View metadata, citation and similar papers at core.ac.uk

brought to you by CORE

provided by University of Maine

The University of Maine
DigitalCommons@UMaine

Electronic Theses and Dissertations

Fogler Library

Summer 8-17-2018

Formate Assisted Pyrolysis of Lignin

Mayank S. Patel
University of Maine, mayank.patel@maine.edu

Follow this and additional works at: https://digitalcommons.library.umaine.edu/etd

Part of the Other Chemical Engineering Commons

Recommended Citation

Patel, Mayank S., "Formate Assisted Pyrolysis of Lignin" (2018). *Electronic Theses and Dissertations*. 2905.
https://digitalcommons.library.umaine.edu/etd/2905

This Open-Access Thesis is brought to you for free and open access by DigitalCommons@UMaine. It has been accepted for inclusion in Electronic Theses and Dissertations by an authorized administrator of DigitalCommons@UMaine. For more information, please contact um.library.technical.services@maine.edu.

FORMATED ASSISTED PYROLYSIS OF LIGNIN

By

Mayank Sureshchandra Patel

B.Tech. Pandit Deendayal Petroleum University, 2015

A THESIS

Submitted in Partial Fulfillment of the

Requirements for the Degree of

Master of Science

(in Chemical Engineering)

The Graduate School

The University of Maine

August 2018

Advisory Committee:

William J. DeSisto, Professor of Chemical Engineering, Advisor

M. Clayton Wheeler, Professor of Chemical Engineering

Douglas W. Bousfield, Professor of Chemical Engineering

FORMATED ASSISTED PYROLYSIS OF LIGNIN

By

Mayank Sureshchandra Patel

Thesis Advisor: Dr. William J DeSisto

An Abstract of the Thesis Presented in Partial
Fulfillment of the Requirements for the
Degree of Master of Science
(in Chemical Engineering)
August 2018

A significant fraction of global energy demand is met through nonrenewable petroleum feedstock, which increases the risk of energy security. The energy production from non-renewable petroleum feedstocks is one of the large contributor to greenhouse gas emissions, which can cause climate change impacts. The energy security can be improved, and the greenhouse gas emissions can be reduced by deriving energy from domestically available renewable lignocellulosic feedstocks such as wood.

Wood has three major components: cellulose, hemicellulose, and lignin. The cellulose is primarily used to produce pulp and paper. The hemicellulose is often utilized to produce a value-added chemical like furfural. However, lignin is an underutilized component of wood, which is primarily used as a boiler fuel. The current economic value of the lignin is very low as its application is greatly limited. The low economic value of lignin can also be limiting the commercialization of biorefineries to produce biofuels. Significant research has been conducted to valorize lignin via fast pyrolysis and catalytic pyrolysis to produce chemicals and fuels. However, problems such as feeding, low energy density of bio-oil due to a high oxygen content, irreversible deactivation of the catalyst due to the presence of ash are hindering the commercialization of these processes. In this study, we explore the possibility of overcoming these problems with the formate assisted pyrolysis (FAsP) of lignin.

The FAsP involves pretreating lignin with two formate salts (calcium formate and magnesium formate) before it is pyrolyzed in a reactor at a temperature of 500 °C. Two different mass concentrations formate salts were considered: 0.5 g and 1 g of formate salt per g of lignin. It was observed that lignin feeding issues can be overcome by pretreating lignin with the formate salts of calcium and magnesium. The highest bio-oil yield of pyrolysis of pretreated lignin with calcium and magnesium formate salts was found to be 7% and 15.5%, respectively. The O/C ratio of bio-oil was found to be 0.08 and 0.16 for the lignin pretreatment with calcium and magnesium formate salts, respectively. By ^{13}-C-NMR it was detected that bio-oil has more than 75% aromatics.

ACKNOWLEDGEMENTS

I would like to express my sincere appreciation to my advisor, Dr. William J. Desisto for his precious ideas, time, advices, and support throughout my research. I would like to thank Dr. Clayton Wheeler for his valuable time and guidance.

I would like to thank my committee member Dr. Douglas Bousfield for his precious time. In addition, I would like to appreciate Dr. Sampath Reddy Gunukula for his important guidance and discussion. Many thanks to Nick Hill for his continuous technical support, Elisha Cram for doing elemental analysis and Ealin Patel for performing NMR.

I would like to acknowledge U.S. Department of Transportation (DTRT-G-UT-C43) for funding this research, and Department of Chemical and Biomedical engineering for giving me this opportunity.

Finally, I would also like to thank my family and friends for their support and love.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

Since the industrial revolution human beings have been largely dependent on different kinds of fossil fuels such as coal, crude oil, and natural gas to produce energy. Of these, coal was the very first source that people started using for energy, followed by crude oil and natural gas. With the advancement in the technology, dependency on coal reduced and more oil was used (1). Energy and fuels are two basic needs of humans; around 81% of total energy is generated by fossil fuel and more than 90% of transportation fuel in the U.S. comes from petroleum oil (2)(3). But along with that, we should also know that fossil fuels are the non-renewable source of energy, as they take millions of years to regenerate. As per BP's report of 2013, the remaining oil supply will last for another 53.3 years at the current rate of extraction, although it might vary a bit because there may still be undiscovered oil reserves (4).

As per population division of the UN, there will be around 9 billion people by 2050 (5), meaning that the global population is increasing daily, therefore the demand for energy and fuel will increase, though we cannot regenerate them as they are non-renewable sources. The rate at which we are using fossil reserves is depleting this limited storage very fast. Also, there is another problem associated with the usage of crude oil. If we look at the life cycle (from extraction to refinement and commercial use) of petroleum products, they are the major source of greenhouse-gas (GHG) emissions, especially when fossil fuels are burnt to produce electricity, heat, and transportation fuel (6). Because of GHG's other problems arise in the form of acid rain which creates many problems, including the major problem of making agricultural land infertile (7).

With the increasing usage of hydrocarbon fuels for our comfort, the negative impacts are increasing as well. This results in global warming because of climate change and the scarcity of petroleum reserves. Therefore, research is being conducted across the world to find an alternative solution for energy and fuels, focused on renewables that generates less CO_2 emission as global warming is a major problem we are facing nowadays. Therefore, options such as solar, and wind are very appropriate as a renewable source to produce energy. It is predicted that after 10 years, up to 19% of electricity will be generated by wind energy and will cover between 25-30% of world's energy need. And by this way, the limit of 2˚C rise by 2100 can also be achieved, as it will help in reducing the release of 3 billion tons of CO_2 a year (8). Likewise, solar energy is also an important source for energy production, and if we look at BP's 2016 report which has mentioned that solar energy is also contributing power generation, increasing steadily in use year after year. It was observed that there was the growth of around 30% in the year 2016 (9). Hence slowly but steadily it also helps in the production of energy and in reducing the usage of a fossil which ultimately decreases the release of harmful gases.

As discussed above, there are many options for the generation of energy. But for transportation fuels and chemicals, biomass may be the sustainable source. So, what is biomass? It is a renewable source of energy obtained by sources such as plants, animals, and municipal waste. Until the mid-1800's biomass was the important source of an energy and still, it is a significant material for energy in many developing countries. The advantage of biomass is that they are renewable and easily available worldwide (10).

There was approximately 450 million dry tons of biomass on the earth. Which makes them a cheap source as well, while also an extensively researched topic to produce renewable sources (11).

Therefore, biofuels such as ethanol and biodiesel are produced from available biomass and blended with gasoline and diesel to reduce the amount of crude oil production and usage along with the reduction of GHG emissions. So, these fuels are divided into different categories based on the type of feedstock. First generation where sugars from different crops such as corn, sugar cane, barley etc. are used to produce ethanol, and most of the ethanol in the United States is produced from corn. In fact, now the majority of the gasoline sold in the U.S. is blended with 10% ethanol by volume and there is no need of changing the vehicle engine. According to the department of energy (DOE) report 2016, the supply of energy crops and crops residue in 2015 was around 100 million of dry tons and will be approximately 600 million of dry tons by the year 2040. Similarly, biodiesel is made from the vegetable oils, fats etc. which can be used in a diesel engine (12).

The second generation of bio-fuels is where lignocellulosic biomass or woody biomass are used to produce fuels. Therefore, renewable fuel standard (RFS) was established in 2005 with the energy policy act (EPA) 2005, where 4 billion gallons of biofuels were required to be used in 2006 by blending it with the transportation fuel. These measures were later extended by the energy independence and security act of 2007, where a requirement of 36 billion gallons of renewable fuel was estimated till the year 2022, with a condition that a maximum limit for the renewable fuel from corn- starch was 15 billion gallons and 16 billion gallons from cellulosic biofuels, all in effort to reduce the emission of GHG (13). Now, when we talk about Maine we can say that it is one of the most forested state in the United States as it is occupied by forest in more than 90% of its land area. The major source of biomass here is the forest residues along with the residue from some pulp and paper mills. Because of this, approximately 10 million metric tons of dry biomass is produced in Maine. Therefore, biomass contributed around 24% of total electricity generation in Maine in 2016 (14). Because of its vast biomass diversity, Maine has the potential to reduce its dependency on non-renewable fuels and use renewable fuel for their energy needs. So, the usage of renewables would not just help in reducing CO_2 emissions and provide clean energy, but it would also help in the energy security of many nations, by reducing the imports from other countries.

Lignocellulosic biomass has three major components: cellulose, hemicellulose, and lignin. The cellulose and hemicellulose are used in pulp and paper mills and also to produce some value-added chemicals. Lignin is an underutilized component and is used as a fuel in the boiler. But lignin has more potential, as lignin is one of the large natural sources of aromatic compounds, which make the lignin very ideal precursor for hydrocarbon fuel. In this study, we are trying to valorize lignin by pretreating with two formate salts (calcium formate and magnesium formate) before pyrolyzing in a reactor at 500 ˚C, to produce bio-oil. Elemental analysis was done to determine the wt% of carbon, hydrogen, nitrogen, and oxygen of the oil. ^{13}C-NMR was performed to detect the groups present in the bio-oil. In next chapter study of different types of lignocellulosic biomass was done with majorly focus on lignin, followed by different pretreatment methods and different thermochemical process for the production of biofuels from the lignocellulosic biomass.

CHAPTER 2

LIGNOCELLULOSIC BIOMASS

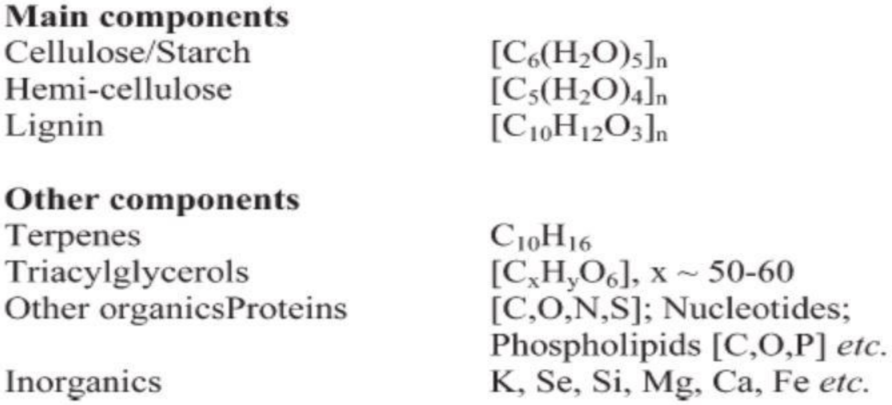
2.1 Introduction

Fossil fuels are the current source of transportation, of which diesel and gasoline are used as fuel for ground transportation, while kerosene and heavy fuel for plane and ships respectively. But, the petroleum reserves are limited, although there is a sufficient amount of coal which can also be used to produce fuel. However, the problem with the use of petroleum fuel is that it is increasing the number of greenhouse gases in the environment. Globally now there is a demand for cleaner and more sustainable fuels. The available options for renewable energy/fuel in the global market are solar, biomass, wind, and geothermal energy. As we have to convert these energy sources into some other form of energy such as electricity, biofuel or hydrogen, it cannot be used directly for transportation. There has been advancement in electrical vehicles but there is the challenge of storing such huge amount of energy efficiently (15).

Hydrogen is a promising source of clean energy as it only generates water as a waste product. Still, the process of converting hydrogen from its source is not very efficient, however, its production from biomass through catalytic conversion has been improved considerably (16) (17). Barriers such as energy densities closer to the petroleum derived fuels and proper storage of hydrogen has come a along the way. Even if these two hinderances are resolved, there is another problem with hydrogen as there is no proper infrastructure for its distribution. All these scenarios make the biomass a suitable candidate for the production of transportation fuels (15). Moreover, hydrogen can also be made from these biofuels by catalytic partial oxidation (18).

Biomass is available in abundance and is renewable in nature which makes it sustainable and a viable option for the production of liquid fuel. Hydrocarbon fuels are used for transportation but, they are blended with the biofuels from biomass. Examples include ethanol and fatty acid methyl esters for gasoline and diesel engine respectively. The benefit of these mixtures are that they can be used for the existing vehicle engine. The use of direct or the total mixture is not an option because when it is compared with the properties such as energy density, viscosity, octane/cetane number of fossil fuels, they are lagging. However, blending of biofuel can be used as it also helps in limiting the usage of fossil fuels (15).

Biomass is the most abundant source of renewable energy, which is available in the form of plants, animals, and municipal wastes. The contribution of biomass as fuel in the year 2017 in the United States was 5%, from which the share of biofuels was 47% and the contribution of wood and municipal waste were 44% and 10% respectively (20). The components of biomass are given in the figure 1. Among which cellulose, hemi-cellulose and lignin are the major components.



Main components	
Cellulose/Starch	$[C_6(H_2O)_5]_n$
Hemi-cellulose	$[C_5(H_2O)_4]_n$
Lignin	$[C_{10}H_{12}O_3]_n$
Other components	
Terpenes	$C_{10}H_{16}$
Triacylglycerols	$[C_xH_yO_6]$, x ~ 50-60
Other organicsProteins	[C,O,N,S]; Nucleotides; Phospholipids [C,O,P] *etc.*
Inorganics	K, Se, Si, Mg, Ca, Fe *etc.*

Figure 2.1 Components of biomass (15)

Lignocellulosic biomass (also known as second generation biofuels) uses woody biomass as a source of energy (23), which is available in the form of agricultural residues, municipal wastes, and forest residues (21). Lignocellulosic biomass (L.C.B) has three major components: cellulose, hemicellulose, and lignin. The composition of these components depends on the type of plant species. The amount of cellulose is greatest in hardwood, while lignin is greatest in softwood (Table 1) (19).

Table 2.1 Composition of lignocellulosic biomass (19)

	Cellulose	Hemicellulose	Lignin
Hardwoods	40-55%	24-40	18-25
Softwoods	45-50	25-35	25-35
Wheat straw	30	50	15
Corn cobs	45	35	15
Grasses	25-40	35-50	10-30
Switchgrass	45	31.4	12

2.2 Components of lignocellulosic biomass

2.2.1 Cellulose

Cellulose is one of the significant components of lignocellulosic biomass, which accounts for 40-45 % of the wood dry weight. They are a polymer of D-glucopyranose units and are connected by β-(1 ----> 4) glucosidic bonds (figure 2). The degree of polymerization can be referred to as how many glucose units are present in the cellulose molecules. An average degree of polymerization of cellulose can be at least 9,000 – 10,000 (22).

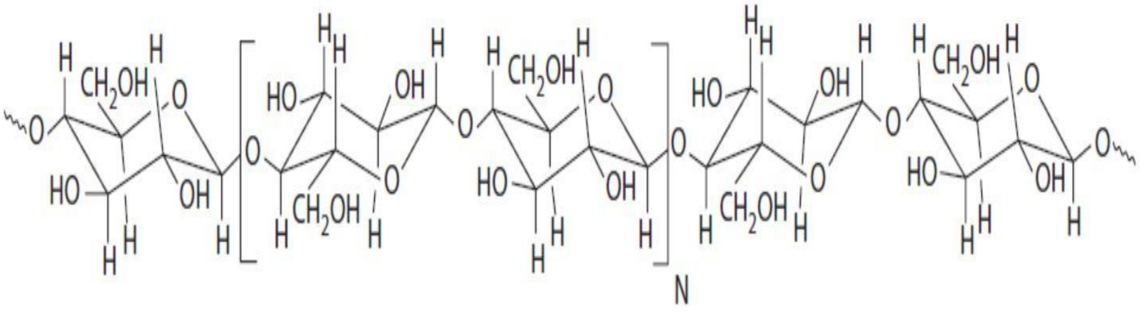


Figure 2.2 Structure of cellulose (22)

As the cellulose molecule tend to form an intra-inter molecular hydrogen bond because of their random orientation, this provides them high tensile strength and hence makes them insoluble to most solvents (21). In cellulose, there are two regions, crystalline and amorphous of which there is a greater crystalline region of cellulose compared to amorphous. Also, because of crystalline nature, it makes cellulose inert and insoluble in most solvents. This structure also helps it for high thermal stability compared to hemicellulose. However, it can be dissolved into strong acids like sulfuric acid, hydrochloric acid, or phosphoric acid, but this may lead to the rapid degradation. It is majorly used as a raw material for pulp and paper industry (22).

2.2.2 Hemicellulose

Like cellulose, hemicellulose is also a polysaccharide polymer but with many different sugars. Hemicellulose generally accounts for 20% - 30 % of wood's dry weight. It has an average degree of polymerization of 100 – 200, making them weaker than cellulose. They are soluble in alkali and easy to hydrolyze (22). Hardwood and softwood have a different composition of hemicellulose (Table 2) (21).

Table 2.2 Percentage of hemicellulose (21)

Hemicellulose	Hardwoods	Softwoods
Xylan	20-30 %	10-15%
Glucomannan	2-5%	15-18%
Galactoglucomannan	-----	5-10%

2.2.2.1 Softwood hemicellulose

Galactoglucomannans: From the above table it can be clearly seen that galactoglucomannan is the main hemicellulose of softwood, comprising between 20% - 25% of wood's weight. The major sugars present are β-D glucopyranose, β-D mannopyranose which is branched linearly (21).

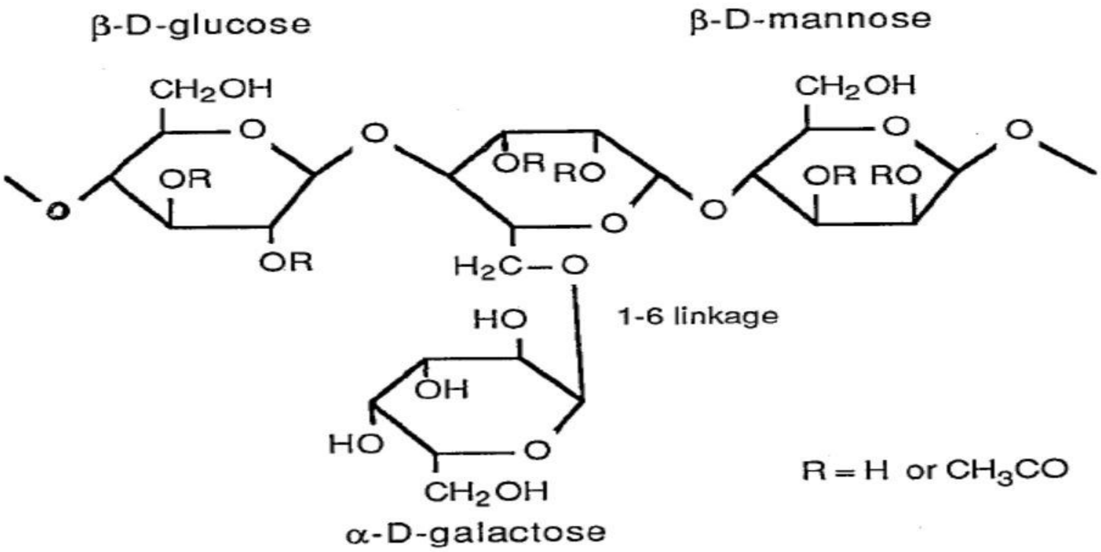


Figure 2.3 Softwood hemicellulose: Galactoglucomannan (21)

2.2.2.2 Hardwood hemicellulose

Xylans: It is the major hemicellulose which is found in hardwood hemicellulose and accounts for 20% - 30% of wood's weight. β-D xylopyranose is the main sugar for the xylans, along with some acetyl and methylglucuronic acid groups (Figure 4) (21).

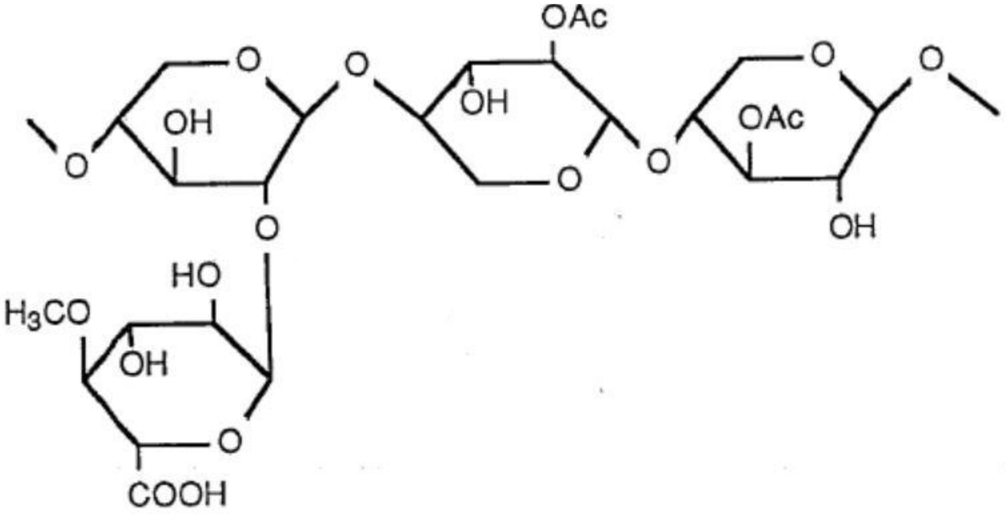


Figure 2.4 Hardwood hemicellulose: Xylan (21)

2.2.3 Lignin

Lignin is the most significant component of lignocellulosic biomass and one of the abundant polymers, usually accounting for 25 – 30 weight % of wood. It is highly complex, amorphous, and mostly aromatic. Unlike cellulose, it does not have any repeating units. The polymers of lignin consist of C-O-C and C-C linkages (Figure 5). In wood, it works as binding material for cellulose and hemicellulose.

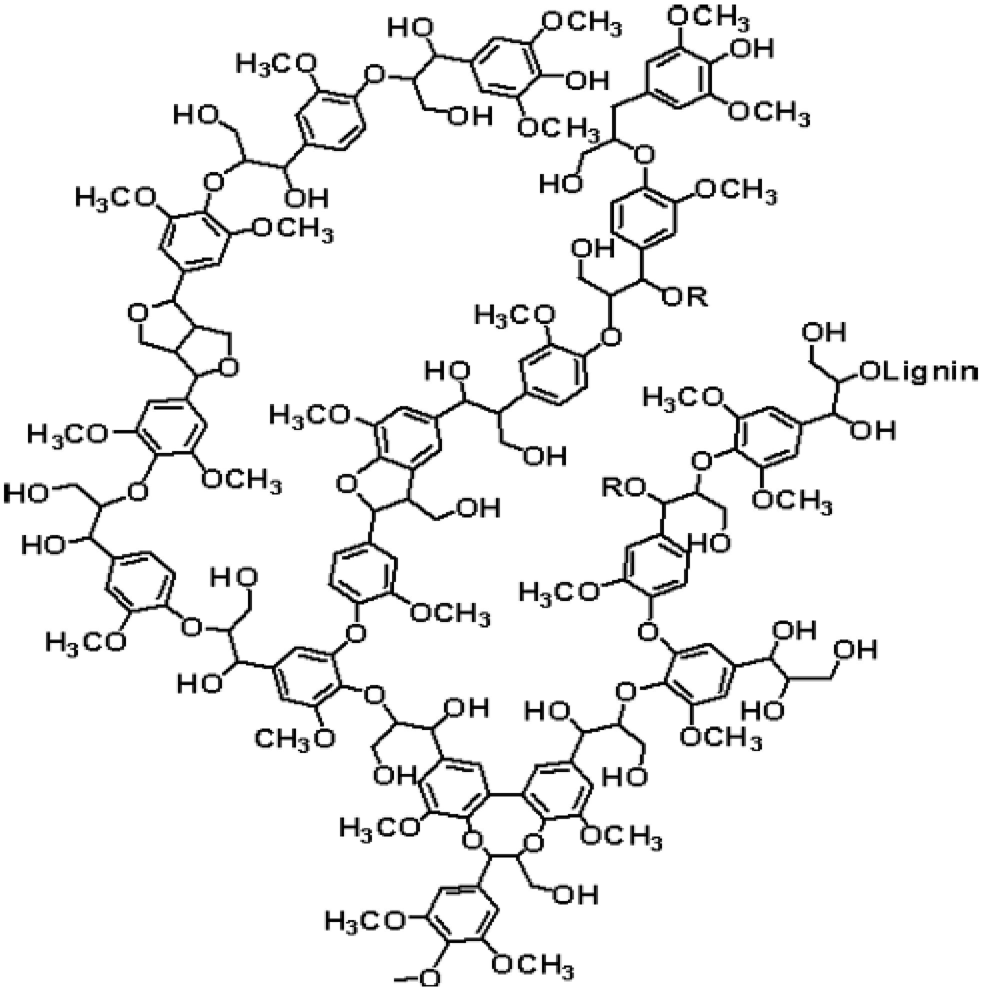


Figure 2.5 Structure of lignin (21)

Similar to cellulose, amount of lignin varies with softwood and hardwood. For softwood it stands between 25% - 35%, and lignin content for hardwood is around 18% - 25%. Basically, Lignin consists of three main buildings blocks or monomers which are p-hydroxyphenyl (p-coumaryl alcohol), guaiacyl (coniferyl alcohol), and syringyl (sinapyl alcohol) as shown in figure 2.6 (21). Its content also varies from softwood to hardwood. Softwood will have more of guaiacyl, whereas hardwood have more syringyl.

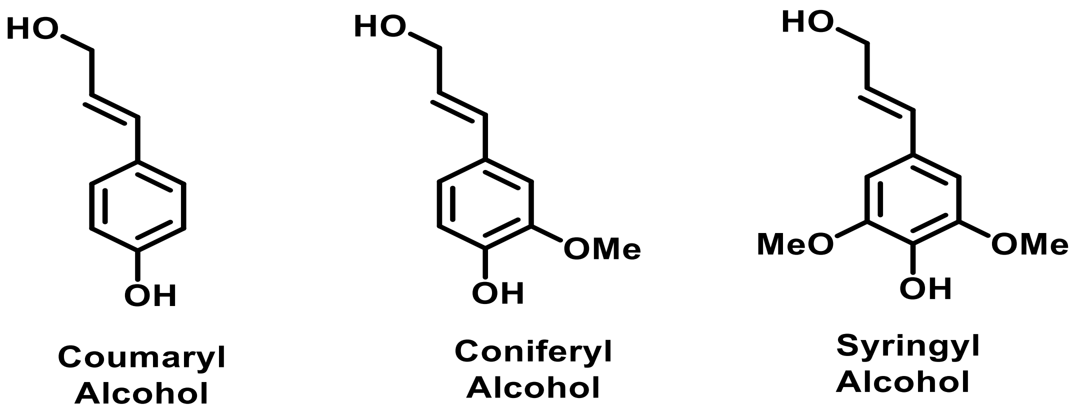


Figure 2.6 Monomers of lignin (21)

Most of the lignin which is produced as a by-product is used as a fuel, while a much smaller amount is used in other applications such as cement, drilling muds, emulsifier etc. (21). Lignin consists of methoxyphenyl propane groups, which provides more energy than that of cellulose and hemicellulose. Being one of the large natural source of aromatic compounds, lignin is a very ideal precursors for hydrocarbon fuels and aromatic chemicals (24) (25).

CHAPTER 3
BIOMASS CONVERSION

3.1 Introduction

The necessity of energy has increased. Due to rapid industrialization and increase in global population, it will not be an easy task to manage energy (26). Also, with the continuous usage of conventional energy, there is also concern about environment. Therefore, renewable energy sources can play an important role to decrease our dependency on fossil fuel by providing an alternative source which will also help in reducing the environment concerns (27). Since ancient times biomass has been used as a source of energy all around the world, whether it is to generate electricity or to be a heat source at some industrial facility. It is the only renewable source which can be either converted into solid, liquid and gaseous fuels. Moreover, biomass contribute to 15% of the worlds primary energy which makes it to the fourth largest of energy (28). Also, the amount of greenhouse gas emissions can be reduced by using biomass fuel sources as they are environmentally friendly and renewable (27). Based on the type, quality or the quantity of feedstock, their end use or any specific environmental conditions or the factors, biomass can be converted into various forms of energy using different processes (29). Basically thermochemical, and biochemical are two processes for converting biomass (30).

3.2 Thermochemical conversion

Thermochemical conversion of biomass is the heating of biomass at high temperature and depending on their end use, different processes such as combustion, gasification, liquefaction, hydrogenation, and pyrolysis are used (27).

3.2.1 Combustion

Combustion involves the heating of biomass in air. The heat generated can be used as a mechanical power or electricity using different equipment. The hot gas generated during combustion are around 800 to 1000 ˚C. It represents oldest utilization of biomass where it can be used on a smaller scale for domestic purpose such as cooking, space heating etc., as well as on an industrial scale to produce heat or generation of steam. Also, generating power on industrial scale by co-combustion with coal is a good option. Upon complete combustion between biomass and oxygen, it produces CO_2, water, and heat (27). Like other process, combustion also has some drawbacks. Biomass which are available in its natural form cannot be used for burning directly. Different pretreatment such as compression, chopping and grinding of biomass need to be done to improve combustion which results in increasing the process cost (31).

3.2.2 Gasification

Gasification is a process which produces mixture of combustion gas by heating biomass with air or steam at the temperature range of 800 to 900 ˚C. The reaction during gasification process are as follows:

$$C + O_2 \rightarrow CO_2$$

$$C + \frac{1}{2} O_2 \rightarrow CO$$

$$CO + \frac{1}{2} O_2 \rightarrow CO_2$$

$$CO_2 + C \rightarrow 2CO$$

Also, methane and hydrogen which are formed by thermal splitting of organic matter may be combusted and can also reduce the carbon due to the presence of hydrogen in the mixture.

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

So, the producer gas while contain a mixture of carbon monoxide, hydrogen, carbon dioxide, methane, and nitrogen. These producer or syngas produced can be either burned directly or can be converted into fuels such as methanol and hydrogen (32). So, in general different phases of gasification can be seen in figure 3.1. Where the moisture or water from biomass is released initially followed by volatiles, the residual carbon reacts slowly. Also, the reactions depend on the types of biomass.

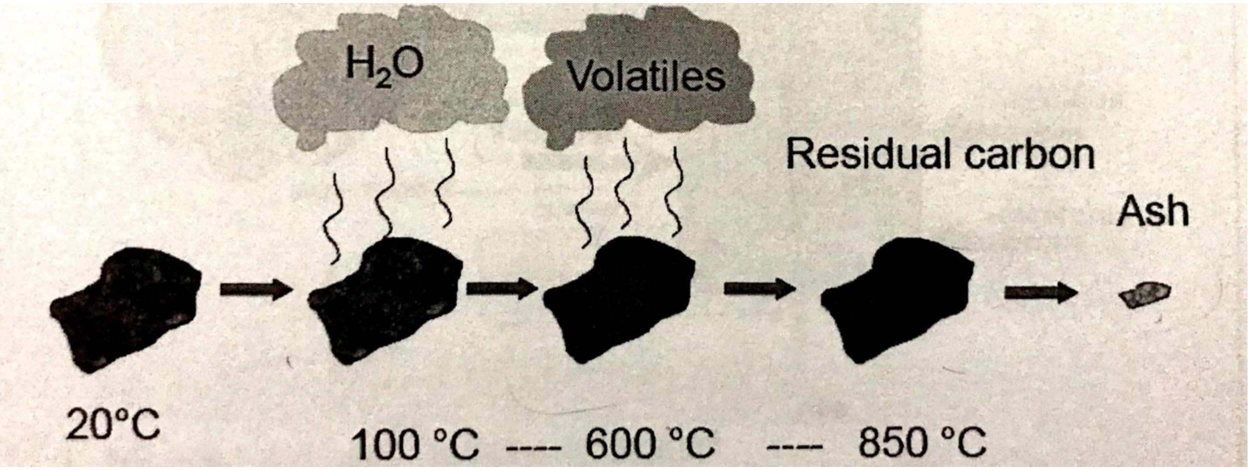


Figure 3.1 Phases of gasification (33)

3.2.3 Liquefaction

Liquefaction is a thermochemical process which uses catalyst along with the hydrogen to make liquid product from biomass at low temperature and high temperature. To secure the liquid phase for proper heat transfer, high pressure is used. Since the reactors and feeding systems are more complex and expensive, there is less interest in this process (34). Also, the liquid product obtained in the process is very viscous, which makes it hard to handle (27).

3.2.4 Hydrogenation

The main product of hydrogenation process is methane which is produced by hydrogasification. It can be produced by two different ways. In first case the synthesis gas produced during the first step is reacted with hydrogen to make methane. While in second case, the biomass is already mixed with hydrogen from the start. Also, whatever amount of char is generated in first step is used to generate hydrogen containing synthesis gases in the second stage reactor (27).

3.2.5 Pyrolysis

Pyrolysis is a thermochemical process, which thermally decomposes biomass at a temperature range of 300 ˚C to 700 ˚C in the absence of oxygen and atmospheric pressure to give char, liquid, and gases. Different parameters such as temperature, pressure, heating rate etc. determine the quality and quantity of products. Low reaction temperature along with long residence time will give more char yield, while high temperature will favor more gas. The moderate temperature along with short residence time will give high liquid yield (35). There are some steps which need to be followed before doing pyrolysis of biomass. They are drying and grinding the feedstock to small particle sizes. Slow pyrolysis and fast pyrolysis are two types of pyrolysis that are used.

3.2.5.1 Slow pyrolysis

It is a conventional pyrolysis, where biomass is heated at varied rate (5 – 7 ˚C/min). The main product in this process is char, because of the slow heating rate. Along with char small amount of liquid and gas product are also produced. Many different types of feedstock can be used for slow pyrolysis (27).

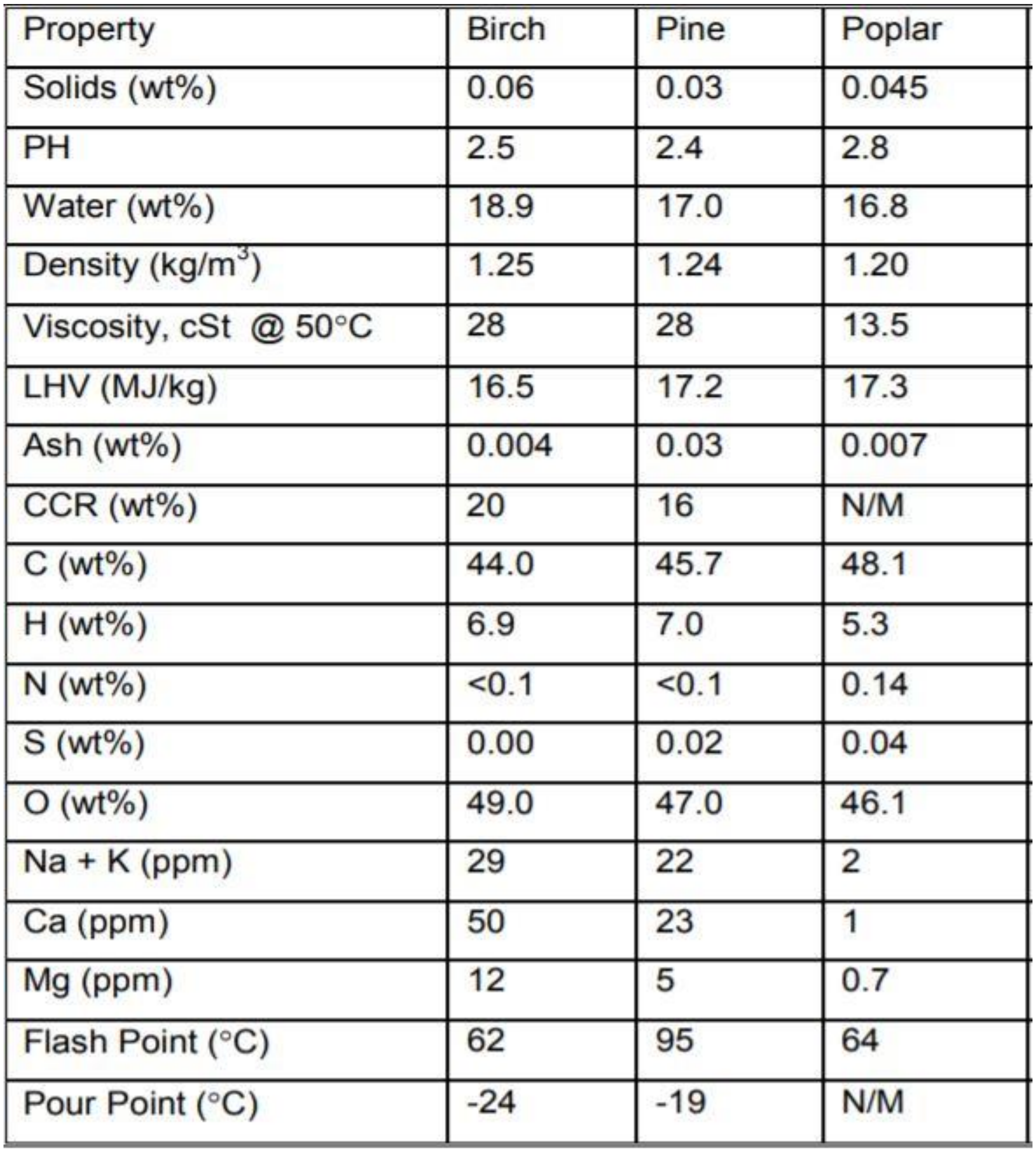
3.2.5.2 Fast pyrolysis

Fast pyrolysis is quite different than slow pyrolysis as the heating rate of fast pyrolysis is very high (300 – 500 ˚C/min), which decomposes biomass very rapidly to give organic vapors, along with char and gases. The vapors are condensed, to collect the liquid known as bio-oil. Fast pyrolysis gives higher liquid yield. The liquid yield depends on the temperature, vapor residence time and char separation (35). But, before doing fast pyrolysis there are some steps which need to be followed. These steps include drying to reduce the moisture content of feedstock (which must be around 10% or less than that to lower the water content in oil), as well as grinding the feedstock into smaller particles size. There are many different biomass feedstocks which have been tested, mostly woody biomass (36).

3.3 Bio-oil properties

Bio-oil is a dark brown, viscous, and smoky-odor liquid. It is a complex mixture of different oxygenated compounds and contains high oxygen (45 – 50 wt%). Also, there is significant amount of water present in oil, along with major groups such as aldehydes, ketones, carboxylic acids, phenols etc. (25). The detailed physical properties of three different biomass pyrolysis oil is given in the table 3.1 (37).

Table 3.1 Physical properties of biomass (37)



Property	Birch	Pine	Poplar
Solids (wt%)	0.06	0.03	0.045
PH	2.5	2.4	2.8
Water (wt%)	18.9	17.0	16.8
Density (kg/m^3)	1.25	1.24	1.20
Viscosity, cSt @ 50°C	28	28	13.5
LHV (MJ/kg)	16.5	17.2	17.3
Ash (wt%)	0.004	0.03	0.007
CCR (wt%)	20	16	N/M
C (wt%)	44.0	45.7	48.1
H (wt%)	6.9	7.0	5.3
N (wt%)	<0.1	<0.1	0.14
S (wt%)	0.00	0.02	0.04
O (wt%)	49.0	47.0	46.1
Na + K (ppm)	29	22	2
Ca (ppm)	50	23	1
Mg (ppm)	12	5	0.7
Flash Point (°C)	62	95	64
Pour Point (°C)	-24	-19	N/M

3.3.1 Viscosity

Viscosity can determine fluidity of a liquid. The bio-oil from pyrolysis is very viscous and it varies from the different types of feedstock, as the amount of cellulose, hemicellulose, and lignin, is different in different biomass (38). Therefore, even if the operating conditions are same for two different types of biomass their viscosity will be different. Hence, difference in operating conditions changes viscosity (39). Ageing is also another factor which affects its viscosity. The water or volatile material from bio-oil gets evaporated when it is stored for a longer duration and makes the oil viscous (40). It has been found that usage of vapor filter actually helps in reducing the viscosity by 13 – 38% in fresh oil and up to 95 % in aged bio-oil (41). Viscosity can also be reduced by adding some polar solvent, but it may affect to some other properties of oil (42).

3.3.2 Heating value

Heating value helps in determining the energy content of fuel. Bomb calorimeter can be used to determine this value. Basically, higher heating value (HHV) and lower heating value (LHV) are two different heating values (43). Factors such as oxygen content, water content, and operating conditions influence the heating value. Bio-oil has HHV in the range between 20 – 25 MJ/Kg (44 – 47). The main reason for low value is the high oxygen content (~50 %) and water content (~30 %) (48). Condensation temperature also plays very vital role in the heating value of oil. The bio-oil condensed at lower temperature has high calorific value compared to that of oil condensed at high temperature (49) (50).

3.3.3 Water content

Presence of moisture in the feedstock and dehydration reaction during pyrolysis are the main reasons for water content in the bio-oil, and because of water content the applications for bio-oil becomes difficult. Therefore, it is necessary to keep the moisture content of feedstock less than 10% in order to reduce the water content in oil. Because of the presence of water, other problems can arise including: lowering of the heating value, premature evaporation, reduction of combustion rate and delays in ignition (51). On the other hand, higher amount of water makes oil less viscous while helps in handling and pumping (42). In general, water content accounts for 10 – 40 wt% of bio-oil from biomass. The difference in water content is due to factors like moisture content of biomass, temperature, vapor residence time, and the type of biomass (38). Bio-oil collected from condensers of low temperature have less water content compare to high temperature condensers (49). The usage of electrostatic precipitator (ESP) also reduces the water content (50).

3.3.4 Oxygen content

Due to the presence of water in bio-oil, there is also presence of oxygen, in the form of oxygenated compounds. The oil becomes immiscible with non-polar petroleum fuels due to such compounds (51). The presence of oxygen makes bio-oil unstable, along with that it also lowers the heating value of oil, and makes liquid corrosive. Therefore, to increase its application oxygen should be removed. It can be removed through hydrotreating where oxygen is removed by forming water and by catalytic cracking in which oxygen is eliminated by forming carbon oxides and water. The amount of oxygen in bio-oil is around 10 – 50 wt%. This number varies because of difference in biomass or different operating conditions (51 – 53). The oxygen content can also be reduced if the vapors are condensed at lower temperature (50).

3.3.5 Acidity/pH

Bio-oil contains significant amount of organic acids. The bio-oil is very acidic as they have pH value between 2 – 4. Therefore bio-oil is very corrosive. The biomass feedstock is one of the factor on which value of pH depends (38). Eucalyptus wood is one of the example, because the pH value of its oil is between 1.8 – 2.9 (54) (55).

3.4 Bio-oil upgrading

As discussed above the properties such as high viscosity or high acidity limits the application of bio-oil. Upon getting some heat or time they polymerize. Also, the high oxygen content makes the oil highly unstable which hinders its application. Despite this, there are various applications and end use of bio-oil, if they are upgraded properly.

3.4.1 Solvent or water addition

Addition of solvents or water is simple yet effective upgrading method. It controls the viscosity of oil by diluting the crude oil. As a result, it will be easier to handle the oil (56). Bridgewater et al. (57) considered adding water and organic solvents, in which they were adding water to bio-oil of initial water content of 17% to make it in three different concentration of 20, 25 and 30%. The following results were reported: i) the viscosity of oil reduced significantly with the addition of small amount of water. ii) No change was observed in the viscosity of oil with 30% water even after four months and very little increment with 25% water. Similar kind of result was also obtained at UCL. The most important result was obtained by the addition of 10% butanol, as there was no change in the viscosity even after eight months. Based on their observations they preferred solvent as better option compared to water (58). This method is easy and cheap and on other hand the heating value of oil is reduced by the addition of water (56).

3.4.2 Catalytic cracking

Another method of upgrading bio-oil is catalytic cracking, where zeolite catalyst is used; as it is proven for deoxygenation of small oxygen compounds dehydration and decarboxylation. Here oxygen was reduced in the form of CO and CO_2 (59). With the decrease in oxygen content it will make oil vary stable, but there are also problem associated with this process; such as the fact that large molecules do not have access to the pores and are not converted selectively. Formation of coke on the catalyst requires the constant regeneration, and due to the presence of alkali metals, it poisons the acidic zeolite, and gives low liquid yields (56). All these complications increase the overall cost.

CHAPTER 4

EXPERIMENTAL SECTION

4.1 Pyrolysis system

The setup for formate assisted pyrolysis was built in house except for condenser which was purchased from chem glass. The detailed discussion for each part is done below. There are five major parts in the system i) feeder, ii) reactor, iii) hot gas filter, iv) condenser, and v) electrostatic precipitator.

4.1.1 Parts of pyrolysis system

The feeder is made up of stainless steel material. It has square opening from the top from where the pretreated feedstock is fed, figure 4.1. At the bottom of the feeder there is rotating screw which is attached to the motor. The motor speed is controlled by power supply. Which also helps in controlling the feed rate which is usually between 1.6 to 2.2 g/min. At the exit of feeder there is inlet for nitrogen gas which carries the feedstock to reactor. Also, at the top of the feeder pressure gauge is put to read the pressure.

Figure 4.1 Biomass feeder

Reactor is made up stainless steel which has 1.5 inch of I.D. and is 12-inch long (figure 4.2). It has one inlet, from there nitrogen brings the feedstock into the reactor which is operated at 500 ˚C. Temperature is monitored by two k-type thermocouple which is at the top of the reactor. The reactor is heated by electric furnace which has three heating zones. The furnace has the heating capacity of 900 ˚C. Reactor is placed in chamber which has 3-inch diameter and length of 16 inches. The bottom of the reactor is filled with sand to provide heat transfer medium. Pre-heated nitrogen from the bottom of the reactor is flown to provide fluidization to the sand and the temperature of the preheater is controlled by variac. After the reaction, pyrolysis vapors and gases along with char goes to the hot gas filter through insulated pipe.

Figure 4.2 Pyrolysis reactor

Figure 4.3 Hot gas filter

The pyrolysis vapors along with char and gases from the reactor goes to the hot gas filter which is made up of stainless steel with 1inch O.D. and 6-inch long (figure 4.3), which fits inside a hot gas filter unit (Bessy) and is 24 inch long with 3 inch O.D. and properly insulated from outside (figure 4.4). The temperature of this unit is set at 500 ˚C. The char will be collected outside the filter and mostly at the bottom of the unit. At the top there one k-type thermocouple to measure temperature.

Figure 4.4 Hot gas filter unit

The vapors along with gases from hot gas filter are carried to the graham type glass condenser. The tubes connected to hoses have 8 mm of O.D. The condenser is set at 3 ˚C and the vapors along with some condensable gases are collected at the bottom of round bottom flask which has two necks as shown in figure 4.5.

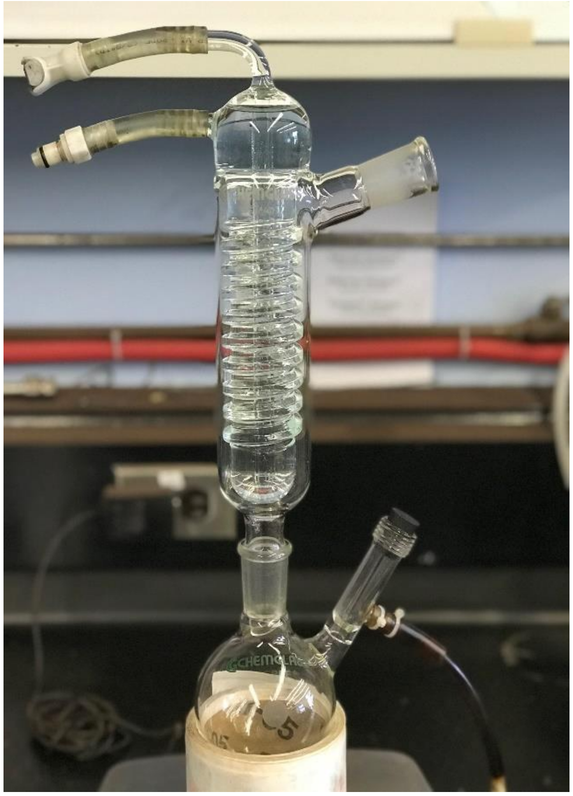


Figure 4.5 Condenser

Figure 4.6 Electrostatic precipitator

After passing through condenser, the non-condensable gases along with aerosols are passed to the electrostatic precipitator. Where aerosols are converted into bio-oil and non-condensable gases leave the system from the outlet of electrostatic precipitator. The middle and bottom part of electrostatic precipitator are made of stainless steel and top with plastic.

4.1.2 Crucible test of pre-treated lignin with different molar ratio

Stoichiometrically, it requires two moles of formic acid and one mole of calcium hydroxide to make one mole of calcium formate. Therefore, lignin was initially pretreated with two moles of formic acid and one mole of calcium hydroxide. The pretreated lignin sample was dried at room temperature followed by sieving at a particle size of 710 μm. Before pyrolyzing the pretreated lignin in a fluidized bed reactor, small sample was collected in a crucible and was heated from outside with nitrogen flowing into the top of the crucible to purge air while heating. The reason for this test was to check whether the pretreated lignin remains in the powder form or is it agglomerating or swelling. If pretreated lignin sample started to agglomerate or swell, that particular sample was not pyrolyzed as it creates plugging problem in the reactor. The stoichiometrically pretreated lignin was not pyrolyzed as this sample has found to be agglomerate when it is heated in a crucible. Similar result has found even for the lignin pretreatment with magnesium formate. Thus, various molar ratios of formic acid to calcium or magnesium formate were tried for the pretreatment of lignin. The table 4.1 and table 4.2 show the results of crucible test for both magnesium and calcium formate pretreatment of lignin, respectively.

Table 4.1 Crucible test results for pretreatment of lignin with magnesium formate

Molar Ratio (F.A.: $Mg(OH)_2$)	Weight Ratio (Lignin/Formic Acid)	Pass the Crucible Test (Yes/No)
2:1	1g/ 1g	No
2:1	1g/ 0.5g	No
1.87:1	1g/ 1g	No
1.87:1	1g/ 0.5g	No
1.6:1	1g/ 1g	Yes
1.6:1	1g/ 0.5g	Yes
1.75:1	1g/ 1g	Yes
1.75:1	1g/ 0.5g	Yes
1.5:1	1g/ 1g	Yes
1.5:1	1g/ 0.5g	Yes
1.4:1	1g/ 1g	No
1.4:1	1g/ 0.5g	No

For the magnesium formate pretreatment, the molar ratio of formic acid to magnesium hydroxide was altered and at the same time for each molar ratio two different loading of lignin to formic acid were used. That is one gram of lignin per gram of formic acid and one gram of lignin per 0.5 gram of formic acid. The results of crucible test for the magnesium formate pretreatment has shown that the ratio of formic acid to magnesium formate as 1.75 and 1.5 can overcome that issues of swelling necessary. Attempts were made to go below 1.5:1 molar ratio of formic acid to magnesium formate and above 1.75:1 molar ratio of formic acid to magnesium formate. However, during crucible test they started to agglomerate or swell and therefore to avoid plugging problems those molar ratios were not used.

Table 4.2 Crucible test results for pretreatment of lignin with calcium formate

Molar Ratio (F.A.: $Ca(OH)_2$)	Weight Ratio (Lignin/Formic Acid)	Pass the Crucible Test (Yes/No)
2:1	1g/ 1g	No
2:1	1g/ 0.5g	No
1.87:1	1g/ 1g	No
1.87:1	1g/ 0.5g	No
1.6:1	1g/ 1g	Yes
1.6:1	1g/ 0.5g	Yes
1.75:1	1g/ 1g	Yes
1.75:1	1g/ 0.5g	No
1.5:1	1g/ 1g	No
1.5:1	1g/ 0.5g	No

Like magnesium formate pretreatment, for the calcium formate pretreatment the molar ratio of formic acid to calcium hydroxide was altered and at the same time for each molar ratio two different loading of lignin to formic acid were used. The results of crucible test for the calcium formate pretreatment has shown that the ratio of formic acid to calcium formate as 1.75 and 1.6 can overcome that issues of swelling necessary. Attempts were made to go below 1.61 molar ratio and above 1.75:1. But, during crucible test faced same problem of agglomeration or swelling as observed in magnesium formate and therefore to avoid plugging problems those molar ratios were not used.

4.2 Formate assisted pyrolysis of lignin

The formic acid salts can provide in situ source of hydrogen for hydrodeoxygenation at atmospheric pressure (60). Here we present a method for the fast pyrolysis of lignin, where it is mixed with magnesium/ calcium formate before pyrolysis. With the addition of calcium formate to the lignin, the feeding problem such as agglomeration, plugging during conventional pyrolysis can be avoided (61). Calcium formate decomposed into calcium carbonate along with CO, CO2, and hydrogen (62), and magnesium formate decomposes at 465 ˚C to give either 2 moles of CO and one mole of water along with magnesium oxide or one mole of CO, CO2, and hydrogen with magnesium oxide (63).

$$Mg(HCOO)_2 \rightarrow MgO + 2CO + H_2O$$

$$Mg(HCOO)_2 \rightarrow MgO + H_2 + CO + CO_2$$

Here we are assuming that magnesium formate decomposed and gave magnesium oxide along with CO, CO2, and hydrogen. In this study lignin was pretreated with the calcium formate or magnesium formate. After mixing, the material was dried in a pan at room temperature. It was then sieved with a pore size of 710 µm before feeding it in the fluidized bed reactor. The moisture content of the samples was measured, and it was between 5 to 10 %. The operating temperature was 500 ˚C and atmospheric pressure. Pretreated lignin was fed into the screw feeder where it was connected with the motor to control the feed rate, usually between 1.6 – 2.2 g/min. Pressure was measured with a pressure gauge installed at the top of the feeder, and two nitrogen tanks were used with a total flow rate of 6LPM. Of which, one was connected at the exit of feeder to carry the pretreated lignin to the reactor at 500 ˚C at 3LPM, and other nitrogen was connected at the bottom of the reactor and heated by preheater prior entering to the reactor at 3LPM. The electric furnace was used as a source to provide heat which three different zones. Two k - type thermocouples were kept at the top of the reactor to watch the reactor temperature. At the bottom of the reactor, fine sand was put for the heat transfer. After the reaction in the reactor organic vapors, char and non-condensable gases move to the hot gas filter unit through insulated pipe. The unit was already set at 500 ˚C and one k – type thermocouple at the top observed the temperature. The char is collected at the hot gas filter and organic vapors along with non- condensable gases would go to the condenser which is at 3 ˚C, the water flows in the counter direction of the gas. Condensed water from the vapor along with some other organics were collected at the bottom of condenser. Finally, the bio-oil was collected at the electrostatic precipitator and non-condensable gases leaves the system from the exit of electrostatic precipitator. The schematic diagram for the same is shown below.

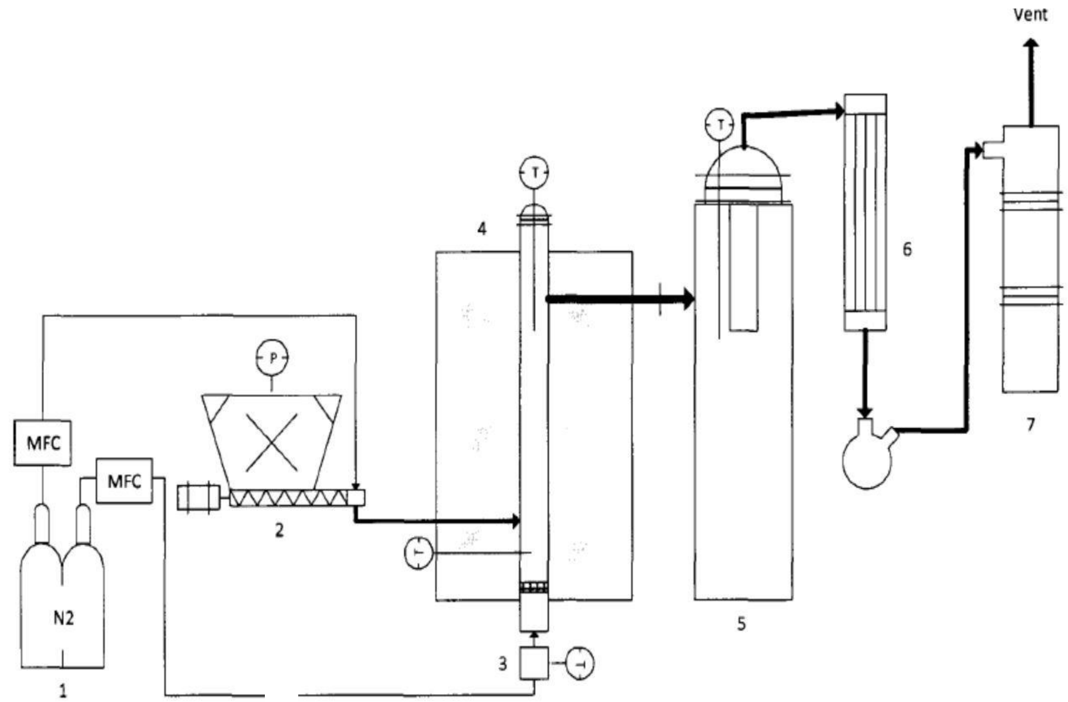


Figure 4.7 Schematic diagram of formate assisted pyrolysis of lignin (60)

Thermo scientific flash 2000 elemental analyzer was used to for elemental analysis. It provides weight farction of carbon, hydrogen, and nitrogen in the oil and weight fraction of oxygen was obtained by difference. For ^{13}-C NMR (Nuclear Magnetic Resonance) analysis bio-oil samples were dissolved in DMSO-d6 solvent and analyzed using varian unity plus 400 NMR, to identify the functional groups present in the bio-oil. Non-condensable gases coming out from the electrostatic precipitator were collected and injected in GC-FID just to detect the gases via gas chromatography (GC). The major gases observed were carbon monoxide, carbon dioxide and methane. The results of lignin pretreated with different salts under different operating conditions is discussed below.

4.3 Pretreatment of lignin with magnesium formate

4.3.1 Molar ratio of 1.6:1 for formic acid to magnesium hydroxide

Two feedstocks with difference in lignin to formic acid wt% (full loading 1g/1g and half loading 1g/0.5g) and same molar ratio (1.6:1) of formic acid to magnesium hydroxide were prepared. In first case 100 g of lignin was mixed with 40 g of magnesium hydroxide and 500 g water in a beaker which is at 60 ˚C. After 1 hour 100 g of formic acid was added to the mixture and left for stirring another hour. After that 40 g of magnesium hydroxide was added to the mixture and stirred for another hour. In second case 160 g of lignin was mixed with 32 g of magnesium hydroxide and 500 g of water and stirred for 1 hour. After that 80 gm of formic acid added to the mixture and wait for another hour to add 32 g magnesium hydroxide. Feedstock was prepared and poured into a pan for drying at room temperature and then sieved at 710 µm size. In the table 4.3 below, bio-oil yield was calculated by the bio-oil collected from the electrostatic precipitator and fraction of condenser (3-6 %). Char yield was calculated by subtracting the amount of magnesium oxide formed during the process from total char produced, to give char formed by lignin. Condenser yield was calculated by subtracting the water formed due to the moisture content in the feed, and the water formed during the decomposition of extra magnesium hydroxide to give water and magnesium oxide. The gas yield was obtained by the difference of bio-oil yield, char yield, and condenser yield. The same calculation was used for other molar ratios of magnesium formate as well. Multiple experiments were performed for this molar ratio and the average value of yield data is presented in the table 4.3.

Table 4.3 Comparision of pretreatment of lignin with magnesium formate at a molar ratio of 1.6:1 for formic acid to magnesium hydroxide

Feed	Lignin / Formic Acid 1 g / 1g	Lignin / Formic Acid 1 g / 0.5 g
Oil Yield (Wt %)	14 (±3)	17 (±3)
Char Yield (Wt %)	29 (±5)	41 (±3)
Gas Yield (Wt %)	27 (± 6)	14 (±2)
Condenser yield (Wt%)	29 (±6)	28 (±6)
O:C	0.19 (±0.03)	0.22 (±0.02)
H:C	1.16 (±0.04)	1.13 (±0.01)
C Yield in oil (Wt %)	16 (±4)	18 (±1)

There is not much difference in the bio-oil yield for both the feedstock. The char yield was more for the half loading (1g lignin/ 0.5g formic acid) and gas yield was high for full loading (1g lignin/ 1g formic acid). However, the O:C ratio in full loading was less compared to that of half loading, suggesting more hydrogen availability due to the addition of extra formic acid. Formate salt decomposes and provides in-situ source of hydrogen for hydrodeoxygenation, which helps in removing more oxygen. Probably decarboxylation, and dehydration have also occurred and helped in removing oxygen as well. The decrease in O:C ratio with varied formate salt loading/ biomass is consistent with the work of Mukkamala et. al. The molar ratio of formic acid to magnesium hydroxide is 1.6:1 for both cases. There is no significant difference in the H:C ratio for both oils. But, the carbon yield in oil for full loading was higher. Hence with all this improvement, the full loading seems more appropriate option for both quality and quantity of oil with the tradeoff of having to use more salt. There is uncertainty of about ± 3-4 % with yield of bio-oil, char, and gas as well as O:C content of bio-oil. The non-uniform heat distribution inside the pyrolyzer and non-uniform flow distribution of feedstock due to stickiness, moisture content of feedstock, and the pressure variation in the pyrolyzer are few reasons for the possible variation in the results of bio-oil, char, and gas yields and there is about ± 2-3% of uncertainty in O:C ratio, because in elemental analysis the average of triplicate of each bio-oil sample are taken. When compared the results of formate assisted pyrolysis of lignin with the results of lignin pyrolysis, the oxygen content of formate assisted pyrolysis oil is found to be lower than that of pyrolysis oil however at the cost of lower mass yields. When compared with results of formate assisted pyrolysis of lignin with that of pine sawdust, it is found that oil with a high quality (less reactive compounds because of less oxygen content) can be attained from lignin. This is probably due to low oxygen content of lignin than the whole biomass sawdust.

4.3.2 Molar ratio of 1.75:1 for formic acid to magnesium hydroxide

Two feedstocks with difference in lignin to formic acid wt% (full loading 1g/1g and half loading 1g/0.5g) and same molar ratio (1.75:1) of formic acid to magnesium hydroxide were prepared. Its preparation is shown in the table 4.4 below.

Table 4.4 Preparation of lignin with molar ratio of formic acid to magnesium hydroxide as 1.75:1

Compound	Lignin / Formic Acid 1 g / 1g	Lignin / Formic Acid 1 g / 0.5 g
Lignin	100 g	150 g
Water	600 g	500 g
Magnesium Hydroxide	36.5 g	27.5 g
Stir for one hour		
Formic Acid	100 g	75 g
Stir for one hour		
Magnesium Hydroxide	36 g	27.5 g
Stir for one hour		

All materials were added according to the detail given in the table above, order of addition following from top to the bottom of the table. Feedstock prepared was then poured into a pan for drying at room temperature and then sieved at 710 µm size. Multiple experiments were performed for this molar ratio and the average value of Yield and comparison results for pyrolysis oil obtained from the above two feedstocks is presented in the table 4.5.

Table 4.5 Comparison of pretreatment of lignin with magnesium formate at a molar ratio of 1.75:1 for formic acid to magnesium hydroxide

Feed	Lignin / Formic Acid 1 g / 1g	Lignin / Formic Acid 1 g / 0.5 g
Oil Yield (Wt %)	12.5	14
Char Yield (Wt %)	24.5	47
Gas Yield (Wt %)	42.5	13
Condenser Yield (Wt %)	20	26
O:C	0.18	0.21
H:C	1.2	1.14
C Yield in oil (Wt %)	15	15.1

Here the molar ratio of formic acid to magnesium hydroxide is 1.75:1. The bio-oil yield is slightly higher for the half loading (1g lignin/ 0.5g formic acid). Along with that it also has more char yield. Gas yield is higher in full loading. However, the O:C ratio in full loading is less compared to that of half loading, indicating extra hydrogen by the addition of extra formic acid which helps in removing the oxygen. The H:C ratio was slightly higher for full loading.

4.3.3 Molar ratio of 1.5:1 for formic acid to magnesium hydroxide

Two feedstocks with difference in lignin to formic acid wt% (full loading 1g/1g and half loading 1g/0.5g) and same molar ratio (1.5:1) of formic acid to magnesium hydroxide were prepared. Its preparation is shown in the table 4.6 below.

Table 4.6 Preparation of lignin with molar ratio of formic acid to magnesium hydroxide as 1.5:1

Compound	Lignin / Formic Acid 1 g / 1g	Lignin / Formic Acid 1 g / 0.5 g
Lignin	120 g	120 g
Water	600 g	500 g
Magnesium Hydroxide	50.5 g	25.5 g
Stir for one hour		
Formic Acid	120 g	60 g
Stir for one hour		
Magnesium Hydroxide	50.5 g	25 g
Stir for one hour		

All materials were added according to the detail given in the table above, order of addition following from top to the bottom of the table. Once the feedstock was prepared it was poured into a pan for drying at room temperature and then sieved at 710 µm size. The pyrolysis yield obtained from the two different feedstocks are shown in the table 4.7.

Table 4.7 Comparison of pretreatment of lignin magnesium formate at a molar ratio of 1.5:1 for formic acid to magnesium hydroxide

Feed	Lignin / Formic Acid 1 g / 1g	Lignin / Formic Acid 1 g / 0.5 g
Oil Yield (Wt %)	11	14
Char Yield (Wt %)	27	18
Gas Yield (Wt %)	33.5	50
Condenser Yield (Wt %)	28.5	18
O:C	0.18	0.23
H:C	1.13	1.09
C Yield in oil (Wt %)	13	15.6

The bio-oil yield here also followed the same trend of previous case, where it was higher in half loading (1g lignin/ 0.5g formic acid). Along with that it has more gas yield compared to full loading. The char yield in full loading (1g lignin/ 1g of magnesium hydroxide) was higher. The molar ratio of formic acid to magnesium hydroxide is 1.5:1. The lower O:C ratio with full loading like previous two cases also suggest that having extra formic acid helps in providing extra hydrogen which helps in removing the oxygen. H:C ratio is high in full loading making full loading a better option.

4.4 Pretreatment of lignin with calcium formate

4.4.1 Molar ratio of 1.6:1 for formic acid to calcium hydroxide

Two feedstocks with difference in lignin to formic acid wt% (full loading 1g/1g and half loading 1g/0.5g) and same molar ratio (1.6:1) of formic acid to calcium hydroxide were prepared were prepared. Its preparation is shown in the table 4.8 below.

Table 4.8 Preparation of lignin with molar ratio of formic acid to calcium hydroxide as 1.6:1

Compound	Lignin / Formic Acid 1 g / 1g	Lignin / Formic Acid 1 g / 0.5 g
Lignin	100 g	120 g
Water	600 g	500 g
Calcium Hydroxide	50 g	30 g
Stir for one hour		
Formic Acid	100 g	60 g
Stir for one hour		
Calcium Hydroxide	50 g	30 g
Stir for one hour		

All materials were added according to the detail given in the table above, order of addition following from top to the bottom of the table. Once the feedstock was prepared it was poured into a pan for drying at room temperature and then sieved at 710 μm size. In the table 4.9 below, bio-oil yield was calculated by the bio-oil collected from the electrostatic precipitator and fraction of condenser (2 - 4 %). Char yield was calculated by subtracting the amount of calcium carbonate formed during the process from total char produced, to give char formed by lignin. Condenser yield was calculated by subtracting the water formed due to the moisture content in the feed, and the water formed during the decomposition of extra magnesium hydroxide to give water and magnesium oxide. The gas yield was obtained by the difference of bio-oil yield, char yield, and condenser yield. The same calculation was used for other molar ratios of calcium formate as well.

Table 4.9 Comparison of pretreatment of lignin with calcium formate at a molar ratio of 1.6:1 for formic acid to calcium hydroxide

Feed	Lignin / Formic Acid 1 g / 1g	Lignin / Formic Acid 1 g / 0.5 g
Oil Yield (Wt %)	6	5
Char Yield (Wt %)	21.4	42.5
Gas Yield (Wt %)	62.8	41.6
Condenser Yield (Wt %)	9.7	10.8
O:C	0.08	0.13
H:C	1.18	1.16
C Yield in oil (Wt %)	7.64	6.03

The bio-oil yield with calcium formate (6%) pretreated lignin is very less compared to magnesium formate (14%), which is possible due to large amount product converted into gas and gave more gas yield in both the loadings, as well as the char. The molar ratio of formic acid to calcium hydroxide is 1.6:1. The O:C ratio of magnesium formate pretreated (0.08) oil is low compared to that magnesium formate pretreatment (0.19). Calcium formate salt decomposes and provide an in-situ source of hydrogen for hydrodeoxygenation. Since full loading has more formic acid it will have more hydrogen, which therefore helps in lowering the O:C ratio compare to the half loading. There is no significant difference in H:C ratio with both feedstocks.

4.4.2 Molar ratio of 1.75:1 for formic acid to calcium hydroxide

Two different feedstocks were attempted to made with difference in lignin to calcium hydroxide wt % (full loading 1g/1g and half loading 1g/0.5g) but only full loading was able to pyrolyze and other started to swell and agglomerate during crucible testing of the sample. Hence, only one type of feedstock was prepared and pyrolyzed and the detailed feedstock preparation is shown in table 4.10 below.

Table 4.10 Preparation of lignin with molar ratio of formic acid to calcium hydroxide as 1.75:1

Compound	Lignin / Formic Acid 1 g / 1g
Lignin	100 g
Water	600 g
Calcium Hydroxide	46 g
Stir for one hour	
Formic Acid	100 g
Stir for one hour	
Calcium Hydroxide	46 g
Stir for one hour	

All materials were added according to the detail given in the table above, order of addition following from top to the bottom of the table. Feedstock prepared was then poured into a pan for drying at room temperature and then sieved at 710 µm size. The yield and composition results for pyrolysis is shown in the table 4.11 below.

Table 4.11 Pretreatment of lignin with calcium formate at a molar ratio of 1.75:1 for formic acid to calcium hydroxide

Feed	Lignin / Formic Acid 1 g / 1g
Oil Yield (Wt %)	6.6
Char Yield (Wt %)	31.1
Gas Yield (Wt %)	47.4
Condenser Yield (Wt %)	4.7
O:C	0.11
H:C	1.16
C Yield in oil (Wt %)	8.1

Here the half loading (1g lignin/ 0.5g formic acid) started to swell and agglomerate and hence it was not able to pyrolyze. But, full loading had no problem. The molar ratio of formic acid to calcium hydroxide is 1.75:1. The difference in bio-oil yield in this case is very less compared to previous feedstock for calcium formate pretreated lignin (1g/ 1g). Other attempts were also made to pretreat lignin with calcium formate with full and half loading and molar ratio of 1.5:1. But, during the crucible test material started to form sticky. Hence it was avoided for pyrolysis as it may cause the plugging problem. Hence the molar ratio of 1.6:1 was appropriate option for calcium formate as well.

4.5 Pretreatment of lignin with magnesium and calcium formate

In this pretreatment lignin was pretreated with both calcium and magnesium formate separately but, after the feedstock preparation both the mixtures were mixed while in aqueous phase and then poured into pan for drying at room temperature. Then sieved at 710 µm size. The molar ratio was kept 1.6:1 for both formic acid to magnesium hydroxide and formic acid to calcium hydroxide. Detailed preparation is given in table 4.12 below.

Table 4.12 Preparation of lignin with molar ratio of formic acid to calcium hydroxide and formic acid to magnesium hydroxide as 1.6:1

Compound	Lignin / Formic Acid 1 g / 0.5 g (Magnesium Hydroxide)	Lignin / Formic Acid 1 g / 0.5 g (Calcium Hydroxide)
Lignin	120 g	120 g
Water	600 g	600 g
Hydroxide (Mg/ Ca)	24.5 g	30 g
Stir for one hour		
Formic Acid	60 g	60 g
Stir for one hour		
Hydroxide (Mg/ Ca)	23 g	30 g
Stir for one hour		

All materials were added according to the detail given in the table above, order of addition following from top to the bottom of the table. Feedstock prepared was then poured into a pan for drying at room temperature and then sieved at 710 μm size. The yield data is shown in the table 4.13 below.

Table 4.13 Pretreatment of lignin with calcium formate and magnesium formate

Feed	Lignin / Formic Acid 1 g / 0.5 g
Oil Yield (Wt %)	13.6
Char Yield (Wt %)	28.9
Gas Yield (Wt %)	38.1
Condenser Yield (Wt %)	19.3
O:C	0.19
H:C	1.15
C Yield in oil (Wt %)	15.6

After finding the yield data separately with calcium and magnesium formate as discussed previously, lignin was mixed with both calcium and magnesium formate in order to find out if the salt mixture has any significant effect. Determining such effect can enable us to improve the oil yield as well as the quality. The result shown in figure 4.8 has shown that calcium formate results in a low liquid oil yield. The liquid oil yield increases as the amount of magnesium formate increases in the salt mixture. However, the amount of oxygen increases and the quality of oil decreases with increase in the amount of magnesium formate increases in the salt mixture (Figure 4.9). We observed the similar trend with the carbon yield for the salt mixture and the individual components (table 4.3, 4.9 and 4.13). Future work is necessary to find optimal ration of calcium and magnesium formate that will result in the high liquid yield with low oxygen content.

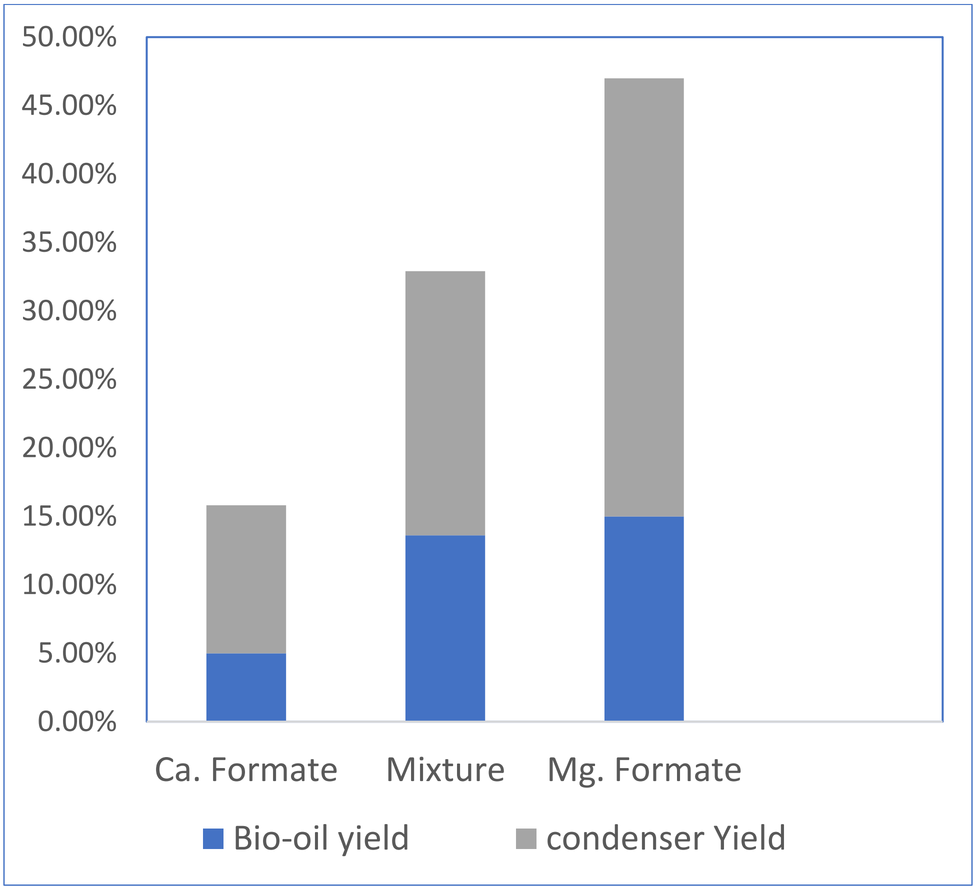


Figure 4.8. Liquid yield comparison of three different salts

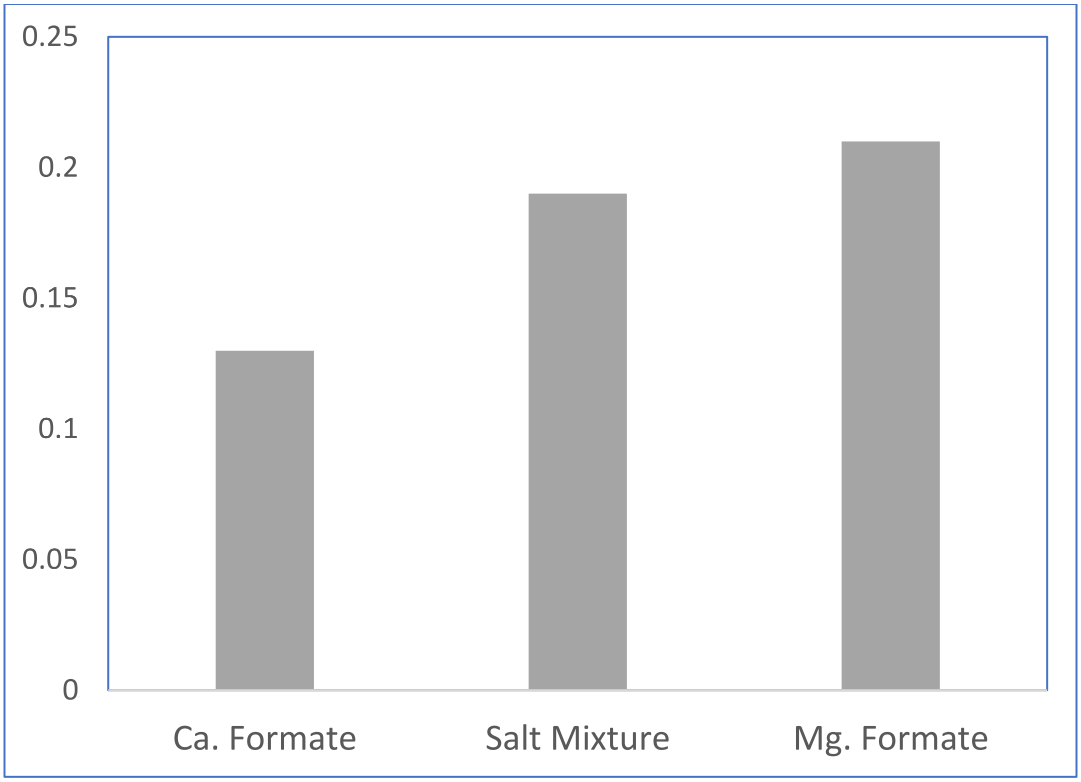


Figure 4.9. O:C ratio comparison of three different salts

4.6 Pretreatment of lignin with magnesium hydroxide

Two different feedstocks were prepared. In first feedstock lignin was mixed with magnesium hydroxide at a wt % of 1g/ 1g. And for second feedstock 1g/ 0.5g ratio was kept to mix lignin and magnesium hydroxide. The detailed preparation is shown in table 4.14 below.

Table 4.14 Preparation of lignin with magnesium hydroxide

Compound	Lignin / Magnesium Hydroxide 1 g / 1g	Lignin / Magnesium Hydroxide 1 g / 0.5 g
Lignin	100 g	120 g
Water	450 g	400 g
Magnesium Hydroxide	50 g	30 g
Stir for one hour		
Magnesium Hydroxide	50 g	30 g
Stir for one hour		

All the materials were mixed in the order discussed int the table. The feedstock prepared were dried at room temperature and the sieved at 710µm size. The pretreated lignin was then pyrolyzed and the yields obtained from the two different feedstocks are shown in the table 4.15 below.

Table 4.15 Comparison of pretreatment of lignin with magnesium hydroxide

Feed	Lignin / Magnesium Hydroxide 1 g / 1g	Lignin / Magnesium Hydroxide 1 g / 0.5 g
Oil Yield (Wt %)	10	18
Char Yield (Wt %)	46	45
Gas Yield (Wt %)	43	33
Condenser Yield (Wt %)	2	4
O:C	0.21	0.23
H:C	1.23	1.11
C Yield in oil (Wt %)	10.9	19.1

After finding the optimized condition with magnesium formate, lignin was pretreated with magnesium hydroxide with both full loading (1g lignin/ g magnesium hydroxide) and half loading (1g lignin/ 0.5 g magnesium hydroxide). The oil yield of half loading is very high compare to the full loading, probably the rate of decomposition is higher in full loading and half loading have more controlled stoichiometry therefore its rate of decomposition is relatively low and gives more bio-oil yield. The char yield was almost same for both. However, the trend of less O:C ratio with full loading was also observed here (0.21 compared to 0.23 for full and half loading respectively). Still, the ratio was high compared to magnesium formate (0.16 and 0.21 for full and half loading respectively) indicating less deoxygenation occurred. Also, the H:C ratio for full loading was high (1.23 and 1.11 for full and half loading respectively).

4.7 Pretreatment of lignin with calcium hydroxide

Two different feedstocks were prepared. In first feedstock lignin was mixed with calcium hydroxide at a wt % of 1:1. And for second feedstock 1g/ 0.5g ratio was kept to mix lignin and calcium hydroxide. The detailed preparation is shown in table 4.16 below.

Table 4.16 Preparation of lignin with calcium hydroxide

Compound	Lignin / Calcium Hydroxide 1 g / 1g	Lignin / Calciium Hydroxide 1 g / 0.5 g
Lignin	100 g	120 g
Water	450 g	400 g
Calcium Hydroxide	50 g	30 g
Stir for one hour		
Calcium Hydroxide	50 g	30 g
Stir for one hour		

All the materials were mixed in the order discussed in the table. The feedstock prepared were dried at room temperature and the sieved at 710μm size. The pretreated lignin was then pyrolyzed. But no oil was obtained when 1:1 ratio was used for calcium hydroxide and lignin. However, with second feedstock (1:0.5) bio-oil was obtained and the result is shown below in table 4.17.

Table 4.17 Yield data for pretreatment of lignin with calcium hydroxide

Feed	Lignin / Calcium Hydroxide (1 g / 0.5 g)
Oil Yield (Wt %)	2
Char Yield (Wt %)	44
Gas Yield (Wt %)	52
Condenser Yield (Wt %)	2
O:C	0.17
H:C	1.22
C Yield in oil (Wt %)	2.23

Similarly, to magnesium hydroxide, lignin was also pretreated with calcium hydroxide hydroxide with both full loading (1g lignin/ g calcium hydroxide) and half loading (1g lignin/ 0.5 g calcium hydroxide). But, no oil was obtained with the full loading. The amount of oil with half loading is also very less as it has very high gas and char yield. However significant amount of deoxygenation was observed as their O:C ratio is less (0.17) compared to magnesium hydroxide (0.23).

Figure 4.10 shows the comparison of bio-oil yields for lignin pretreated with different magnesium salts. The brown and blue bars in figure 4.10 indicate the results of lignin pretreatment with magnesium hydroxide and remaining bar graphs represent the results of lignin pretreatment with magnesium at different molar ratios. The highest bio-oil yield was obtained when lignin was pretreated with magnesium hydroxide (1g/ 0.5g) (Figure 4.10). However, the oxygen content of the resulting bio-oil for the lignin pretreatment with magnesium hydroxide (1g/ 0.5g) is found to be higher than that of other tested samples (Figure 4.11). The second highest bio-oil yield was obtained when the molar ratio for formic acid to magnesium hydroxide was 1.6:1 and full loading (1g/ 1g) and while sample has lowest O:C ratio compared to all other samples making it most favorable option.

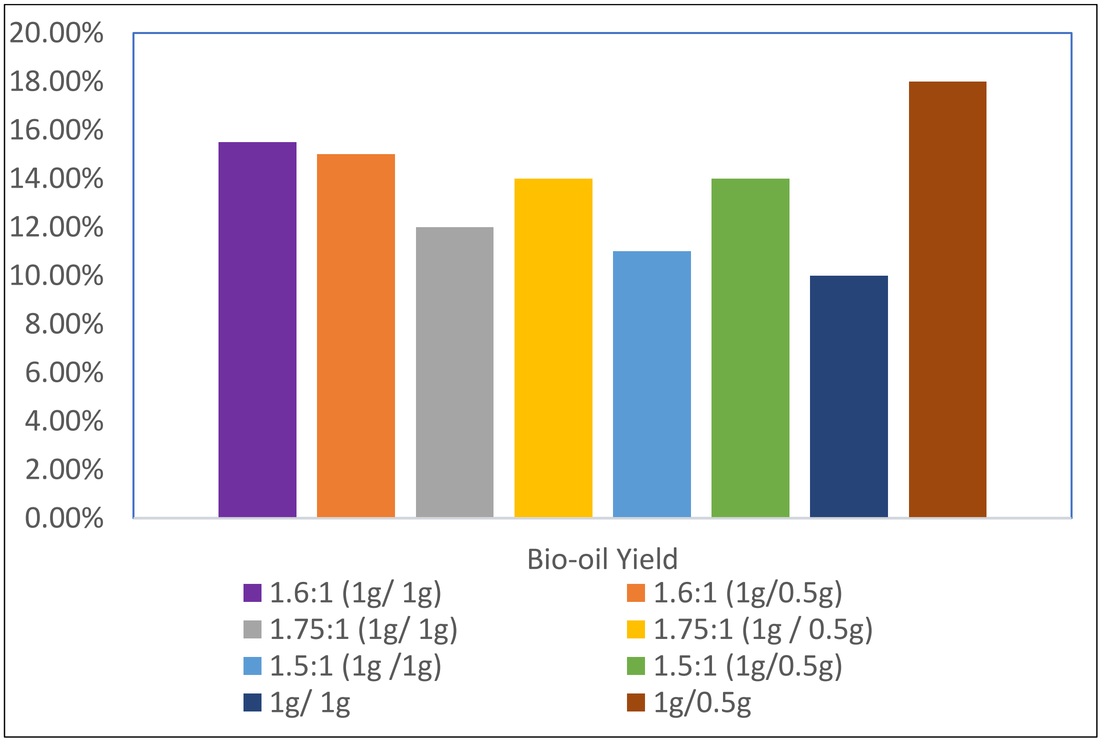


Figure 4.10 Bio-oil yield comparison for lignin pretreated with magnesium salts

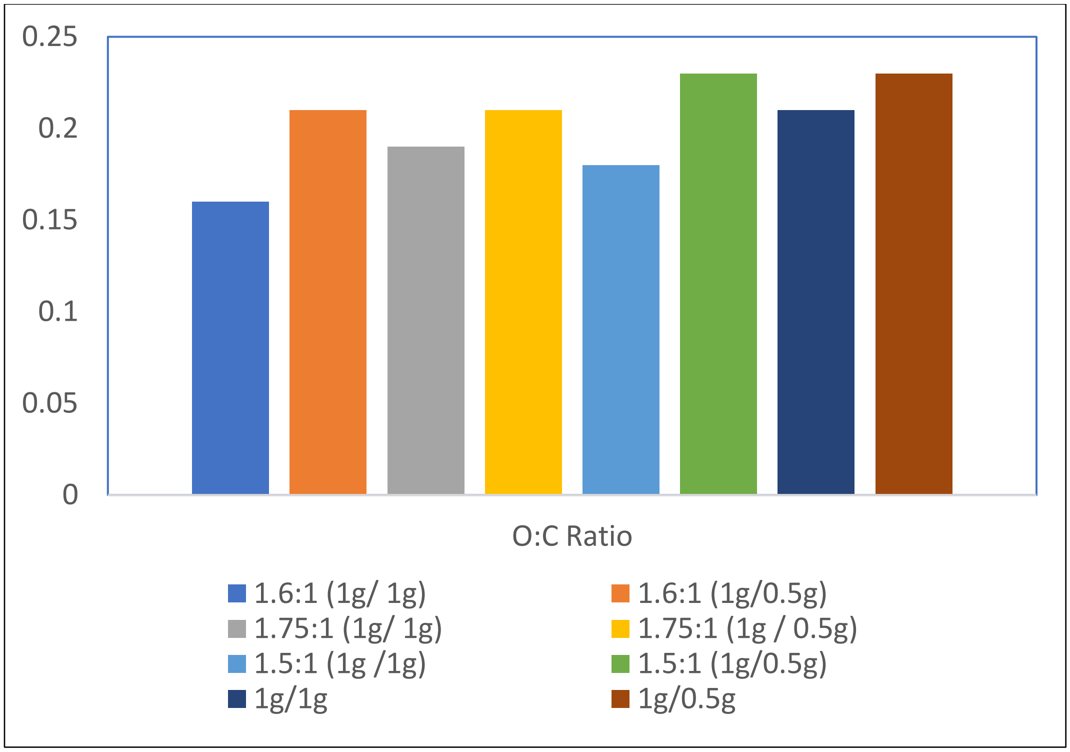


Figure 4.11 O:C ratio comparison for lignin pretreated with magnesium salts

Figure 4.12 shows the bar graph which compares the bio-oil yield for lignin pretreated with calcium salts. The yellow bar represents the results of lignin pretreatment with calcium hydroxide and remaining bars represent the results of lignin pretreatment with calcium formate pretreated with different molar ratios. The maximum bio-oil yields were obtained when lignin was pretreated with calcium formate at molar ratio of 1.75:1 and 1.6:1. Since the minimum oxygen content of bio-oil is found to be low with the molar ratio of calcium formate to lignin of 1.6:1, making the bio-oil sample with 1.6:1 molar ratio and full loading (1g/ 1g) makes favorable option for the production of oil from lignin with less oxygen content and more oil yield.

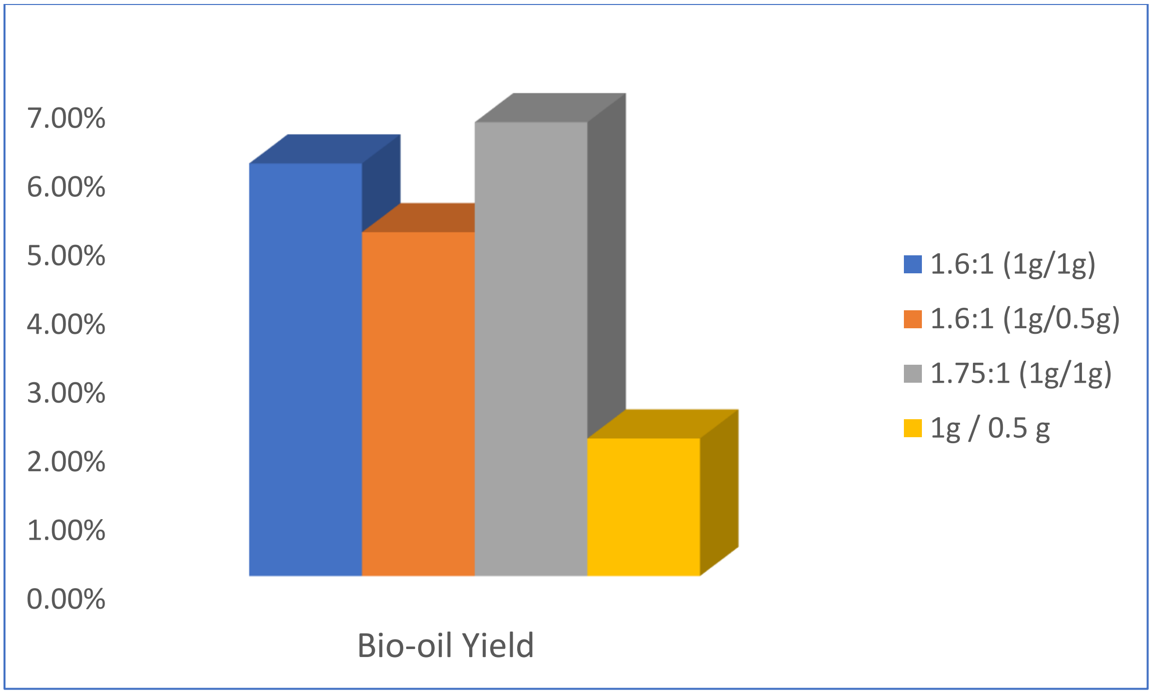


Figure 4.12 Bio-oil yield comparison for lignin pretreated with calcium salts

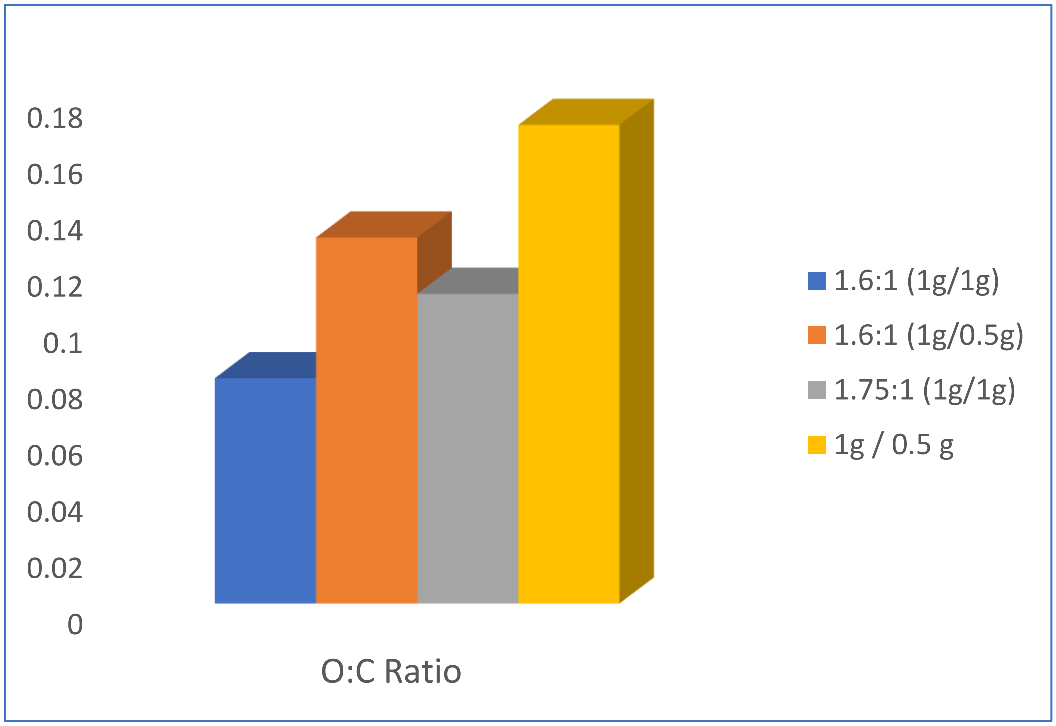


Figure 4.13 O:C ratio comparison for lignin pretreated with calcium salts

4.8 Conclusion

Lignin was pretreated with both magnesium formate and calcium formate. The reason for pretreating lignin with different molar ratios was to find their optimized ratios which gives both high yield as well as higher quality of oil. Among all different ratios, 1.6:1 molar ratio of formic acid to magnesium/calcium hydroxide showed the best results. The oxygen is removed by hydrodeoxygenation, decarboxylation and decarbonylation. The bio-oil yield was higher in magnesium formate (15.5%) compared to that of calcium formate (6%). Similar to calcium formate, magnesium formate pretreated lignin also showed deoxygenation but the amount of oxygen removed by magnesium formate was less. Hence their O:C ratio was higher in magnesium formate (0.16) compared to calcium formate (0.08). By the addition of proper amount of formate salt, O:C ratio is decreased and H:C ratio is increased with the addition of more formic acid i.e. in full loading compared to half loading. Hence, oil with magnesium formate is good in quantity and oil with calcium formate is good in quality as it has oxygen which makes oil stable. Also, calcium salt may create more reactive atmosphere than magnesium salt and therefore more cracking reaction occurs with calcium. This cracking phenomenon explains the result of a high gas yields. In addition to the cracking, decarboxylation and dehydration can also be dominant with calcium, therefore the O:C ratio of resulting bio-oil is less when lignin is pretreated with calcium formate.

4.9 ^{13}-C NMR Data

The ^{13}-C NMR was done on the collected bio-oil samples and their spectra is shown in figure 4.14. The fraction of aromatic groups was the highest among all the samples obtained and were observed in the range between 102 to 160 ppm. The highest fraction observed was aromatic group in the oil. From the magnesium formate pretreated lignin oil bio-oil, the integrated area in the table 4.18, it was observed that ratio of aromatic to alkyl group was 4.8:1 for full loading (1g/1g) and 6:1 for half loading(1g/0.5g) for molar ratio of 1.6:1. More deoxygenation was observed in full loading compared to half loading as we can see the amount of methoxy/hydroxy group is 0.9% for full loading and 3.7% for half loading. It is also supported by the elemental analysis as O:C ratio for full loading (0.16) is less to that of half loading (0.21). For table 4.19 the molar ratios were 1.75:1 and 1.5:1 for full loading. The ratio of aromatic to alkyl group was same 7.5:1 for both molar ratios. More deoxygenation was observed in 1.5:1 molar ratio compared to 1.75:1 molar ratio as we can see the amount of methoxy/hydroxy group is 1.4% for 1.5:1 molar ratio and 3.5% for 1.75:1 molar ratio. It is also supported by the elemental analysis as O:C ratio for 1.5:1 molar ratio (0.18) is less to that of 1.75:1 (0.19). From all the four different feedstocks, oil with full loading and molar ratio of 1.6:1 is better option as it showed the highest amount of deoxygenation and makes bio-oil more stable.

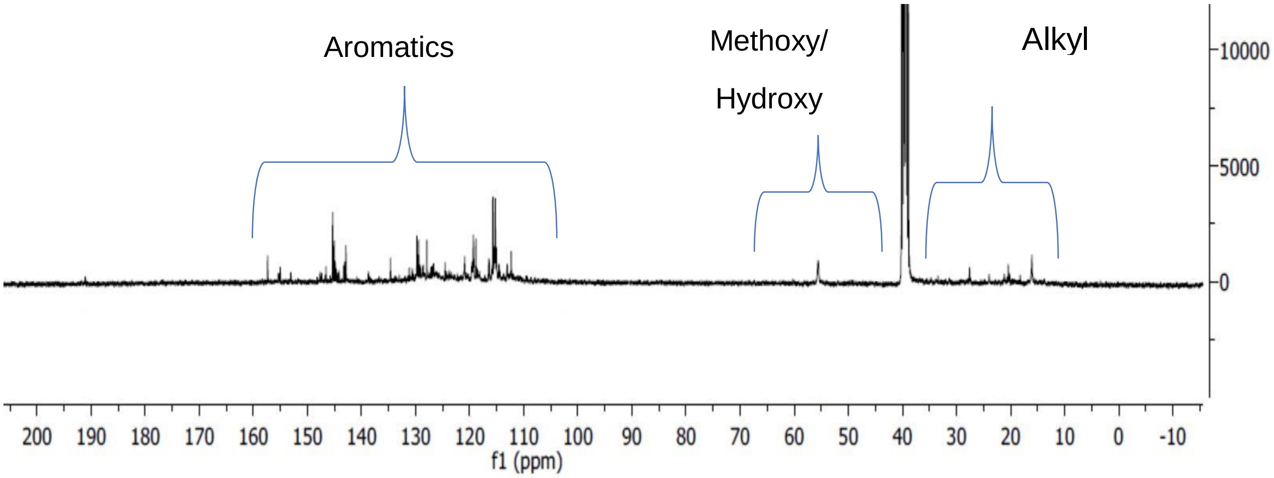


Figure 4.14 ^{13}-C NMR spectra of magnesium formate pretreatment of lignin bio-oil.

The integrated area for the above four different feedstocks is tabulated below.

Table 4.18 ^{13}-C NMR data for magnesium formate pretreated lignin pyrolysis oil (molar ratio of 1.6:1)

Type of carbon	**Chemical Shifts**	**Lignin/F.A. (1g/1g) F.A./$Mg(OH)_2$ (1.6:1 moles)**	**Lignin/F.A. (1g/0.5g) F.A./$Mg(OH)_2$ (1.6:1 moles)**
Alkyl	0-54	16.8%	13.7%
Methoxy/Hydroxy	54-70	1.2%	3.0%
Aromatic	103-163	82.0%	83.3%
Carbonyl	163-215	0.0%	0.0%

Table 4.19 ^{13}-C NMR data for magnesium formate pretreated lignin pyrolysis oil (molar ratio of 1.75:1 and 1.5:1)

Type of carbon	**Chemical Shifts**	**Lignin/F.A. (1g/ 1g) F.A./$Mg(OH)_2$ (1.75:1 moles)**	**Lignin/F.A. (1g/1g) F.A./$Mg(OH)_2$ (1.5:1 moles)**
Alkyl	0-54	11.2%	11.5%
Methoxy/Hydroxy	54-70	3.5%	1.4%
Aromatic	103-163	85.4%	87.2%
Carbonyl	163-215	0.0%	0.0%

From the calcium formate pretreated lignin oil bio-oil, the integrated area in the table 4.20, it was observed that ratio of aromatic to alkyl group was 3:1 for full loading (1g/1g) and 5:1 for half loading (1g/0.5g). More deoxygenation was observed in full loading compared to half loading as we can see the presence of methoxy/hydroxy group is very negligible for full loading, therefore it was not able to detect in full loading and 0.5% for half loading. It is also supported by the elemental analysis as O:C ratio for full loading (0.08) is less to that of half loading (0.13). From the two different feedstocks of calcium formate, oil with full loading and molar ratio of 1.6:1 is better option as it showed the highest amount of deoxygenation and makes bio-oil more stable

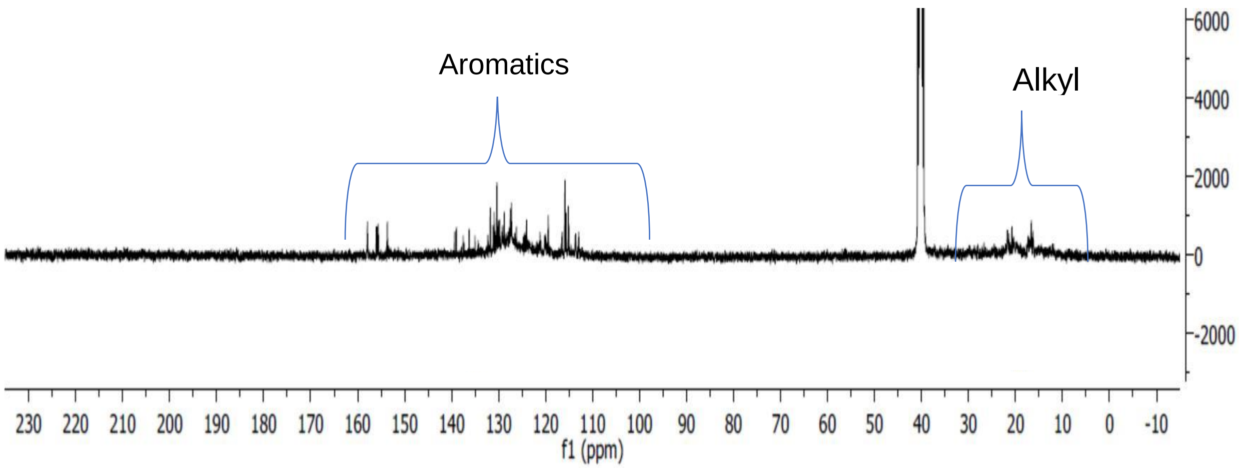


Figure 4.15 ^{13}-C NMR spectra of calcium formate pretreatment of lignin bio-oil

The integrated area for two different feedstocks is tabulated below.

Table 4.20 ^{13}-C NMR data for calcium formate pretreated lignin pyrolysis oil (molar ratio of 1.6:1)

Type of carbon	**Chemical Shifts**	**Lignin/F.A. (1g/g) F.A./Ca(OH)$_2$ (1.6:1 moles)**	**Lignin/F.A. (1g/0.5g) F.A./Ca(OH)$_2$ (1.6:1 moles)**
Alkyl	0-54	25.8%	16.5%
Methoxy/Hydroxy	54-70	0.0%	0.5%
Aromatic	103-163	74.2%	83.0%
Carbonyl	163-215	0.0%	0.0%

From the salt mixture pretreated lignin pyrolysis oil (half loading and molar ratio 1.6:1) the integrated area result is shown in table 4.21 which shows that ratio of aromatic to alkyl group was 6.5:1. The fraction of methoxy/hydroxy group was 1.9% in the oil. This amount of hydroxy/methoxy is less than magnesium formate pretreated oil (3.7%) and more than calcium formate pretreated oil (0.5%). So, after comparing the data for all formate pretreated lignin, it was found that lignin pretreated with calcium formate (full loading and 1.6:1 molar ratio) gave the best quality of oil as it showed highest deoxygenation. Hence, it has very negligible methoxy/ hydroxy groups.

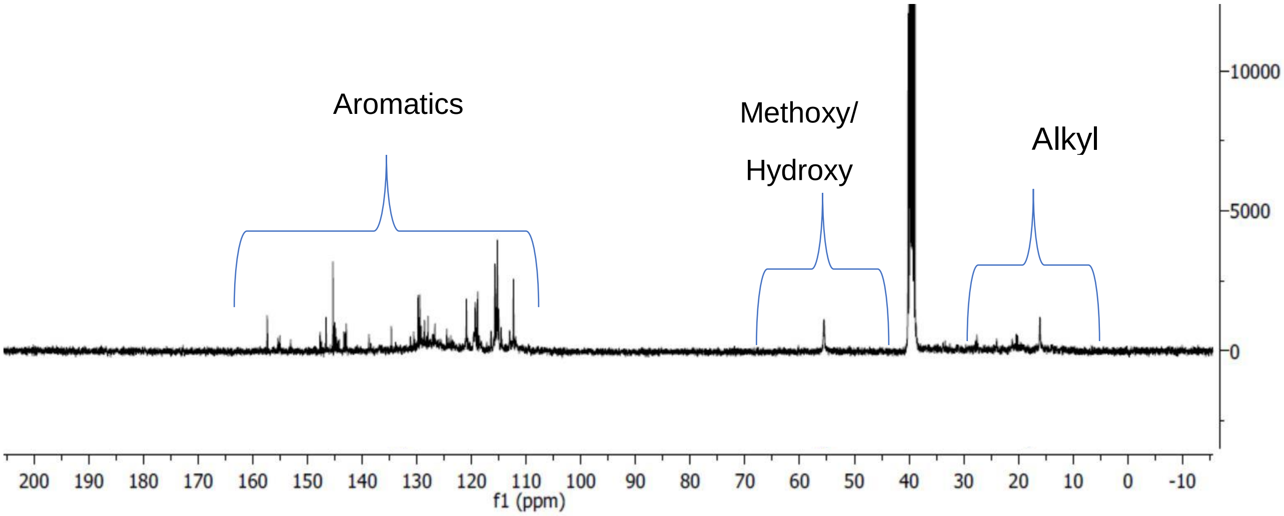


Figure 4.16 ^{13}-C NMR spectra of pretreated lignin bio-oil. (Mixture of two salts)

The area for above spectra is integrated and tabulated below

Table 4.21 ^{13}-C NMR data for salt mixture pretreated lignin pyrolysis oil (molar ratio of 1.6:1)

Type of carbon	**Chemical Shifts**	**Lignin/F.A. (1g/0.5g) F.A./Ca(OH)$_2$, F.A/Mg(OH)$_2$ (1.6:1 moles)**
Alkyl	0-54	12.7%
Methoxy/Hydroxy	54-70	1.9%
Aromatic	103-163	85.4%
Carbonyl	163-215	0.0%

The integrated area for ^{13}-C-NMR spectra for bio-oil collected by the pretreatment of magnesium and calcium hydroxide are shown in table 4.22. Oil was not formed when full loading i.e. 1g/1g of calcium hydroxide to lignin was taken. Here also the trend is similar as that of calcium and magnesium formate pretreatment. As the relative abundance of aromatic fraction was highest. The ratio of aromatic to alkyl group was 5:1 for full loading (1g/1g) and 7.5:1 for half loading. More deoxygenation was observed in full loading compared to half loading as we can see the amount of methoxy/hydroxy group is 2.1%

for full loading and 4.1% for half loading. Similar, comparison was done with half loading of calcium and magnesium hydroxide. The ratio of aromatic to alkyl group was 4.6:1 for half loading of calcium hydroxide. More deoxygenation was observed in calcium hydroxide compared to magnesium hydroxide pretreated lignin bio-oil as we can see the amount of methoxy/hydroxy group is 3.4% for calcium hydroxide and 4.1% for magnesium hydroxide.

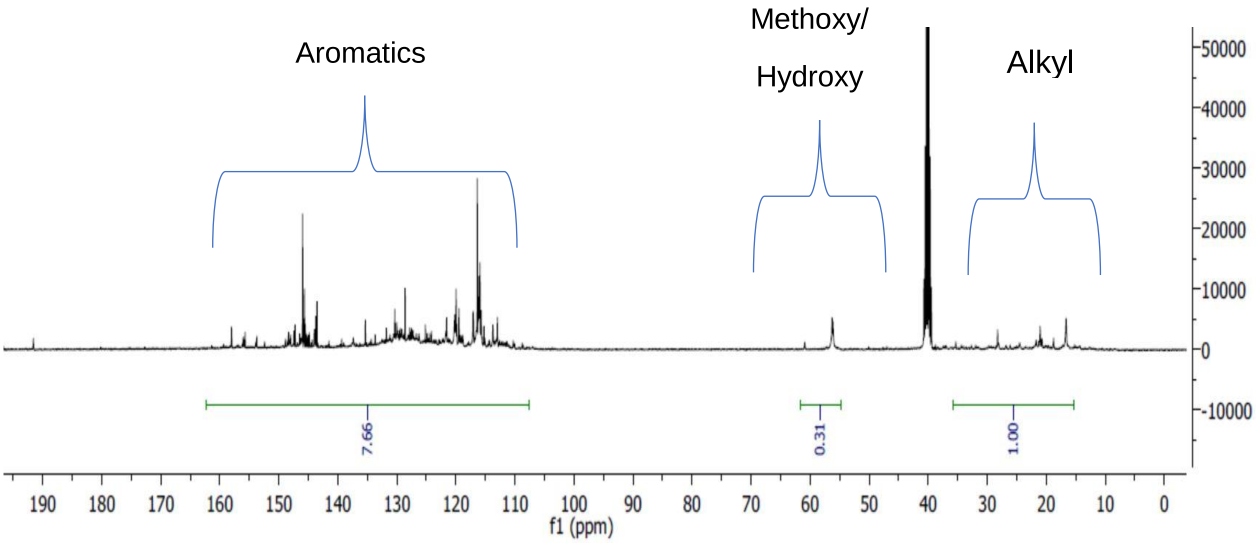


Figure 4.17 ^{13}-CNMR spectra of magnesium hydroxide pretreatment of lignin bio-oil

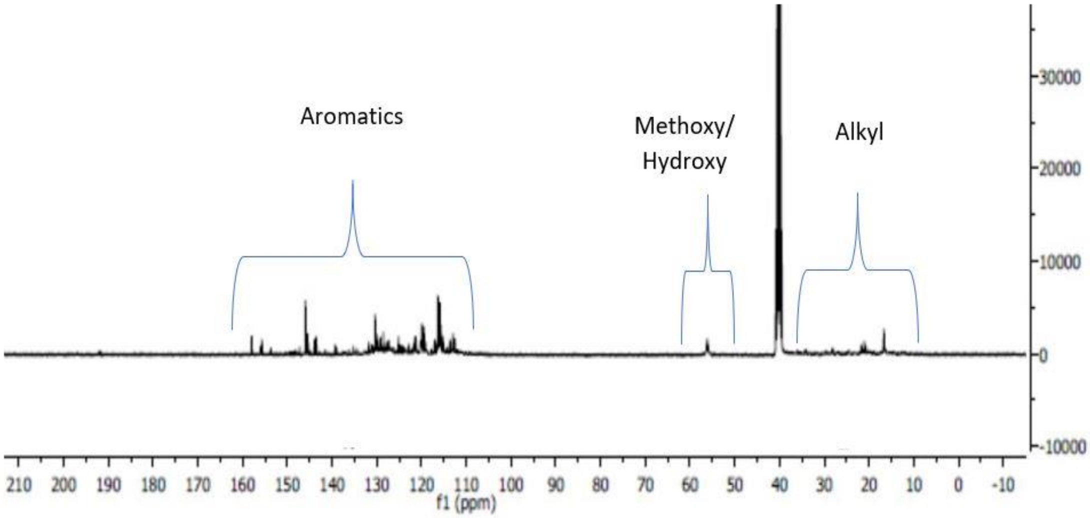


Figure 4.18 ^{13}-C NMR spectra of calcium hydroxide pretreatment of lignin bio-oil.

The area for above spectra is integrated and tabulated below

Table 4.22 ^{13}-C NMR data for magnesium and calcium hydroxide pretreated lignin pyrolysis oil

Type of carbon	**Chemical Shifts**	**Lignin/Mg(OH)$_2$ (1g / g)**	**Lignin/Mg(OH)$_2$ (1g / 0.5g)**	**Lignin/Ca(OH)$_2$ (1g / 0.5g)**
Alkyl	0-54	16.8%	11.4%	17.2%
Methoxy/Hydroxy	54-70	2.1%	4.1%	3.4%
Aromatic	103-163	81.1%	84.5%	79.4%
Carbonyl	163-215	0.0%	0.0%	0.0%

Carbon – 13 isotopes in nature is only 1.1% abundant, therefore ^{13}C-NMR is less sensitive then other nucleus such as proton or fluorine. ^{13}C NMR signal for aromatic carbons and carbons attached to heteroatoms is usually weak. In addition, a significantly higher number of scans need to be done to get a higher signal to noise ratio. Due to these limitations ^{13}C-NMR is more qualitative than quantitative.

CHAPTER 5

CONCLUSION

In this study, the various problems with lignin such as agglomeration, plugging was handled. Along with maintaining the proper pressure and temperature for the process. Lignin was pretreated with magnesium formate as well as calcium formate. The maximum oil yield (15.5 wt%) was observed with magnesium formate (with 1.6:1 molar ratio) pretreated lignin. And lowest O:C ratio (0.08) was obtained with calcium formate (with 1.6:1 molar ratio) which means more deoxygenation was observed. The formate salt decomposes and provide in-situ source of hydrogen for hydrodeoxygenation to remove oxygen. Because of the same reason of decreasing oxygen content, methoxy/hydroxy groups proportion was also reduced in the oil. The addition of appropriate amount of formic acid with calcium/magnesium hydroxide will give better oil both in terms of quality and the quantity. The optimized molar ratio was obtained, and it was 1.6:1 for formic acid to calcium/magnesium hydroxide, because at this ratio the oil yield as well as O:C ratio is better compared to other molar ratios. Apart from that knowledge of pyrolyzing lignin with the mixture of both salts was also gained. And with the pretreatment of magnesium and calcium hydroxide more possibilities can be explored. The oil obtained during pyrolysis can also be used to make aromatic chemicals. Hence, formate assisted pyrolysis of lignin is simple yet promising method for reducing the oxygen from bio-oil. Also, it does not require any catalyst and can operate at atmospheric pressure for deoxygenation.

REFERENCES

1. Golas, Peter J and Needham, Joseph *Science and Civilisation in China*. Cambridge University Press. (1999): 186-91.

2. United States Energy Information Administration-(EIA). (2011) https://www.eia.gov/totalenergy/data/annual/pdf/aer.pdf

3. United States Energy Information Administration-(EIA). (2018) https://www.eia.gov/energyexplained/?page=us_energy_transportation

4. Reserves Production and others, BP Statistical Review of World Energy About This Review Contents, 2013 <http://large.stanford.edu/courses/2013/ph240/lim1/docs/bpreview.pdf>.

5. Prediction of world population by UN. (2015)http://www.un.org/en/development/desa/news/population/2015-report.html

6. United Nations Intergovernmental Panel on Climate Change IPCC (2014). *Climate Change 2014: Mitigation of Climate Change*

7. United States Environmental Protection Agency- (EPA). (2017) https://www.epa.gov/nutrientpollution/sources-and-solutions-fossil-fuels

8. Greenpeace and the Global Wind Energy Councils report on wind energy. (2014) https://www.ecowatch.com/wind-energy-could-generate-nearly-20-percent-of-worlds-electricity-by--1881962962.html

9. BP statistical review of world energy. (2017) https://www.bp.com/en/global/corporate/energy-economics/statistical-review-of-world-energy/renewable-energy/solar-energy.html

10. Huber, George W., Sara Iborra, and Avelino Corma. "Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering." *Chemical reviews* 106.9 (2006): 4044-4098.

11. U.S. Department of Energy (2011). U.S. Billion-Ton Update: Biomass Supply for a Bioenergy and Bioproducts Industry. R.D. Perlack and B.J. Stokes (Leads), ORNL/TM-2011/224. Oak Ridge National Laboratory, Oak Ridge, TN. 227p. https://www.eia.gov/energyexplained/index.php?page=biofuel_home

12. United States EPA-Renewable Fuel Standard (RFS).http://www.epa.gov/OTAQ/fuels/renewablefuels/

13. United States Energy Information Administration-(EIA). (2018) https://www.eia.gov/state/print.php?sid=ME

14. PETRUS, Leo, and Minke A. NOORDERMEER. "Biomass to biofuels, a chemical perspective." *Green chemistry* 8.10 (2006): 861-867.

15. Freni, S., et al. "Production of hydrogen for MC fuel cell by steam reforming of ethanol over MgO supported Ni and Co catalysts." *Catalysis Communications* 4.6 (2003): 259-268.

16. Huber, George W., J. W. Shabaker, and J. A. Dumesic. "Raney Ni-Sn catalyst for H2 production from biomass-derived hydrocarbons." *Science* 300.5628 (2003): 2075-2077.

17. Brown, Lee F. "A comparative study of fuels for on-board hydrogen production for fuel-cell-powered automobiles." *International Journal of Hydrogen Energy* 26.4 (2001): 381-397.

18. Bajpai, Pratima. *Pretreatment of lignocellulosic biomass for biofuel production*. Singapore: Springer, 2016.

19. "Biomass - Energy Explained, Your Guide To Understanding Energy - Energy Information Administration". *www.eia.gov*.

20. Sjostrom, Eero. *Wood chemistry: fundamentals and applications*. Elsevier, 2013.

21. Rowell, Roger M. *Handbook of wood chemistry and wood composites*. CRC press, 2012.

22. Darby, Thomas. "What Is Biomass Renewable Energy." *Real World Energy* (2014).

23. Rinaldi, Roberto, et al. "Paving the way for lignin valorisation: recent advances in bioengineering, biorefining and catalysis." *Angewandte Chemie International Edition* 55.29 (2016): 8164-8215.

24. Ragauskas, Arthur J., et al. "Lignin valorization: improving lignin processing in the biorefinery." *Science* 344.6185 (2014): 1246843.

25. Adhikari, D. K., et al. "Biomass based fuel/energy." *J Petrotech Soc* 3.1 (2006): 28-42.

26. Pandey, Ashok. *Handbook of plant-based biofuels*. CRC press, 2008.

27. Chen, G., J. Andries, and H. Spliethoff. "Catalytic pyrolysis of biomass for hydrogen rich fuel gas production." *Energy Conversion and Management* 44.14 (2003): 2289-2296.

28. Garcìa-Pèrez, Manuel, Abdelkader Chaala, and Christian Roy. "Vacuum pyrolysis of sugarcane bagasse." *Journal of analytical and applied pyrolysis* 65.2 (2002): 111-136.

29. Saxena, R. C., D. K. Adhikari, and H. B. Goyal. "Biomass-based energy fuel through biochemical routes: a review." *Renewable and Sustainable Energy Reviews* 13.1 (2009): 167-178.

30. McKendry, Peter. "Energy production from biomass (part 2): conversion technologies." *Bioresource technology* 83.1 (2002): 47-54.

31. Asadullah, Mohammad, et al. "Role of catalyst and its fluidization in the catalytic gasification of biomass to syngas at low temperature." *Industrial & engineering chemistry research*41.18 (2002): 4567-4575.

32. Kouhia, Mikko. "Biomass Gasification." (2011).

33. Demirbaş, Ayhan. "Biomass resource facilities and biomass conversion processing for fuels and chemicals." *Energy conversion and Management* 42.11 (2001): 1357-1378.

34. Bridgwater, A. V. "Catalysis in thermal biomass conversion." *Applied Catalysis A: General* 116.1-2 (1994): 5-47.

35. Crocker, Mark, ed. *Thermochemical conversion of biomass to liquid fuels and chemicals*. Royal Society of Chemistry, 2010.

36. Elliot, D. C. "Analysis and Comparison of Biomass Pyrolysis/Gasification Condensates." *Final Report, No. PNL-5943. Northwest Laboratory, Richland, WA* (1986).

37. Bardalai, Monoj. "A review of physical properties of biomass pyrolysis oil." *International Journal of Renewable Energy Research (IJRER)* 5.1 (2015): 277-286.

38. Sipilä, Kai, et al. "Characterization of biomass-based flash pyrolysis oils." *Biomass and Bioenergy* 14.2 (1998): 103-113.

39. Lu, Qiang, Xu-lai Yang, and Xi-feng Zhu. "Analysis on chemical and physical properties of bio-oil pyrolyzed from rice husk." *Journal of Analytical and Applied Pyrolysis* 82.2 (2008): 191-198.

40. Suttibak, Suntorn, Keartisak Sriprateep, and Adisak Pattiya. "Production of bio-oil via fast pyrolysis of cassava rhizome in a fluidised-bed reactor." *Energy Procedia* 14 (2012): 668-673.

41. Bridgewater, Anthony V. "Biomass fast pyrolysis." *Thermal science* 8.2 (2004): 21-50.

42. Pattiya, Adisak, James O. Titiloye, and Anthony V. Bridgwater. "Fast pyrolysis of agricultural residues from cassava plantation for bio-oil production." *Carbon* 51 (2009): 51-59.

43. Biswal, Bijayani, Sachin Kumar, and R. K. Singh. "Production of hydrocarbon liquid by thermal pyrolysis of paper cup waste." *Journal of Waste Management* 2013 (2013).

44. Mullen, Charles A., et al. "Bio-oil and bio-char production from corn cobs and stover by fast pyrolysis." *Biomass and bioenergy* 34.1 (2010): 67-74.

45. Bertero, Melisa, et al. "Characterization of the liquid products in the pyrolysis of residual chañar and palm fruit biomasses." *Fuel* 116 (2014): 409-414.

46. Demiral, İlknur, Alper Eryazıcı, and Sevgi Şensöz. "Bio-oil production from pyrolysis of corncob (Zea mays L.)." *Biomass and Bioenergy* 36 (2012): 43-49.

47. Xiujuan, Guo, et al. "Properties of bio-oil from fast pyrolysis of rice husk." *Chinese Journal of Chemical Engineering* 19.1 (2011): 116-121.

48. Asadullah, M., et al. "Production of bio-oil from fixed bed pyrolysis of bagasse." *Fuel* 86.16 (2007): 2514-2520.

49. Yin, Renzhan, et al. "Characterization of bio-oil and bio-char obtained from sweet sorghum bagasse fast pyrolysis with fractional condensers." *Fuel* 112 (2013): 96-104.

50. Zhang, Qi, et al. "Review of biomass pyrolysis oil properties and upgrading research." *Energy conversion and management* 48.1 (2007): 87-92.

51. French, Richard, and Stefan Czernik. "Catalytic pyrolysis of biomass for biofuels production." *Fuel Processing Technology*91.1 (2010): 25-32.

52. Li, Lin, Hongxun Zhang, and Xuliang Zhuang. "Pyrolysis of waste paper: characterization and composition of pyrolysis oil." *Energy Sources* 27.9 (2005): 867-873.

53. Mohanty, Pravakar, et al. "Fuel production from biomass: Indian perspective for pyrolysis oil." (2011).

54. Kumar, Gaurav, Achyut K. Panda, and R. K. Singh. "Optimization of process for the production of bio-oil from eucalyptus wood." *Journal of Fuel Chemistry and Technology*38.2 (2010): 162-167.

55. Bridgwater, Anthony V., and D. G. B. Boocock, eds. *Developments in Thermochemical Biomass Conversion: Volume 1*. Vol. 2. Springer Science & Business Media, 2013.

56. Bridgwater, AV et al. " 4th Progress Report Contract AIR-CT92- 0216. " (1995).

57. Maggi, R. et al. " 1st Progress Report Contract JOR3-CT95-0025. " (1996).

58. Chang, Clarence D., and Anthony J. Silvestri. "The conversion of methanol and other O-compounds to hydrocarbons over zeolite catalysts." *Journal of catalysis* 47.2 (1977): 249-259.

59. Case, P. A. (2015) Fundamentals of pyrolysis of pretreated biomass (Doctoral dissertation). Retrieved from Fogler Library Digital Commons

60. http://digitalcommons.library.umaine.edu/cgi/viewcontent.cgi?article=3369&context=etd.

61. De Wild, Paul, et al. "Lignin valorisation for chemicals and (transportation) fuels via (catalytic) pyrolysis and hydrodeoxygenation." *Environmental Progress & Sustainable Energy: An Official Publication of the American Institute of Chemical Engineers* 28.3 (2009): 461-469.

62. Mukkamala, Saikrishna, et al. "Formate-assisted fast pyrolysis of lignin." *Energy & Fuels* 26.2 (2012): 1380-1384.

63. Dollimore, D., J. P. Gupta, and D. V. Nowell. "The thermal decomposition of metal formates. II. Solid state thermal decomposition studies on magnesium formate dihydrate." *Thermochimica Acta* 30.1-2 (1979): 339-350.

APPENDIX A. ELEMENTAL ANALYSIS OF BIO-OIL

The elemental analysis of bio-oil was done to determine carbon, hydrogen, nitrogen, and oxygen. Flash 2000 elemental analyzer was used for analysis.

Operating procedure

- Turn on the computer
- Open the eager xperience software
- Open the analyzer
- If the instrument is in standby mode off, then it can be turn on by following these steps. First go to edit option → edit elemental analyzer parameter → send
- After instrument is started, leak test is performed before running analysis.

Leak testing

- Click view
- After that select view elemental analyzer status
- Click on special function tab
- Click on leak test
- Start and click OK

It takes about 90 seconds to complete the leak test.

Creating sample table

- Go to edit then click sample table
- Name the sample
- Click on unknown for the sample type
- Click on weight to receive the weight of the sample

Sample preparation

- All instruments must be clean with acetone before using, also the counter
- Before running actual sample, a standard check run is done
- The sample for standard check is prepared as follows:
- Turn on the helium gas and set the flow at 300 ml/min
- Open the balance door
- Put an empty capsule in the balance and close the balance door
- Zero/tare the weight of capsule
- Take the capsule out
- Add 1-2 mg sample in the capsule
- If the weight is not between 1-2 mg make another sample and if it between the range, then put the capsule in capsule sealing device
- Purge the sample with helium gas inside the device for 30 seconds
- Seal the capsule and take it out

- Put it in balance and close the balance door
- Wave the hand from left side of the balance to add the weight of your sample in the sample table
- Place sample in the first auto sampler position
- Each sample is prepared three times by the same procedure
- After running standard sample, the bio-oil samples will be prepared and run by same procedure mention above
- The approximate time for each sample is 360 seconds.

Figure A.1 Elemental analyzer for CHNO

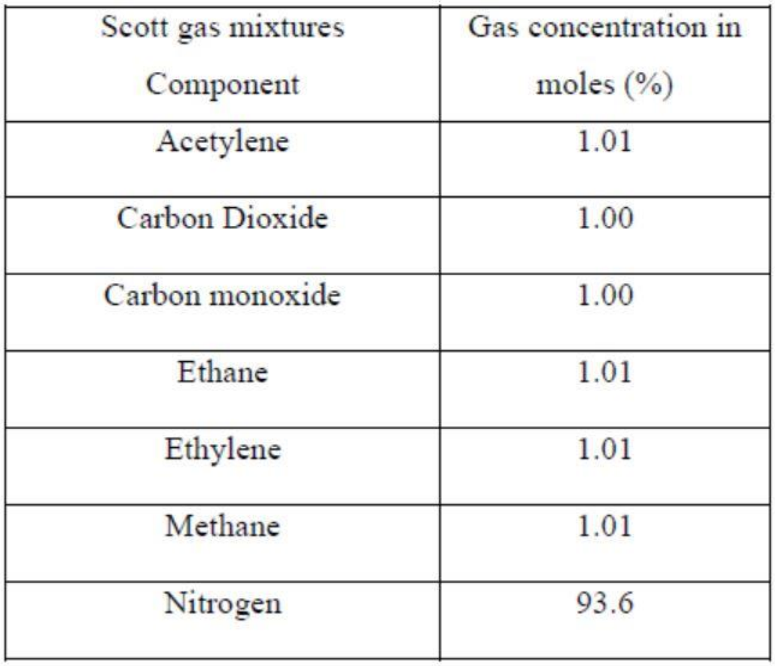
APPENDIX B. GAS CHROMATOGRAPHY

Gas Chromatography done to detect the non-condensable gases leaving the system during pyrolysis. GC analyzer has TCD detector and FID mechanizer. It has two packed column and equipped with four channels pick simple data system. Columns used are molecular sieve and Hayesep-D column. Helium was used as a carrier gas.

Operating procedure

- Turn on helium and hydrogen gas
- Turn on GC
- Four channels will display on the computer screen
- Right click on the channel 1 and click on events to add events
- Right click on channel 1 and click on temperature to add the temperature
- Temperature was set at 40 ˚C, and held for 15 minutes
- After that wait for 40 – 50 minutes until everything gets stable
- The standard scott gas mixture with following specifications was used as calibration gas

Table B.1 Gas component and concentrations



Scott gas mixtures Component	Gas concentration in moles (%)
Acetylene	1.01
Carbon Dioxide	1.00
Carbon monoxide	1.00
Ethane	1.01
Ethylene	1.01
Methane	1.01
Nitrogen	93.6

After that the non-condensable gases from pyrolysis is injected in the analyzer and usually performed thrice.

Figure B.1 GC analyzer

APPENDIX C. NMR SAMPLE PREPARATION AND MEASUREMENT PROTOCOL

Bio-oil sample (15-20 mg) was pipetted into a vial and dissolved in d^6-DMSO (0.8-1.0 mL) (*Sigma-Aldrich©)*. Sample was transferred to an NMR tube and capped. NMR-sample was loaded onto a green spinner (gradient 4-nuke broadband type probe) and depth of the solution was measured with the golden depth gauge (minimum volume ~0.7 mL). NMR-sample with probe was inserted into a Varian/Agilent NMR (400 MHz). ^{1}H-NMR was done on the sample with gradient shimming and 'nt' (number of transients) equal to 8. Gradient shimming was done for ^{13}C nucleus for a sample in DMSO. While setting up the experiment, ^{1}H- decoupler was used to avoid splitting of carbon peaks and to reduce NOE (Nuclear Overhauser Effect). Delay time between successive scans was kept at two seconds and number of transients was kept >5000 to get better signal to noise ratio, as the ^{13}C abundance is low (~1%). Once the NMR scan was done, the results were analyzed by M-Nova version 12.0. Baseline correction and phase corrections were done, followed by referencing the d^6-DMSO peak at 39.52(±0.06) ppm. For qualitative analysis alkyl (0-35 ppm), alkoxy/hydroxy (50-70 ppm), aromatic (100-165 ppm) and carbonyl (165-215 ppm) were integrated. Area integration intensities were normalized and tabulated.

Figure C.1 Varian Unity NMR

APPENDIX D. YIELD DATA OF ALL EXPERIMENTS

Table D.1 Molar ratio of 1.6:1 for formic acid to magnesium hydroxide (1g lignin/ 1g formic acid)

Feed	Run-1	Run-2	Run-3	Run-4	Run-5	Run-6
Oil Yield (Wt %)	15.5	13	12	14	14	11
Char Yield (Wt %)	33.5	33	20	31	31	28
Gas Yield (Wt %)	15.7	21	43	26	30	32
Condenser yield (Wt%)	35.2	32	25	29	25	30
O:C	0.16	0.17	0.22	0.20	0.17	0.18
H:C	1.13	1.21	1.11	1.14	1.25	1.11
C Yield in oil (Wt %)	18.2	15.4	13.1	15.5	16.6	12.8

Table D.2 Molar ratio of 1.6:1 for formic acid to magnesium hydroxide (1g lignin/ 0.5g formic acid)

Feed	Run-1	Run-2	Run-3
Oil Yield (Wt %)	15	18	17
Char Yield (Wt %)	40	40	44
Gas Yield (Wt %)	13	13	16
Condenser yield (Wt%)	32	32	22
O:C	0.21	0.21	0.23
H:C	1.12	1.13	1.13
C Yield in oil (Wt %)	17	19.7	18.5

Table D.3 Molar ratio of 1.75:1 for formic acid to magnesium hydroxide (1g lignin/ 1g formic acid)

Feed	Run-1	Run-2
Oil Yield (Wt %)	12	13
Char Yield (Wt %)	34	15
Gas Yield (Wt %)	25	50
Condenser yield (Wt%)	29	11
O:C	0.19	0.15
H:C	1.14	1.37
C Yield in oil (Wt %)	13.9	15.7

Table D.4 Molar ratio of 1.5:1 for formic acid to magnesium hydroxide (1g lignin/ 1g formic acid)

Feed	Run-1	Run-2
Oil Yield (Wt %)	11	11
Char Yield (Wt %)	29	25
Gas Yield (Wt %)	33	34
Condenser yield (Wt%)	27	30
O:C	0.18	0.18
H:C	1.12	1.13
C Yield in oil (Wt %)	12.9	12.2

BIOGRAPHY OF THE AUTHOR

Mayank S. Patel was born in Himmatnagar, India. He graduated from Pandit Deendayal Petroleum University, India in May 2015 with a Bachelor of Technology in Chemical Engineering. He is a Co-founder of Innovation and Incubation Centre, India. In June 2016, he enrolled in the Chemical Engineering program at the University of Maine, Orono. Mayank Patel is a candidate for the Master of Science degree in Chemical Engineering from the University of Maine in August 2018.