Understanding The Effect of Catalytic Pyrolysis Bio-oil Produced Using CaO During Hydrotreatment

by

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A thesis submitted to the Graduate Faculty of
Auburn University
in partial fulfillment of the
requirements for the Degree of
Master of Science

Auburn, Alabama
December 16, 2017

Keywords: Fast pyrolysis, biomass, upgrading, catalyst, friction, wear

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Abstract

Energy is very important for sustaining human life, and mankind is dependent on fossil fuels for energy need. Since fossil fuels reserves are limited and are depleting in a rapid rate, there is a surge for alternative fuel sources. Wind, solar, hydropower, and geothermal are some of the key alternative sources of energy. However, the carbon based liquid form of alternative energy can be obtained only form biomass. Biomass can be converted to liquid intermediates such as bio-oil and then upgraded it to "drop-in" and "fungible" biofuels. There are different methods for converting biomass to biofuels, and a fast pyrolysis is touted as one of the promising technologies. The fast pyrolysis is carried out at moderate temperature (400 – 600^{o}C) in the absence of oxygen with a very short residence time to convert solid biomass into chars, condensable vapors and non-condensable gases.

There are different parameters that play influential role in fast pyrolysis process such as temperature, residence time, type of biomass, heating rate and type of reactor. However, bio-oil obtained from fast pyrolysis process has high acidity, high viscosity, high oxygen content and low heating value, which make it incompatible to be used as a transport fuel. In order to improve these properties, bio-oil needs to be upgraded over catalyst(s), and hydrotreating is one the effective methods. Hydrotreating process is carried out at high pressure where hydrogen helps to remove oxygen from bio-oil in order to obtain biofuels that is comparable to fuels obtained from crude oil. Instead of conducting convectional pyrolysis followed by hydrogen treatment, catalytic fast pyrolysis, in which biomass is reacted with catalysts during pyrolysis, is an efficient method to improve bio-oil properties. Chapter 1 gives brief introduction about the basis of study and overall research objective. Chapter 2 summarizes brief information of energy scenario, fast pyrolysis, list of parameters affecting fast pyrolysis, bio-oil properties, upgrading technique along with tribological aspect of bio-oil.

Chapter 3 included comparative study of upgraded non-catalytic and catalytic bio-oils. In this study, non-catalytic (quartz sand) and catalytic (CaO) fast pyrolysis process were performed to produce two types of bio-oil from hybrid poplar biomass. Bio-oil collected from electrostatic precipitator (ESP) were upgraded in three conditions: Pt/C catalyst, ZSM-5 catalyst and control (without any catalyst). Product distribution and major biofuel properties were compared between upgraded bio-oils from both catalytic and non-catalytic fast pyrolysis process (Chapter 3). From this study, it was observed that higher liquid yields were obtained when bio-oils were upgraded over Pt/C catalyst for both non-catalytic (69.79 wt. %) and catalytic (68.67 wt. %) bio-oils. Higher heating value of original ESP bio-oil from catalytic fast pyrolysis (33.4 MJ/kg) was higher than non-catalytic (27 MJ/kg) fast pyrolysis bio-oil although there was no significant effect on upgraded catalytic bio-oils. The upgraded as well as original ESP bio-oils included higher fraction (52 - 66%) of vacuum gas oil range in both catalytic and non-catalytic. Acidic nature of original ESP oil reduced to around 53 for both catalytic and non-catalytic upgraded bio-oils. Viscosity of original ESP bio-oils was reduced from non-catalytic (98.22 cSt) to catalytic (68.07 cSt) bio-oils.

Friction and wear tests were performed using original ESP bio-oils based on their viscosity values and compared with the standard base oils from Petro Canada. Friction coefficient of the original catalytic bio-oil was lower compared to standard and non-catalytic bio-oil. Wear volume results showed that catalytic original ESP bio-oil performed better than any other oils tested.

Acknowledgements

First of all, I would like to thank Dr. Sushil Adhikari for allowing me to work under his supervision. His persistent support and guidance has always helped me to work hard, and I feel lucky to be part of his successful career. I would also like to thank Dr. Robert L. Jackson and Dr. Brian Via for their valuable suggestions. I would specially like to thank Rajdeep Shakya, Dr. Zhouhong Wang and Ujjain Pradhan for suggesting and helping me during this study. I am grateful to Dr. Hyungseok Nam and Dr. Saravanan Shanmugam for their support and guidance during this study. I also want to express my sincere thanks to Dawayne "Doc" Flynn and Bobby Epling for their support during experimental works. I have great appreciation towards all my colleagues in the Biosyestems Engineering Department– Thomas Loxley, Ritesh Karki, Vivek Patil, Sourov Sajib, Nikhil Jain, Khalida Harun and Philip Cross. I am grateful for my parents Mr. Krishna K C and Mrs. Sujata K C for their love and support. I would like to thank my brothers Mr. Sudeep K C and Mr. Tikaram Adhikari, and sisters, Miss Upama Shrestha and Mrs. Indu Dhakal, for their support. I would specially like to thank Binita Bohara for always being there for me. Lastly, I would like to acknowledge Southeastern Sun Grant Center and the US Department of Transportation, Research and Innovative Technology Administration (Grant No. DTO559-07-G-00050) and entire staff of Biosystems Engineering Department for their support and making this research possible.

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CHAPTER ONE

Introduction

This chapter includes brief introduction about necessity of alternative energy sources. Biomass is the only carbon based liquid fuel energy source. A short introduction about the conversion of biomass into liquid fuels using non-catalytic and catalytic fast pyrolysis followed by hydrotreatment process is discussed. This chapter also includes research objective along with a scheme to carry out research objective.

1.1. Rationale

In this 21st century, energy demand is continuously increasing with the rise in population. The majority of energy demand is currently fulfilled by fossil fuels and partially by renewable energy. The thrust for the production of alternative energy is very imperative in order to address climate change and reduction on the dependency of fossil fuels. There are various sources of alternative energy such as hydropower, wind, solar, geothermal and biomass. Among these sources, biomass only has the potential to supply carbon based liquid form of energy, which is particularly important in transportation and industrial sectors. Biomass consumes carbon dioxide (CO_2) during photosynthesis process and releases during combustion, which makes biofuels carbon neutral. A conversion of solid biomass into liquid form can be done through various processes but a fast pyrolysis is preferred mainly because it can produce higher amount of liquid intermediates at moderate temperatures (450-500°C). The fast pyrolysis process converts solid biomass to liquid, also known as bio-oil, along with bio-char and non-condensable gases. Bio-oil can be used as a feedstock for heat generation and transportation fuels, while biochar can be applied to the agricultural lands as a soil amendment or utilized to produce activated carbon and non-condensable gases to produce liquid fuels and chemicals. Bio-oil is in the liquid form containing high amount of aromatic compounds, which makes it as a potential source for alternate energy. However, bio-oil produced via fast pyrolysis is acidic in nature, highly viscous, contains high oxygen, high viscosity and also suffers from aging problem. These problems present in bio-oil restrict its application in commercial equipment that are being operated using liquid fossil fuels. Polymerization, corrosion, and lower heating value are the major hurdles associated with the bio-oil application. Therefore, there is a need to improve the quality of bio-oil particularly by removing oxygen presents in it, and deliver it as an alternative to conventional fossil fuel.

1.2. Research Objective

The overall objective of this research was to study the effectiveness of hydrotreament of bio-oil collected from electrostatic precipitator (ESP) for reducing oxygen content and other biofuels properties. The specific objective was to understand the effect of hydrotreatment on catalytic pyrolysis bio-oil produced using CaO on biofuels and tribological properties.

This study was focused to produce bio-oil via two pathways: one with quartz sand as bed material and other with CaO as bed material (in-situ pyrolysis) in order to produce non-catalytic and catalytic pyrolysis oils, respectively. Bio-oil collected from ESP for both non-catalytic and catalytic bio-oil was hydrotreated in the presence of hydrogen and catalyst to understand the efficacy of hydrotreatment. The major tasks of the study were to (i) evaluate product distribution of non-catalytic and catalytic upgraded bio-oils; (ii) compare properties between non-catalytic and catalytic upgraded bio-oils; and (iii) compare friction and wear properties between non-catalytic and catalytic original ESP bio-oils. Figure 1.1 shows the experimental scheme of the proposed work in this study.

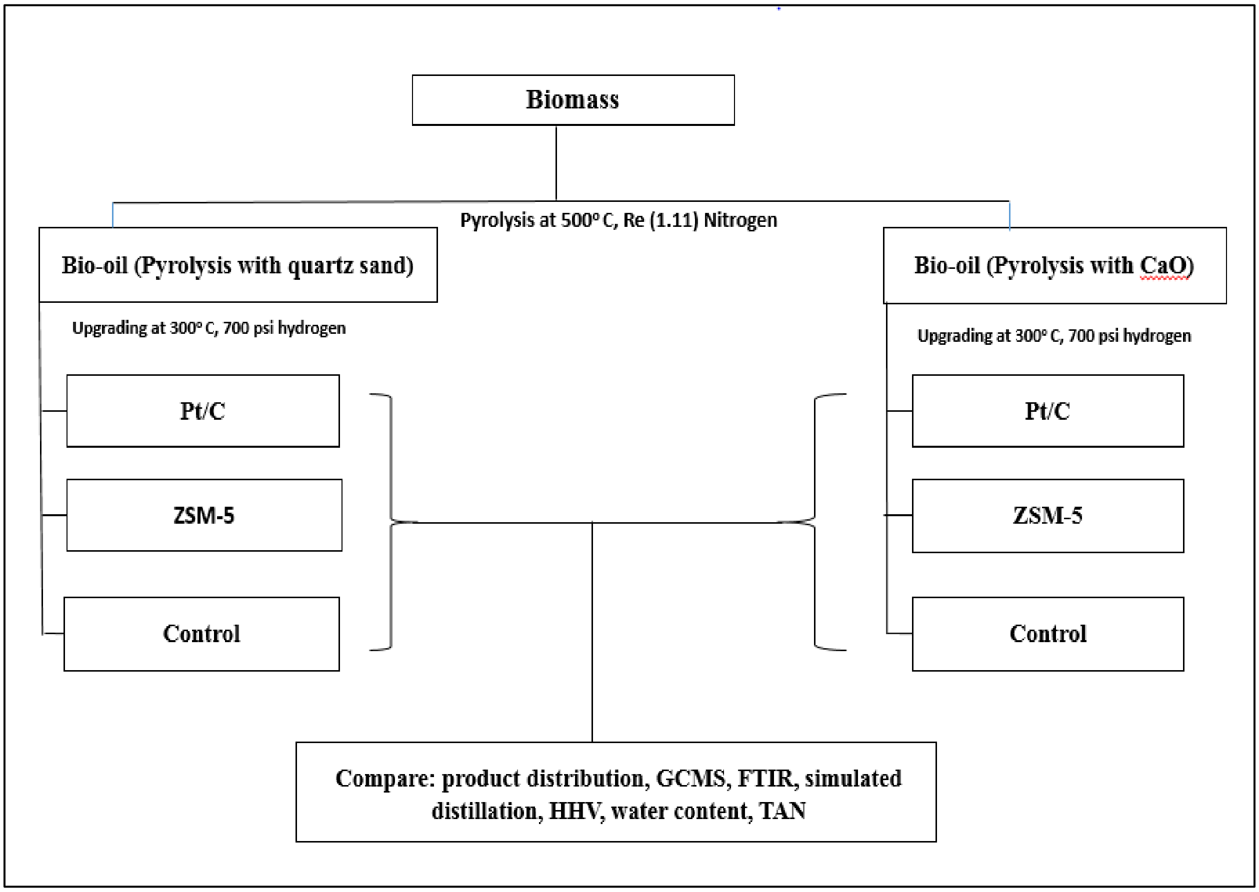

Figure 1.1: Experimental scheme of the objective

CHAPTER TWO

Literature Review

2.1. Energy Background

The population of the world including the U.S. is in increasing pattern. According to the U.S. Census Bureau [1], the population of the world is projected to be 8 billion in 2025, which is 0.6 billion more than that of current population (7.4 billion). With an increase in population, there is a looming increase in the energy demand. Majority of the energy demand is fulfilled by fossil fuels, which have limited or finite sources. According to the U.S. Energy Information Administration (EIA), the total energy consumption by the U.S. at the end of 2016 was 88.34 quadrillion Btu of which 71.19 quadrillion Btu was obtained from fossil fuels [2], which clearly indicates high dependency on fossil fuels for meeting energy demand. Majority of the fossil fuels is being consumed in transportation and industry sectors [3]. Although fossil fuels are being used to meet our energy demand, their combustion has led to an increase amount of greenhouse gases, working as a proponent for global warming. Major greenhouse gas that is being produced during combustion is carbon dioxide (CO_2). Transportation sector has been the major source of carbon dioxide emissions since 1990, and has reached its highest level in 2007 [4]. Liquid fossil fuel is the major energy source for the transportation sector.

Liquid fuel plays a vital role in energy consumption and also in environment. The U.S. total primary energy consumption by fuel could increase from 97.1 quadrillion Btu in 2013 to 105.7 quadrillion Btu in 2040 [5], in which consumption of petroleum and liquid fuel is expected to increase from 35.9 quadrillion Btu in 2013 to 37.1 quadrillion Btu in 2020. But this increasing consumption pattern is projected to decrease to 36.2 quadrillion Btu from 2020 to 2040. This decrease in consumption pattern from 2020 to 2040, is expected to be from the use of alternate fuels and blending of petroleum liquid fuels with biodiesel. Another key thing that is to be considered with this pattern is the carbon dioxide emission from various sectors. There is a decrease in carbon dioxide emission, which would be mainly because of the shift from coal to natural gas for electricity generation and also shift towards renewable energy, an increase in efficiency of appliances and vehicle technology advancement. The trend of carbon dioxide emission indicates that it was about 6% higher between 1990 and 2015, which is primarily due to massive use of the fossil fuels [5].

There are various influencing factors for change in carbon dioxide emission trend such as population growth, technological advancement, economy and behavioral change. There is a decrease in the U.S. carbon dioxide emission from 419 million metric tons in 2009 to 5447 million metric tons in 2009 [6]. This decreasing trend in carbon dioxide emission is also due to shift towards renewable energy sources for energy needs. The amount of carbon dioxide emission can also be related to the type of transportation fuel that is being consumed for end-use. There is a huge reduction in terms of carbon dioxide emission by the combustion of transport fuels produced from sources such as algae, sugarcane and cellulosic matters. The reduction in carbon dioxide emission in comparison to petroleum is 78% and 86% for fuels produced from sugarcane and cellulosic biomass respectively [7]. Figure 2.1 shows the biomass energy consumption by type and indicates that there is an increase in biomass energy. The trend in Figure 2.1 clearly indicates that there is an increase in the use of biomass for energy particularly from 2008. The growth in biomass energy consumption is mainly because of the use of biomass to produce biofuels, primarily ethanol, for the transportation sector. There was a massive increase in the production of ethanol, which has been one of the key contributors for shift towards alternate fuels.

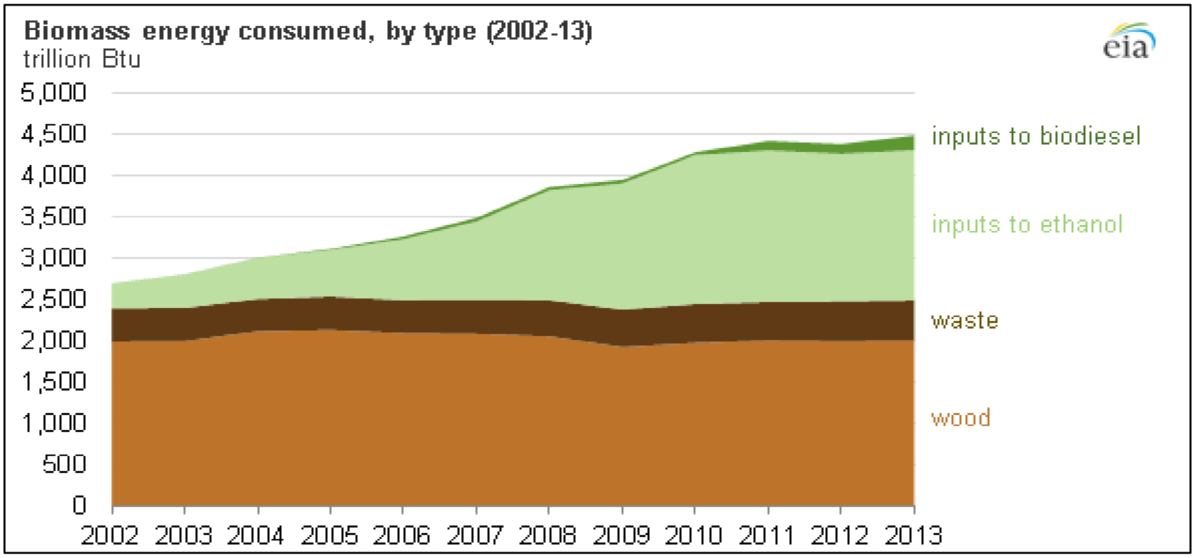

Figure 2.1: Biomass energy consumption by type including inputs to biodiesel and ethanol industries [8]

2.2. Biomass as fuel

Fossil fuels have primarily two major issues: finite source and its contribution towards greenhouse effect [2,7]. There is a necessity to shift towards alternate fuels, and biomass is the only alternative source for the production of carbon based liquid fuel. Biomass are organic matters which are mainly derived from living organisms. There are various sources of biomass such as wood, food and agricultural wastes, which are readily accessible throughout the world. The major components of biomass are cellulose, hemicellulose and lignin. Biomass feedstocks varies with the amount of these major components. Most often lignocellulosic biomass consists of 85-90% of these components in which hemicellulose, cellulose and lignin are in 20-40, 40-60, and 10-25 wt%, respectively [9]. Cellulose is a long chain of glucose molecules which are interlinked together by glycosidic bonds. This is the dominant form of biomass found in the planet. Glucose from one chain to another is connected by hydrogen bond with oxygen atoms attached either on same or associated chains, which is shown in Figure 2.2. The bond between the glucose units is strong, and it is difficult to break with temperature below 350^{o}C. Typically, cellulose under thermal decomposition is converted into aerosols, chars, vapors and gases, while vapors yield are higher at 500^{o}C [10]. The functional compounds that are obtained from thermal decomposition of cellulose are light oxygenates, furans, levoglucosan and gases through primary reaction mechanism while levoglucosan sometimes undergoes secondary reactions to yield aldehydes and hydroxyl groups [11].

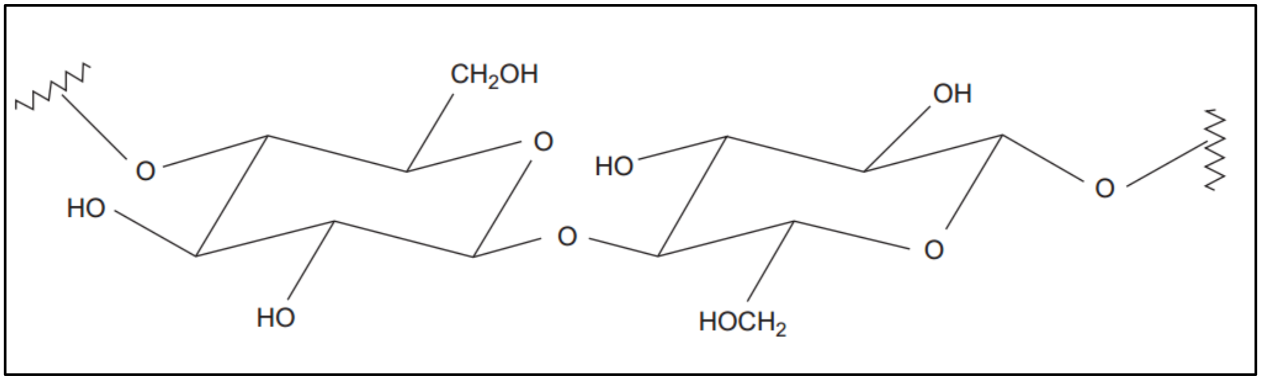

Figure 2.2: Schematic of a cellulose molecule [12]

Hemicellulose is complex combination of polysaccharides, which is particularly present in the vicinity of cell wall. Unlike cellulose, its structure is random with very little strength, and bonds can be easily destroyed even by hydrolysis with dilute acids. The schematic of hemicellulose is shown in Figure 2.3. These polysaccharides are mainly composed of xylose, mannose, galactose, rhamnose and arabinose. They have shorter chains consisting of 500-3000 sugar units as compared to 7000-15000 glucose units per polymer of cellulose [13]. Since the bonding between glucose units are not strong, the temperature required for thermal decomposition is much lower than cellulose.

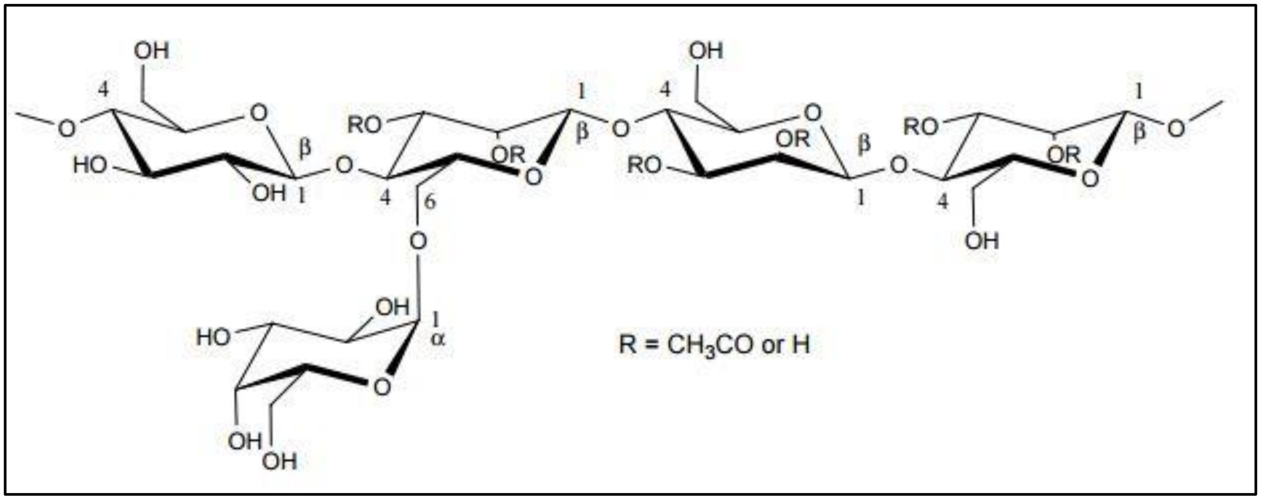

Figure 2.3: Schematic of hemicellulose [14]

Lignin is complex organic polymers, which are crossed linked mainly by phenolic polymers [15]. The intricate linking between the polymers makes lignin very rigid and difficult to break, which is particularly important for the formation of cell walls. It is basically made up of three carbon chains attached to rings of six carbon atoms, while there may be one or more methoxyl groups attached to the rings as shown in Figure 2.4 [9]. The thermal decomposition of lignin extends over a wider range compared to cellulose and hemicellulose [16]. Phenolic compounds, 4-,5-,6-, methyl derivatives and 2-6-dimethylphenol are the main products from the thermal decomposition of lignin [17].

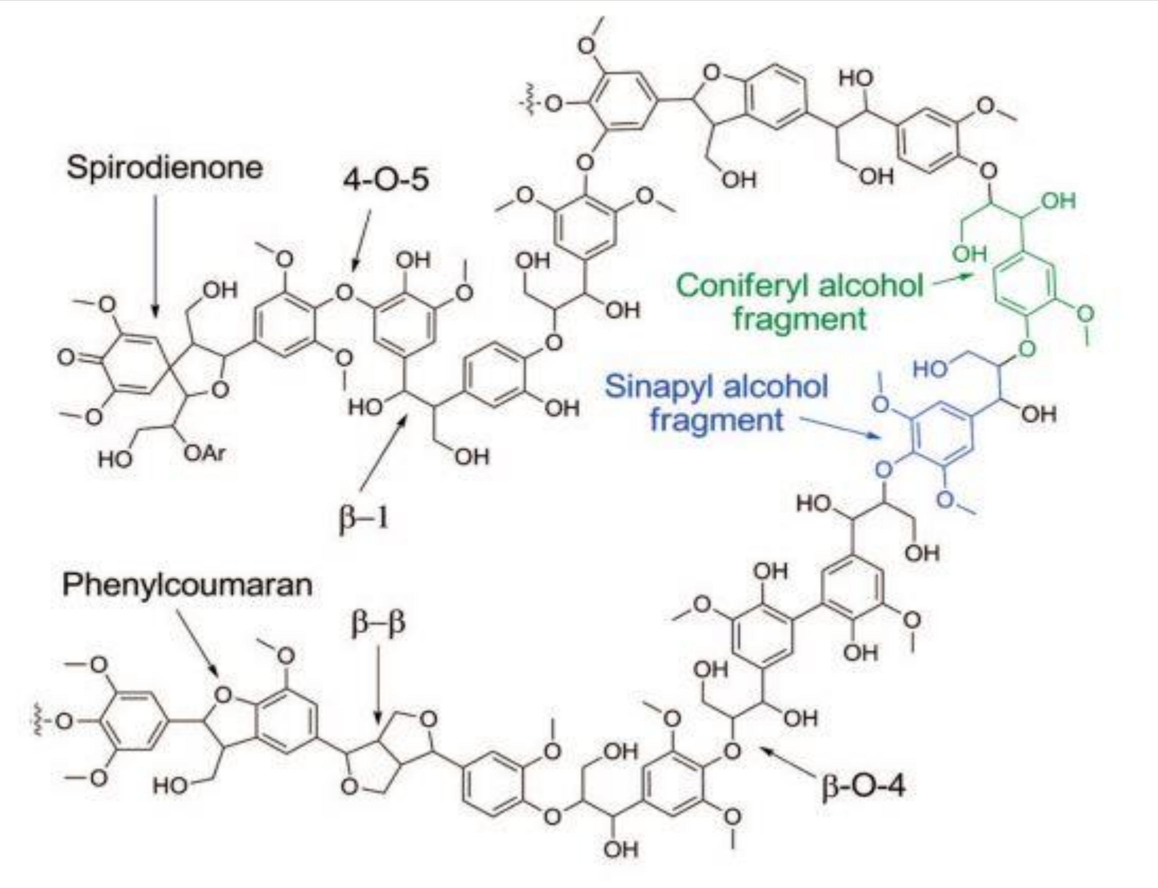

Figure 2.4: Schematic of lignin [18]

From 2002 to 2013, conversion of biomass as biofuels increased by 500% in the U.S. primarily for the production of ethanol [8]. Although there are many other renewable energy sources such as hydropower, wind, solar which are available in specific locations, biomass is abundantly found throughout the world and can be utilized to generate energy. Hence, biomass can be effectively implemented even at local level [19]. This accessibility of biomass makes it as one of the viable sources for energy production. Biomass can be used for energy production through different pathways as follows:

- **Direct combustion of biomass:** Combustion is the reaction process to produce thermal energy and flue gas in presence of oxygen. Through direct combustion, biomass can be used to produce heat, which can be utilized to produce steam for electricity generation. These combustion process is mainly targeted to the current electricity production plant. A simple modification to power generation plant would allow for direct combustion of biomass. The disadvantage associated with direct combustion of biomass comes with moisture content in biomass and ash content present in the biomass.

- **Gasification:** Gasification is a thermal conversion process of converting biomass at high temperature in limited supply of oxygen in order to produce syngas – carbon dioxide, carbon monoxide, hydrogen and methane. Any carbonaceous solids or liquids can be used as raw materials for gasification so it is a very useful process in areas having plenty of waste woods. Gasification is one of the flexible application processes for hydrogen production, synthesis of fuels, chemical and thermal power generation. Heat is supplied to gasifier only at the initial stage and gets regenerated throughout the process making it more energy efficient. The disadvantage associated with gasification is related with clean-up process. Gasification is associated with tars and other undesirable compounds and efficiency of overall process is reduced.

- **Fast pyrolysis:** Fast pyrolysis is a thermochemical conversion of biomass into bio-oils, chars and gases in absence of oxygen. Fast pyrolysis is particularly favorable for the production of liquid fuel. Biomass gets rapidly heated at around 500^{o}C to convert into solid chars, condensable and non-condensable gases. The condensable gases are passed through condenser train to get dark brown liquid commonly known as bio-oil. Bio-oil is a complex mixture of organic compounds such as carboxylic acids, phenols, alcohols, aldehyde, esters, and other lignin oligomers. The production and upgrading of liquid fuel into different petroleum range is widely applicable for transportation and electricity production sector. The problems associated with bio-oil are its high acidic nature, corrosiveness, low heating value sand instability. In order to convert bio-oil into biofuels further processing, also known as upgrading process, is required, which increases the overall process cost.

There are many advantages of converting biomass to biofuel such as: (i) one of the major advantage of biomass based fuel is that it significantly helps to reduce the carbon dioxide emission, which reduces greenhouse effect, and (ii) it reduces the dependency on fossil fuel and thrives towards sustainable energy. About 40% or less of the organic matter is removed from farm fields for ethanol production while the rest is returned back to soil which increases fertility and helps to decrease soil erosion [20]. Biofuels are classified in three generations: first, second and third. The primary characteristic of the first generation biofuel is that it is mainly derived from food products such as corn and soybean, which can blend with other petroleum fuels making it compatible with existing IC engine [21].

As an alternative to the first generation, the second generation biofuel is produced primarily from lignocellulose feedstocks, which are cheap and abundantly found in nonedible parts in plants. Plant biomass are found abundantly and are not considered as useful source. But plant biomass is one of the potential raw materials for the second generation biofuel and can be utilized to produce energy. Plant biomass can undergo through various heating process to extract heat and can be used for energy generation. The overall conversion of biomass to bio-oil and its subsequent conversion to gasoline, diesel and jet fuel range will have positive impact on environmental issues. Therefore, there is an increasing demand towards agricultural byproduct which has uplifted farmers for the production of dedicated biomass production [22]. The major advantage of this second generation biofuel is that it does not collide with demand of food crops, and at the same time exhibits the advantages of using biofuel. The problem associated with the second generation biofuel is its bio-oil properties such as high acidity, high viscosity and lower heating value, which has been a hindrance for commercial production of biofuels [23].

Third generation biofuels are mainly produced from algal biomass, which has very high oil yield compared to the best oilseed crops [24]. Biomass having higher lipid content are mainly targeted for the production of biofuels. Algal biomass also avoids the food versus fuel debate. Microalgae has the potential for rapid growth and it helps for the biofixation of CO_2 [25]. A huge positive impact can be made that can address energy security, environmental impact and economy with the advancement of these second generation biofuels. A comparative scenario of petroleum fuel, first generation, second and third generation biofuel is represented in Table 2.1.

Table 2.1: Comparison of first generation, second generation biofuel and petroleum fuel

Petroleum fuel	First generation biofuel	Second generation biofuel	Third generation biofuel
Feedstock Crude petroleum	Feedstock Corn, sugars, vegetable oils	Feedstock Agricultural byproducts, wastes, woody crops	Feedstock Algae
Advantages Better performance, commercially used for energy production	Advantages Environment friendly, means of energy security, economic	Advantages Environment friendly, Technological advancement will reduce cost, Not competing with food	Advantages Environmental friendly, Can be produced throughout the year, can be cultivated in brackish water or non-arable land
Products Diesel, Petrol, Kerosene, Jet fuel, LPG, CNG	Products Corn ethanol, biodiesel	Products Bio-oil, lignocellulosic ethanol, hydrotreating oil	Products Bio-oil, syngas, ethanol, methane and hydrogen
Problems Greenhouse effect, environmental	Problems Food crop for production, partial	Problems Require more technological	Problems Species selection and production, technological

pollution, limited resource	blend with petroleum fuel	advancement for blending and use.	advancement for conversion

Biomass, which is in solid form, is converted to liquid bio-oil directly by pyrolysis process. Pyrolysis process can be categorized into mainly three types: slow, fast and flash pyrolysis. The variation in pyrolysis categories depend on parameters such as heating rates, residence time, particle size and temperature. Fast pyrolysis is mainly focused on the production of liquid while slow pyrolysis favors the production of charcoal.

2.3. Fast Pyrolysis

Fast pyrolysis is a process of direct conversion of biomass to liquid oil via thermal decomposition in absence of oxygen. Biomass is mainly composed of lignin, hemicellulose and cellulose which degrade at different temperatures. Cellulose and hemicellulose degrade in short temperature while lignin decompose in a wide temperature range [16]. The products from fast pyrolysis are mostly vapors, aerosols and char. Controlled cooling and condensation of vapors with shorter residence time results higher amount of bio oil that has half the heating value of petroleum liquid fuel. The biomass is fed to the reactor through screw feed mechanism which is set at a predetermined temperature. Research indicates that the optimum temperature for higher liquid yield is about 500^{o}C with very short residence time and high heating rate [16]. Fast pyrolysis prevents primary decomposition of products which are cracked thermally/catalytically and also prevents polymerization resulting in higher amount of condensable vapors. The essential features of fast pyrolysis process are: (1) high heating rate and temperature which requires finely ground and dried biomass feed; (2) controlled reactor temperature and shorter residence time in order to prevent secondary reaction; and (3) rapid condensation of vapors results in production of bio-oil. Fast pyrolysis requires very high heating rate, which is done mainly by preheated bed material, and when biomass is fed in the reactor, heat is transferred to biomass for decomposition. The reactor designs were explored to improve high heat transfers rate and particle size of biomass were screened in order reduce high heat penetration depth. It is endothermic process and heat is being supplied externally during the process. There has been prime focus on increasing the yield of bio-oil, process improvement but less research in improving the characteristics properties of bio-oil [26].

2.4. Fast pyrolysis process parameters

2.4.1. Temperature

Temperature is one of the key parameters in fast pyrolysis process and research indicates that the optimum temperature for maximum yield is around 500^{o}C [16]. The decomposition temperature of various components of biomass occurs at different temperature so optimum temperature to obtain higher yield of liquid is very critical. Temperature also plays a vital role in order to vary product distribution such as higher temperature resembles to higher gas production whereas char for lower temperature. The reaction temperature plays vital role with higher heat transfer requirement for decomposition of biomass.

2.4.2. Residence time

Residence time is another significant factor for the product distribution in pyrolysis process. It has been reported that very short residence time of around 0.5-2 s is considered to increase the liquid yield [27]. Longer residence time results in secondary vapor cracking, which reduces the bio-oil yield and also has negative impact on the quality of bio-oil. Time and temperature profile determines the quality of the bio-oil being produced since secondary cracking adds to the instability of bio-oil [28].

2.4.3. Biomass characteristics

Biomass particle size, moisture content and shape are some of the key factors associated with improving the yield of bio-oil. The moisture content of biomass prevents for maximum heat transfer for decomposition since most of the heat energy would be consumed for removing moisture. It has been reported that the moisture content of biomass should be below 10% unless the biomass is naturally dry [29]. Biomass particle size also enhances the decomposition rate since smaller particle size causes less hindrance on the flow of condensable and non-condensable gases while it gets high in the case of bigger particle size. Variation in particle size usually depends on the type of reactor being used for pyrolysis process.

2.4.4. Heating rate

Heating rate plays a pivotal role in order to supply desired amount of heat flux for decomposition of biomass. Higher heating rate can influence the product distribution by increasing the gas formation while bio-oil yield gets decreased [30]. Slow heating rate favors for higher char production but the bio-oil yield gets decreased. Onay et al. [31] found out that the heating rate of around 300^{o}C min^{-1} resulted higher yield than heating rate of 100^{o}C min^{-1} while yield remained constant beyond 300^{o}C min^{-1} heating rate.

2.4.5. Reactor

Numerous research work has been carried out to improve reactors design in order to maximize higher bio-oil yield. Higher heating rate, temperature control, de-volatilization are the parameters that are important for the reactor design. Fast pyrolysis can be carried out mainly by three main methods: ablative pyrolysis; fluid bed pyrolysis and vacuum pyrolysis. Ablative pyrolysis is performed by pressing the wood directly to the heated surface leaving behind evaporative oil film. The heat is transferred by solid–solid conductive method as performed in NREL [32]. The advantage of using this method is that even larger particle size biomass and wood can be used. Fluidized bed pyrolysis uses good mixing of solids to transfer heat by solid-solid conduction and gas-solid convective heat transfer method. Around 90% of heat transfer is done by conductive method while 10% contribution is done by convective heat transfer [33]. The limitations with this method is that smaller particle size biomass is required around 3mm with carrier gas for fluidization. Vacuum pyrolysis has slow heating rates but the products are comparable to that of fast pyrolysis. The major drawback of this method is high cost on vacuum and piping which makes it not a viable option for liquid production. Table 2.2 summarizes bio-oil properties (HHV, yield, water) from different biomass in terms of the reactors used for combustion.

Table 2.2: Overview of bio-oil from various biomass

	Corn cobs	Corn stover	Pine	Softwood	Hardwood
Temperature (^oC)	500	500	500	500	510
Reactor	Fluidized bed	Fluidized bed	Continuous auger reactor	Rotating cone	Transported bed
HHV (MJ/kg)	19.5	22.1	-	18-20	17-20
Yield (%)	61.0	61.7	57.8	60-70	60-70
Water (%)	25	9	30.9	29-32	20-21
Reference	[34]	[34]	[35]	[36]	[36]

2.5. Bio-oil

Fast pyrolysis process results in the formation of dark, brown, viscous liquid, which is referred as bio-oil. It is the result of thermal decomposition of biomass in absence of oxygen to form chars, vapors/aerosols and non-condensable gases. The vapors/aerosols 16are condensed by rapid quenching to form liquid product which is referred as bio-crude or bio-oil. It consists of more than 200 compounds such as acids, sugars, esters, ketones, aldehydes, furans, phenols, guaiacols, and water [37]. The properties of bio-oil may vary with type of biomass, heating rates, residence time and temperature. The application of bio-oil has been tested in boiler, furnaces, turbines and diesel engines for energy generation and can be upgraded to liquid fuel. In order to commercialize bio-fuel it has to meet ASTM D 7544-09 standard [38]. The standard requirement needs properties of bio-oil to be improved which are discussed in following section.

2.6. Bio-oil properties

- Heating value:

Heating value is the amount of energy released during combustion of bio-oil and is generally expressed in MJ/kg. The energy content of the bio-oil is described by its heating value. Higher heating value of bio-oil ranges from 16-19 MJ/kg compared to 44 MJ/kg of crude oil normally evaluated using bomb calorimeter [39]. It is clear that the higher heating value of bio-oil is about half of the crude bio-oil.

- Viscosity:

Viscosity is related to the flow characteristic of bio-oil. Highly reactive compounds such as olefins tend to polymerize for thermodynamic equilibrium which increases the molecular mass of the bio-oil. Compounds such as ketones, aldehydes and acids tend to form ethers, and acetales due to polymerization. These circumstances leads to increased viscosity of bio-oil making it unsuitable for alternative to liquid fuel. Viscosity depends on the type of biomass and water content so the viscosity may vary depending on these criteria. Typical wood pyrolysis bio-oil has viscosity of 40-100 cP while it is 180 cP for heavy fuel oil at 50^{o}C [40]. Viscosity of bio-diesel falls within the range of 1.9 – 6.0 mm^2/s at 40^{o}C [41], while viscosity of diesel Grade LS#1, No. 1-D is 1.3 - 2.4 (mm^2/s), Grade LS#2, No. 2-D is 1.9 – 4.1 (mm^2/s) and Grade No. 4-D is 5.5 – 24.0 (mm^2/s) at 40^{o}C according to ASTM D975.

- Water and oxygen content

The water content in bio-oil is mainly due to the moisture content in biomass feedstock and during pyrolysis process via dehydration [42]. Water content on bio-oil reduces the heating value and flame temperature which is unsuitable for modern transportation vehicle and other equipment. The lower molecular weight oxygenates in bio-oil are not miscible with water which indicates polar nature of bio-oil [43]. The high water content and oxygenates in bio-oil result immiscibility with petroleum fuels and reduces heating value of the bio-oil.

- Acidic

The presence of organic acids such as formic acid and acetic acids is a major reason for bio-oil to be of acidic in nature. It has a pH of about 2-4, which makes it very unsuitable for alternative fuel [17, 44]. Corrosion of metals have proven that bio-oil is difficult to handle and store due to acidic nature. Acids in lignocellulosic biomass are mainly due to thermal decomposition of hemicellulose which mainly contains acetic and formic acids [44]

Table 2.3 summarizes the bio-oil properties from different biomass. Water content, pH and HHV are some of the key properties of bio-oil which varies according to different biomass. Rice-husk, switch grass, eucalyptus bark and poplar have higher water content which also includes higher pH values. Bio-oils having higher water content have relatively lower heating values whereas it’s vice versa for bio-oils having lower water content. Nanocholoropsis algae exhibits better bio-oil properties having realatively lower water content, nearly neutral pH and higher heating value.

Table 2.3: Selected bio-oil properties from different biomass

Bio-oil	Water (wt. %)	pH	HHV (MJ/kg)	Viscosity (cSt, 40^{o}C)	Ref
Rice-husk	28	3.2	16.5	13.2	[45]
Corn stover	15.2	2.87	185	17.51	[46]
Nanochloropsis algae	7.63	6.61	33.4	-	[47]
Sludge	10.9	6.8	36.4	-	[48]
Switch grass	21.8	2.97	19.6	25.6	[49]
Eucalyptus bark	32.86	2.87	12.23	16.28	[50]
Poplar	29.7	3.1	19	22	[51]
Oak	16.1	2.8	18.9	115	[51]
Pine	18.5	2.9	18.7	44	[51]

2.7. Catalytic fast pyrolysis

Bio-oil is unstable, acidic, highly viscous, highly oxygenated, immiscible with other petroleum fuels and has half the heating value of petroleum fuels. There are various technique that has been followed to upgrade bio-oil among which in-situ catalytic pyrolysis has been promoted as one of the effective pathways [52]. Catalyst are placed directly in the reactor as bed material or with mixture of other bed material and reacts with pyrolysis vapors. This pathway converts biomass into bio-oil while vapor phase are catalytically upgraded in the same reactor before condensation. Numerous research work has been carried out in order to analyze the effect of different cracking catalyst such as zeolites, metal-modified zeolites, and alumina but with this process there is reduction in yield due to increased cracking [26]. Catalytic pyrolysis process can be done with inexpensive base metal such as CaO, MgO, ZnO and dolomite, which reduces undesirable components from bio-oil. The use of CaO and CaO.MgO (dolomite) reduce acidity and oxygen content [53]. Accelerated aging test of bio-oil produced using CaO, MgO and ZSM-5 catalysts in a fluidized bed reactor showed that CaO used bio-oil was more stable compared to two other bio-oils [26] . Wang et al. [54] in their experiment using CaO catalysts for catalytic pyrolysis of corncob showed that it helped to effectively reduce acids while improving the production of hydrocarbons. Even after the catalytic pyrolysis, oxygen content in the bio-oil is still high and makes it incompatible to petroleum fuels. Therefore, catalytic pyrolysis followed by upgrading is another important step for producing “fungible” transportation fuels.

2.8. Bio-oil upgrading to biofuels

Bio-oil either from catalytic or non-catalytic pyrolysis needs to be upgraded in order to convert it into transportation fuels. There are various techniques that are followed to upgrade bio-oil primarily catalytic and non-catalytic. Non-catalytic upgrading includes emulsification [55], solvent addition [56] and treating with supercritical fluids [57]. Catalytic upgrading is mainly done by hydrotreatment and zeolite cracking. Hydrotreatment is a process in which high pressure is applied in order to catalytically react with hydrogen and remove oxygen as water from bio-oil. The issue related with hydrotreatment is that it produces char, coke and tar resulting catalyst deactivation. Zeolite cracking is a process in which zeolite such as H^+ZSM-5 are used to remove oxygen as CO_2. But there are some problems related to zeolite cracking such as carbon deposition is higher, low H/C ratio and approximately 25% lower heating value than crude oil [39]. The effectiveness of the upgrading process is mainly analyzed by two important parameters: oil yield and degree of deoxygenation (DOD).

The oil yield indicates selectivity toward oil product (quantity) and DOD indicates the effectiveness of the process in removing the oxygen (quality). The operating condition for hydrotreatment requires high pressure which is in the range of around 10-120 bar [49,51]. The increase in pressure implies higher solubility of hydrogen making it accessible in locale of catalyst for hydrotreatment [59]. In case of batch reactor, the reaction is carried out in certain time frame usually (2-10h) while DOD is directly related with the residence time as well as temperature which is normally between 250 to 450^{o}C [53,54]. But kinetic aspects is more determining factor for the selection of the temperature. Another important aspect of hydrotreatment is the amount of hydrogen being consumed in the reaction. Venderbosch et al. [62], studied the consumption of hydrogen with respect to DOD over Ru/C catalyst and found out that the hydrogen consumption was increased with higher DOD. This trend is mainly because of highly reactive oxygenates such as ketones were reacted with low hydrogen, while complex molecules have higher consumption for the reaction in order to leverage out oxygen which increases hydrogen consumption at high DOD[61]. Thus, the two main impacts of hydrotreatment are eliminating oxygen and saturation of double bonds that helps to increase H/C ratio improving the quality of bio-oil [62] . The catalyst that are used for the hydrotreatment are basically sulfide/oxide catalysts, transition metal catalysts and supports. The catalyst that fall under sulfide/oxide catalyst are Co-MoS_2 and Ni-MoS_2 while transition metal catalyst include Rh, Co, Pd, Pt [62]. Table 2.4 represents the overview of catalysts used for upgrading, operating parameters and properties. This catalytic action helps to upgrade bio-oil to improve its characteristics property.

Table 2.4: Various upgraded oil and their properties

Catalytst	Setup	P [bar]	T^o [C]	DOD [%]	O/C	H/C	Y_{oil} [wt%]	Ref
$Pt/Al_2O_3/SiO_2$	Continuous	85	400	45	-	-	81	[63]
Ru/C	Batch	200	350	86	0.8	1.5	53	[64]
HZSM-5	Continuous	1	380	50	0.2	1.2	24	[65]
$Co\text{-}AMoS_2/Al_2O_3$	Batch	200	350	81	0.8	1.3	26	[64]
$Ni\text{- }MoS_2/Al_2O_3$	Batch	200	350	74	0.1	1.5	28	[64]

2.9. Tribological properties of bio-derived oils

Lubrication is very critical factor to avoid machinery failure particularly in automobile and industrial sectors. All these machines are continuously moving so proper lubrication is very important for smooth operation. The machine components which are in motion are mainly affected by load, temperature, speed, sliding time, base oil and additives. The nature of the motion between these machines surfaces causes wear, seizure, fretting and structure failure. Therefore, a proper lubrication is critical for smooth operation. Heat transfer, friction reduction, wear resistance and shock absorption are the important gained features of using a lubricant. Most of the commercial lubricants available on the market are derived from fossil sources. Bio-derived oil lubricants can be an alternative to these commercial ones and several investigations are carried out on the friction, wear and lubrication properties of bio-based oils. Kodali [66] studied the lubricating properties of oil derived from vegetable oils which exhibited excellent performance at low temperature flow properties and oxidation stability. Siniawski et al. [67] compared the tribological properties (abrasion rate and friction) between soybean, sunflower and base oils. Soybean oil was superior in terms of tribological nature and the deduced reason for the difference is fatty acid composition. Particularly, a lower content of linoleic and oleic acids played a vital role. Reeves et al. [67] studied the worn surface roughness of bio-based lubricants along with varying additives and found out that higher particle sizes caused rougher worn surfaces. The important properties for lubricating oil are friction and wear reduction.

2.9.1 Friction

Friction is resistance to motion, which is related in everyday work. In the case of moving machine components, friction is undesirable since it consumes energy, reduces the overall performance and also deteriorates materials. One of the tests that is used to determine the coefficient of friction of lubricating oil is by a tribometer such as a ball-on-disk tribometer, cylinder liner-piston ring tribometer and engine cylinder piston tribometer. Figure 2.5 represents the schematic of a ball-on-disk tribometer. The test specimen lies at the bottom while the testing oil is placed at the top and a specific load is applied through the ball on to the disk. The sliding motion is carried out at a specific speed and for a specific time frame. The results are obtained for coefficient of friction with relation to sliding speed and load.

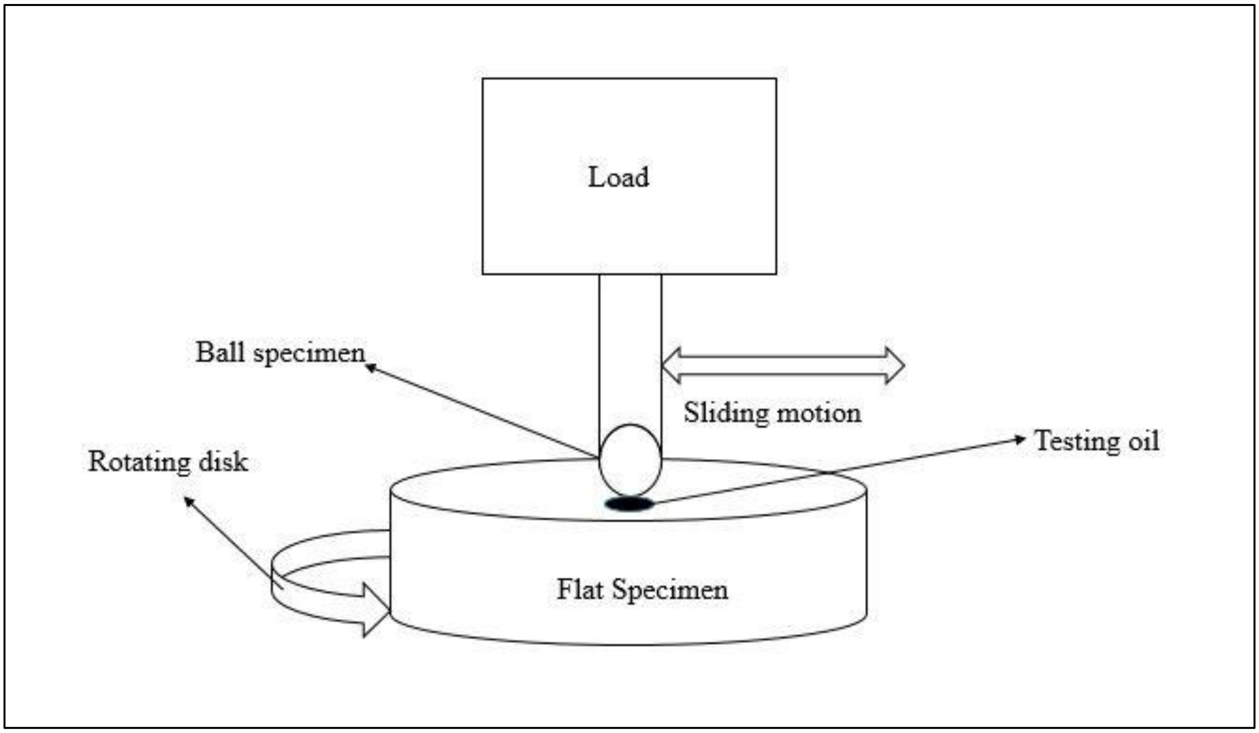

Figure 2.5: Schematic of ball on disk tribometer

2.9.2 Wear

The removal of material due to interaction between solid surfaces during motion is referred to as wear. It is one of the undesirable material removal cases while there are desirable material removal operations performed such as in the case of polishing and machining. Wear is directly related to material properties, the nature of motion, load and temperature. The wear volume of a surface can be evaluated by profilometer as represented in Figure 2.6. Surface roughness is evaluated by surface profiler obtained from the profilometer. The wear surface can also be evaluated from a scanning electron microscope which gives the morphological surface structure of the test specimen.

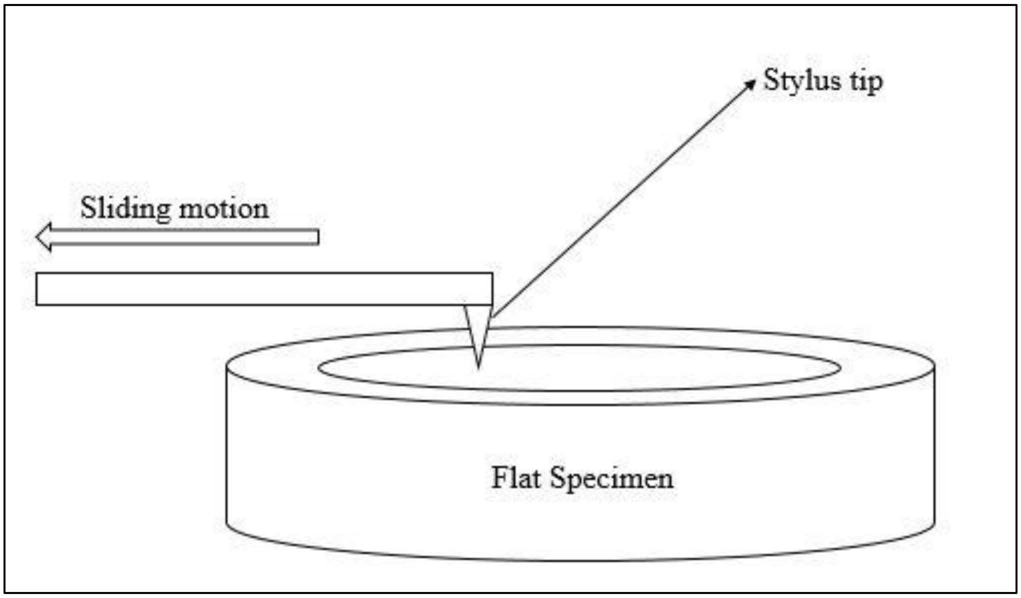

Figure 2.6: Schematic of stylus profilometer

2.10. References

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CHAPTER THREE

Hydrotreatment of ESP Pyrolysis Bio-oil

Abstract

In-situ catalytic fast pyrolysis process is touted as one of the promising techniques to improve the properties of bio-oil during its production process. The negative properties such as low heating value, high acidity as well as unstable nature of bio-oil are improved during catalytic fast pyrolysis process. In this study, hydrotreating effect on catalytic fast pyrolysis bio-oil produced using CaO was studied over Pt/C, ZSM-5 and control (without any catalyst). Quartz sand was used as bed material for non-catalytic fast pyrolysis while CaO was used for catalytic fast pyrolysis in a fluidized bed reactor and bio-oils obtained from electrostatic precipitator (ESP) were used for hydrotreating operation. The upgraded bio-oils were compared for their product distribution, chemical composition, heating value, total acid number, oxygen content and water content. Higher liquid yield was obtained when upgraded with Pt/C catalyst for both non-catalytic (69.79%) and catalytic (69.67%) bio-oils. The chemical composition of bio-oil were analyzed using a gas chromatography mass spectroscopy where phenols were higher in both catalytic and non-catalytic upgraded bio-oil, while oxygenated compounds were reduced during hydrotreating. Catalytic original ESP oil (33.4 MJ/kg) heating value was higher than non-catalytic original ESP oil (27 MJ/kg), while upgrading catalytic bio-oil had no significant improvement in heating value with values remaining around the proximity of 33 MJ/kg. Total acid number of original ESP bio-oils were reduced from 131.46 to 53.45 for non-catalytic and 107.53 to 53.08 catalytic bio-oil, which indicated improvement in reducing acidic nature of bio-oil. Tribological tests were performed to compare friction and wear properties of original ESP bio-oils with standard base oils, and it was observed that the catalytic original ESP bio-oil had low friction coefficient and wear volume when compared with base oils and non-catalytic bio-oils.

Keywords: Fast pyrolysis, biomass, upgrading, catalyst, friction, wear

3.1. Introduction

The conversion of solid biomass to gasoline, diesel and jet fuel ranged fuels over thermal conversion process addresses environmental issues as well as reduces dependency on fossil fuels [68]. There are various sources for renewable energy such as hydropower, wind, solar but biomass is the only potential carbon source which can be converted into transportation liquid fuel [69]. Poplar as biomass has several advantages since it is one of the fast growing trees. Since last 50 years, it has been grown commercially for the pulp and paper industries [70]. Rigorous research works using poplar are being carried out for watershed protection, carbon sequestration and commercial conversion of biomass to biofuels for energy [71]. Biomass can be converted to liquid fuels via fast pyrolysis process since it favors higher liquid yield [72]. In fast pyrolysis, biomass is thermally decomposed in the absence of oxygen at atmospheric pressure and controlled temperature at around 500^{o}C within very short residence time [10]. The products of fast pyrolysis are solid chars, non-condensable gases (or syn gas) and liquid products (bio-oil and aqueous phase). The problems associated with pyrolysis oil, which constrains it from being used commercially are instability, acidity, char particles inclusion, high oxygen content, lower heating value, high viscosity and immiscibility with petroleum fuels [54]. Therefore, bio-oil must be upgraded in order to eliminate oxygenates, reduce acidic nature, improve viscosity, reduce aging and increase heating value so that it can be used as liquid transportation fuel [73]. Bio-oil upgrading is mostly done by catalytic upgrading such as zeolite cracking and hydrotreatment, while there are non-catalytic technique such as emulsification, solvent addition and treating with superficial fluids. [39]. Various reactions occur during hydrotreatment upgrading process such as cracking, decarbonylation, hydrocracking, hydrodeoxygenation, decarboxylation and hydrogenation [10, 11]. Hydrodeoxygenation (HDO) reactions are carried out to increase H:C ratios and decrease O:C ratios with a support from catalysts and hydrogen gas.

Bio-oil yield is one of the major concerns during the conversion of solid biomass to liquid bio-oil. Various noble catalysts such as: Ru/C, Pt/C, Pd/C and Ru/TiO_2 were used for bio-oil upgrading in order to study the effect of catalysts on product yield. Bio-oil from beech wood was for study and Ru/C performed better while hydrotreating in terms of quantity (up to 60% yield) and quality (deoxygenation up to 90%) when operated at 350^{o}C and at 200 bar for 4 h [64]. Elliott et al. [75] studied the effect of temperature on upgrading bio-oil produced from poplar over a Pd/C catalyst in a fixed bed reactor and found out that the oil yield is decreased with increase in temperature. Kim et al. [76] performed experiment on the production of bio-oil via fast pyrolysis process using yellow poplar wood and subsequently upgrade it using a Pd/C catalysts in supercritical ethanol. The heavy fraction of liquid yield had lower O/C ratio than that of crude bio-oil. Busetto et al. [77] used bio-oil produced from white poplar wood chips in fixed bed tubular quartz reactor and upgraded it with Shvo catalysts. HDO altered the chemical composition of bio-oil by hydrogenating oxygen containing compounds such as aldehydes, ketones and non-aromatic double bonds.

Catalytic pyrolysis has been touted as a better approach to produce bio-oil where catalysts are used as bed material during fast pyrolysis. Catalytic pyrolysis involves the conversion of biomass into vapors and catalytic reactions of vapors-phase upgrading in same reactor. Kantarelis et al. [78] used modified zeolites as catalysts for the production of bio-oil showing less oxygenated liquid product yield with a decreased bio-oil yield. Veses et al. [79] used low cost materials like clay minerals as catalysts and found out that there was a reduction in total acid number and aging test showed that stability of bio-oil was also improved. They also found out a higher heating value of bio-oil was obtained but with a decrease in bio-oil yield. Aho et al [80] studied the effect of catalyst during catalytic pyrolysis of pine wood and found that there was an increase in gas production mainly because of decarbonylation reaction, reducing oxygen via CO formation. Cheap base metals such as CaO, MgO and ZnO, could be used for decarbonylation reaction and few studies [18, 19] have shown the effectiveness of these base metals. Reduction in acidity and oxygen content of bio-oil was reported when CaO and CaO.MgO were used as catalysts [83]. Mahadevan et al. [26] studied the effect of three different catalysts (CaO, ZSM-5 and MgO) as bed materials and concluded that bio-oil from CaO catalytic pyrolysis was comparatively stable and had lowest TAN. They found ZSM-5 had very less effect on acidic property even though it produced less acidic oil.

Despite numerous studies on catalytic pyrolysis on bio-oil production, Elkasabi et al. [84] extended his work hydrotreating catalytically pyrolyzed (HZSM-5) switchgrass bio-oil. Hydrotreating operation was carried out by mixing 9g of ESP bio-oil with 0.5g of catalyst and 40 mL of deionized water at 320 ^oC at 2100 psi for 4h. They observed that catalytically pyrolyzed bio-oil hydrogenated performed better at hydrogenating than any other oils.

Tribological property of bio-oil is also very important since every machining surface has to be properly lubricated in order operate properly. Friction and wear are the key properties to evaluate the tribological competency of the bio-oil. Xu et al. [85] compared the friction and wear behavior of bio-oil, emulsified bio-oil and diesel oil with engine cylinder piston ring tribotester and concluded that emulsified bio-oil performed better in terms of reducing wear. Friction coefficient of bio-oil were lower while emulsified bio-oil had comparable friction coefficient with diesel oil. Suarez et al. [86] performed lubricity test pyrodiesel from soybean oil and their blends with petroleum diesel. They concluded that lubricity property of diesel fuels were improved by the addition of pyrodiesel. Similarly, Lu et al. [87] studied the effect of solid char content and emulsification of bio-oil from rice husk. They found out that solid char particles in bio-oil helped to improve the lubricity, and a higher bio-oil content in emulsification improve lubrication properties. Xu et al. [87] studied the friction and wear behavior with the upgraded microalgae (spirulina) bio-oil. They found out that the upgraded bio-oil in the presence of KF/Al_2O_3 catalysts performed better in terms of lubrication than the upgraded oil with KF/HZSM-5 catalysts. The study concluded that crude spirulina and esterified spirulina bio-oil can be attributed for corrosion and boundary layer lubrication respectively.

Therefore, the objective of this work was to study the effect of catalytic fast pyrolysis bio-oil produced using CaO during hydrotreatment and compare its properties with non-catalytic fast pyrolysis bio-oil.

3.2. Materials and methods

3.2.1. Bio-oil production

Figure 3.1 represents the schematic of fast pyrolysis process for both non-catalytic and catalytic experiment. Quartz sand (Macron, State, USA) showed particle density of 2650 kg/m^3; a bulk density of 1570 kg/m^3 and particle size distribution of 150-300 µm, which was used as fluidizing bed material for non-catalytic pyrolysis. For catalytic experiment, marble small lump of CaO (3-20 mm; Millipore sigma, State, USA) was crushed and sieved to obtain particle size of 150-300 µm (ASTM E-11 mesh 50+ and 100-). The experimental setup for pyrolysis consists of a hopper with a twin screw auger, an injection screw, a fluidized bed reactor, a high temperature filter unit (HTF), pair of condensers, an electrostatic precipitator connected to gas analyzer. Biomass with moisture content less than 10% in hopper and was supplied to the main reactor with the help of auger feeder at around 3.5 g/min. Around 300g of quartz sand as bed material was used for the non-catalytic pyrolysis and the same amount of CaO was also used for the catalytic experiment. The fluidized bed reactor has diameter of two inches (0.0508 m) and a freeboard with diameter of 4 inches (0.1016 m). The overall height of the setup was 30 inches (0.762 m) with a freeboard of 6 inches (0.1524 m) high. The fluidized bed reactor was supplied with nitrogen to exclude oxygen from the system at 15 L/min which corresponds to superficial velocity of 0.12 m/s with Reynolds number of 1.11 at NTP. Multiple orifice distribution plate was placed at the bottom of the reactor through which nitrogen was passed. The temperature inside the reactor was measured using thermocouple and was maintained at 500^{o}C by a set of electrical heaters. HTF was maintained at 350^{o}C and chars were collected at the bottom. The pyrolysis vapor passed through the pipe into condenser train was cooled by a mixture of ethylene glycol and water. The condenser temperature was maintained at 2^{o}C by circulating water and ethylene glycol mixture through a chiller where the pyrolysis vapor condensed to form bio-oil. The non-condensable gases passed through electrostatic precipitator (ESP) with a 20 kV supply to the rod, where oil phase is precipitated at the bottom of ESP. Activated charcoal filters were used to absorb moistures form non-condensable gases while gas analyzer was used to evaluate the quality of non-condensable gases. Bio-oil collected at the bottom of the ESP was used for the study.

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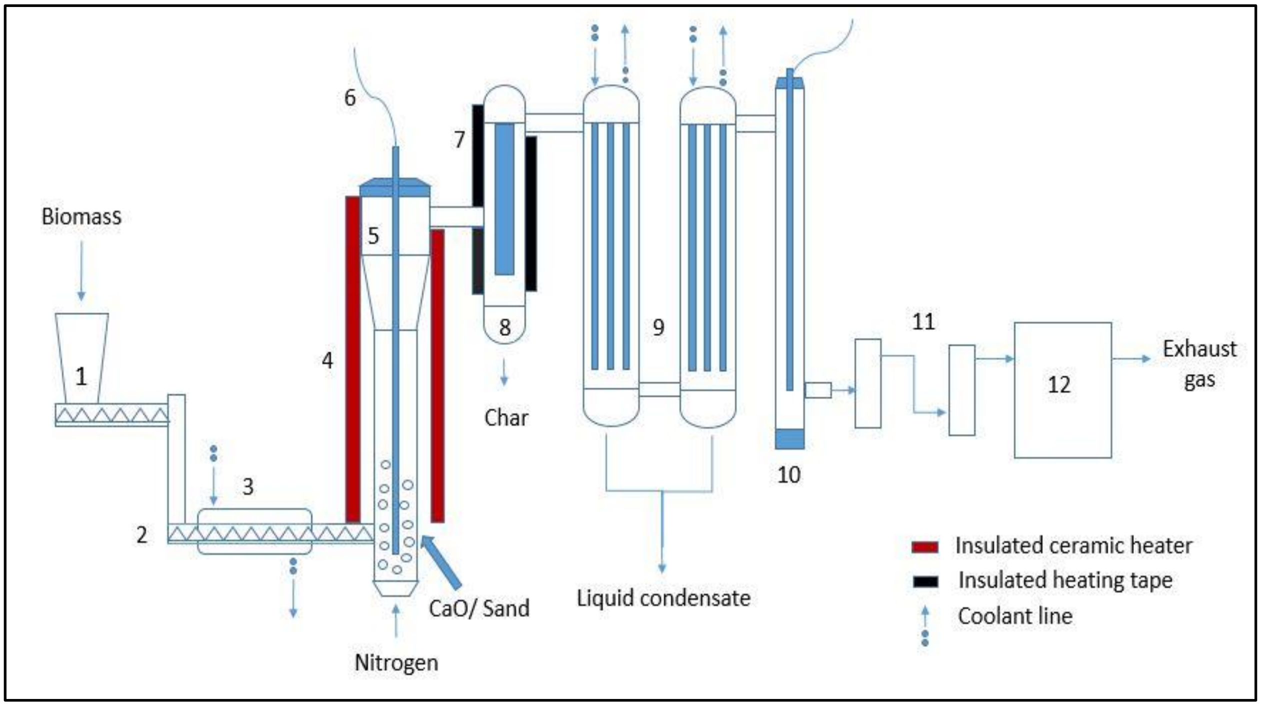


Figure 3.1: Schematic of bench-scale fluidized bed pyrolysis setup: 1, hopper; 2, injection screw; 3, heat exchanger; 4, pyrolysis heater; 5, reactor; 6, thermocouple; 7, filter heater; 8, high temperature filter; 9, condensers; 10, electrostatic precipitator; 11, moisture absorbers; 12, gas analyzer for CO, CO_2, CH_4 and H_2

The poplar chip sample used for the experiment was obtained from ForestConcepts, LLC. (Auburn, WA). The poplar chip was processed through Crumble M24 rotary shear two times to get uniformity in chip size. The samples were screened with a mesh 30 + pass and mesh 60 - no pass. The initial moisture content of wood was 16.75%. The particle size distribution of poplar biomass can be seen in Figure 3.2.

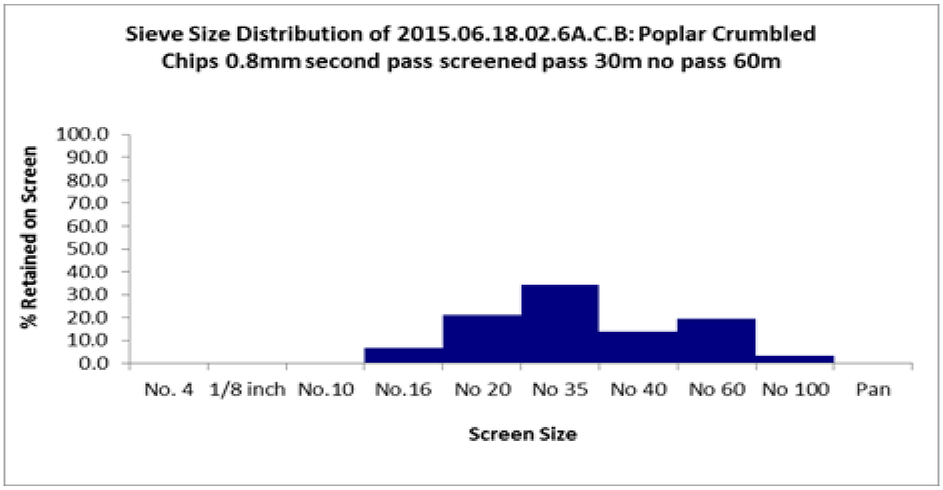


Figure 3.2: Sieve size distribution of poplar

3.2.2. Hydrodeoxygenation

Bio-oil obtained from ESP underwent batch hydrodeoxygenation reaction employing 450 ml bench-top Parr reactor in presence of Pt/C (5 wt. % Pt on C), ZSM-5 and control (H_2 only). The mini bench top reactor (Parr model 4567) can withstand a pressure of 2950 psi at 350 ^oC. The reactor consists of a glass liner, vessel, governable stirrer and heating mantle. A number of parameters such as internal temperature, vessel pressure, stirrer speed were monitored using a controller (Parr model 4843). Hydrogen and nitrogen were ultrahigh pure grade (99.999 %)

purchased from Airgas Inc. (Charlotte, NC). In each experiment, 1 g of catalysts was loaded and purged with nitrogen thrice to create inert environment inside the reactor. ZSM-5 was initially calcined for 2 hr at 550^{o}C prior before reducing it in Parr reactor. Hydrogen was purged three times in order to confiscate residual nitrogen and initial hydrogen pressure was maintained at 1000 psi for reduction. Catalysts was reduced at 300^{o}C for 1 hr in presence of hydrogen and subsequently cooled down to room temperature followed by purging with nitrogen. Approximately 36 g of bio-oil was carefully loaded in the reactor in presence of argon to prevent oxidation. Nitrogen gas followed by hydrogen gas were again purged once the vessel was connected with the main frame. The hydrogen pressure was maintained at 700 psi and heated to 300^{o}C at 500 RPM for 4 hr. For the control experiment, 36 g of bio-oil was loaded without any catalysts and followed the same experimental parameters. After the experiment, the reactor was cooled down to 21^{o}C, internally by flowing chilled water through cooling chambers and externally by fan. Final pressure was recorded in order to identify the pressure created by the residual gas formation during the experiment. Initial and final mass of the reactor, glass liner, catalysts and products fractions were recorded. Products remained on stirrer and cap of the reactor were wiped out by paper and included in final mass. The liquid product from the reactor was decanted in a separate vial while the slurry portion was mixed with acetone and collected on a separate vial. The liquid fraction was vacuum filtered to obtain upgraded oil while slurry mixed with acetone was vacuum filtered to obtain solid as product. Organic phase/ acetone mixture filtrate were separated by IKA rotary evaporator operated at 50^{o}C and 556 mbar to obtain extracted oil. All experiments were performed in duplicates.

3.2.3. Bio-oil analysis

The upgraded bio-oil were analyzed for higher heating value (HHV), water content, total acid number (TAN), simulation distillation and chemical composition. Higher heating value was measured using approximately 0.5g of bio-oil in an IKA C2000 bomb calorimeter. Fourier Transform Infrared (FTIR) spectroscopic was performed using Thermo Nicolet iS10 (Thermo Scientific, Waltham, MA). The sample were analyzed for 32 scans, between 4000 to 700 cm $^{-1}$ at a resolution of 4 cm $^{-1}$. The results obtained from FTIR were improved in Spectra 10 software and evaluated in Microsoft excel.

Water content of bio-oil was performed using Karl Fischer titration method. Mettler Toledo V20 was used for evaluating water content of bio-oil. Combititrant 5 keto as titrant and Combisolvent keto (EMD Millipore) as solvent were used for analysis while calibration was done using deionized water. Thermogravimetric (TGA) analysis was performed using PerkinElmer Pyris TGA with 20 μL alumina crucible. Around 9.1 g of sample was carefully loaded in crucible and heated from below 25^{o}C to 600^{o}C at a heating rate of 20 ^{o}C/min in the presence of nitrogen, flowing at 20 mL/min.

Boiling point distribution of upgraded bio-oil was performed using Agilent 7890A GC, equipped with split and splitless inlet, Agilent DB-2887 column (10 m × 0.53 mm, 3.00 μm), and a FID detector following standard procedure of ASTM D2887. Upgraded bio-oil were diluted with carbon disulfide to 1% with a split ratio of 1:2. The program was sequenced to start from 40^{o}C with a heating ramp of 20^{o}C/min to 350^{o}C with helium as carrier gas flowing at 14 mL/min. FID was set to operate at 350^{o}C and equipment was calibrated with standard mixture purchased from Ultra Scientific and Restek. Mettler Toledo T50 Titrator was used to measure ASTM D664.

Samples were sent to Mississippi State University for ultimate analysis in order to determine the elemental composition of biomass as well as bio-oils.

Chemical composition of upgraded bio-oil was evaluated using an Agilent 7890 GC/5975 MS equipped with a DB -1701 column (30 m × 0.25 mm, 25 µm). Each sample was prepared by diluting approximately 150 mg of upgraded bio-oil with 3 mL of methanol and 7 mL of dichloromethane. The initial temperature of the column was maintained at 50^{o}C for 2 min and the temperature increased to 250^{o}C at a ramped rate of 3^{o}C/min. Ultrahigh-purity helium (99.999%) was purchased from Airgas Inc. (Charlotte, NC) and was used as carrier gas flowing at 1 mL/min. National Institute of Standards and Technology (NIST) mass spectral library data were used to compare and identify the compounds from the analysis.

3.2.4. Tribological tests

Bio-oils from ESP were first filtered using a 0.2 µm filter in order to remove the char particles present in the bio-oil. A Bruker/CETR UMT-3 was used to conduct the friction and wear test of the bio-oil on the test specimen as shown in Figure 3.3. About 1 ml of each lubricant sample was poured on the surface test specimen and a load of 50N was applied for 30 min. Bio-oil was placed on the contacting surface between the ball and the test specimen. Load was supplied through the ball making a point contact while each specimen was placed on the disk which was rotating at a speed of 63.7 rev/min. Base oils (HT-68 and HT-100) from Petro Canada were used as standards in order to compare the results from the test. The data was instantly obtained through the CETR data viewer software where coefficient of friction, time, loading condition and speed were obtained in a CSV file for exportation and analysis.

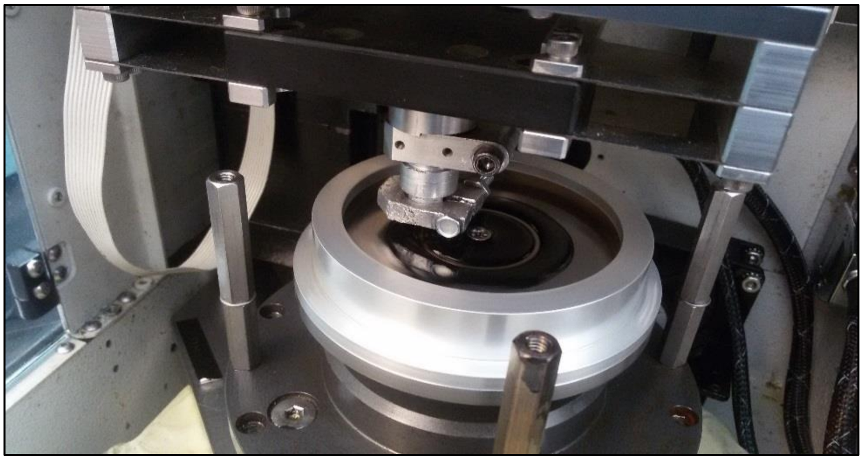
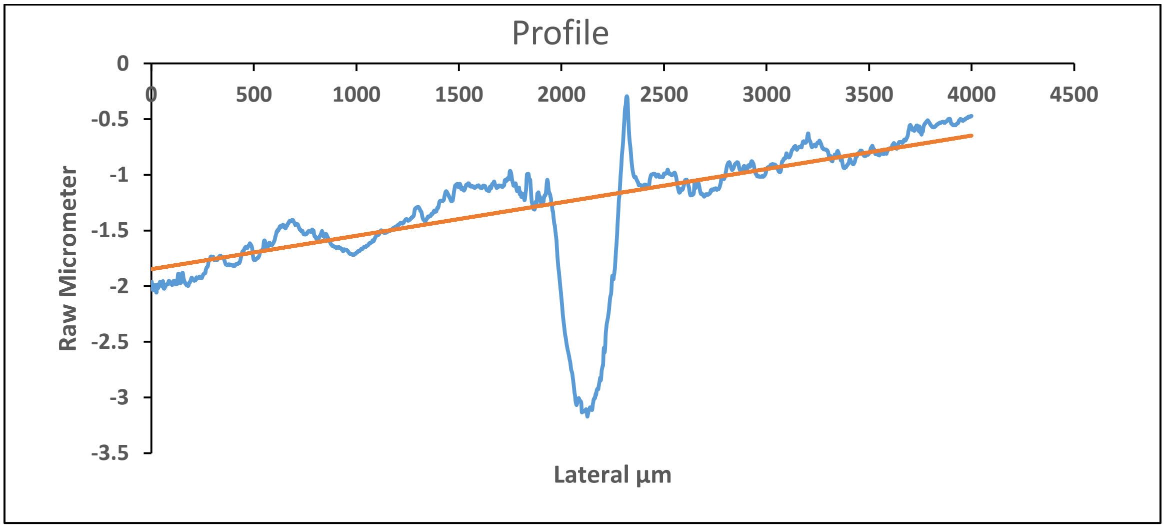


Figure 3.3: Friction test of bio-oil on Brunker/CETR UMT-3

A Veeco Dekatak 150 stylus surface profilometer was used to study the wear of the test specimen as shown in Figure 3.4 a. The machine is fitted with stylus tip which is slid across the worn part of the UMT test specimen. The stylus radius was 12.5 µm and the duration for the test was 45 sec with a force of 3.00 mg. The length of the radial measurement of each test specimen was 4000.0 µm. The data from the test were instantly obtained through Dektak software in a CSV format. The csv data were plotted in excel as shown in Figure 3.4 b. The dent between 1800-2500 µm was first removed from profile and rest of the data was fitted linearly. The dent and linear line was plotted separately for calculating the wear area between the dent and the fitted linear line in MATLAB. The wear area was thus multiplied by the radius to obtain wear volume.

a)



b)

Figure 3.4: a) Stylus profilometer Bruker/Vecco Dektak 150 and b) Profilometer data

3.3. Results and discussions

3.3.1. Biomass characterization

Proximate and ultimate analysis of biomass were performed for poplar which is depicted in Table 3.1. Poplar had higher amount of volatile component (82.59 wt. %), while ash content was pretty low (0.74 wt. %). Ultimate analysis shows that there is higher percentage of carbon present (47.94 ± 0.23) in bio-oil and significantly less amount of nitrogen present in bio-oil. The wt. % of oxygen in poplar is relatively higher and S wt. % is relatively low in poplar [88], so the remaining wt. % might include more of oxygen. The higher heating value was evaluated using bomb calorimeter and had an average value of 19.57 MJ/kg. These properties indicated that poplar could be used as feedstock for bio-oil production.

Table 3.1 Proximate and ultimate analysis of biomass

Proximate analysis (a.r)	**Analytical standard**	**Biomass**
Ash content (wt. %)	ASTM E1755	0.74 ± 0.69
Volatile matter (wt. %)	ASTM E872	82.59 ± 1.41
Moisture content (wt. %)	ASTM E871	4.171 ± 0.31
Fixed carbon (wt. %)	By balance	12.49 ± 0.77
HHV (MJ/kg)	Bomb calorimeter	19.57 ± 0.28
Ultimate analysis (a.r)	**Analytical instrument**	**Biomass**
C (wt. %)	Elemental Analyzer	47.94 ± 0.23
H (wt. %)		6.16 ± 0.02
N (wt. %)		0.57 ± 0.40
Remaining (wt. %)	By balance	45.35 ± 0.18

a.r – as received, wt. – weight

3.3.2. Influence of catalysts on product distribution

The catalytic and non-catalytic bio-oil could be influenced by catalysts during hydrotreatment. A typical pressure and temperature profile with respect to time during hydrotreatment of non-catalytic bio-oil over Pt/C catalyst is shown in Figure 3.5. The temperature was set to 350°C with a ramping rate of 5°C/min. The pressure increased with increases in temperature along with the stirrer speed of 500rpm. There was rapid increase in pressure and reached its maximum (1080 psi) value within 1 h after which the pressure slight start to decrease. The trend is similar over other catalyst, however there were variations for maximum values of pressure.

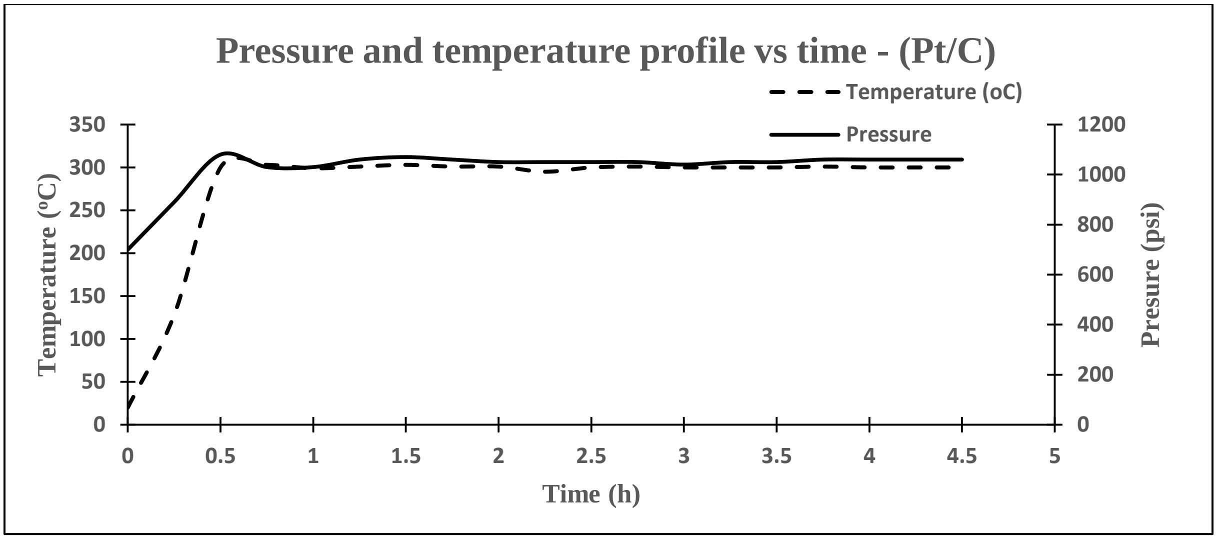


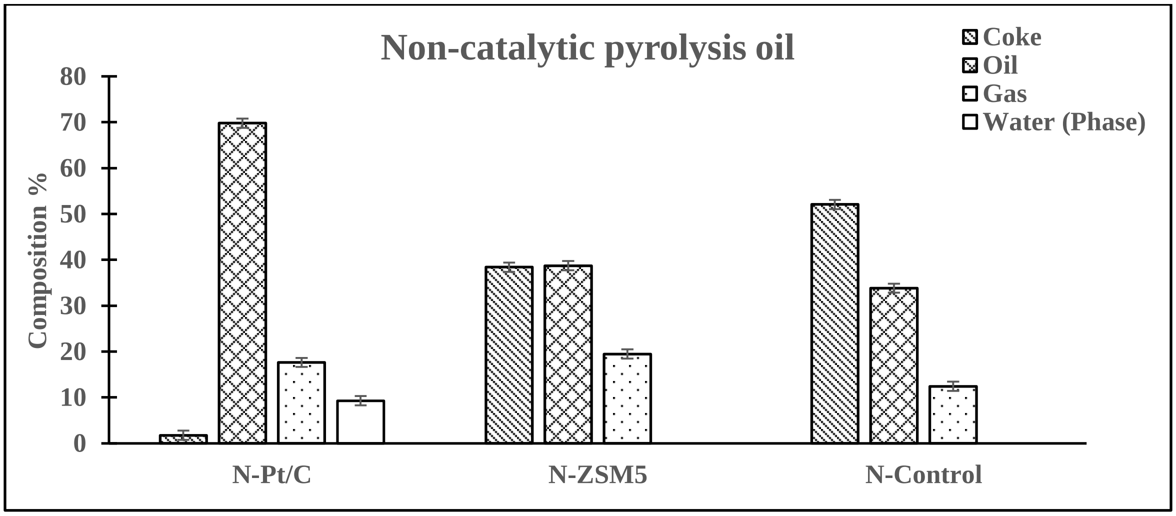
Figure 3.5: Pressure and temperature profile vs time for Pt/C (non-catalytic hydrotreatment)

The products obtained after upgrading were characterized in terms of gas, liquid and solids (coke). Figure 3.6 shows the effect of catalysts on product distribution obtained after upgrading of catalytic and non-catalytic bio-oils operated at 300°C with an initial hydrogen pressure of 700 psi. A complete mass balance was not possible due to experimental errors, loss of liquid during pressure relief, coke stuck at the immobilized reactor parts, losses while cleaning with solvents and also some losses while decanting the products. Lighter fractions were recovered from the glass liner while others were obtained from in between glass liner and vessel.

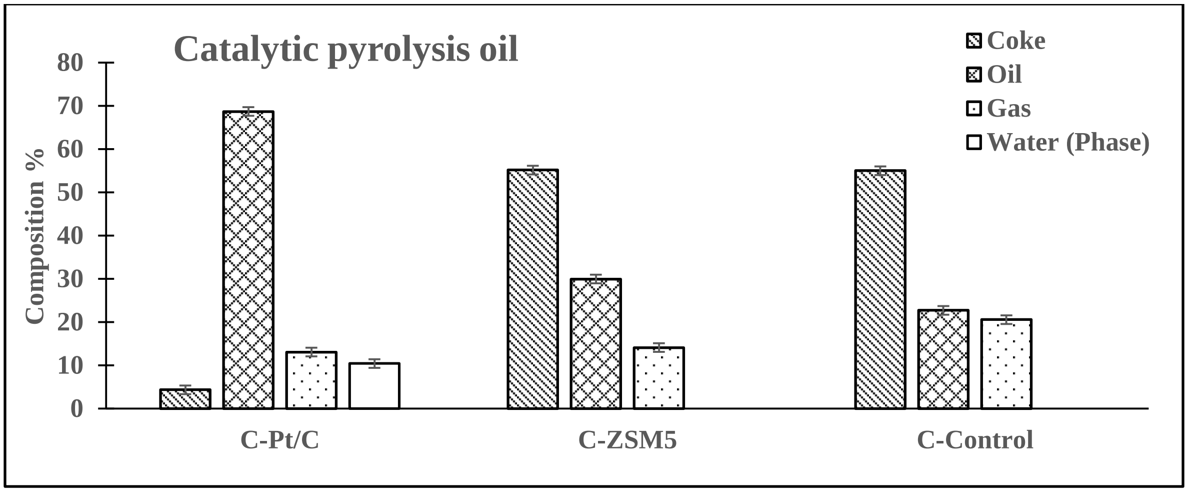
The liquid oil yield were comparatively higher while treating with Pt/C catalysts than ZSM-5 and control for both catalytic (68.67 wt. %) and non-catalytic (69.79 wt. %) bio-oil. Wildschut et al. [64] obtained higher bio-oil yield using Pt/C catalysts during mild hydrotreament (250^{o}C and 100 bar H_2 pressure for 4 h reaction time) while gas yield was higher using Pt/C catalysts during deep hydrotreatment (300^{o}C and 200 bar pressure for 4 h reaction time). They used bio-oil produced from beech wood for HDO and found that Pt/C consumed higher H_2 indicating higher decarboxylation actions for organic acids. In this study, there was formation of water phase for both type of bio-oils when upgraded with Pt/C which indicates hydrodeoxygenation reaction. It was referred as water phase since it included around 85.225 wt. % and 86.71 wt. % for non-catalytic and catalytic bio-oils respectively. The water phase product could be the lighter fraction of oil which were obtained during decanting glass liner, while heavier fractions were obtained between vessel and glass liner. There was no distinct water phase obtained during decanting with ZSM-5 and control experiment. The oil yields were lower for ZSM-5 (29.93 wt. %) for catalytic and (38.72 wt. %) for non-catalytic bio-oils. The reduction on oil yield could be because of deoxygenation, decarboxylation and decarbonylation reaction of bio-oil which might have been increased by acidic sites of zeolite thus resulting in the formation of more coke [89]. The oil yields were lowest for hydrogen experiment with 22.73 wt. % for catalytic and 33.81 wt. % for non-catalytic bio-oils, which indicates the influence of catalysts for oil yields.

The coke formation during hydrotreatment varies with the influence of catalysts. The coke formation was lowest for both catalytic (4.37 wt. %) and non-catalytic (1.75 wt. %) bio-oils when upgraded with Pt/C. This action of noble metal catalysts with carbon support on upgrading lignocellulosic bio-oil is similar to algal bio-oil which promote hydrogen adsorption and hydrogenation reaction leading to a reduction in coke formation [90]. Solid residue or coke formation was the highest for control (52.06 wt. %) using non-catalytic pyrolysis oil, indicating the catalytic effect on pyrolysis oil. However, the effect of catalysts (ZSM-5) on the coke formation was not observed in case of catalytic pyrolysis oil, since ZSM-5 and control had relatively similar values of around 55 wt. %. Kerstem et al. [91] found higher quantities of coke formation when ZSM-5 was used as catalysts for upgrading. They obtained improved bio-oil with low in acids, less corrosive, more stable due to decarboxylation of organic acids.

Gas formation was the highest for ZSM-5 catalysts (18.15 wt. %) with non-catalytically upgraded pyrolysis oil, while the lowest for control run (11.41 wt. %). The results were almost similar for catalytically upgraded pyrolysis oil as the control run showed the highest (18.95 wt. %) gas formation while Pt/C (11.64 wt. %) run had the lowest gas formation.



a)



b)

Figure 3.6: Product distribution after hydrotreatment: a) non-catalytic and b) catalytic pyrolysis oil

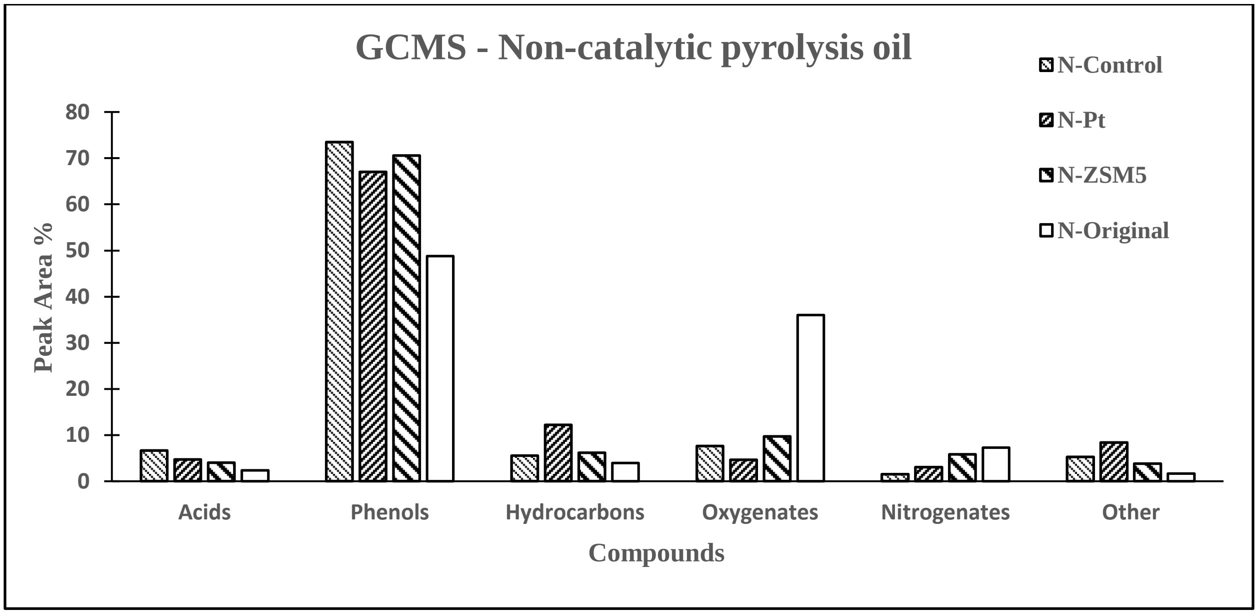
3.4. Influence of catalyst on bio-oil property

Hydrotreated fast pyrolysis bio-oils along with original ESP oils were analyzed in terms of elemental composition, moisture, TAN and HHV. Table 3.2 summarizes overall elemental composition, moisture, TAN and HHV of hydrotreated bio-oils. Carbon content of bio-oil were increase during upgrading process for both non-catalytic and catalytic oils. The remaining portion of from original biomass (45.35 wt. %) was reduced after hydrotreatment indicating reduction in oxygen and sulphur content. The TAN was comparatively lower for hydrotreated catalytic (52.58-58.08) than non-catalytic (53.45-89.93) bio-oil. The HHV value of catalytic original ESP (33.41 MJ/kg) bio-oil was higher than non-catalytic original (27 MJ/kg). In terms of HHV, the values for hydrotreated catalytic oils were similar to original catalytic bio-oils which is around 33 MJ/kg, while there is increase in hydrotreated non-catalytic bio-oil than original ESP (27 MJ/kg to 33.46 MJ/kg).

Table 3.2: Ultimate properties of upgraded bio-oil

Properties	**Non-catalytic pyrolysis oils**			
	Pt/C	**ZSM-5**	**Control**	**Original**
C (wt. %)	76.60 ±2.21	75.50 ± 3.76	73.19 ±0.43	62.55
H (wt. %)	9.22 ± 0.66	8.82 ± 1.22	7.90 ± 0.03	6.95
N (wt. %)	0.69 ± 0.28	0.64 ± 0.34	0.39 ± 0.02	1.27
Remaining (wt. %)	13.55 ± 3.08	15.09 ± 5.25	18.53 ± 0.36	29.23
Moisture (wt. %)	4.31 ± 0.34	8.68 ± 0.29	7.83 ± 0.2	4.17 ± 0.25
TAN	53.45 ± 0.42	89.93 ± 3.19	81.96 ± 1.45	131.46 ± 5.02
HHV (MJ/kg)	33.46 ± 0.29	31.15 ± 0.07	31.86 ± 0.29	27 ± 0.01
	Catalytic pyrolysis oils			
	Pt/C	**ZSM-5**	**Control**	**Original**
C (wt. %)	73.91 ± 0.44	74.44 ± 2.26	75.94 ± 1.71	64.79
H (wt. %)	8.59 ± 0.09	7.94 ± 0.03	7.88 ± 0.17	6.91
N (wt. %)	0.75 ± 0.36	0.42 ± 0.02	0.41 ± 0.03	0.43
Remaining (wt. %)	16.76 ± 0.71	17.21 ± 2.25	15.77 ± 1.57	27.87
Moisture (wt. %)	4.43 ± 0.27	5.99 ± 0.57	14.47 ± 0.68	3.68 ± 0.37
TAN	53.61 ± 0.88	58.08 ± 3.68	52.58 ± 3.94	107.53 ± 1.50
HHV (MJ/kg)	33.32 ± 0.06	32.74 ± 0.19	32.82 ± 0.40	33.41 ± 0.02

More than 100 compounds of bio-oils and upgraded oils were detected with GC/MS analysis based on their mass spectra with a NIST library. The GCMS peaks corresponding to different chemicals were chosen based on the area percentage exceeding 0.1% of total ion chromatogram. The bio-oil compounds were categorized into six major groups: acids, phenols, hydrocarbons, oxygenates, nitrogenates and others (compounds which could not be included in these major groups). Appendix A includes the list of chemical information categorized in each chemical group. Figure 3.7 depicts the peak area percentage of various compounds between upgraded oil, control oil (without catalysts) and original bio oil from ESP. One of the major compounds of bio-oils is phenols which are mainly derived from lignin having higher molecular weights and contribute to viscosity of bio-oil [92]. Heavy molecules of phenols are mainly cracked at a higher temperature (around 350^{o}C) and high pressure (around 1500 psi) where hydrogen solubility is high [73], while some phenolic ethers are reactive even at 300^{o}C. Since the experiment was carried out at 300^{o}C with initial hydrogen pressure of 700 psi, phenols might not have cracked and remained as higher proportion even after upgrading bio-oil in the presence of catalysts. There is a slight decrease in phenol when upgraded with Pt/C catalysts both in catalytic and non-catalytic bio-oil, which could be due to the reactivity action of phenolic ethers during hydrotreatment condition.



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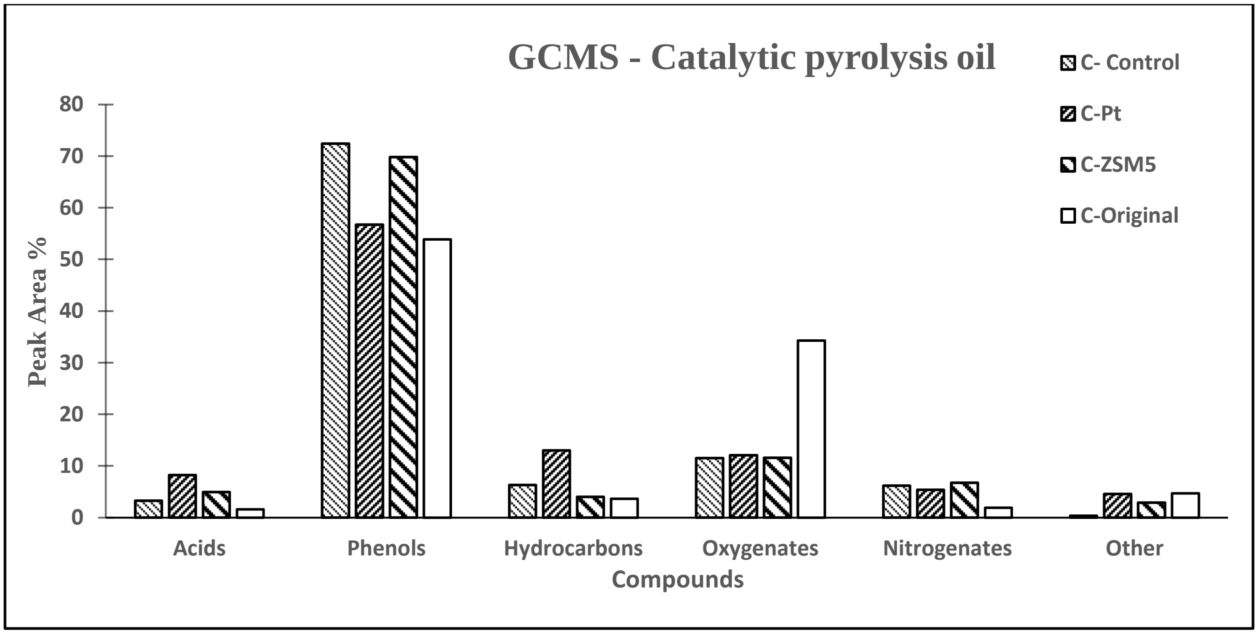


b)

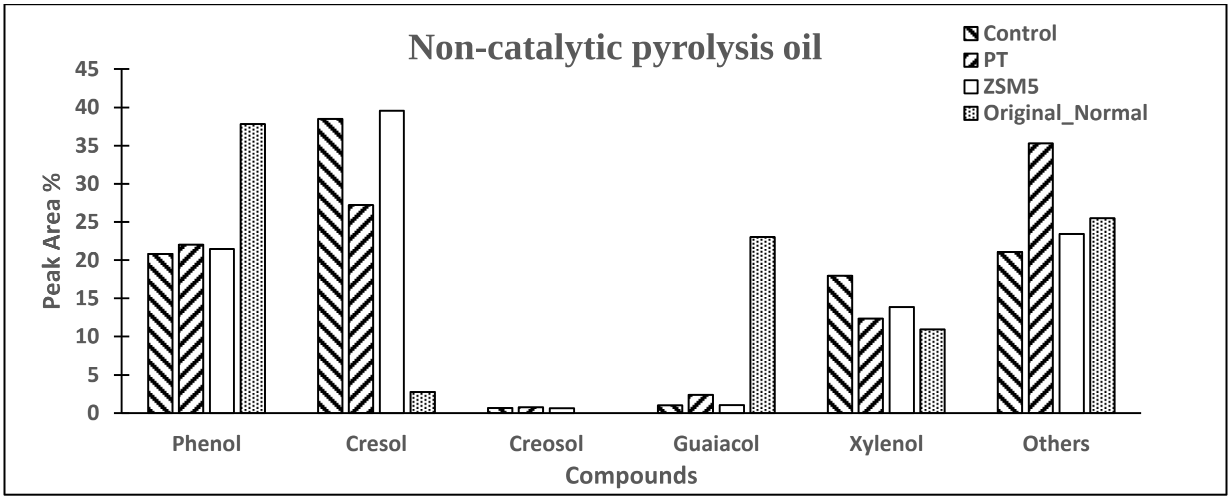
Figure 3.7: GC/MS results for a) non-catalytic and b) catalytic pyrolysis oil

Studies [25,26] showed that vapor phase as well as aqueous phase hydrodeoxygenation of phenols favors towards the hydrogenation route which reduces phenol, when treated with catalysts such as Pt, Pd and Ni. Noble metal catalyst helps to reduce the phenolic content during hydrotreatment on catalytic pyrolysis oil than non-catalytic pyrolysis oil. The catalytic pyrolysis oil contains more light chemical phenols than the non-catalytic oil. Subsequent upgrading process would help converting phenols to aromatic hydrocarbons [26]. The overall phenols have again been categorized to five different groups: phenol, cresol, cresol, guaiacol, xylenol and rest are placed into others as shown in Figure 3.8. The phenol content is decreased for both catalytic and non-catalytic bio-oils after hydrotreatment. The reason behind a decrease in phenol could be due to vapor phase and aqueous phase HDO, which favored more to catalytic hydrogenation route

[26,27]. There is an increase in cresol which may be due to an increase in light chemical compounds such as 2-methylphenol, 4-methylphenol, dimethyl and trimethyl. The reason for an increase in these light compounds may be due to the conversion of heavier oxygenated compounds to light ones over HDO process. Mahadevan et al. [26] also observed a decrease in heavier oxygenated compounds while an increase in lower oxygenated compounds when used with catalytic pyrolysis with CaO. HDO reaction is also converting higher oxygenated compounds to lower oxygenated compounds indicating the elimination of oxygen content from the compounds. Similarly, there is a decrease in xylenol when upgraded with catalyst indicating the conversion of higher oxygenate compounds to lower oxygenated compounds.

A higher amount of acids present in non-catalytic bio-oil were obtained than that in the catalytic pyrolysis oil, which was also reported in several studies [20,21]. Carboxylic acids are one of the major compound present in bio-oil which is responsible for acidic and corrosive property of bio-oils. Acids such as acetic acid, formic acid and butanoic acid are present in bio-oil which needs to be removed in order to make transportation biofuel. CaO has been an effective bed material as well as catalysts to convert acid vapors to ketones via ketonization reaction [96]. The total acid number of catalytic pyrolysis bio-oil and its upgraded one showed less as compared to that of non-catalytic pyrolysis bio-oil and its upgraded oils.

The overall oxygenate compounds in both the catalytic and non-catalytic bio-oil after upgrading decreased. The oxygenate compound is categorized into furans, aldehyde, ketones, anhydrosugars, anisole and rest are grouped into others. There is a reduction in furans in both non-catalytic and catalytic bio-oils compared to the control runs. Reports on the hydrotreatment of furans suggest that it follows both hydrogenation and direct deoxygenation routes in order to remove oxygen content [29,30]. This reaction mechanism could be the reason for the reduction of furans during hydrotreatment process. The amount of ketones in catalytic upgraded oil also decreased as compared to that in the non-catalytic bio-oils, which indicates a reduction in the overall oxygenate contents.



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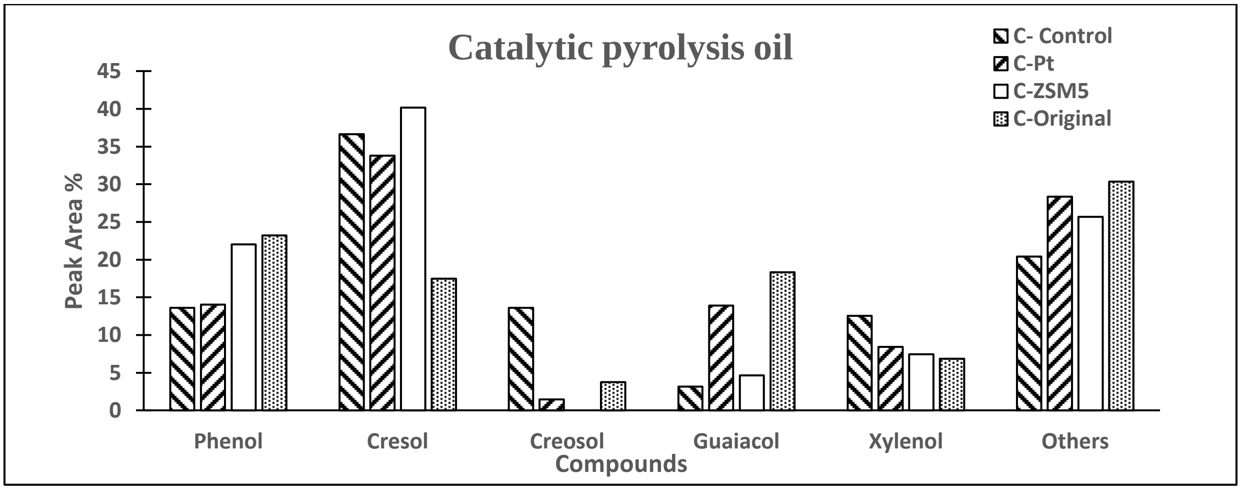
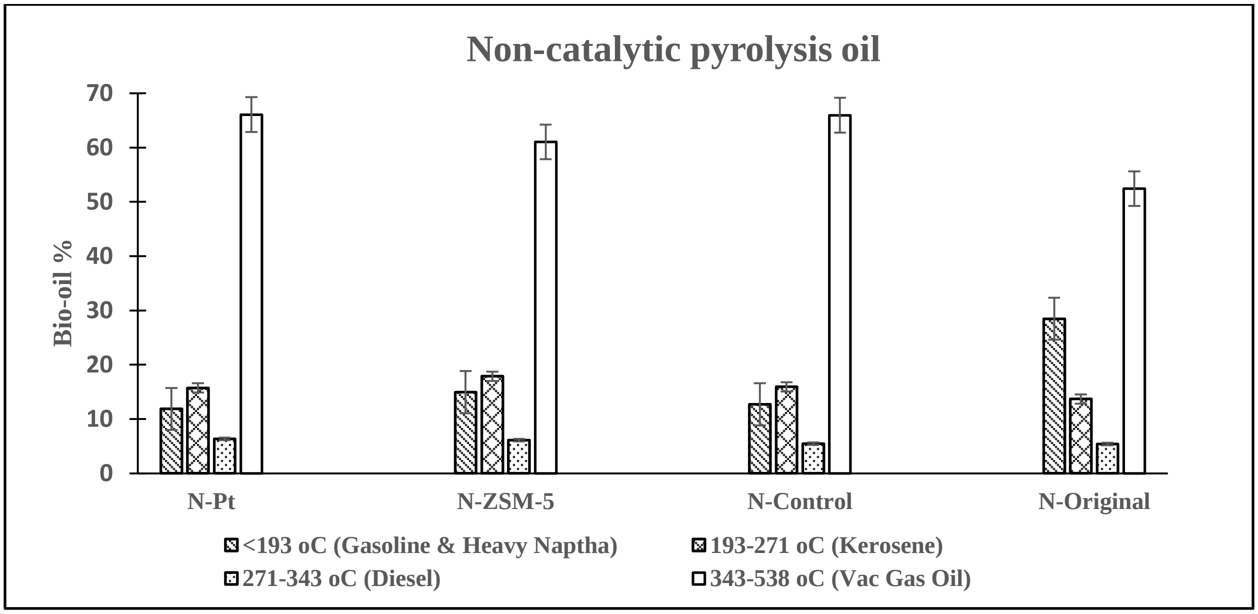


b)

Figure 3.8: Phenols composition for a) non-catalytic and b) catalytic pyrolysis oil

Boiling point distribution was mainly divided into four different groups – gasoline and heavy naptha range (<193^{o}C), kerosene range (193-271^{o}C), diesel range (271-343^{o}C) and vacuum gas oil range (343-538^{o}C) as shown in Figure 3.9. The highest fraction were for vacuum gas oil range (343-538^{o}C) for both catalytic and non-catalytic bio-oils. The ESP oils consists of heavier fraction which could be the reason for higher proportion of vacuum gas oil range. This trend for boiling point distribution were similar to medium oxygen content fraction from Christensen et al. [99]. The pyrolysis oil was upgraded using Pd/C which is still a noble catalyst and the results can be compared with Pt/C. The lowest fraction was for diesel range (271-343^{o}C) range which was similar in this experiment. Analyzing the boiling point distribution of catalytic and non-catalytic bio-oil, there is reduction on light and naptha (<193^{o}C) fraction of original bio-oil while slight increase in diesel range for control. The variation for the upgraded oil might not have been that prominent since the bio-oil used in both cases were from ESP which itself was heavier fraction.



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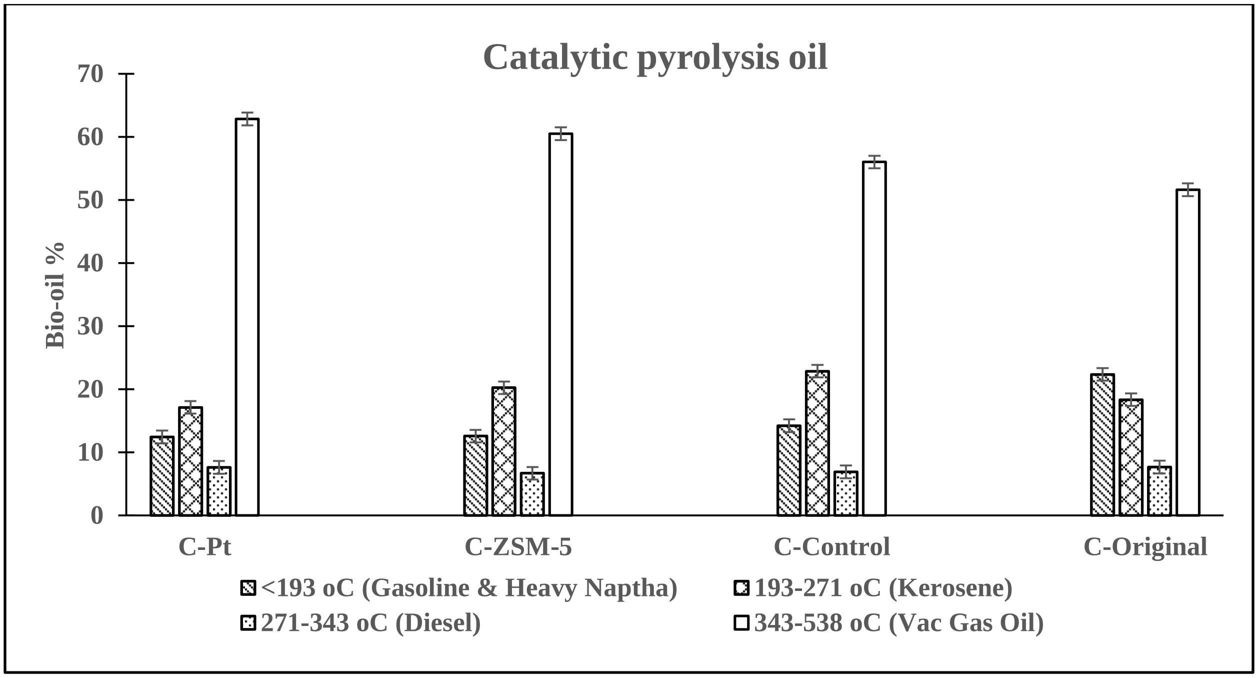
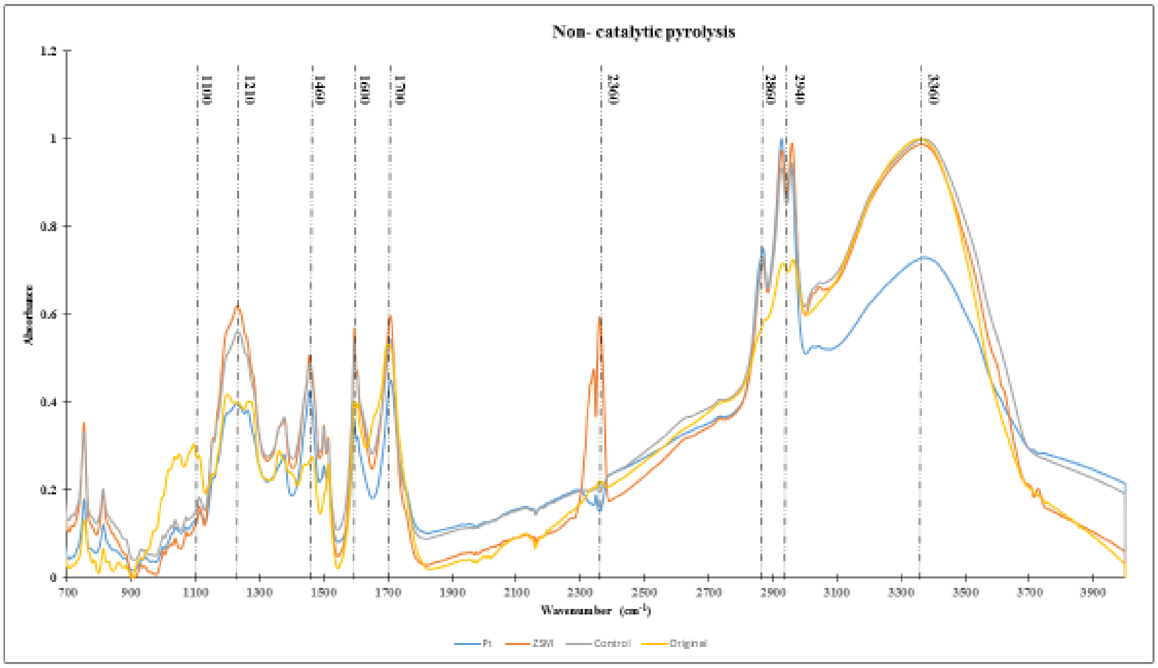


b)

Figure 3.9: Simulated distillation for a) non - catalytic and b) catalytic bio-oils

Figure 3.10 shows the FTIR data of non-catalytic and catalytic bio-oils along with original oils. The FTIR data here shows the functional groups in upgraded and original bio-oils. Significant stretching occurred at 3500-3100 cm $^{-1}$ which confirm O-H functional group. There is lack of band peak in between 3100-3000 cm $^{-1}$ (aromatic C-H stretch) region. The peaks present in 1600-1450 cm $^{-1}$ region indicates the presence of C-C stretching vibration. The peaks in between band of 1300-1000 cm $^{-1}$ represent in-plane bending vibration of aromatic-hydrogen. The stretching observed between 3000-2800 cm $^{-1}$ represents antisymmetric and symmetric stretching of C-H bonds. The peaks present in bands of 900-650 cm $^{-1}$ region represents out-of-plane bending vibration of aromatic-hydrogen. The presence of oxygenated compounds is confirmed by the large peak of intermolecular hydrogen bond O-H stretching vibration at 3360 cm $^{-1}$, along with in-plane bending at 1220 cm $^{-1}$ and out-of-plane bending at 720 cm^{-1}. The upgraded oil in presence of Pt/C catalyst has some reduced stretching for both catalytic and non-catalytic oils indicating removal of phenols, which resembles with the results from GC/MS. Ketonic functional group is confirmed by 1700 cm^{-1} stretching vibration which is also identified in GC/MS data. The stretching vibration of C-H at 2860 and 2920 cm $^{-1}$ confirms the paraffinic structure of bio-oil and stretching at 1460 and 1500 cm $^{-1}$ refers to methyl and methylene groups. The FTIR data here represents the presence of phenolic (alcoholic groups), ketonic and carboxylic functional groups. The overall pattern of both catalytic and non-catalytic upgraded oil is almost similar except the reduction on stretching vibration for Pt/C upgraded bio-oils.



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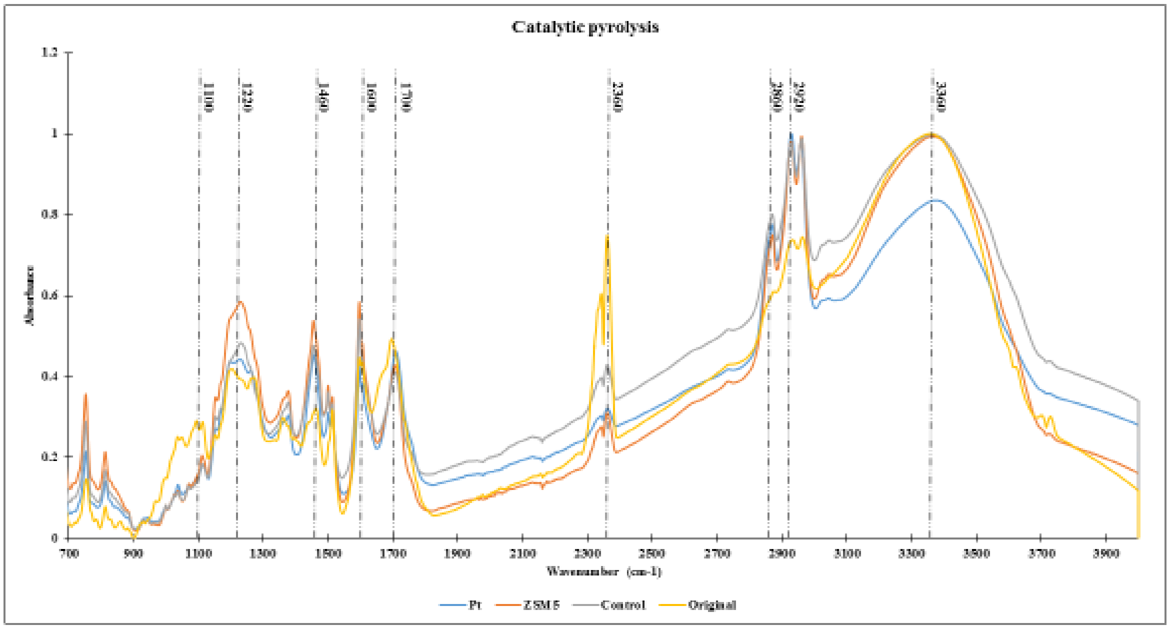
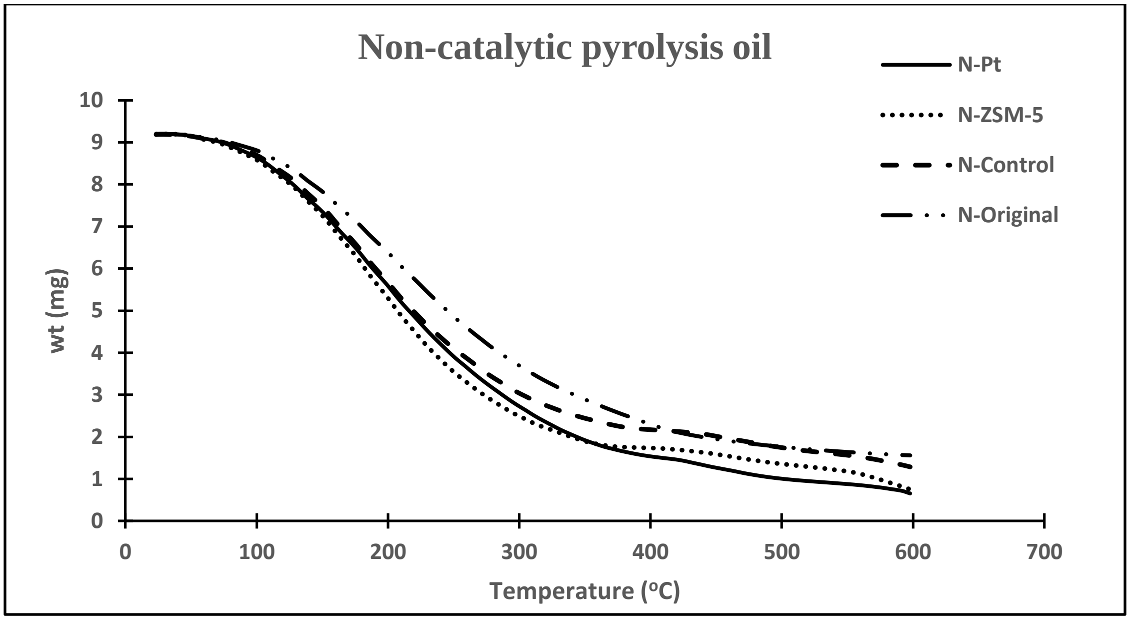


b)

Figure 3.10: FTIR data for a) non- catalytic and b) catalytic pyrolysis bio-oils

The thermogravimetric analysis of bio-oil represents the mass loss with temperature as shown in Figure 3.11. Major mass loss occurred below 400°C, and the residue of all samples were below 2 mg when the temperature reached 600°C. The lowest residue was for Pt/C run in both catalytic and non-catalytic experiments while the highest residue was for original bio-oils. The mass loss rate information is given by DTGA curve shown in Figure 3.12. The majority of mass loss rate occurred in the temperature range of 25 – 400°C and suppressed thereafter. The maximum mass loss was for the original oil of catalytic bio-oil which supports the results from the simulated distillation where comparatively less fraction of vacuum gas oil was present so that most of the gasoline, diesel and kerosene range were burned out.



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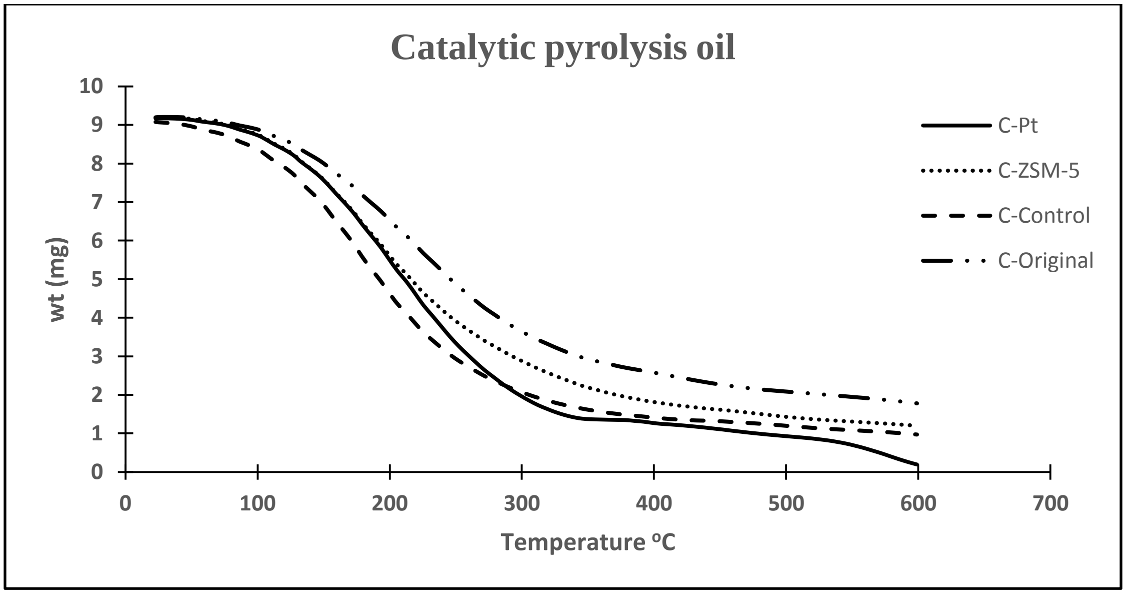

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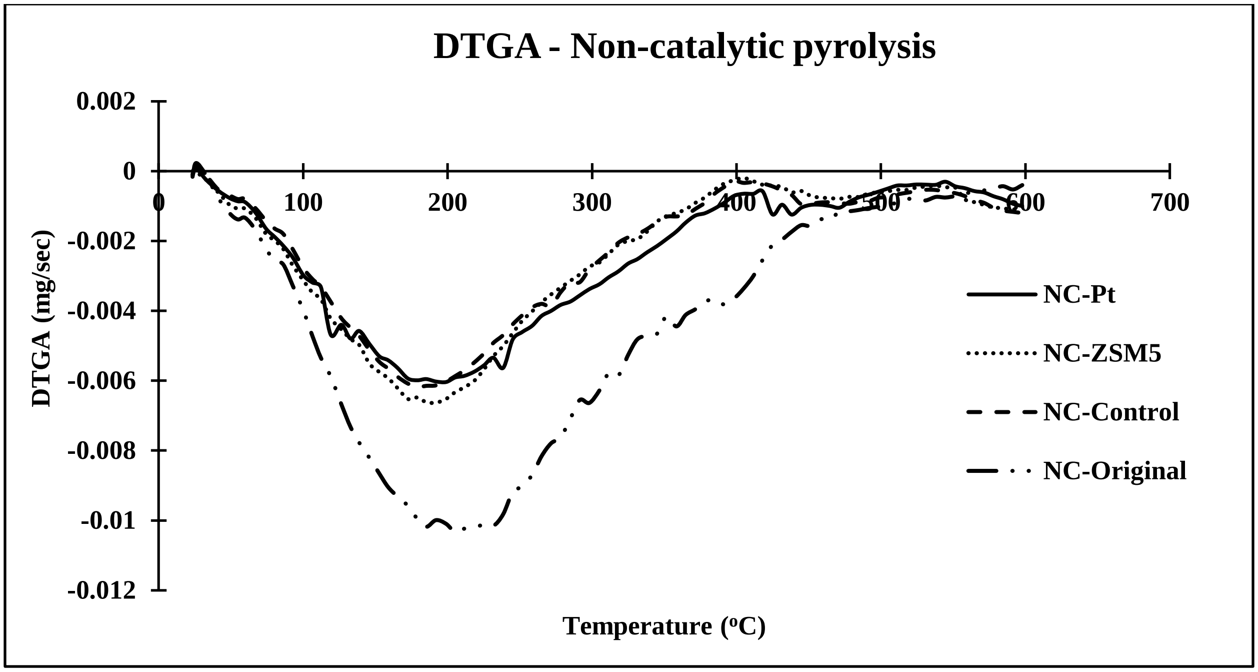
Figure 3.11: TGA data for a) non-catalytic and b) catalytic pyrolysis bio-oils



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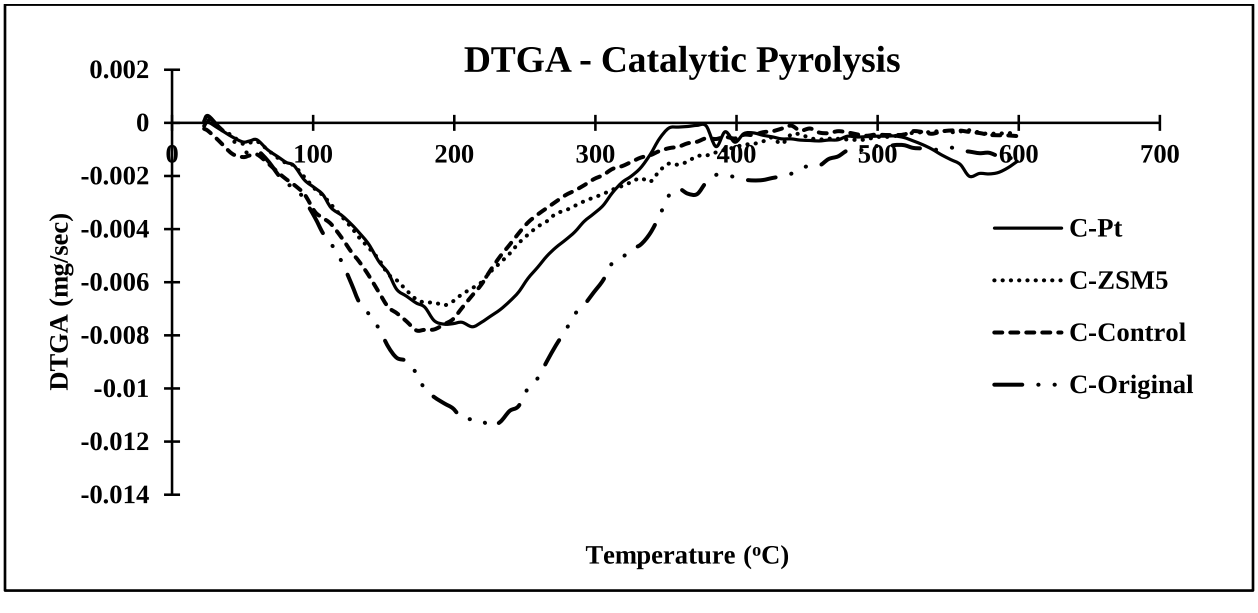
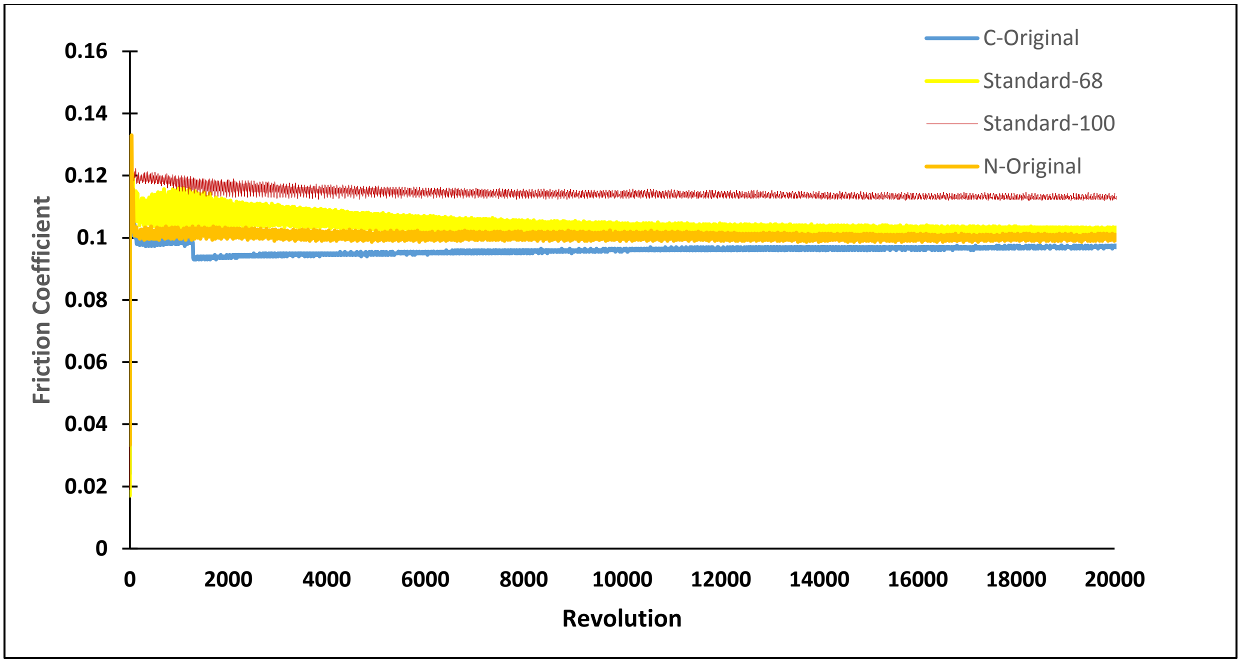


b)

Figure 3.12: DTGA data for a) non-catalytic and b) catalytic pyrolysis bio-oils

3.5. Influence of oils on tribological properties

The friction and wear behaviors of the original ESP oils were analyzed and compared with the standard base oils. Base oils are the lubrication grade oils that are initially produced from refining crude oil to improve the performance without any additives. The kinematic viscosity of catalytic bio-oil was measured as 65.076 ± 0.302 cSt and non-catalytic bio-oil was 98.225 ± 0.302 cSt at 40^{o}C. The base oils (ISO-68 and ISO-100) were obtained from Petro Canada based on the viscosity of bio-oils at 40^{o}C. Figure 3.13 represents the comparison of the measured friction coefficients between bio-oils and standard base oils. It can be clearly seen that the bio-oils had slightly lower coefficient of frictions than the base oils. This contradicts the result from Xu et al.'s study where the bio-oil had an unstable friction coefficient [85]. The reason could be the removal of char particles and a heavier fraction of ESP bio-oil which could have formed a film layer on the surface. The film on the surface could have reduced any solid contact between surfaces. Both catalytic and non-catalytic bio-oils were stable and there coefficients of friction were slightly lower than the standard base oils which indicates that they could have a promising future as a lubricant base oil. From the FTIR, it is clear that there is the presence of slightly higher ketonic groups in catalytic bio-oils than non-catalytic. These polar ketonic groups can be easily adsorbed onto metal surfaces and form a thin oil film between the surfaces, which could be the reason for the slightly lower friction coefficient of the catalytic bio-oil than non-catalytic bio-oil [100]. Another reason could be also due to the lower viscosity.



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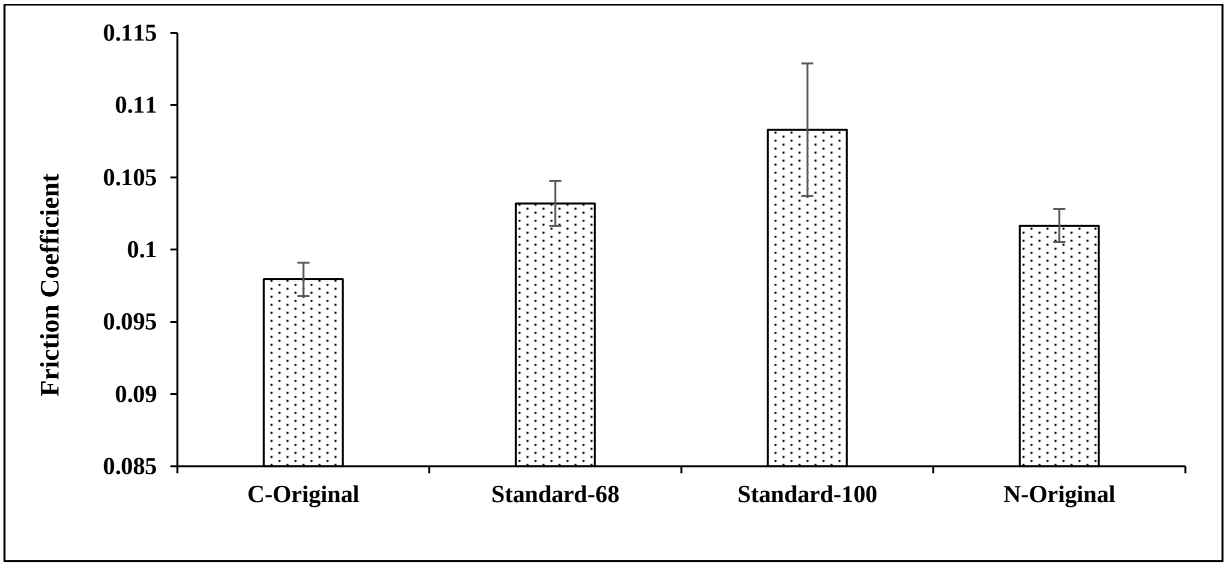

b)

Figure 3.13.: a) Comparison of friction coefficients between original bio-oils and standard base oils and b) average value of coefficients of friction

The test specimens from the UMT-3 were analyzed for wear by using the stylus profilometer. The surface profile was used to evaluate the cross-sectional area of the wear groove. The wear volume were calculated as described in section 2.9.2. The catalytic bio-oil performed better in terms of wear since it had the lower wear volume where as a standard (base oil – 68) had the highest wear volume as shown in Figure 3.14. Therefore, the bio-oils performed better than the standard base oils. The reason could be the adsorption film formation on the surface due to heavier fraction of ESP bio-oil preventing higher contact between two surfaces.

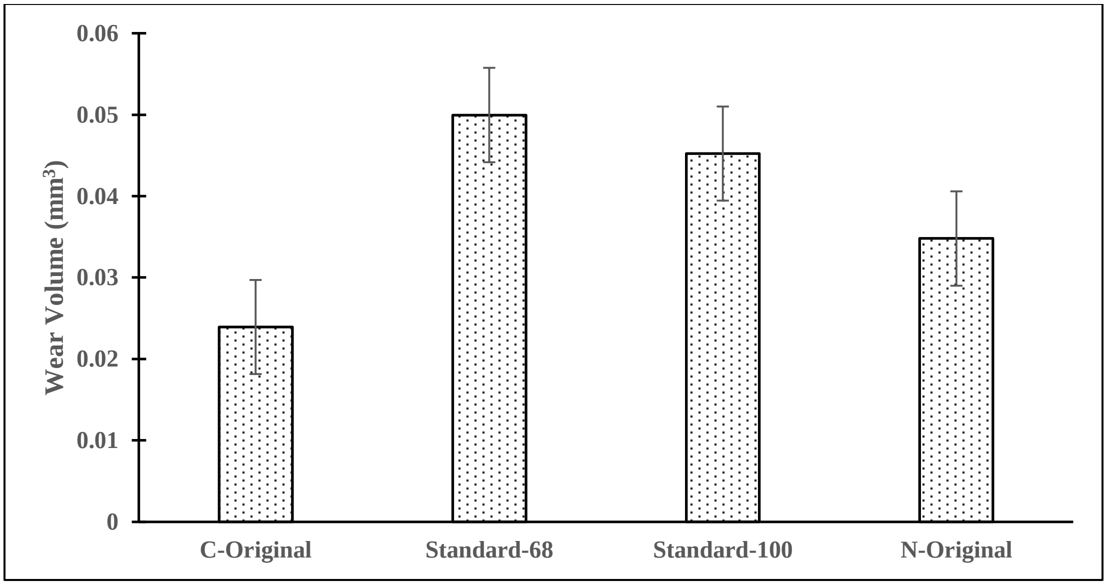

Figure 3.14: Comparison of wear between original ESP bio-oils and standard base oils

3.6. Conclusion

Upgrading operation was carried out in a Parr reactor in three different conditions: Pt/C, ZSM-5 and control (without catalyst), where Pt/C proved to be a better catalyst in terms of bio-yield production. Among the catalyst tested, ZSM-5 was observed to be mild catalyst, which did not have a distinct role in product distribution and results were comparable to control experiment. In terms of chemical composition, phenols were dominant in both the upgraded bio-oils, while oxygenates were reduced compared to the original ESP bio-oils of both non-catalytic and catalytic pyrolysis. Upgraded catalytic pyrolysis bio-oils had reduced TAN value than original ESP bio-oil in all three conditions which indicates the reduction in acidic nature of catalytic pyrolysis bio-oil. Viscosity of original catalytic ESP bio-oil was less than non-catalytic original ESP bio-oil which indicates positive step towards commercial bio-fuels production. Original catalytic pyrolysis bio-oil had a lower friction coefficient and wear volume than the standard base oils representing a positive lubricity property of the bio-oil.

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CHAPTER FOUR

Summary and Future Directions

4.1. Summary

Bio-oil production from in-situ catalytic fast pyrolysis process has been presented as an effective method to improve bio-oil properties. In this process, catalyst is used as the bed material and vapor phase catalytic upgrading action occurs during combustion process to convert solid biomass into non-condensable gases, bio-oil (reduced acidic) and solid residue often termed as char. The main objective of this study was to understand the effect of catalytic pyrolysis bio-oil during hydrotreatment. The specific objectives of this study were to: (i) analyze the product distribution of non-catalytic (quartz sand) and catalytic (CaO) pyrolysis bio-oil upgraded over two different catalyts: Pt/C, ZSM-5 and control (without any catalyst); (ii) compare the properties of upgraded bio-oils; and (iii) compare friction and wear behavior of the catalytic and non-catalytic original ESP bio-oils.

Two types of bio-oils were produced using poplar as biomass in a fluidized bed reactor with quartz sand and CaO as bed material, respectively. The reactor was maintained at 500^{o}C to convert biomass into solid char, condensable vapors and non-condensable gases. Condensable vapors turns to form bio-oil and for this study, bio-oil present at the bottom part of ESP were used for hydrotreatment. Hydrotreatment process was performed in a Parr reactor maintained at 300^{o}C for 4 h over Pt/C, ZSM-5 and control (without any catalyst) conditions. Maximum bio-oil yield for non-catalytic (69.79 %) and catalytic (68.67 %) were obtained when hydrotreated over Pt/C catalyst. This may be because H_2 was consumed in order to eliminate oxygen compounds which helped to improve bio-oil properties. A distinct water phase obtained during hydrotreatment over Pt/C, which indicates that Pt/C was able to reduce oxygenates present in bio-oil. The reduced stretching vibration at 3360 cm^{-1} during FTIR test also indicates effectiveness of Pt/C catalysts. This study also shows that ZSM-5 was not effective in terms of product distribution since the results were similar to control experiment for catalytic bio-oil. Bio-oils obtained after hydrotreatment were analyzed for TAN and found that the upgraded catalytic bio-oils had reduced TAN then non-catalytic upgraded bio-oils. The TAN value was less for original ESP bio-oil of catalytic fast pyrolysis bio-oil than its counterpart non-catalytic one. This indicates that the vapor phase catalytic upgrading in fluidized bed reactor helped to reduce the acidic nature of bio-oil during combustion process. The original ESP bio-oils along with upgraded bio-oils were analyzed for heating value, and it was observed that the catalytic original ESP bio-oil (33.41 MJ/kg) were higher than the non-catalytic original ESP (27 MJ/kg) one. The HHV of upgraded non-catalytic bio-oil had maximum value of (33.4 MJ/kg) while it was similar to upgraded catalytic pyrolysis bio-oil. There was no significant increase in HHV of upgraded catalytic bio-oil than catalytic original ESP bio-oil since the values were within the periphery of 33 MJ/kg. This could be because hydrotreating action could not crack strong bonds, since bio-oil contains higher proportion of heavier fractions. This reason is supported by GCMS data which includes higher proportion of phenols. There was reduction in oxygenates of upgraded bio-oils than original ESP bio-oils which indicates the hydrotreating action. Also, there was slight increase in hydrocarbons when upgraded over Pt/C catalyst which supports its effective role during hydrotreatment.

The simulated distillation results also shows the presence of heavier fraction of bio-oil since more than 50% boiling point distribution falls in vacuum gas oil range. Another significance of simulated distillation was that the original ESP bio-oil had relatively higher proportion of gasoline and heavy naptha range while upgraded oils had higher proportion of kerosene range. Viscosity of catalytic original ESP bio-oil were less viscous (68.072 cSt) than non-catalytic original ESP (98.225 cSt), which leaded to friction and wear tests. The results obtained from the tribological tests showed that catalytic original ESP bio-oils were better than non-catalytic original ESP and standard oils. Friction coefficient were less than 0.1 while wear volume was 0.029 mm^3, which was comparatively lower than other oils.

4.2. Future Directions

In-situ catalytic pyrolysis has been studied extensively in order to improve the properties of bio-oil and to make the overall conversion process efficient and economically viable. But there are still problems associated with the properties of catalytic fast pyrolysis bio-oils. So, this research helps to reduce the knowledge gap in literature about how hydrotreating catalytic fast pyrolysis can influence its properties compared to upgraded non-catalytic fast pyrolysis bio-oil. This study helps to build a bridge about the possibility of using lignocellulosic bio-oil as lubricating oil which is still in its naïve stage. The knowledge gained from this research would be helpful to further explore the possibility of improving bio-oil properties and also towards its application. The following topics are recommended for further studies.

- Biomass exploration

This study was conducted using poplar as biomass, however there are lots of biomass such as pine, switchgrass, douglas fir, eucalyptus which can be used to perform the experiment. The results obtained from different biomass would be compared with this research and help to identify the higher liquid yielding biomass with better bio-oil properties.

- Changing experimental parameters

  In this study, the hydrotreatment operation was conducted in a Parr reactor which could withstand only 2100 psi at 350°C, which restricted the flexibility of operating at higher temperatures and pressures. This upgrading process can be performed at higher temperature (320°C or 350°C) which could crack heavier fraction of bio-oil and could give different results. Another parameters which could be modified is the initial hydrogen pressure which is 700 psi in this study. The initial pressure of hydrogen can be increased to 1000 psi which would make the availability of hydrogen during hydrotreatment. The reaction with higher pressure and higher temperature could bolster cracking and hydrotreating operation in order to improve the bio-oils properties. Another key parameters which could be explored is the residence time since this study was only conducted for 4 h. The variation in residence time to maintain WHSV of 0.5 can be used as reference and results could be analyzed which would help to identify the optimum residence time for conducting further research.

- Using solvents during hydrotreatment

This study included only ESP bio-oil for upgrading process however, solvent addition such as cyclohexane, isoparafin, hydrocarbon solvent (dodecane) could be used along with bio-oil. This action could help to extract the organic components of bio-oil and improve its properties. Researchers have used supercritical water for hydrotreatment which could be another possible pathways.

- Exploring catalyst

  This study included only two types of catalyst Pt/C and ZSM-5 however, numerous catalyst are available in order to explore this experiment. Sulphide/oxide catalysts (Co-MoS_2, Ni-MoS_2); metal catalysts (Pd/C, Ru/C, Pt/Al_2O_3) could be used to explore properties of bio-oil upgraded over these catalyst.

- Test condition for friction and wear

  In this study, the friction test were performed using only 50 N load for 30 min at room temperature. However, bio-oil performance for longer duration of time could be an interesting topic to explore regarding friction test. Another approach could be changing the loading condition such as 100 N, 150N could be used to explore the friction and wear test of the bio-oil and also the temperature of the bio-oil could also play significant role in friction test followed by its wear analysis.

Appendix A

Furans	Aldehydes	Ketones	Phenols	Hydrocarbons	Acids
Benzofuran, 2-methyl-	Benzeneacetaldehyde, 2-methoxy-.alpha.,5-dimethyl-	1H-Inden-1-one, 2,3-dihydro-3,4,7-trimethyl-	Phenol	Indan, 1-methyl-	Butanoic acid
Dibenzofuran	1,4-Benzenedicarboxaldehyde, 2,5-dimethyl-	1(2H)-Naphthalenone, 3,4-dihydro-5,8-dimethyl-	Phenol, 2-methoxy-	1H-Indene, 2,3-dihydro-1,3-dimethyl-	Benzoic acid, methyl ester
Benzofuran, 3-methyl-2-(1-methylethenyl)-		Butyrolactone	Phenol, 2-methyl-	Benzene, (2-methyl-1-butenyl)-	n-Hexadecanoic acid
Furfural		Ethanone, 1-(2-hydroxy-5-methylphenyl)-	Phenol, 2,3-dimethyl-	1H-Indene, 2,3-dihydro-1,6-dimethyl-	Heptadecanoic acid, 16-methyl-, methyl ester
Furan-2-methyl			Benzeneethanol, 3-hydroxy-	Naphthalene, 1-methyl-	
4-methyl furan			Phenol, 2-methoxy-4-methyl-	Naphthalene, 2,3-dimethyl-	
Benzofuran			Phenol, 2-ethyl-4-methyl-	Naphthalene, 2,3,6-trimethyl-	
2-Dibenzofuranol			Phenol, 2,4,6-trimethyl-	Benzene, 1-methyl-2-[(4-methylphenyl)methyl]-	
			Phenol, 4-(1-methylethyl)-	7,8-Diphenylbicyclo[4.2.1]nona-2,4,7-triene	
			Phenol, 2-ethyl-4,5-dimethyl-	Anthracene, 2-methyl-	
			Thymol	Heptadecane	