – 300 psi) a reduction in acid sites (metal occupied acid site and it was not active), provided lower yield for aromatic hydrocarbons as that of H^+ZSM-5. At higher pressure (400 psi) the presence of active site helped more compounds for cyclization. A reduction in xylene selectivity was noticed as pressure increased from 100 psi to 400 psi in presence of H^+ZSM-5 catalyst whereas in presence of Mo/ZSM-5, a reduction was noticed only when hydrogen pressure increased from 100 psi to 200 psi, and it was almost similar for further increase in pressures.

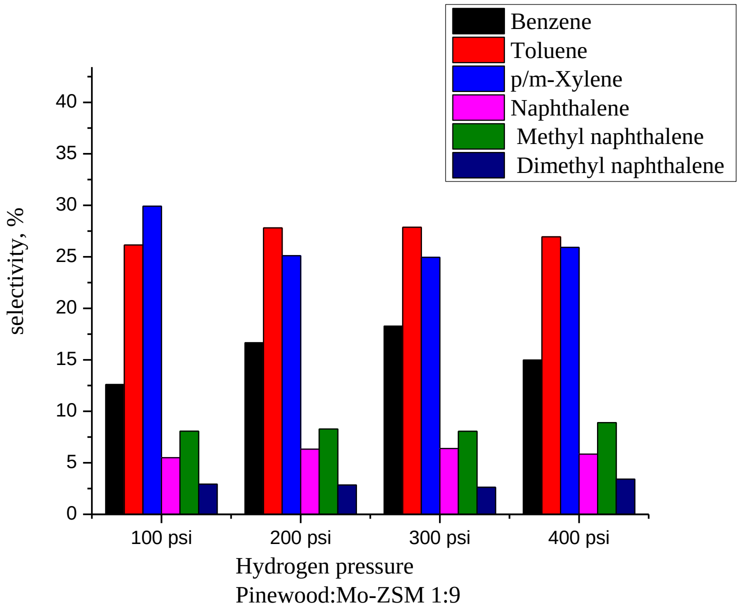


Figure 6.2: Aromatic selectivity of major hydrocarbons produced during catalytic pyrolysis of pinewood with Mo/ZSM-5 catalysts under different hydrogen pressures

Recent study [25] on catalytic pyrolysis of biomass utilized a bifunctional catalyst (Ga/ZSM-5) for increasing the aromatic yield. Their study showed that while Ga promoted the desired decarbonylation and olefin aromatization reactions, the ZSM-5 catalyzed the oligomerization and cracking reactions. Therefore Ga/ZSM-5 catalyst provided 15 – 23% more aromatic yield than that with normal acid (H^+ZSM-5) catalyst. Ga increased the rate of aromatic production without changing the overall reaction mechanism [25]. In contrast to this result, current study provided higher aromatic yield with acid/metal catalysts only at high hydrogen pressure (400 psi). This would be because Mo promotes hydrogenation rather than decarbonylation. Hydrogenation of free radicals or ions (formed due to thermal cracking) is stabilized so that more compounds can go for hydrocarbon production.

The carbon yield of major aromatic compounds produced from the catalytic pyrolysis of pine wood at 650^{o}C (probe temperature) under 400 psi hydrogen pressures in presence of metal impregnated-ZSM-5 catalysts is shown in Table 6.3.

There was an increase in the yield of aromatic hydrocarbons when the metal impregnated-ZSM-5 powder used for catalytic pyrolysis. However, the differences in the influence of metals were not visible because of high standard deviations. High standard deviation for yields of compounds during pyroprobe studies were noticed elsewhere [26]. The high carbon yield with metal impregnated-ZSM-5 catalysts confirmed that the metal impregnated on H^{+}ZSM-5 helped to hydrogenate some of the compounds to produce more aromatic hydrocarbons. However, none of the aliphatic compounds were noticed as major compound during the pyrolysis; which indicates that the carrier (H^{+}ZSM-5 powder) had higher catalytic activity than impregnated metals. Therefore, deoxygenation due to cracking was the major reaction occurred during catalytic-pyrolysis and hydrogenation of aromatic hydrocarbons was not observed.

Table 6.3: Carbon yield of aromatic hydrocarbons during catalytic pyrolysis of pinewood with metal impregnated-ZSM-5 catalysts at 400 psi hydrogen pressure‡

Bio-oil compounds	C yield, wt.%			
	Co-ZSM	Ni-ZSM	Mo-ZSM	Pt-ZSM
Benzene	8.0±2.0	7.4±3.1	6.4±1.3	6.7±2.1
Toluene	11.1±1.2	10.6±1.4	11.5±1.2	12.0±1.7
Ethylbenzene	0.6±0.1	0.7±0.2	0.7±0.1	0.6±0.2
p/m - Xylene	9.6±1.5	10.0±1.9	11.0±1.1	11.9±1.2
Benzene, 1-ethyl-2-methyl-	1.0±0.1	1.1±0.4	1.2±0.2	1.1±0.3
Benzene, 1,3,5-trimethyl-	1.5±0.3	2.2±1.3	2.2±0.6	2.6±0.7
Indane	0.5±0.1	0.6±0.1	0.6±0.1	0.6±0.2
Indene	0.5±0.1	0.5±0.1	0.5±0.1	0.5±0.1
Methyl indene	0.6±0.1	0.6±0.1	0.6±0.1	0.7±0.2
Naphthalene	2.1±0.3	2.5±0.3	2.5±0.3	3.0±0.4
Methyl naphthalene	2.9±0.5	3.7±0.7	3.8±0.3	4.8±0.4
Dimethyl naphthalene	1.0±0.2	1.4±0.5	1.4±0.2	1.8±0.4
Anthracene	0.1±0.0	0.1±0.0	0.1±0.1	0.2±0.1
Total	39.8±4.7	41.3±4.5	42.5±3.3	46.4±5.1
Hydrogen yield , wt.%				
Total	25.0±2.8	25.9±2.0	25.9±2.0	28.2±3.0

‡ Number after ± is the standard deviation

Normally bimetallic catalysts (Ni-Mo or Co-Mo) are used for hydrodeoxygenation of bio-oil compounds and Mo loading on carriers is higher than Nickel or Cobalt [27-28]. Noble metals (Pt, Pd) as monometallic catalysts showed a high selectivity towards hydrodeoxygenation [29]. Masalska studied the hydrogenation of toluene in presence of Ni/ZSM-5 catalyst and noticed an increase in the overall toluene conversion from 35 to 60 % when the NiO content increased from 8 – 12 wt. % [30]. Similar increase in benzene hydrogenation was noticed as the platinum load increased on zeolite carrier [31]. In current study, the carrier catalyst activity dominated (cracking) over the metal catalyst activity (hydrogenation), therefore, it was difficult to distinguish the difference in the activity of metals.

The aromatic selectivity of major hydrocarbons was described in Figure 6.2. The aromatic distribution for each case of metal impregnated zeolite catalyst was almost similar which was even similar to that of H^+ZSM-5 (graph was shown by avoiding the error bars). The major compounds in all cases were toluene and xylene; benzene and naphthalene were next major compounds.

One catalytic hydropyrolysis study of rice husk in presence of an inexpensive catalyst (nickel-loaded brown coal char catalyst) was reported in which hydropyrolysis under atmospheric pressure with and without catalyst had done [18]. A 10% decrease in oxygen content of bio-oil was observed when catalyst used for pyrolysis than non-catalytic pyrolysis. The aromatic yield during non-catalytic pyrolysis was negligible and in catalytic pyrolysis, aromatic yield increased upto 14.09 area % in GC-MS chromatogram [18]. The maximum aromatic in their study was very less compared to current study. This could be due to low hydrogen pressure (atmospheric pressure); even a hydrogenating element (Ni) could not hydrogenate the bio-oil compounds.

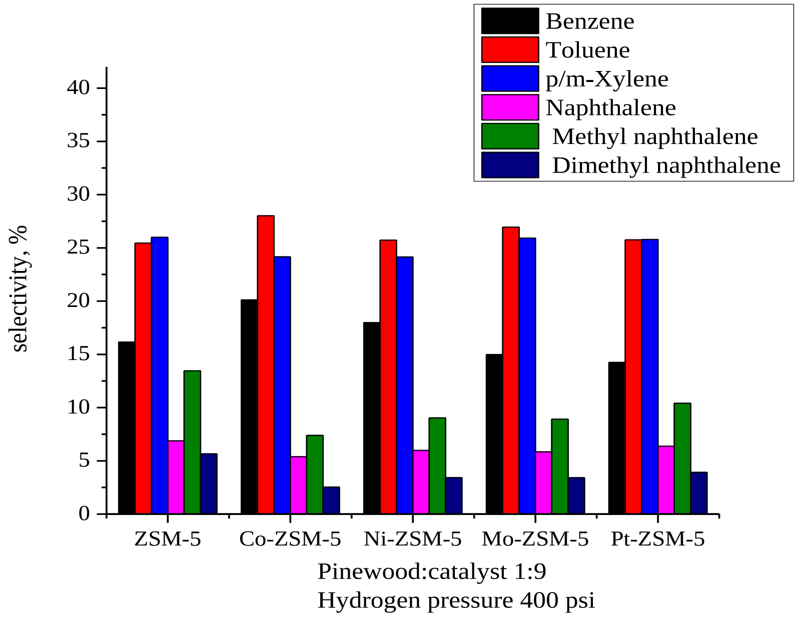


Figure 6.3: Aromatic selectivity of major hydrocarbons produced during hydrocatalytic pyrolysis of pinewood at 400 psi with metal impregnated ZSM-5 catalysts

A study [32] on bio-oil upgrading with Ni/ZSM-5 catalyst had reported about 95% of carbon in liquid product. Ni promoted hydrogenation and dehydro-aromatization reactions while Brønstead acids in ZSM-5 catalyzed dehydration and hydrolysis. The Ni/ZSM-5 catalysts showed high activity for hydrodeoxygenation of various C-O and C=O bonds. Their study under hydrogen pressure (725 psi) with 20 wt.% Ni on ZSM-5 catalyst resulted more cyclic alkanes than aromatic hydrocarbons [32]. In contrast to their result, current study reported only aromatic hydrocarbons. The reason can be the amount of metal sites available may be very low for hydrogenation of aromatic hydrocarbons.

Recently, Gas Technology Institute (GTI) has invented a new process to produce fungible blend-stocks for transportation fuel named Integrated Hydropyrolysis and Hydroconversion (IH^2) process [33]. The first step in IH^2 process (Hydropyrolysis) is similar to current study where hydropyrolysis occurred at 14-35 bar (200-500 psi) and resulted gasoline diesel range product with less than 2.7 wt.% oxygen content. One of their catalytic hydropyrolysis with mixed wood

(68% hardwood and 32% softwood) in presence of CRI-S-4211 catalyst at 396°C and 22.4 bar (325 psi) resulted a bio-oil with 0.48 wt.% oxygen content [34-36]. The principle to select the catalyst for this process was balanced CO_x and H_2O production which means balancing decarboxylation & decarbonlyation reactions (CO_x removal) with hydrodeoxygenation reaction (H_2O removal). If the decarboxylation & decarbonlyation reactions exceeds, the liquid yield will be decreased due to the removal of carbon and if hydrodeoxygenation reaction exceeds, large amount of external supply of hydrogen will be required due to the removal of hydrogen as water [34]. In this approach the selection of current catalyst could play a major role where oxygen removal as CO_x removal would occur by catalyst carrier (H^+ZSM-5) and metals part could utilize the hydrogen environment for hydrodeoxygenation. In current study, more than 42 wt. % of biomass carbon was converted as aromatic hydrocarbon (only high peak compounds in GC chromatogram were identified, other compounds were ignored) which showed that the carbon loss due to the activity of H^+ZSM-5 was less. However, the hydrodeoxygenation reaction was not a major process which may be because of low amount of hydrogenating element (~5 wt. % in current study and about 24 wt. % Ni in GTI catalyst) compared to the carrier. Therefore, in order to improve the HDO activity, the metal dispersion has to be improved.

6.5. Conclusions

Catalytic pyrolysis of pine wood biomass in presence of H^+ZSM-5 catalyst was carried out under different pressures in order to investigate the effect of pressure on bio-oil compounds. There was no increase in aromatic hydrocarbons as the hydrogen pressure increased from 100 psi to 400 psi. The catalytic pyrolysis of biomass in presence of Mo/ZSM-5 catalyst under different hydrogen pressures showed an increase in aromatic hydrocarbons as pressure increased. Nevertheless, the metal site was active only after 300 psi hydrogen pressure. Therefore, a series of hydrogenating metal catalysts (Ni, Co, Mo, and Pt) were impregnated on ZSM-5 catalyst and had taken for catalytic pyrolysis under hydrogen pressure (400 psi). Aromatic yield was higher in presence of metal impregnated ZSM-5 catalysts (~ 42.5wt.% carbon yield) than in the presence of H^+ZSM-5 catalyst (36.2wt.% carbon yield). In the case of metal impregnated-ZSM-5 catalysts, metals sites were available in addition to acid sites on H^+ZSM-5. Therefore, there was hydrogenation of some oxygenated compounds would have happened before going to aromatization. However, hydrogenation reaction for aromatic compounds were not evident (no aliphatic compounds were identified as major compounds). No major difference in aromatic selectivity was noticed by changing the metal content on ZSM-5 catalyst.

6.6. Acknowledgement

The authors would like to thank the Alabama Agricultural Experiment Station (AAES) and the Center for Bioenergy and Bioproducts of Auburn University for funding this study. However, only the authors are responsible for the opinions expressed in this paper and for any remaining errors.

6.7. References

1. Luo, Z., et al., *Research on Biomass Fast Pyrolysis for Liquid Fuel.* Biomass and Bioenergy, 2004. **26**: p. 455 - 462.

2. Onay, O., *Fast and Catalytic Pyrolysis of Pistacia Khinjuk Seed in a Well-Swept Fixed Bed Reactor.* Fuel, 2007. **86**: p. 1452 - 1460.

3. Bridgwater, A.V. and M.L. Cottam, *Opportunities for Biomass Pyrolysis Liquids Production and Upgrading.* Enegry & Fuels, 1992. **6**(2): p. 113-120.

4. Czernik, S. and A.V. Bridgwater, *Overview of Applications of Biomass Fast Pyrolysis Oil.* Enegry & Fuels, 2004. **18**(2): p. 590-598.

5. Bridgwater, A., *Review of Fast Pyrolysis of Biomass and Product Upgrading.* Biomass and Bioenergy, 2011: p. 1 - 27.

6. Carlson, T.R., et al., *Production of Green Aromatics and Olefins by Catalytic Fast Pyrolysis of Wood Sawdust.* Energy and Environmental Science, 2011. **4**(1): p. 145 - 161.

7. Pattiya, A., J.O. Titiloye, and A.V. Bridgwater, *Fast pyrolysis of cassava rhizome in the presence of catalysts.* Journal of Analytical and Applied Pyrolysis, 2008. **81**(72 - 79).

8. Carlson, T.R., et al., *Aromatic Production from Catalytic Fast Pyrolysis of Biomass-Derived Feedstocks.* Topics in Catalysis, 2009. **52**: p. 241 - 252.

9. Torri, C., I.G. Lesci, and D. Fabbri, *Analytical Study on the Pyrolytic Behaviour of Cellulose in the Presence of MCM-41 Mesoporous Materials.* Journal of Analytical and Applied Pyrolysis, 2009. **85**: p. 192 - 196.

10. Thangalazhy-Gopakumar, S., et al., *Production of Hydrocarbon Fuels from Biomass using Catalytic Pyrolysis under Helium and Hydrogen Environments.* Bioresource Technology, 2011. **102**(12): p. 6742 - 6749.

11. French, R. and S. Czernik, *Catalytic Pyrolysis of Biomass for Biofuels Production.* Fuel Processing Technology, 2010. **91**: p. 25 - 32.

12. Costa, E., et al., *Conversion of n -Butanol-Acetone Mixtures to C1-Cl0 Hydrocarbons on HZSM-5 Type Zeolites.* Industrial and Engineering Chemistry Research, 1992. **31**(4): p. 1021 - 1025.

13. Sharma, R.K. and N.N. Bakhshi, *Catalytic Upgrading of Biomass-Derived Oils to Transportation Fuels and Chemicals.* The Canadian Journal of Chemical Engineering, 1991. **69**: p. 1071 - 1081.

14. Gunawardena, D.A. and S.D. Fernando, *Deoxygenation of Methanol over ZSM-5 in a High-Pressure Catalytic Pyroprobe.* Chemical Engineering & Technology, 2011. **34**(2): p. 173-178.

15. Adjaye, J.D. and N.N. Bakhshi, *Production of Hydrocarbons by Catalytic Upgrading of a Fast Pyrolysis Bio-Oil. Part II: Comparative Catalyst Performance and Reaction Pathways.* Fuel Processing Technology, 1995. **45**(3): p. 185-202.

16. Carlson, T.R., et al., *Catalytic Fast Pyrolysis of Glucose With HZSM-5: The Combined Homogeneous and Heterogeneous Reactions.* Journal of Catalysis, 2010. **270**: p. 110 - 124.

17. Canel, M., Z. Mısırlıogˇlu, and A. Sınagˇ, *Hydropyrolysis of A Turkish Lignite (Tunçbilek) and Effect of Temperature and Pressure on Product Distribution.* Energy Conversion and Management, 2005. **46**(13–14): p. 2185-2197.

18. Meesuk, S., et al., *The Effects of Temperature on Product Yields and Composition of Bio-Oils in Hydropyrolysis of Rice Husk Using Nickel-Loaded Brown Coal Char Catalyst.* Journal of Analytical and Applied Pyrolysis, 2012.

19. Pindoria, R.V., et al., *A Two-Stage Fixed-Bed Reactor for Direct Hydrotreatment of Volatiles from the Hydropyrolysis of Biomass: Effect of Catalyst Temperature, Pressure and Catalyst Ageing Time on Product Characteristics.* Fuel, 1998. **77**(15): p. 1715-1726.

20. Chareonpanich, M., T. Boonfueng, and J. Limtrakul, *Production of Aromatic Hydrocarbons from Mae-Moh Lignite.* Fuel Processing Technology, 2002. **79**(2): p. 171-179.

21. Li, B., S.C. Mitchell, and C.E. Snape, *Effect of Heating Rate on Normal and Catalytic Fixed-Bed Hydropyrolysis of Coals.* Fuel, 1996. **75**(12): p. 1393-1396.

22. Chang, C.D., et al., *Synergism in acetic acid/methanol reactions over ZSM-5 zeolites*, in *American Chemical Society National meeting*. 1983: Seattle, WA, USA. p. 146-152.

23. Biscardi, J.A. and E. Iglesia, *Reaction Pathways and Rate-Determining Steps in Reactions of Alkanes on H-ZSM5 and Zn/H-ZSM5 Catalysts.* Journal of Catalysis, 1999. **182**(1): p. 117-128.

24. Bartholomew, C.H., *Mechanisms of catalyst deactivation.* Applied Catalysis A: General, 2001. **212**(1–2): p. 17-60.
25. Cheng, Y.-T., et al., *Production of Renewable Aromatic Compounds by Catalytic Fast Pyrolysis of Lignocellulosic Biomass with Bifunctional Ga/ZSM-5 Catalysts.* Angewandte Chemie International Edition, 2012. **51**(6): p. 1387-1390.

26. Thangalazhy-Gopakumar, S., et al., *Influence of Pyrolysis Operating Conditions on Bio-Oil Components: A Microscale Study in a Pyroprobe.* Enegry & Fuels, 2011. **25**: p. 1191 - 1199.

27. Ferrari, M., et al., *Como/Carbon Hydrodeoxygenation Catalysts: Influence of the Hydrogen Sulfide Partial Pressure and of the Sulfidation Temperature.* Catalysis Today, 2001. **65**(2–4): p. 257-264.

28. Kwon, K.C., et al., *Catalytic Deoxygenation of Liquid Biomass for Hydrocarbon Fuels.* Renewable Energy, 2011. **36**(3): p. 907-915.

29. Zhao, C., et al., *Highly Selective Catalytic Conversion of Phenolic Bio-Oil to Alkanes.* Angewandte Chemie International Edition, 2009. **48**: p. 3987 - 3990.

30. Masalska, A., *Ni-Loaded Catalyst Containing ZSM-5 Zeolite for Toluene Hydrogenation.* Applied Catalysis A: General, 2005. **294**(2): p. 260-272.

31. Wang, J., Q. Li, and J. Yao, *The Effect of Metal–Acid Balance in Pt-Loading Dealuminated Y Zeolite Catalysts on the Hydrogenation of Benzene.* Applied Catalysis A: General, 1999. **184**(2): p. 181-188.

32. Zhao, C. and J.A. Lercher, *Upgrading Pyrolysis Oil over Ni/HZSM-5 by Cascade Reactions.* Angewandte Chemie International Edition, 2012. **51**.

33. GTI. *Converting Biomass to Gasoline and Diesel Using* IH^2. 2011 Jan-30-2012]; Available from: http://www.gastechnology.org/webroot/app/xn/xd.aspx?it=enweb&xd=1ResearchCap/1_8GasificationandGasProcessing/MajCurrentProj/Biomass-to-Diesel.xml.

34. Marker, T., L. Felix, and M. Linck. *Integrated Hydropyrolysis and Hydroconversion Process for Production of Gasoline and Diesel Fuel from Biomass*. AICHE 2009; Available from: http://www.aicheproceedings.org/2009/Fall/data/papers/Paper171241.pdf.

35. Marker, T., M. Linck, and L. Felix. *Integrated Hydropyrolysis and Hydroconversion (IH2) Process for Direct Production of Gasoline and Diesel Fuel from Biomass*. 2010 Jan-30-2012]; Available from: www1.eere.energy.gov/biomass/biomass2010/pdfs/biomass2010_track3_s2_marker.pdf.

36. Marker, T.L., et al., *[Tcbiomass2011] integrated hydropyrolysis and hydroconversion (IH2) for the direct production of gasoline and diesel fuels or blending components from biomass, part 1: Proof of principle testing.* Environmental Progress & Sustainable Energy, 2011.

7. Catalytic Pyrolysis of Green Algae for Hydrocarbon Production

7.1. Abstract

Microalgae are considered as an intriguing candidate for biofuel production due to their high biomass yield. Studies on bio-oil production through fast pyrolysis and upgrading to hydrocarbon fuels using algal biomass are limited as compared to other terrestrial biomass. Therefore, in this study, a fresh water green alga, *Chlorella vulgaris,* was taken for pyrolysis study. The average activation energy for pyrolysis zone was found to be 109.1 kJ/mol. Fixed-bed pyrolysis of algae gave a bio-oil yield of 52.7 wt.%, which accounts for 60.7 wt.% carbon yield. In addition, analytical pyrolysis of *C. vulgaris* was carried out in a Py/GC-MS to identify major compounds present in bio-oil with and without catalyst (H^+ZSM-5). The study found that in catalytic-pyrolysis, as the catalyst loading increased from zero to nine times of the biomass, the carbon yield of aromatic hydrocarbons increased from 0.9 to 25.8 wt.%.

7.2. Introduction

Biomass, a renewable source for carbon based liquid fuels, has a potential to alleviate the dependency on fossil fuels, and related environmental problems. Therefore, biofuels are considered as an important candidate for the national energy security and energy sustainability. In addition, biofuels can be a major factor for the nation's economy in creating more job opportunities in rural areas. Biochemical and thermochemical techniques have been developed to convert biomass into electricity and liquid fuels. Fast pyrolysis, a thermochemical conversion, gives high liquid yield (*i.e.,* bio-oil) up to 70 wt.% (dry weight) from biomass. The liquid can be utilized as an energy carrier, source for many commodity chemicals, or can be upgraded as a transportation fuel. However, bio-oil has some negative properties such as high density, acidity, water content, and, oxygen content together with low heating value.

Catalytic pyrolysis is one of the methods to produce hydrocarbon fuels from bio-oil where C-C bonds in bio-oil compounds are ruptured in presence of some shape selective catalysts. Cracking reactions involve dehydration, decarboxylation, and decarbonylation of compounds to produce aromatic hydrocarbons, water, and carbon dioxide. Catalytic pyrolysis produces better quality of bio-oil at atmospheric pressure without of the need of hydrogen gas as opposed to hydrodeoxygenation process, which makes this process less expensive [1-2]. Recently, a few micro-scale studies [3-6] have reported high aromatic yields (30-45 wt.% carbon yield) from the catalytic pyrolysis of lignocellulosic biomass or its structural units.

The major challenge for the utilization of biomass is the uncertainty on the continuous supply of biomass. Therefore, researchers have tested different types of biomass such as agriculture wastes, forest wastes, municipal wastes, animal manure, algae, and energy crops for different biomass conversion techniques. Currently, utilization of algae as a source of biofuel has attracted a great interest due to a number of reasons [7-10]. For example, algae have higher growth rate and higher efficiency for CO_2 fixation than terrestrial plants. Water consumption of algae is lower than terrestrial plants, and algae help to reduce eutrophication from water bodies by consuming nitrogen and phosphorus. Another advantage of algae is high temperature tolerance and can grow in a wide range of environmental conditions [9, 11-12].

Current algal biofuel research is mainly focused on extraction of lipids and transesterification to produce biodiesel. In biodiesel production, only a part of organic content of algae (lipid content) is utilized for biofuel production; rest is considered as waste. On the other hand, thermochemical treatment can utilize complete organic content of algae biomass for biofuel production. High ash content of algae (~10 wt. %) is considered as an inferior characteristic for biomass. However, fast pyrolysis has the flexibility over ash content of biomass, and both bio-oil and bio-char (products of fast pyrolysis) can be utilized for a number of applications. A number of studies [13-20] have reported pyrolysis products from lignocellulosic biomass and its basic constituents (cellulose, hemicelluloses and lignin). The major components of algae biomass are proteins, lipids, and carbohydrates, which are different from the main components of lignocellulosic biomass. Therefore, the pyrolysis behavior and bio-oil components from algae biomass are expected to be different from terrestrial biomass. *Chlorella* species is a promising strain for biofuel production [21], and can be cultivated in industrial scale. *Chlorella vulgaris* is freshwater green algae which is cultivated in wastewater streams for the degradation of pollutants [22-23], and can fix around 18.3 mg CO_2 L^{-1} day^{-1} [24]. In addition, *C. vulgaris* is one of the species which can give high yield of biomass and oil [25].

Herein, *C. vulgaris* algae were taken for the pyrolysis study to investigate the possibility of producing hydrocarbons using catalytic pyrolysis process. The first objective was to find the possibility of producing bio-oil from microalgae. A fixed-bed reactor was used for algae pyrolysis and the chemical properties of bio-oil were studied. The quality of bio-oil produced from this study was compared with the bio-oil from woody biomass (Van-Krevelen diagram). The second objective of this study was to investigate the catalytic pyrolysis of algae biomass to produce hydrocarbons. An analytical pyrolysis of *C. vulgaris* was carried out to evaluate the major compounds in algae bio-oil with and without catalyst.

7.3. Materials and Methods

7.3.1. Sample Characterization

Algal biomass (*Chlorella Vulgaris*) used for this study was obtained in dry powder and was purchased from an online store (www.nutsonline.com). Moisture content of a biomass sample (wet basis) was determined by calculating weight loss after heating in an oven at 103°C for 16 h according to ASTM E 871 standard, and the ash content was measured using ASTM E 1755 standard. The higher heating value (HHV) of the biomass sample was measured using an oxygen bomb calorimeter (IKA, model C200). Ultimate analysis of biomass sample was analyzed in a CHNS/O analyzer (Perkin Elmer model 2400). Carbon, hydrogen, oxygen and nitrogen contents of a sample were reported on "as received" basis. Algae sample was sent to an outside laboratory (Midwest Laboratories, Inc., Omaha, NE) for analyzing fat and protein content.

7.3.2. Catalyst

ZSM-5 catalyst (SiO_2/Al_2O_3= 50 and surface area = 425 m^2/g) used in this study was purchased from a commercial supplier (Zeolyst International, Conshohocken, PA, USA). ZSM-5 powder was received in ammonium cation form, and, in order to obtain in H^+ZSM-5 form, the catalyst was calcined in air at 550°C for 2 h prior to use.

7.3.3. Thermogravimetric Analysis

Pyrolytic behavior of algal biomass was analyzed in a thermogravimetric analyzer (Shimadzu, TGA 50H) under nitrogen environment. A known amount (approximately 10 mg) of biomass was taken for the analysis, and biomass was heated from 30°C to 800°C at different heating rates of 10, 20, 30, and 40 °C/min and hold at final temperature for 10 min. Nitrogen flow rate of 30 mL/min was maintained during the pyrolysis. All experiments were run in triplicates to confirm reproducibility of the data.

If m_0 is the initial weight of the sample, m is the instantaneous weight for a specified time, t, and m_∞ is the weight remaining without decomposition, the biomass conversion (α) can be defined as $(m_0 - m)/(m_0 - m_\infty)$. The rate of degradation (dα/dt) is a linear function of rate constant (k) and conversion (α), where the temperature dependency of the rate constant is given as $k=Ae^{(-E/RT)}$. The rate of degradation (dα/dt) can be expressed as

$$\frac{d\alpha}{dt} = A\, e^{\left(-E/_{RT}\right)}\, f(\alpha) \quad \text{.................................. (Equation 7.1)}$$

where A is a pre-exponential factor, E is the activation energy, R is the universal gas constant, and T is the absolute temperature. Since the heating rate (β) is dT/dt, Equation 7.1 can be expressed as follows:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{\left(-E/_{RT}\right)}\, f(\alpha) \quad \text{.................................. (Equation 7.2)}$$

The integrated form of this Equation 7.2 would be

$$G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^{T} e^{\left(-E/_{RT}\right)}\, dT \quad \text{............. (Equation 7.3)}$$

The apparent activation energy can be found out by two methods without knowing the reaction mechanism. The methods are Flynn-Wall-Ozawa (FWO) and Kissinger's (Kissinger-Akahira-Sunose or KAS) methods can be applied. The Flynn-Wall-Ozawa equation [26-27] is given as follows:

$$ln\,\beta = ln\left(\frac{0.0048AE_a}{R\,G(\alpha)}\right) - 1.0516\frac{E_a}{RT} \quad \text{.................. (Equation 7.4)}$$

The KAS [28] equation is given as

$$ln\frac{\beta}{T^2} = ln\left(\frac{AR}{E_a\,G(\alpha)}\right) - \frac{E_a}{RT} \quad \text{.......................... (Equation 7.5)}$$

From Equations (7.4) and (7.5), the linear plots of ln(β), ln(β/T^2) vs 1/T at fixed α will give the apparent activation energy, E_a, for the given value of conversion.

7.3.4. Fixed-Bed Pyrolysis

Fixed-bed pyrolysis experiment was performed in a packed-bed reactor to find the yield and properties of bio-oil from *C.vulgaris*. The reactor set-up for a fixed-bed pyrolysis is shown in Figure 7.1. A stainless steel tubular reactor (0.5" OD and 18" length) was filled with 5 g of biomass sample supported with quartz wools on both sides. A handful of studies on algae pyrolysis [7, 29-31] were conducted at 500°C and therefore, the current study of algae pyrolysis was also carried out at 500°C (set point); whereas the actual temperature inside the reactor was was 510 ± 5°C and the heating rate was 48.0 ± 0.3 °C/min. Once the reactor was loaded with algae, it was purged with nitrogen gas for 5 min in order to maintain an inert condition inside the reactor. Once the furnace temperature reached the set point (500°C), the reactor was placed on the furnace after 10 min. A low nitrogen flow was maintained throughout the experiments to direct the pyrolysis vapors towards the condensers. Two glass condensers were used in series to condense the vapors, and the condensers were placed in ice-bath where the temperature was around 2°C to 4°C. The noncondensed gas was vented out. The reactor was left in the furnace for 30 min to make sure that the complete pyrolysis was occurred. Weight of bio-oil and bio-char was measured and calculated as the weight percentage of biomass whereas gas yield was calculated by difference.

Chemical properties of bio-oil, such as ultimate analysis and HHV were performed as described in Section 7.3.1. In a GC/MS analysis, a representative bio-oil sample (200 mg) was weighed and mixed with 2 mL of methanol and diluted to 10 mL with dichloromethane. The GC-MS method for bio-oil analysis in this study was similar to the method described for Py-GC/MS in the Section 7.3.5. Instead of split injection in Py-GC/MS, splitless mode was selected to inject 0.2μl of bio-oil. The ash content of bio-oil was measured in a TGA under oxidizing (air) environment. In the TGA experiments, a known amount of bio-oil was placed in a crucible and the sample temperature was increased from 30°C to 550°C, and was held at the final temperature for 30 min. The final weight remained was attributed to the ash content of the bio-oil. The sample was heated at a heating rate of 20 °C/min, and the air flow of 20 mL/min was maintained during the heating process. Carbon content of bio-char was analyzed using an elemental analyzer.

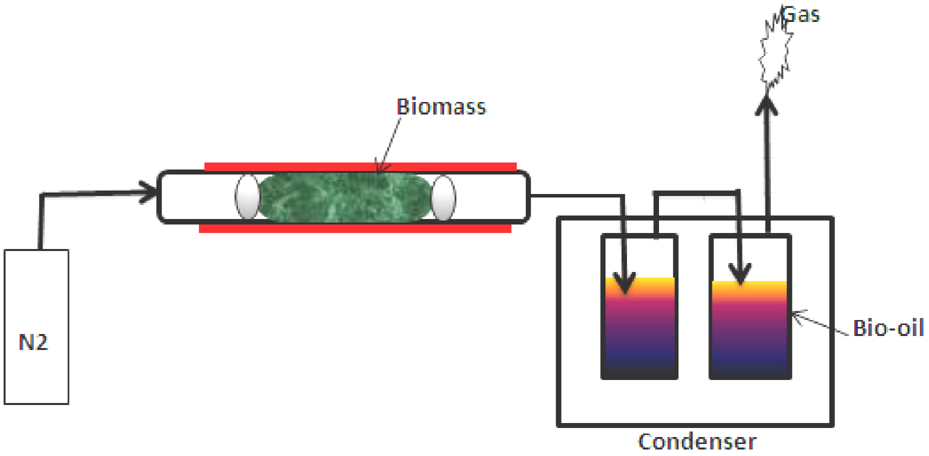


Figure 7.1: Experimental set-up for the fast pyrolysis of algae in fixed-bed reactor

7.3.5. Py/GC-MS

Pyrolysis studies were carried out using a commercial pyrolyzer (Pyroprobe model 5200, CDS Analytical Inc., Oxford, PA), which was interfaced with a gas chromatograph/mass spectrometer (GC/MS). A detailed description of an experimental procedure is available in the published documents elsewhere [17, 32]. Briefly, about 2 mg of samples were pyrolyzed at 650^{o}C, which is a filament temperature but the actual biomass temperature was about 100^{o}C lower than the filament temperature and the filament ramping rate was 2000 ^{o}C/s with a holding time of 1.5 min. The bio-oil compounds were analyzed with an Agilent 7890GC/5975MS using a DB-1701 column (30 m; 0.25 mm i.d.; 0.25 mm film thickness). The initial temperature of the column, 40^{o}C, was maintained for 2 min and was subsequently increased to 250^{o}C at 5 ^{o}C/min and hold at the final temperature for 8 min. Bio-oil compounds were identified by comparing the mass spectra with the NIST (National Institute of Standards and Technology) mass spectral library. Noncondensable gases and the solids left after the pyrolysis were not analyzed in the study.

The effect of catalyst during pyrolysis was investigated at different biomass to catalyst ratios (1:1, 1:4, and 1:9). The premixed biomass and catalyst mixture was inserted between the quartz wool in a quartz tube for the pyrolysis, and catalyst and biomass mixing was performed using a method described elsewhere [32]. Char (solids left from pyrolysis) and coke (solids deposited on catalyst's surface during the catalytic-cracking reaction) formation were not quantified in this study. It was observed that the amount of char is typically higher in a pyroprobe than the bench-scale reactors [33].

7.4. Results and Discussion

7.4.1. Biomass Characterization

The chlorella sample (particle size < 150µm) used for this study had 8.4±0.2 wt.% (wet basis) moisture content, 10.3±0.2 wt.% ash content, and a higher heating value of 19.4±0.02 MJ/kg. The carbon, hydrogen, oxygen, and nitrogen contents of algae sample were found to be 44.5±0.3%, 6.2±0.0%, 29.3±0.5%, and 9.6±0.2%, respectively. Based on the ultimate analysis, the chemical formula can be written as $(C_{3.7}H_{6.2}O_{1.8}N_{0.7})_n$. Ash and nitrogen content of algae biomass was higher than that of terrestrial plants whereas oxygen content was less [34-36]. Literature reported the composition of *C. vulgaris* was protein (51 – 58%), carbohydrates (12 – 17%), lipids (14 – 22%), and nucleic acids (4 – 5%) [37-38]. However, the analysis of current algal sample showed that the protein content was 58.13% and fat content was 1.04%. Fat content was significantly low compared to the values reported in literature. The algae powder used for this study was processed as a protein supplement and this could be the reason for low fat content.

7.4.2. Thermogravimetric Analysis

Figure 7.2(a) and (b) depict mass loss and the rate of thermal degradation of *C. vulgaris* at different heating rates under nitrogen atmosphere, respectively. Weight loss curve shows that the weights remaining after 600^{o}C were 35.5, 32.2, 31.4, and 30.8 wt.% for heating rates 10, 20, 30, and 40 ^{o}C/min, respectively. The degradation curve can be distinguished as three stages where the first stage (30^{o}C to 200^{o}C) shows a slight thermal degradation, which was mainly due to the loss of moisture. The weight loss at this stage was 8.4 ±0.6, which was equal to the moisture content of biomass. The second stage (200^{o}C to 600^{o}C) corresponds to the major weight loss where main pyrolysis occurred, and the third stage (600^{o}C to 800^{o}C) corresponds to the slow degradation of carbonaceous material. Most of the organic materials were decomposed during the second stage. As the heating rate increased a shift in the rate of degradation curve occurred towards the higher temperature. Similar shift was noticed for algae and other types of biomass [39-40]. This shift can be due to the temperature gradient inside the biomass (due to low thermal conductivity of biomass) at higher heating rates [40-41]. High heating rates supplied more thermal energy to overcome the temperature gradient which leads to the high conversion of biomass. Therefore, as the heating rate increased, the maximum rate of degradation increased.

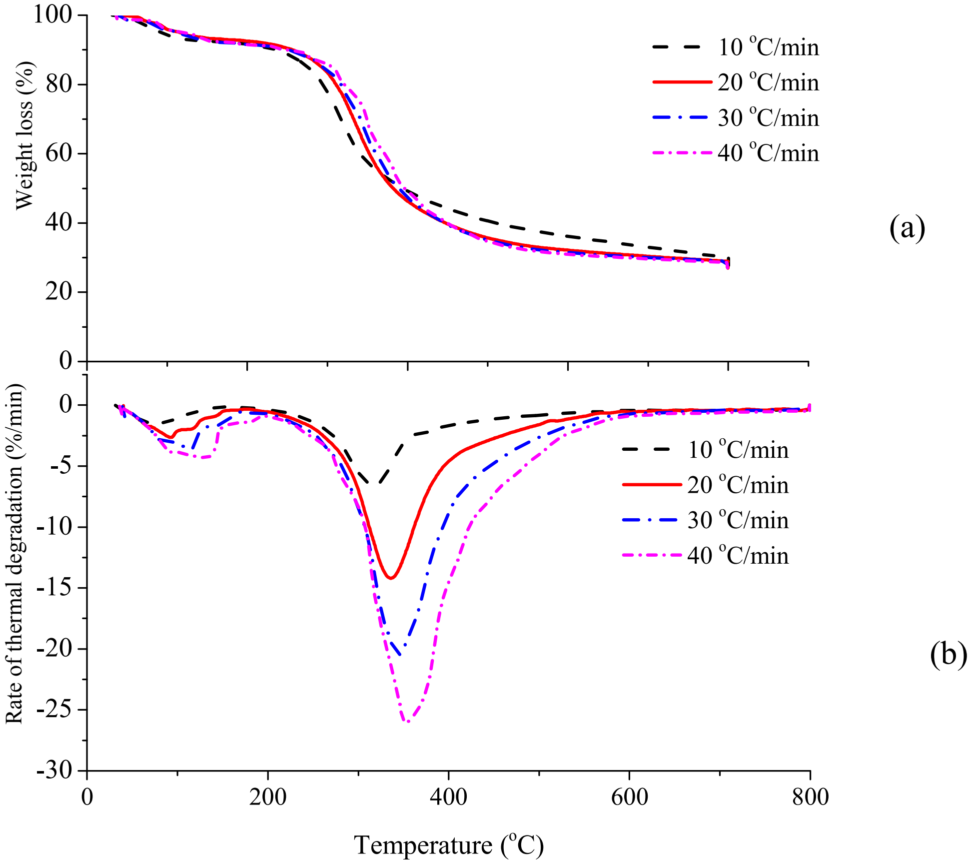


Figure 7.2: Thermogravimetric behavior of algae biomass under different heating rates (a) mass loss, % (b) mass loss rate, %/min

Using Equations 7.4 and 7.5, the plots of ln (β), ln (β/T^2) vs 1/T for different conversions (α) during the second stage of degradation (α is from 0.1 to 0.6) are given in Figures 7.3 (a) and (b). The values of apparent activation energy are presented in Table 7.1.

The average of apparent activation energy from both the methods was 109.1 kJ/mol. The values of activation energy at different conversion rates are almost similar in both the methods. As the conversion increased, the activation energy increased. A similar approach was used for kinetic analysis for another algae sample but the activation energies did not vary much (average activation energy was 146.07 kJ/mol from both the methods) with the conversion in that study

[39]. However, the increase in the activation energy with the increase in conversion rates was noticed for algae and other biomass samples [42-43].

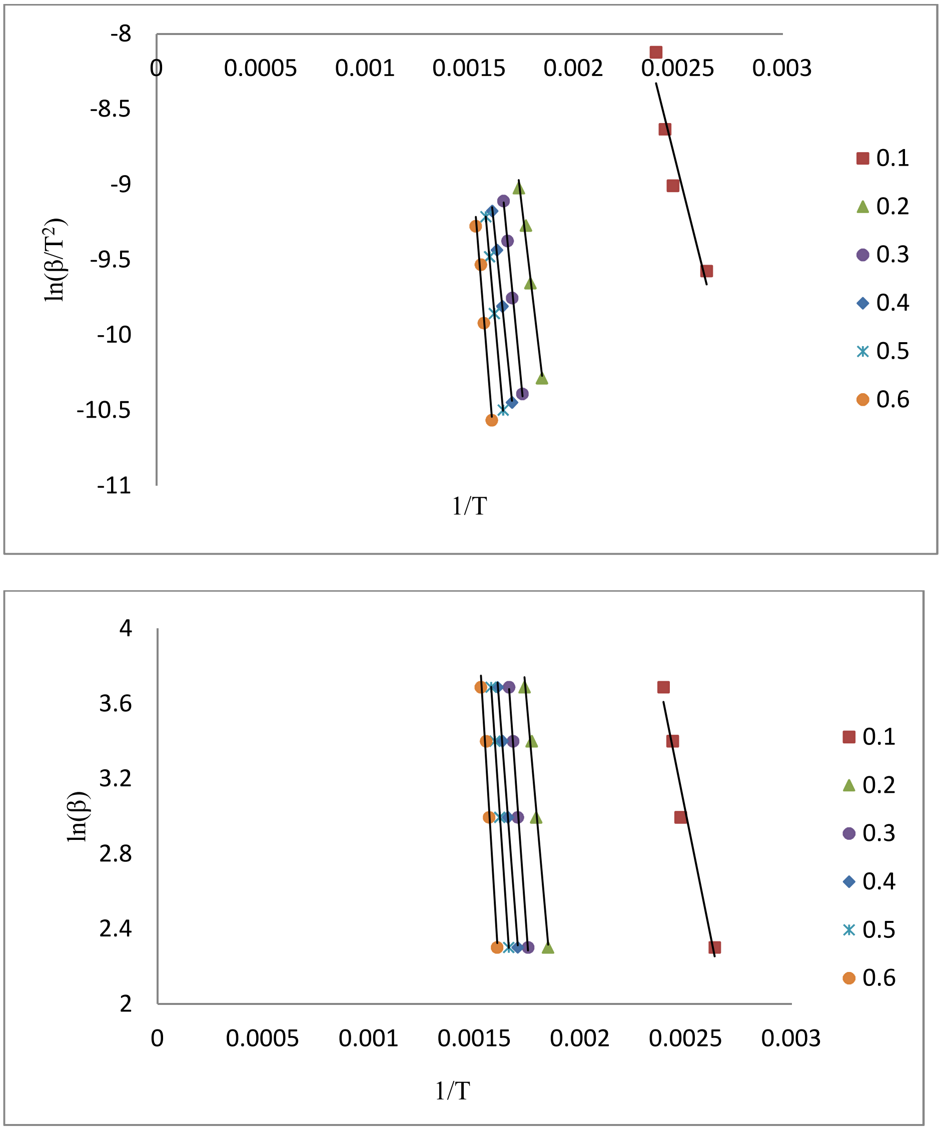


Figure 7.3: Plots for the determination of activation energy at different conversions (a) KAS method (b) FWO method

Table 7.1: Activation energies obtained for algae biomass at different conversions

	KAS		FWO	
Conversion rate, α	E, kJ/mol	Related coefficient	E, kJ/mol	Related coefficient
0.10	45.8	0.9029	44.2	0.9673
0.20	97.1	0.9839	101.2	0.9866
0.30	118.3	0.997	121.7	0.9974
0.40	112.4	0.9984	116.4	0.9987
0.50	129.4	0.9996	132.8	0.9997
0.60	143.5	0.9809	146.5	0.9865
Average	107.7±34.1		110.5±35.9	

7.4.3. Fixed-Bed Pyrolysis

The pyrolysis of algae was performed in a fixed-bed reactor at 500^{o}C to understand the yield and properties of bio-oil. The product yields of bio-oil, bio-char, and gas were 52.7± 4.7, 25.7± 0.8, and 21.6± 4.5, respectively. Fixed-bed operations are normally in batch mode; hence these operations are limited to laboratory scale studies. Another major drawback of fixed-bed pyrolysis is a long residence time of vapors, which results in high yield of bio-char and gas, and low yield of bio-oil [44]. Within the limitations of fixed-bed reactor and the high ash content biomass, algae pyrolysis yielded relatively high amount of bio-oil [45-47]. Other studies [30, 48] have reported lower yield for bio-oil than the current study (52.7±4.7 wt.%) using the fixed-bed pyrolysis system. Literature suggests [29] that the genetic modification of algae can give higher liquid yield than that from normal algae. The higher heating value and ultimate analysis of bio-oil are presented in Table 7.2.

Table 7.2: Selected properties of algae bio-oil[†]

Properties	
HHV, MJ/kg	18.6 ± 0.3
Ultimate analysis, wt.%	
C	51.4± 2.3
H	10.4± 0.4
N	12.4± 1.1
O (by difference)	24.8± 1.6
Ash content, wt.%	1.0± 0.4

[†] values are means of repeated analyses and numbers after ± are standard deviations.

Heating value of bio-oil conveyed that the heat recovery from pyrolysis was 51.6%, and the higher heating value of algae bio-oil was similar to the heating value of bio-oil from terrestrial biomass [15, 49]. The heating values of alage bio-oils were reported in the range of 19 to 25 MJ/kg after excluding its water content [30]. Genetically modified algae can provide bio-oil with high HHV (41MJ kg^{-1}) [29]. The oxygen content of algae bio-oil was lower than the oxygen content of bio-oil produced from terrestrial biomass (35-40 %), however high nitrogen content (68.1% of nitrogen in biomass) was found in algae bio-oil. The presence of nitrogen in bio-oil was assumed to be derived from proteins, which is the prominent chemical constituent of *C.vulgaris* [38]. Since, the current biomass had very low fat content, major bio-oil compounds were formed from the thermal cracking of protein, which could be the reason for higher percentage of nitrogen in the current bio-oil than that reported in literature [7]. Therefore, algae bio-oil upgrading includes the removal of nitrogen in addition to the removal of oxygen.

Van-Krevelen diagram (Figure 7.4) compares the quality of algae bio-oil with the bio-oil from pinewood biomass produced in auger reactor [49]. Even though, algae biomass has similar H/C ratio as that of pine wood biomass, algae bio-oil had a higher H/C ratio than that of pine wood bio-oil, which is very favorable fuel property. The O/C ratio of algae bio-oil was lower than that of pine wood bio-oil, however, algae bio-oil had N/C ratio of 0.2 which was negligible for pinewood bio-oil.

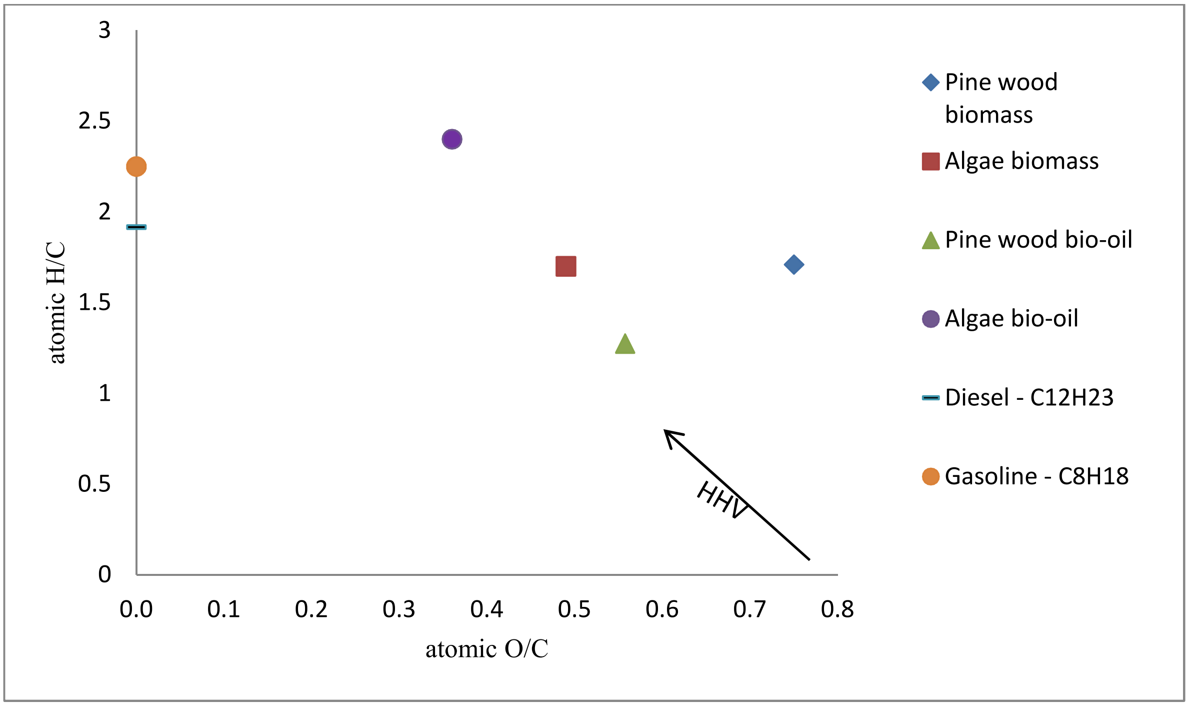


Figure 7.4: Van-Krevelen diagram for algae bio-oil in comparison with pine wood bio-oil

The ultimate analysis of bio-char had 47.8± 1.6 wt. % carbon, 2.9± 0.2 wt. % hydrogen, and 7.6± 0.3 wt. % nitrogen. The ultimate analysis of bio-oil and bio-char showed that about 60.7wt% of carbon in biomass was recovered as liquid fuel, whereas about 27.5 wt. % as recovered as bio-char.

7.4.4. Py/GC-MS

Analytical pyrolysis of *C. vulgaris* was carried out at different temperatures (550^{o}C, 650^{o}C, and 750^{o}C) and the relative areas of the selected compounds (higher quality in mass spectral database) were compared. There was not much difference in their area percentage. The area percentage of major components in total chromatogram for the pyrolysis at 650^{o}C is shown in Table 7.3.

Table 7.3: Compounds present in bio-oil during different conditions of pyrolysis

Compound groups	Pyrolysis at 650^{o}C (probe temperature)				Pyrolysis at 500^{o}C
	Non-catalytic pyrolysis	Catalytic pyrolysis (biomass:catalyst)			Bio-oil from fixed-bed pyrolysis
		1:1	1:4	1:9	
Alkane/alkene	8.4	4.2	0.4	0.2	7.8
Alkane with Nitrogen	10.3	12.1	2.4	1.2	13.7
Carbonyl	11.5	5.0	3.6	3.8	5.1
Aromatic	19.8	23.0	44.9	50.8	2.7
Aromatic with Nitrogen	6.4	8.3	2.9	1.9	9.2
Furan	1.4	0.3	0.1	0.2	2.2
Phenol	14.8	5.0	1.4	1.3	14.6
Total	72.5	58.1	55.6	59.4	55.4

The major compounds from analytical pyrolysis (Py/GC-MS) of algae were carbonyls, aromatic hydrocarbons, phenols, and nitrogen containing compounds. Most of these compounds were absent in bio-oil from terrestrial biomass. In addition, there were higher alkane compounds which are desirable compounds for transportation fuel. Bio-oil from lignocellulosic biomass has number of compounds and contains guaiacyl group which has low conversion rate compared to carboxyl or carbonyl compounds during hydrodeoxygenation [50]. Further, guaiacyl compounds cause high coke formation but these compounds are absent in algae bio-oil, upgrading could be easier. More aromatic hydrocarbons were present in algae bio-oil compared to the bio-oil from terrestrial plants [17]. The presence of alkane and aromatic hydrocarbons in bio-oil showed that the fuel quality of bio-oil derived algae would be better than the bio-oil obtained from terrestrial biomass.

The compounds from analytical pyrolysis were compared with the bio-oil produced from the fixed-bed pyrolysis. The relative concentrations (area %) of most of the groups were almost similar for bio-oil from both the fixed-bed and analytical pyrolysis. However, the aromatic and carbonyl concentrations were less in fixed-bed bio-oil. Some major compounds in both the cases were heptadecane, hexadecanoic acid, and phenol compounds whereas toluene and pyrrole compounds were dominant in analytical pyrolysis while hexadecanamide, octadecanamide, indole were major compounds in fixed-bed bio-oil. This could be due to the difference in the heating method, heating rate and the cooling processes in both fixed-bed and analytical pyrolysis.

7.4.5. Catalytic Pyrolysis

The studies of catalytic pyrolysis of algal biomass using shape selective catalysts are limited. ZSM-5 has some unique features such as medium pore size, strong acid sites, and high silica alumina ratio for its catalyst activity towards cracking and aromatization and therefore it provides better aromatic yield than other zeolite catalysts [3-4, 51-52]. Therefore, the current study conducted catalytic pyrolysis of *C. vulgaris* with H^+ZSM-5 catalyst for hydrocarbons production. Table 7.4 depicts the carbon yield of aromatic hydrocarbons produced during the catalytic pyrolysis of algae at different biomass to catalyst ratios. Here, three ratios of biomass to catalyst were selected such as 1:1, 1:4, and 1:9 (50%, 20%, and 10% biomass in mixture), respectively) and also compared with the aromatic yield from non-catalytic pyrolysis. As the catalyst loading increased from 50% to 80%, the total yield of aromatic hydrocarbons increased significantly.

Table 7.4: Carbon yield of aromatic hydrocarbons during catalytic pyrolysis†

Aromatic hydrocarbons from pyrolysis	Carbon yield, wt. %			
	Biomass:Catalyst			
	1:0	1:1	1:4	1:9
Benzene	*	0.1±0.03	1.9±0.1	4.0±0.7
Toluene	0.5±0.02	0.6±0.1	2.0±0.1	4.2±0.6
Ethylbenzene	0.1±0.0	0.1±0.01	0.4±0.03	0.9±0.2
p/m - Xylene	0.1±0.01	0.5±0.04	3.4±0.4	7.7±1.1
Styrene	0.2±0.0	0.3±0.04	0.5±0.1	0.9±0.3
o-Ethyltoluene	*	0.1±0.03	0.8±0.1	1.7±0.3
Benzene, 1,2,3-trimethyl-	*	0.1±0.01	0.5±0.1	1.2±0.1
p/m-Methylstyrene	*	0.04±0.0	0.1±0.02	0.2±0.05
Indane	*	*	0.3±0.03	0.7±0.1
Indene	*	0.1±0.02	0.5±0.1	1.0±0.2
1H-Indene, 2-methyl-	*	*	0.2±0.02	0.5±0.1
Naphthalene	*	*	0.3±0.04	0.6±0.1
Naphthalene, 2-methyl-	*	0.1±0.01	0.4±0.1	0.8±0.2
Naphthalene, 2-ethyl-	*	*	*	0.1±0.01
Naphthalene, 2,6-dimethyl-	*	*	0.1±0.03	0.3±0.1
Total	0.9±0.05	2.6±0.5	15.3±1.7	25.8±4.2

* not found in chromatogram. †values are means of repeated analyses and numbers after ± are standard deviations.

The major compounds in catalytic pyrolysis of algae were benzene, toluene, and xylene, and these compounds accounted for more than 60% of total aromatic yield. In addition to these hydrocarbons, there were other compounds present in the bio-oil (see Table 7.4). A reduction the total area of compounds (other than aromatic hydrocarbons) and a similar increase in the yield of aromatics was noticed when equal amount of catalyst (1:1) was introduced for algae pyrolysis. A significant change in bio-oil composition was noticed when catalytic pyrolysis was performed for algae to catalyst ratio of 1:4 and 1:9. The presence of compounds other than aromatic hydrocarbon was reduced significantly at this condition of catalytic pyrolysis.

Fast pyrolysis and catalytic conversion of pyrolysis vapors from algae extracted lipids on ZSM-5 had reported the production of alkane, alkene and aromatics [53]. A high yield of hydrocarbons (~ 25% carbon yield) in the current study showed the potential of catalytic pyrolysis of algae for hydrocarbons production. Another study [54] on catalytic pyrolysis of algae biomass over ZSM-5 catalyst reported a reduction in the bio-oil yield (from 25.1 to 20.7 wt. %) when the catalyst:biomass ratios increased from 0:1 to 1:1. On the other hand, a reduction in oxygen content in bio-oil was noticed (from 30.1 to 19.5 wt.%) and improved the quality of bio-oil in terms of heating value (24.4 – 32.2 MJ/kg). Nonetheless, nitrogen content in bio-oil did not change in both the catalytic and non-catalytic processes. The GC-MS analysis in the current study also showed similar area percentage for nitrogen containing compounds for non-catalytic and catalytic (1:1) pyrolysis. As the catalyst load increased to four times of biomass, a sudden decrease in nitrogen containing compounds was noticed, which shows that the high amount of catalyst is required to remove nitrogen content in the bio-oil. This means, although deoxygenation happened for low catalyst loading (1:1) for hydrocarbon formation, denitrogenation started only at high catalyst:biomass ratio of 1:4.

A reduction in alkane compounds was noticed during catalytic pyrolysis (1:1) and as the catalyst ratio increased, the concentration of alkane compounds reduced. An earlier study [51] reported that ZSM-5 catalyst favors aromatic hydrocarbons but the cracking of bio-oil with

ZSM-5 catalyst at higher temperatures (>340°C) would decrease the amount of aliphatic hydrocarbons. This could be the reasons for reduced concentration of alkanes during the catalytic pyrolysis.

7.5. Conclusions

Chlorella vulgaris, fresh water green algae, was taken for pyrolysis studies. The kinetic study gave the average activation energy for the pyrolysis (200°C – 600°C) as 109.1 kJ/mol. The fixed-bed pyrolysis of *C. vulgaris* yielded 52.7 wt.%. The catalytic pyrolysis of algae using ZSM-5 (biomass:catalyst ratio of 1:9) resulted 25 wt.% of carbon in biomass as aromatic hydrocarbons. The change in the composition of bio-oil for catalytic and non-catalytic pyrolysis confirmed that negative attributes of algae bio-oil, such as high nitrogen and oxygen content can be reduced by using ZSM-5 catalyst.

7.6. Acknowledgement

The authors would like to acknowledge the Alabama Agricultural Experiment Station (AAES) and the Center for Bioenergy and Bioproducts of Auburn University for funding this study. However, only the authors are responsible for the opinions expressed in this paper and for any remaining errors.

7.7. References

1. Williams, P.T. and N. Nugranad, *Comparison of Products from the Pyrolysis and Catalytic Pyrolysis of Rice Husks.* Energy, 2000. **25**: p. 493 - 513.
2. KiOR. *http://www.kior.com/content/?s=11&t=Technology*. 2011 12-12-2011].

3. Carlson, T.R., et al., *Aromatic Production from Catalytic Fast Pyrolysis of Biomass-Derived Feedstocks.* Topics in Catalysis, 2009. **52**: p. 241 - 252.

4. French, R. and S. Czernik, *Catalytic Pyrolysis of Biomass for Biofuels Production.* Fuel Processing Technology, 2010. **91**: p. 25 - 32.

5. Pattiya, A., J.O. Titiloye, and A.V. Bridgwater, *Evaluation of Catalytic Pyrolysis of Cassava Rhizome by Principal Component Analysis.* Fuel, 2010. **89**: p. 244 - 253.

6. Torri, C., I.G. Lesci, and D. Fabbri, *Analytical Study on the Pyrolytic Behaviour of Cellulose in the Presence of MCM-41 Mesoporous Materials.* Journal of Analytical and Applied Pyrolysis, 2009. **85**: p. 192 - 196.

7. Miao, X., Q. Wu, and C. Yang, *Fast Pyrolysis of Microalgae to Produce Renewable Fuels.* Journal of Analytical and Applied Pyrolysis, 2004. **71**(2): p. 855-863.

8. Brennan, L. and P. Owende, *Biofuels from Microalgae—A Review of Technologies for Production, Processing, and Extractions of Biofuels and Co-products.* Renewable and Sustainable Energy Reviews, 2010. **14**(2): p. 557-577.

9. Li, Y., et al., *Biofuels from Microalgae.* Biotechnology Progress, 2008. **24**: p. 815 - 820.

10. Babich, I.V., et al., *Catalytic Pyrolysis of Microalgae to High-Quality Liquid Bio-fuels.* Biomass and Bioenergy, 2011. **35**(7): p. 3199-3207.

11. Demirbas, A., *Use of Algae as Biofuel Sources.* Energy Conversion and Management, 2010. **51**(12): p. 2738-2749.

12. Mata, T.M., A.A. Martins, and N.S. Caetano, *Microalgae for Biodiesel Production and Other Applications: A Review.* Renewable and Sustainable Energy Reviews, 2010. **14**(1): p. 217-232.

13. Radlein, D., J. Piskorz, and D.S. Scott, *Fast Pyrolysis of Natural Polysaccharides as a Potential Industrial Process.* Journal of Analytical and Applied Pyrolysis, 1991. **19**: p. 41-63.

14. Shafizadeh, F., *Introduction to Pyrolysis of Biomass.* Journal of Analytical and Applied Pyrolysis, 1982. **3**: p. 283-305.

15. Mohan, D., C.U.P. Jr., and P.H. Steele, *Pyrolysis of Wood/Biomass for Bio-Oil: A Critical Review.* Energy & Fuels, 2006. **20**: p. 848-889.

16. Branca, C., P. Giudicianni, and C.D. Blasi, *GC/MS Characterization of Liquids Generated from Low-Temperature Pyrolysis of Wood.* Industrial and Engineering Chemistry Research, 2003. **42**(14): p. 3190-3202.

17. Thangalazhy-Gopakumar, S., et al., *Influence of Pyrolysis Operating Conditions on Bio-Oil Components: A Microscale Study in a Pyroprobe.* Enegry & Fuels, 2011. **25**: p. 1191 - 1199.

18. Varhegyi, G., et al., *Kinetic Modeling of Biomass Pyrolysis.* Journal of Analytical and Applied Pyrolysis, 1997. **42**: p. 73-87.

19. Shafizadeh, F., G.D. Mcginnis, and C.W. Philpot, *Thermal Degradation of Xylan and Related Model Compounds.* Carbohydrate Research, 1972. **25**: p. 23 - 33.

20. Nowakowski, D.J., et al., *Lignin Fast Pyrolysis: Results from an International Collaboration.* Journal of Analytical and Applied Pyrolysis, 2010. **88**: p. 53 - 72.

21. Tran, N.H., et al., *Catalytic Upgrading of Biorefinery Oil from Micro-algae.* Fuel, 2010. **89**(2): p. 265-274.

22. Lima, S.A.C., P.M.L. Castro, and R. Morais, *Biodegradation of p-nitrophenol by Microalgae.* Journal of Applied Phycology, 2003. **15**(2): p. 137-142.

23. Kim, J., et al., *Removal of Ammonia from Wastewater Effluent by Chlorella Vulgaris.* Tsinghua Science & Technology, 2010. **15**(4): p. 391-396.

24. Chinnasamy, S., et al., *Biomass Production Potential of a Wastewater Alga Chlorella vulgaris ARC 1 under Elevated Levels of CO_2 and Temperature.* International Journal of Molecular Sciences, 2009. **10**: p. 518 - 532.

25. Araujo, G.S., et al., *Bioprospecting for Oil Producing Microalgal Strains: Evaluation of Oil and Biomass Production for Ten Microalgal Strains.* Bioresource Technology, 2011. **102**(8): p. 5248-5250.

26. Flynn, J.H. and L.A. Wall, *A quick, direct method for the determination of activation energy from thermogravimetric data.* Journal of Polymer Science Part B: Polymer Letters, 1966. **4**: p. 323 - 328

27. Ozawa, T., *A New Method of Analyzing Thermogravimetric Data.* Bulletin of the Chemical Society of Japan, 1965. **38**(11): p. 1881 - 1886.

28. Kissinger, H.E., *Reaction Kinetics in Differential Thermal Analysis.* Analytical Chemistry, 1957. **29**(11): p. 1702-1706.

29. Miao, X. and Q. Wu, *High Yield Bio-oil Production from Fast Pyrolysis by Metabolic Controlling of Chlorella protothecoides.* Journal of Biotechnology, 2004. **110**(1): p. 85-93.

30. Bae, Y.J., et al., *The Characteristics of Bio-oil Produced from the Pyrolysis of Three Marine Macroalgae.* Bioresource Technology, 2011. **102**(3): p. 3512-3520.

31. Grierson, S., et al., *Thermal Characterisation of Microalgae under Slow Pyrolysis Conditions.* Journal of Analytical and Applied Pyrolysis, 2009. **85**(1-2): p. 118-123.

32. Thangalazhy-Gopakumar, S., et al., *Production of Hydrocarbon Fuels from Biomass using Catalytic Pyrolysis under Helium and Hydrogen Environments.* Bioresource Technology, 2011. **102**(12): p. 6742 - 6749.

33. Torri, C., et al., *Investigation on catalytic pyrolysis of pine sawdust: Catalyst screening by Py-GC-MIP-AED.* Journal of Analytical and Applied Pyrolysis, 2010. **88**(1): p. 7-13.

34. McKendry, P., *Energy production from biomass (part 1): overview of biomass.* Bioresource Technology, 2002. **83**(1): p. 37–46.

35. Jenkins, B.M., et al., *Combustion Properties of Biomass.* Fuel Processing Technology, 1998. **54**: p. 17 - 46.

36. Jenkins, B.M. and J.M. Ebeling (1985) *Thermochemical Properties of Biomass Fuels*.

37. Demirbas, M.F., *Biofuels from Algae for Sustainable Development.* Applied Energy, 2011. **88**(10): p. 3473-3480.

38. Bruton, T., et al., *A Review of the Potential of Marine Algae as a Source of Biofuel in Ireland*. 2009, Sustainable Energy Ireland.

39. Shuping, Z., et al., *Pyrolysis Characteristics and Kinetics of the Marine Microalgae Dunaliella tertiolecta using Thermogravimetric Analyzer.* Bioresource Technology, 2010. **101**(1): p. 359-365.

40. Maiti, S., S. Purakayastha, and B. Ghosh, *Thermal Characterization of Mustard Straw and Stalk in Nitrogen at Different Heating Rates.* Fuel, 2007. **86**(10-11): p. 1513-1518.

41. Zhang, X., et al., *Study on Biomass Pyrolysis Kinetics.* Journal of Engineering for Gas Turbines and Power, 2006. **128**(3): p. 493-496.

42. Li, D., et al., *Pyrolytic characteristics and kinetic studies of three kinds of red algae.* Biomass and Bioenergy, 2011. **35**(5): p. 1765-1772.

43. Kim, S.-S. and F.A. Agblevor, *Pyrolysis characteristics and kinetics of chicken litter.* Waste Management, 2007. **27**(1): p. 135-140.

44. Basu, P., *Pyrolysis* in *Biomass Gasification and Pyrolysis* 2010, Academic Press: Burlington, MA, USA. p. 65 - 92.

45. Şensöz, S. and İ. Kaynar, *Bio-oil Production from Soybean (Glycine max L.); Fuel Properties of Bio-oil.* Industrial Crops and Products, 2006. **23**(1): p. 99-105.

46. Özbay, N., et al., *Biocrude from Biomass: Pyrolysis of Cottonseed Cake.* Renewable Energy, 2001. **24**(3-4): p. 615-625.

47. Kim, S.-S., F.A. Agblevor, and J. Lim, *Fast Pyrolysis of Chicken Litter and Turkey Litter in a Fluidized Bed Reactor.* Journal of Industrial and Engineering Chemistry, 2009. **15**(2): p. 247 - 252.

48. Maddi, B., S. Viamajala, and S. Varanasi, *Comparative study of pyrolysis of algal biomass from natural lake blooms with lignocellulosic biomass.* Bioresource Technology, 2011. **102**(23): p. 11018-11026.

49. Thangalazhy-Gopakumar, S., et al., *Physiochemical properties of bio-oil produced at various temperatures from pine wood using an auger reactor.* Bioresource Technology, 2010. **101**(21): p. 8389 - 8395.

50. Laurent, E. and B. Delmon, *Study of the Hydrodeoxygenation of Carbonyl, Carboxylic and Guaiacyl Groups over Sulfided CoMo/γ-*Al_2O_3 *and NiMo/γ-*Al_2O_3 *Catalysts: I. Catalytic Reaction Schemes* Applied Catalysis A: General, 1994. **109**(1): p. 77 - 96.

51. Adjaye, J.D. and N.N. Bakhshi, *Production of Hydrocarbons by Catalytic Upgrading of a Fast pyrolysis Bio-Oil. Part I: Conversion Over Various Catalysts.* Fuel Processing Technology, 1995. **45**: p. 161-183.

52. Adjaye, J.D. and N.N. Bakhshi, *Production of Hydrocarbons by Catalytic Upgrading of a Fast Pyrolysis Bio-Oil. Part II: Comparative Catalyst Performance and Reaction Pathways.* Fuel Processing Technology, 1995. **45**(3): p. 185-202.

53. Milne, T.A., R.J. Evans, and N. Nagle, *Catalytic Conversion of Microalgae and Vegetable Oils to Premium Gasoline, with Shape-Selective Zeolites.* Biomass, 1990. **21**(3): p. 219-232.

54. Pan, P., et al., *The Direct Pyrolysis and Catalytic Pyrolysis of Nannochloropsis sp. Residue for Renewable Bio-oils.* Bioresource Technology, 2010. **101**(12): p. 4593-4599.

8. Summary and Future Work

Bio-oil was produced from pine wood in the Auburn pyrolyzer and physicochemical properties were studied. The physical properties of bio-oil produced at four (425, 450, 475, and 500°C) temperatures met the specifications listed in ASTM D 7544. The bio-oil produced at 475°C had better composition than the bio-oil produced at 450°C which would make the downstream process easier. Study on the influence of pyrolysis parameters showed that the yield of each group of compounds would be different for different feedstocks. The change in their behavior for the change in temperature is mainly due to the change in their lignin structure. Catalytic pyrolysis of biomass with HZM-5 catalyst provided aromatic hydrocarbons. Mixing could provide good surface contact between biomass and catalyst and therefore bio-oil compounds undergo simultaneous cracking as they formed. Therefore, a homogeneous mixture of catalyst and biomass provided a high yield for aromatics than passing bio-oil vapors through a catalyst bed. There was no significant change in the yield of hydrocarbons during the catalytic pyrolysis with HZSM-5 catalyst for the change in the gas environment from inert helium gas to reduced hydrogen gas. Next studies on catalytic pyrolysis were carried out under hydrogen pressure and metals were incorporated to utilize the hydrogen from environment.

Hydrodeoxygenation metals (nickel, cobalt, molybdenum, and platinum) were used for impregnation on ZSM-5 catalyst. An increase in the yield of aromatic hydrocarbon was noticed when metal impregnated ZSM-5 catalyst used for catalytic pyrolysis of pine wood biomass under hydrogen pressure. Therefore, hydrocatalytic pyrolysis can be considered as a promising process for biofuel production which provide high yield of hydrocarbon fuel directly from solid biomass. Microalgae, another intriguing candidate as biomass, were taken for pyrolysis study. A high yield of bio-oil obtained from *Chlorella vulgaris*, fresh water microalgae. The algae bio-oil had better H/C ratio than that of lignocellulosic bio-oil and algae bio-oil contained higher alkane compounds which are rarely available in bio-oil from terrestrial biomass. The catalytic pyrolysis of algae biomass provided good yield for aromatic hydrocarbons.

The present research opened an advanced process for catalytic pyrolysis after going through some fundamental studies on conventional and catalytic pyrolysis. Hydrocatalytic pyrolysis, a new term for biomass pyrolysis, can have good impact for future biofuel production. Hydrocatalytic pyrolysis had many advantages. Since the cracking of bio-oil compounds are integrated with pyrolysis, it can avoid reheating the condensed bio-oil compounds and go for vapor phase cracking. The presence of metal compounds can act as hydrogenating elements in simultaneous with cracking reaction. In addition, the hydrogen pressure is less than that of hydrodeoxygenation and the presence of hydrogen pressure can reduce the coke formation on catalyst. However, this study has to be further explored in the following concepts

I. *Selection of catalysts hydrocatalytic pyrolysis:* Eventhough this study explored the concept of bifunctional catalyst (metal impregnated ZSM-5 catalyst) for hydrocatalytic pyrolysis, the contribution of each metal could not be explored. Therefore, a detailed study is required to select the best catalytic system for hydrocatalytic pyrolysis. The

H^+ZSM-5 is considered to be better catalyst among molecular sieve catalysts which provide high yield for hydrocarbons. Therefore the selection of the metal is required for further study. In addition to the selected metals, noble metals such as palladium, rhodium, and ruthenium, gallium (promotes Brønstead acid sites on zeolite network), and bimetallic hydrodeoxygenation catalysts (Ni-Mo, Co-Mo) have to be used to find the best catalytic system. Catalyst preparation can give differences in the properties of bifunctional catalysts. Therefore in addition to metal impregnation method, ion-exchange method has to be studied for the preparation of above catalytic system.

II. *Catalytic upgrading of bio-oil:* The catalysts developed for hydrocatalytic pyrolysis can be used for catalytic upgrading studies. Bio-oil produced during conventional fast pyrolysis can be upgraded through hydrodeoxygenation process using above catalysts. Here the yield of hydrocarbons has to be compared with that of hydrocatalytic pyrolysis. Catalytic upgrading studies can be applied to synthetic bio-oil compounds in order to understand the chemistry in detail. Moreover, the bio-oil produced from the conventional pyrolysis can be fractionated to different boiling point range compounds and each fraction can be taken for catalytic upgrading. In addition to lignocellulosic bio-oil, bio-oil from other types of biomass (algae, poultry litter) can be used for this study. Therefore, the catalytic upgrading study also helps for large scale production of bi-oil from hydrocatalytic pyrolysis.

III. *Optimization of hydrocatalytic pyrolysis parameters for large scale pyrolysis:* After selecting the best catalytic system from objective I and understanding the chemistry of the catalytic system for each group of components in bio-oil from objective II, the hydrocatalytic pyrolysis parameters such as temperature, hydrogen pressure, catalyst loading have to be optimized for high yield of hydrocarbons and low yield of coke for large scale pyrolysis. Kinetic studies are required for optimization of parameters. In addition, large scale operation will be accompanied with continuous operation and catalyst regeneration.

Appendix A: Typical Chromatograms

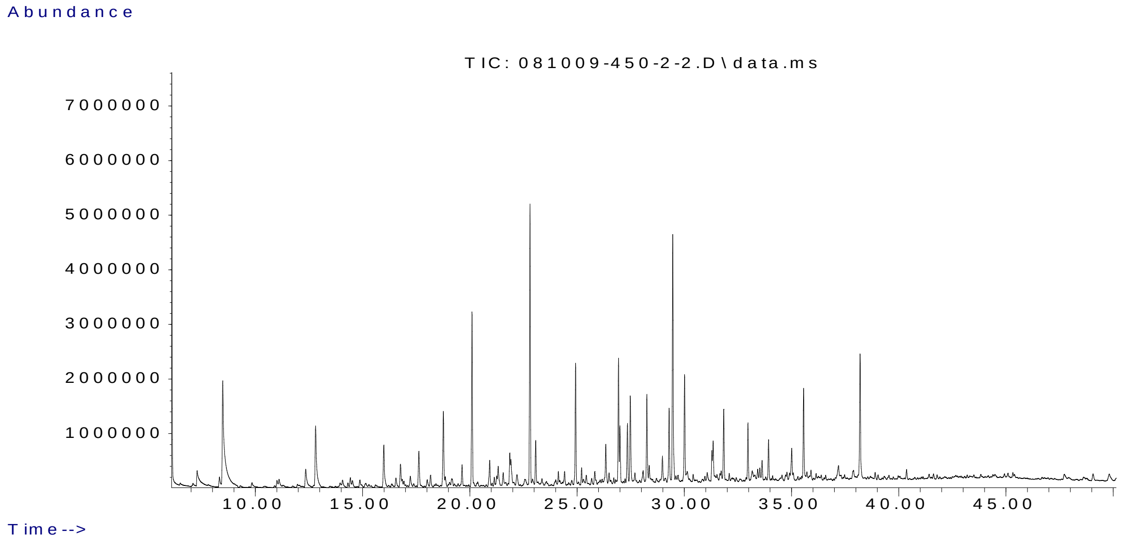


Figure A.1: Pine wood bio-oil produced from Auger reactor at 450 ^{o}C (For Table 3.2)

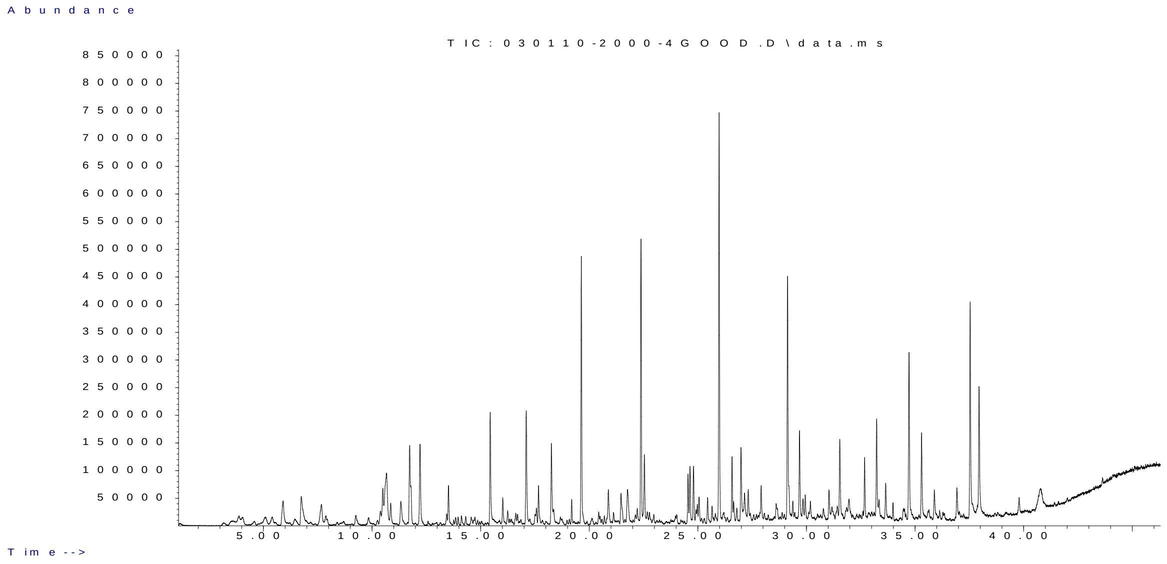


Figure A.2: Bio-oil produced at 450 ^{o}C and 2000 ^{o}C/s from pine wood in pyroprobe (For Table 4.4)

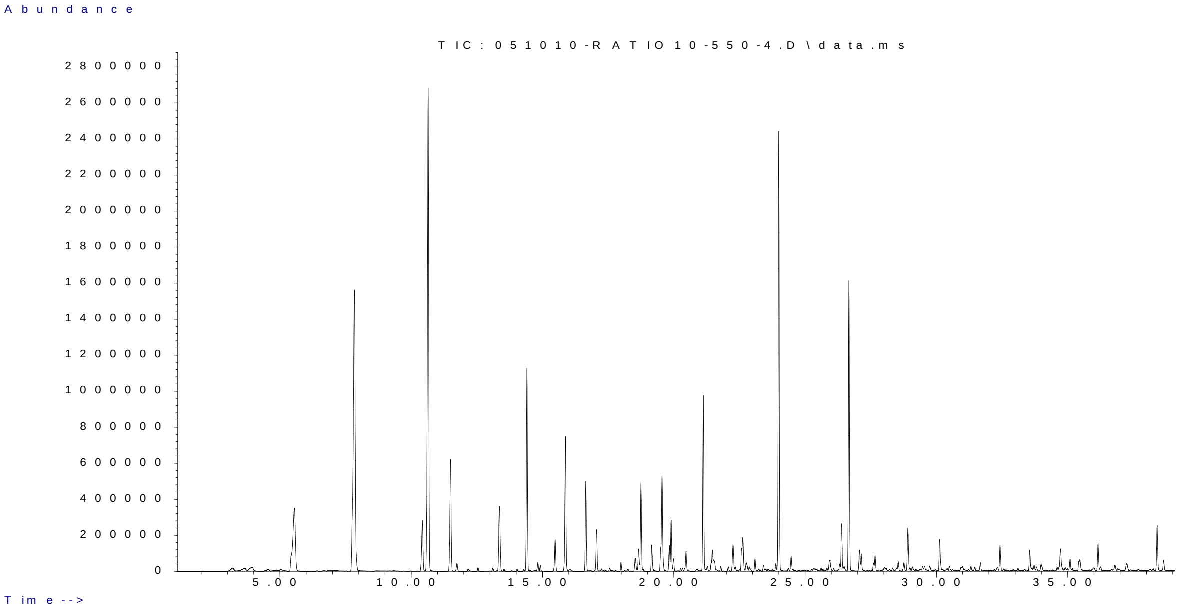


Figure A.3: Bio-oil produced from catalytic pyrolysis (mixing method) of pine wood over ZSM-5 catalyst under helium environment (For Table 5.3)

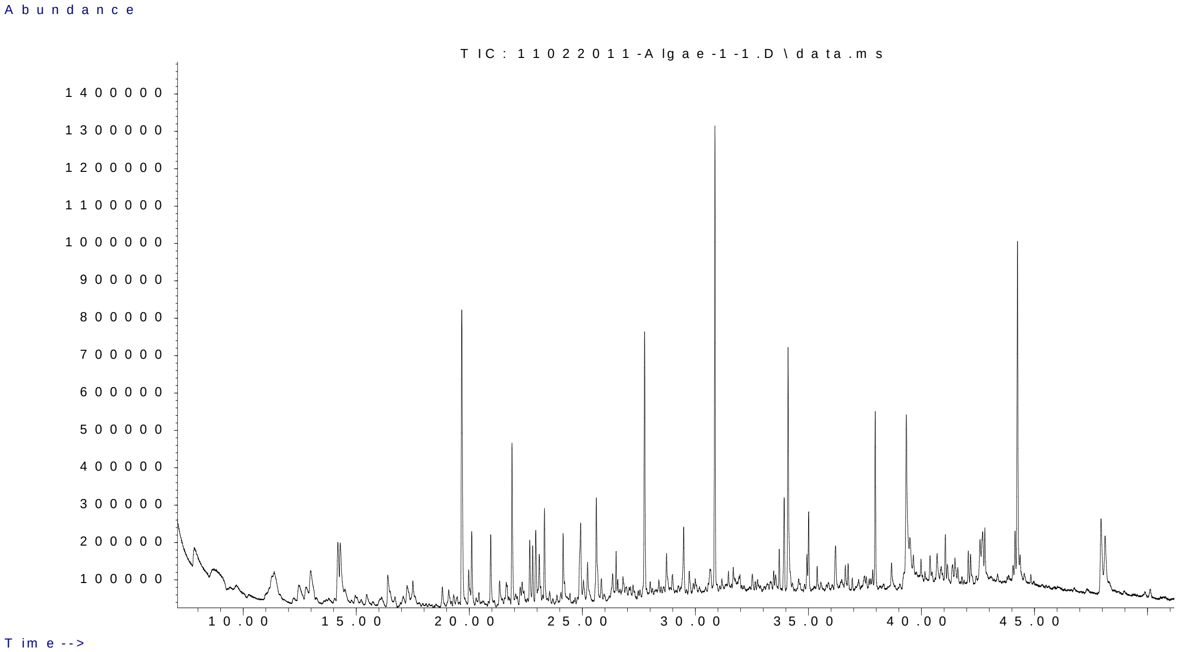


Figure A.4: Bio-oil produced from fixed bed pyrolysis of algae at 500 ^{o}C (For Table 7.3)

Appendix B: Data for graphs

Table B.1: Data for Figure 3.2

Temperature ^{o}C	bio-oil	char	gas
425	45.3±5.3	34.9±7.3	19.9±2
450	50.3±1.4	26.3±3.4	23.5±3.9
475	45.33±5.1	23.2±6.3	31.5±6.0
500	36. 7±6.5	20.1±2.0	43.3±5.7

Table B.2: Data for Figure 3.5

(1/T)*1000	ln(μ)
3.531697	-1.62232
3.411223	-2.54033
3.298697	-3.29414
3.193358	-4.21855
3.094538	-4.32451
3.001651	-4.64599
2.914177	-4.94344
2.831658	-5.13365

Table B.3: Data for Figure 4.1

Particle size (μm)	Pinewood	Switchgrass
< 149	25.0	7.5
149 - 177	21.9	19.4
177 - 210	13.5	25.4
210 - 250	5.2	19.4
250 - 420	34.4	28.4
> 420	0	0

Table B.4: Data for Figures 5.4 and 7.4

	H/C	O/C
Biomass	1.71	0.75
Bio-oil (H2)	1.01	0.33
Bio-oil (He)	1.01	0.34
1:5 Cata-bed-bio-oil (He)	1.04	0.13
1:5 Cata-bed-bio-oil (H2)	1.05	0.13
1:9 Cata-mix-bio-oil (He)	1.04	0.01
1:9 Cata-mix-bio-oil (H2)	1.05	0.01
Diesel - $C_{12}H_{23}$	1.92	0
Gasoline - C_8H_{18}	2.25	0
Ethanol – C_2H_5OH	3	0.5
Butanol – C_4H_9OH	2.5	0.25
Algae biomass	1.7	0.5
Algae bio-oil	2.4	0.4

Table B.5: Data for Figure 6.1

Pyrolysis pressure, Psi	Benzene	Toluene	p/m-Xylene	Naphthalene	Methyl naphthalene	Dimethyl naphthalene
100	6.7	15.1	27.5	9.1	18.4	8.3
200	7.1	17.4	17.2	11.8	24.1	10.4
300	5.7	16.5	17.7	12.8	23.4	13.0
400	15.3	26.5	24.2	9.7	13.1	5.0

Table B.6: Data for Figure 6.2

	Benzene	Toluene	p/m-Xylene	Naphthalene	Methyl naphthalene	Dimethyl naphthalene
Co-ZSM-5	16.2	24.4	23.5	13.0	7.6	2.9
Ni-ZSM-5	16.3	23.4	22.0	14.5	8.2	3.1
Mo-ZSM-5	12.9	24.7	24.4	13.3	8.0	3.3
Pt-ZSM-5	12.4	23.0	23.8	14.9	9.5	3.7

Table B.7: Data for Figure 7.3

α	ln (β)	ln (β/T^2)	1/T
0.1	2.302585	-9.57405	0.002636
	2.995732	-9.00759	0.002475
	3.401197	-8.63279	0.002438
	3.688879	-8.12129	0.002394
0.2	2.302585	-10.285	0.001848
	2.995732	-9.65339	0.001792
	3.401197	-9.27137	0.001771
	3.688879	-9.023	0.001736
0.3	2.302585	-10.3895	0.001754
	2.995732	-9.75308	0.001705
	3.401197	-9.37387	0.001682
	3.688879	-9.10906	0.001663
0.4	2.302585	-10.4466	0.001704
	2.995732	-9.80812	0.001658
	3.401197	-9.43441	0.001632
	3.688879	-9.17507	0.001609
0.5	2.302585	-10.4973	0.001662
	2.995732	-9.85597	0.001619
	3.401197	-9.47865	0.001597
	3.688879	-9.2134	0.001579
	2.302585	-10.5643	0.001607
0.6	2.995732	-9.91916	0.001569
	3.401197	-9.53154	0.001555
	3.688879	-9.27616	0.00153

Appendix C: Compounds in Group

Table C.1: Compounds in each group for Table 7.3

Alkane/alkene
Limonene
Pentadecane
Hexadecane
Heptadecane

Carbonyl
Butanal, 2-methyl-
Propanoic acid
2-Cyclopenten-1-one
2-Cyclopenten-1-one, 2-methyl-
2-Cyclopenten-1-one, 3-methyl-
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-
2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-
Hexadecanoic acid, methyl ester
Hexadecenoic acid, Z-11
n-Hexadecanoic acid
9,12-Octadecadienoic acid (Z,Z)-

Aromatic
Benzene
Toluene
Ethylbenzene
p-Xylene
Styrene
Benzene, 2-propenyl-
1H-Indene, 3-methyl-
Naphthalene
Naphthalene, 2,6-dimethyl-
Naphthalene, 1,2,3,4-tetrahydro-1,1,6-trimethyl-
Naphthalene, 1,2-dihydro-1,1,6-trimethyl-

Furan
2-Furanmethanol
Ethanone, 1-(2-furanyl)-
Benzofuran
2(5H)-Furanone

Alkane with Nitrogen
Pyrrole
Pentadecanenitrile
Pentanenitrile, 4-methyl-
1H-Pyrrole, 2-methyl-
1H-Pyrrole, 3-methyl-
1H-Pyrrole, 2,3-dimethyl-
1H-Pyrrole, 2,5-dimethyl-
1H-Pyrrole, 2-ethyl-
2,3,4-Trimethylpyrrole
1H-Pyrrole, 2-ethyl-4-methyl-
9-Octadecenamide, (Z)-
Hexadecanamide

Aromatic with Nitrogen
Pyridine
Pyridine, 2-methyl-
Pyridine, 3-methyl-
Aniline
Benzenamine, 3-methyl-
2-Pyridinecarbonitrile
Benzyl nitrile
Benzenepropanenitrile
Indole
1H-Indole, 5-methyl-
Adenine

Phenol
Phenol
Phenol, 2-methyl-
Phenol, 4-methyl-
Phenol, 2-ethyl-
Phenol, 2,3-dimethyl-
Phenol, 4-ethyl-
2,5-Diethylphenol
3-(4-Hydroxyphenyl)propionitrile

Appendix D: Quantification factor[‡]

Table D.1: Quantification factor for each compound

Retention Time		Compounds	Quantification factor		
			ALS	Pyro	
Pyro	ALS			Old	new
6.81	7.28	Acetic acid	$1*10^{-5}$		
9.28	9.85	Propoinic acid	$4*10^{-6}$	$2*10^{-5}$	
13.77	13.94	Crotonic acid	$3*10^{-5}$	$1*10^{-5}$	
	9.08	Butanoic acid, 3-methyl-, methyl ester		$2*10^{-6}$	
12.16	12.96	2-Cyclopenten-1-one		$4*10^{-6}$	
13.88	14.42	2-Cyclopenten-1-one, 2-methyl-	$2*10^{-5}$	$2*10^{-6}$	
18.28	18.76	1,2-Cyclopentanedione, 3-methyl-	$3*10^{-5}$	$3*10^{-6}$	
34.77	34.99	1,6-Anhydro-.beta.-D-glucopyranose (levoglucosan)	$4*10^{-5}$	$4*10^{-6}$	
12.21	12.80	Furfural	$2*10^{-5}$	$4*10^{-6}$	
16.27	16.76	2-Furancarboxaldehyde, 5-methyl-	$4*10^{\wedge-6}$	510^{-6}	
17.13	17.62	2(5H)-Furanone	$4*10^{-5}$	$6*10^{\wedge-6}$	
27.00	27.34	2-Furancarboxaldehyde, 5-(hydroxymethyl)-	$2*10^{-5}$	$6*0^{-6}$	
15.48	16.28	2,3-Benzofuran	$8*10^{-6}$	$2*10^{-6}$	$6*10^{-7}$
18.53	19.46	2-Methylbenzofuran	$8*10^{-6}$	$1*10^{-6}$	$4*10^{-7}$
29.75	30.43	Dibenzofuran	$6*10^{-6}$	$7*10^{-7}$	
19.21	19.63	Phenol	$9*10^{-6}$	$2*10^{-6}$	$8*10^{-7}$
20.51	20.92	Phenol, 2-methyl-; (o-Cresol)	$7*10^{-6}$	$1*10^{-6}$	$5*10^{-7}$
21.49	21.86	Phenol, 4-methyl-; (p-Cresol)	$7*10^{-6}$	$1*10^{-6}$	$5*10^{-7}$

20.90	21.32	Phenol, 2,6-dimethyl-	$6*10^{-6}$	$9*10^{-7}$	
22.70	23.07	Phenol, 2,4-dimethyl-; (m-Xylenol)	$7*10^{-6}$	$1*10^{-6}$	$5*10^{-7}$
23.66	24.01	Phenol, 2,3-dimethyl-; (2,3-Xylenol)	$7*10^{-6}$	$1*10^{-6}$	
22.54	22.92	Phenol, 2-ethyl-	$6*10^{-6}$	$8*10^{-7}$	
23.76	24.12	phenol, 4 ethyl	$6*10^{-6}$	$9*10^{-7}$	
	21.55	2-Hydroxy-5-methylbenzaldehyde	$7*10^{-6}$	$1*10^{-6}$	
27.16	27.48	1,2-Benzenediol; (pyrocatechol)	$1*10^{-5}$	$4*10^{-6}$	
29.03	29.28	1,2-Benzenediol, 4-methyl-; (Homocatechol)	$1*10^{-5}$	$4*10^{-6}$	
30.78	31.07	1,4-Benzenediol, 2-methyl-; (2-Methylcatechol)	$1*10^{-5}$	$1*10^{-6}$	
	31.29	1,3-Benzenediol, 4-ethyl-; (4-Ethylcatechol)	$2*10^{-5}$	$4*10^{-6}$	
19.65	20.10	Phenol, 2-methoxy (Guaiacol)	$8*10^{-6}$	$1*10^{-6}$	
22.40	22.80	Phenol, 2-methoxy-4-methyl- (Homoguaiacol)	$7*10^{-6}$	$1*10^{-6}$	
24.56	24.93	Phenol, 4-ethyl-2-methoxy- (p-ethyl guaiacol)	$6*10^{-6}$	$8*10^{-7}$	
25.99	26.34	2-Methoxy-4-vinylphenol (p-vinyl guaiacol)	$9*10^{-6}$	$2*10^{-6}$	
26.59	26.93	Eugenol; (Phenol, 2-methoxy-4-(2-propenyl))	$7*10^{-6}$	$1*10^{-6}$	
27.95 & 29.14	28.25 & 29.46	cis & trans -Isoeugenol	$7*10^{-6}$	$7*10^{-6}$	
29.69	30.00	Vanillin (Benzaldehyde, 4-hydroxy-3-methoxy)	$7*10^{-6}$	$1*10^{-6}$	
31.55	31.84	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-; (Acetoguaiacone)	$7*10^{-6}$	$9*10^{-7}$	
27.31	27.85	2,6-Dimethoxyphenol	$1*10^{-5}$	$1*10^{-6}$	
35.84	36.30	syringaldehyde	$4*10^{-5}$	$2*10^{-6}$	
5.56	6.21	Benzene		$2*10^{-6}$	$7*10^{-7}$
7.84	8.47	Toluene	$8*10^{-6}$	$1*10^{-6}$	$5*10^{-7}$

10.43	11.31	Ethylbenzene	$8*10^{-6}$	$1*10^{-6}$	$4*10^{-7}$
10.65	11.54	P-Xylene	$3*10^{-6}$	$2*10^{-6}$	$5*10^{-7}$
11.74	12.63	Styrene	$8*10^{-6}$	$2*10^{-6}$	
13.37	14.93	2-Ethyltoluene	$7*10^{-6}$	$1*10^{-6}$	$4*10^{-7}$
14.28	15.18	Alpha-Methylstyrene	$7*10^{-6}$	$1*10^{-6}$	
14.83	15.641	3-Methylstyrene	$6*10^{-6}$	$1*10^{-6}$	
14.41	16.254	1,2,3-Trimethylbenzene	$6*10^{-6}$	$1*10^{-6}$	$4*10^{-7}$
15.87	16.63	indane		$1*10^{-6}$	$4*10^{-7}$
16.65	17.53	Indene	$8*10^{-6}$	$1*10^{-6}$	$4*10^{-7}$
19.56	20.60	1H-Indene, 1-methyl-		$7*10^{-7}$	$3*10^{-7}$
21.13	21.91	Napthalene	$6*10^{-6}$	$8*10^{-7}$	
24.00	25.186	1-Methylnaphthalene	$5*10^{-6}$	$9*10^{-7}$	$3*10^{-7}$
26.06	26.82	Biphenyl	$6*10^{-6}$	$7*10^{-7}$	
26.40	27.01	Naphthalene, 2-ethyl-		$6*10^{-7}$	
27.60	28.3	2-Vinylnaphthalene	$7*10^{-6}$	$9*10^{-7}$	
28.78	29.13	1,1'-Biphenyl, 4-methyl-		$6*10^{-7}$	
	29.14	Biphenylene	$6*10^{-6}$	$7*10^{-7}$	
26.68	29.31	1,8-Dimethylnaphthalene	$5*10^{-6}$	$7*10^{-7}$	$2*10^{-7}$
27.99	29.57	Acenaphthene	$5*10^{-6}$	$5*10^{-7}$	
32.43	31.90	Fluorene		$5*10^{-7}$	$2*10^{-7}$
34.73	34.52	9H-Fluorene, 2-methyl-		$5*10^{-7}$	
36.16	36.69	Anthracene		$5*10^{-7}$	$3*10^{-7}$
38.66	39.93	Phenanthrene, 2-methyl-		$4*10^{-7}$	$2*10^{-7}$

[‡] subject to change with the GC and MS parameters. Old-until chapter 6 – 100,200, 300 psi, new – chapter 6- 400 psi experiments for pyroprobe pyrolysis, ALS – direct injection to GC

Appendix E: Instruments and materials

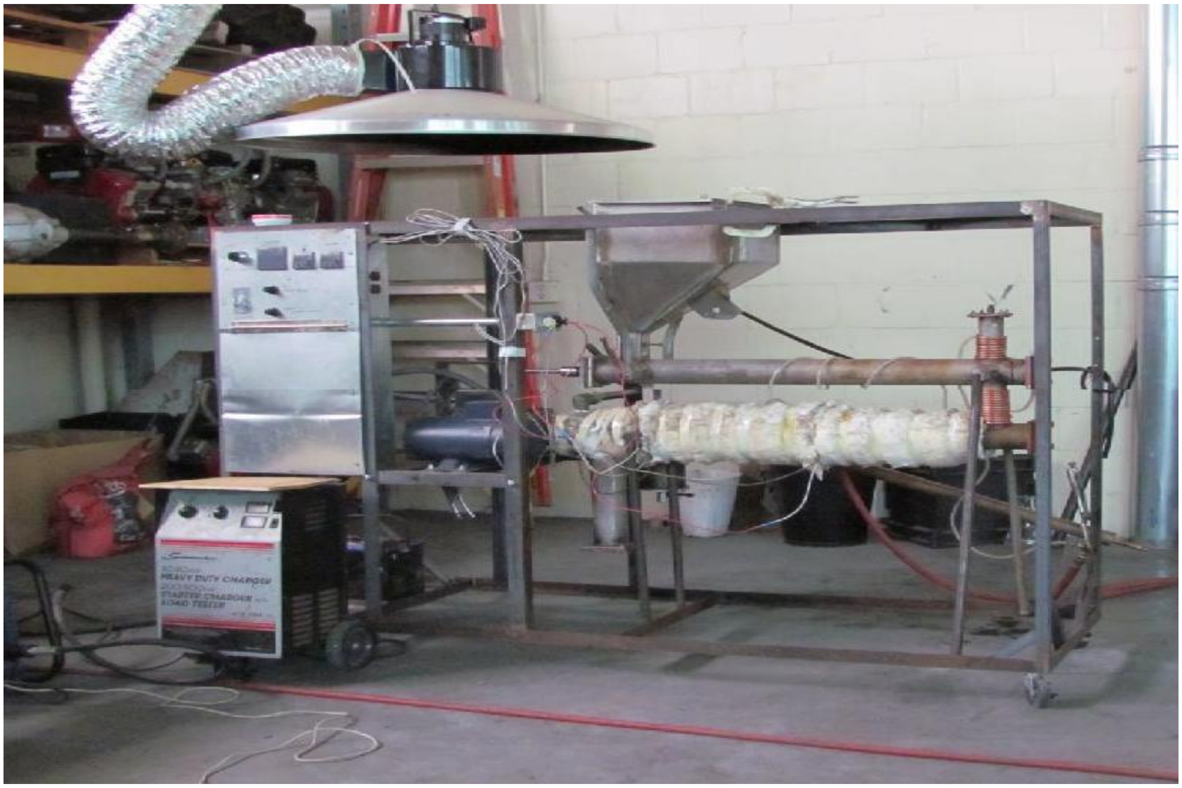
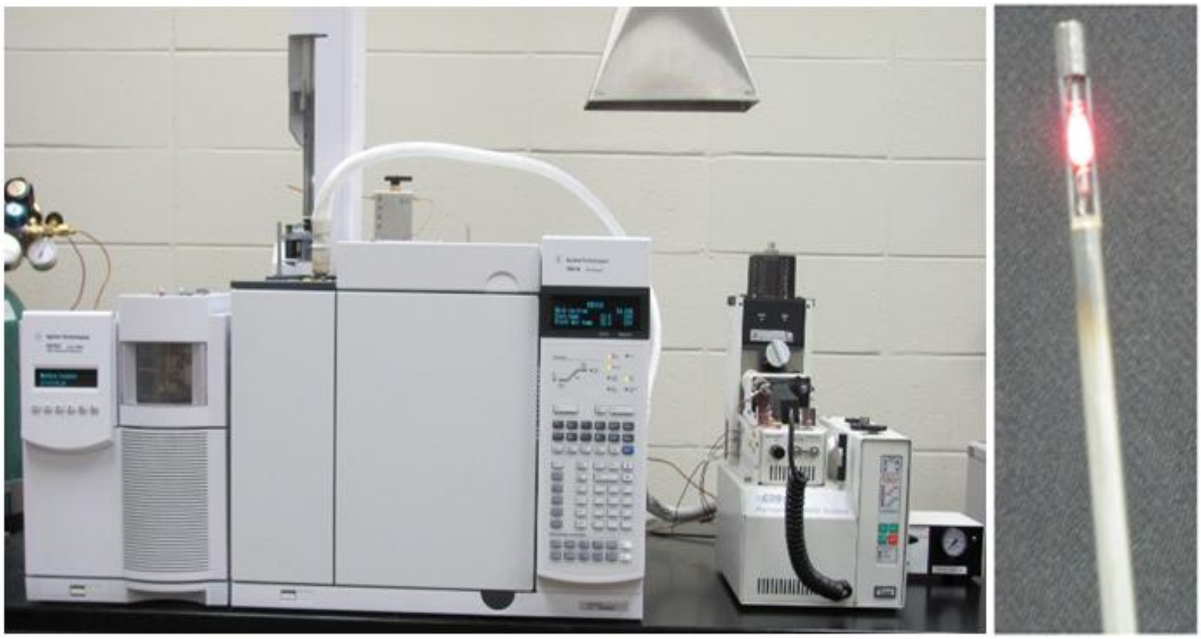


Figure E.1: Auger reactor at Auburn University used for pine wood pyrolysis in Chapter 3

Figure E.2: Bio-oil obtained from pine wood



(a) (b)

Figure E.3: (a) Agilent 7890GC/5975MS for bio-oil chemical analysis connected to CDS 2000 for biomass pyrolysis. (b) Probe with filament where quartz tube inserts for pyrolysis

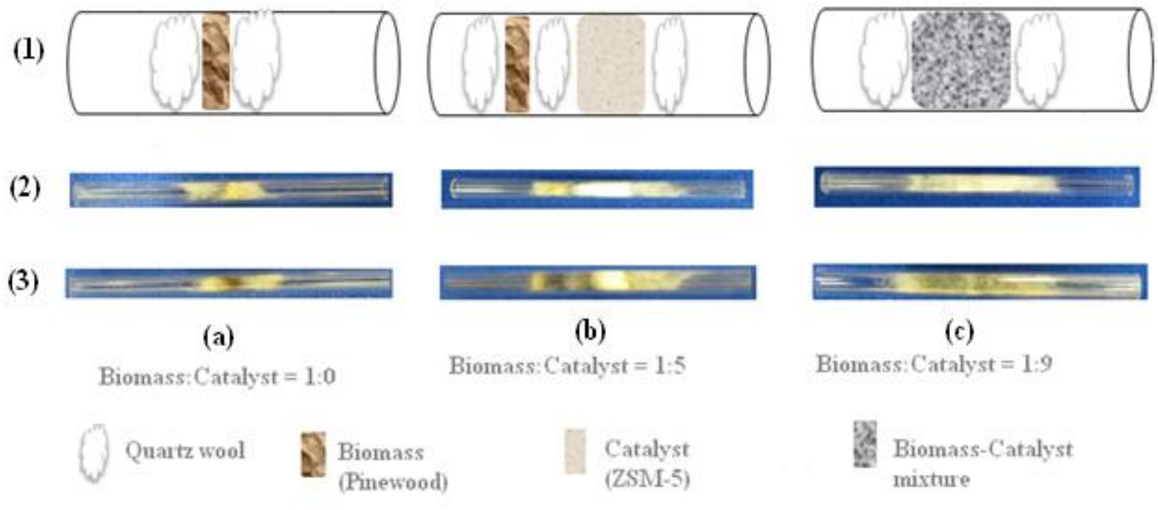
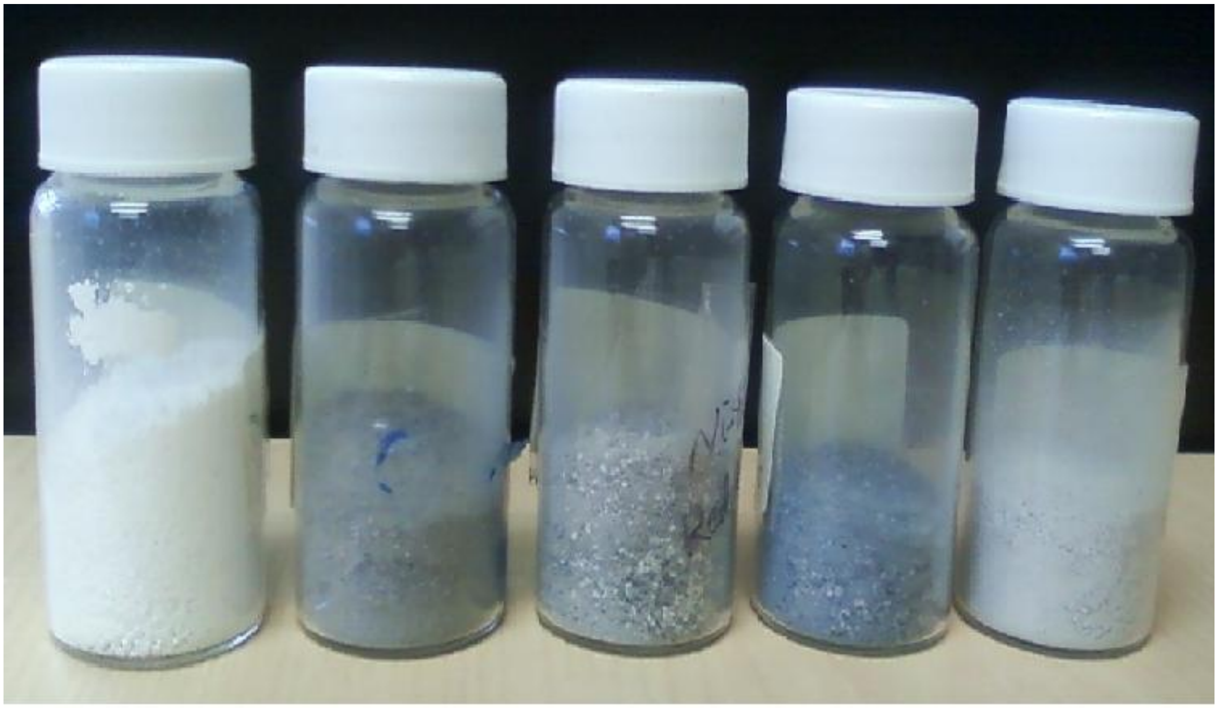


Figure E.4: Reactor set up in Chapter 5 for pyrolysis (a) non-catalytic pyrolysis, (b) catalyst-bed method, (c) catalyst-mixing method, (1) schematic diagram (2) reactor image before pyrolysis, (3) reactor image after pyrolysis



H$^+$ZSM-5 Co/ZSM-5 Ni/ZSM-5 Mo/ZSM-5 Pt/ZSM-5

FigureE.5: Zeolite and metal impregnated zeolite catalysts in Chapter 6

Figure E.6: Reactor set up for fixed bed pyrolysis of algae in Chapter 7

Figure E.7: Bio-oil obtained from algae