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Improving bio-oil quality and stability based on capping reactions

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Improving bio-oil quality and stability based on capping reactions

by

Wenqi Li

A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Major: Mechanical Engineering

Program of Study Committee:
Xianglan Bai, Major Professor
Arthur Winter
Mark Mba-Wright

Iowa State University

Ames, Iowa

2016

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DEDICATION

Dedicated to my beloved mom for her love, endless support, encouragement and sacrifices.

TABLE OF CONTENTS

	Page
DEDICATION	ii
NOMENCLATURE	iv
ACKNOWLEDGMENTS	v
ABSTRACT	vi
CHAPTER 1 INTRODUCTION	1
1. Overview of biomass	2
2. Overview of fast pyrolysis	7
3. Overview of bio-oil.....	8
4. Reference	11
CHAPTER 2 UNDERSTANDING HYDROGEN TRANSFER EFFECT DURING LIGNIN PYROLYSIS FOR STABILIZED PYROLYTIC OIL USING DEUTERATED SODIUM FORMATE	15
Abstract	15
1. Introduction.....	17
2 Materials and Methods.....	20
2.1 Materials	20
2.2 Pyrolysis.....	20
2.3 Collection of pyrolysis vapor.....	21
2.4 Bio-oil aging test.....	22
2.5 Gel Permeation Chromatography	22

3. Results and Discussion	22
3.1 Distribution of pyrolysis products	22
3.2 Stability of bio-oil.....	27
3.3 Deuterated MS data.....	30
3.4 Pyrolysis of model compounds with sodium formate.....	37
4 Conclusion	38
References	39
CHAPTER 3 THE EFFECT OF HYDROQUINONE TO IMPROVING	
BIO-OIL STORAGE STABILITY.....	44
Abstract	42
1. Introduction.....	42
2 Materials and Methods.....	45
2.1 Materials	45
2.2 Pyrolysis test and vapor collection	46
2.3 Bio-oil aging test.....	47
2.4 GC / MS analysis for bio-oil.....	47
2.5 Gel Permeation Chromatography analysis.....	48
2.6 Electron Paramagnetic Resonance analysis	48
3. Results and Discussion	49
3.1 Co-pyrolysis red oak with HQ	49
3.2 GC/MS analysis of HQ treated bio-oil.....	49
3.3 GPC analysis of HQ treated bio-oil	52

3.4 The effect of HQ addition to condensed oil.....	52
3.5 EPR analysis of HQ treated bio-oil	54
4 Conclusion	55
References	56
CHAPTER 4 CONCLUSIONS.....	59

LIST OF FIGURES

	Page
Figure 1 Chemical Structure of Cellulose	3
Figure 2 Chemical structure of hemicellulose.....	4
Figure 3 Main composition of hemicellulose.....	5
Figure 4 Lignin segment structure.....	6
Figure 5 Three major precursor monomers build up lignin (From left to right, p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol).....	7
Figure 6 Acetic acid yields from lignin co-pyrolysis with sodium formate at different ratios.....	23
Figure 7 Fresh oils produced from pyrolysis of lignin and the mixture of lignin and sodium formate.....	28
Figure 8 Aging study of the oil products produced from (a) lignin and (b) the mixture of lignin and sodium formate.....	29
Figure 9 Presence of deuterium atoms in pyrolysis products of lignin (2-methylphenol).....	34
Figure 10 Presence of deuterium atoms in pyrolysis products of lignin (Phenol).....	35
Figure 11 Presence of deuterium atoms in pyrolysis products of lignin (2, 6-dimethoxyphenol).....	36
Figure 12 Hydrogen transfer in phenolic compounds during co-pyrolysis of lignin and sodium formate.....	37
Figure 13 Pyrolysis-GC/MS chromatogram of 2-methoxy-4-vinylphenol w/o sodium formate	38
Figure 14 Pyrolysis-GC/MS chromatogram of phenol w/o sodium formate	38

Figure 15 GC/MS chromatograms for aged red oak bio-oils collected in a solvent with no HQ and with HQ (1. Glycolaldehyde; 2. Acetic Acid; 3. Acetol; 4. Furfural; 5. 2-Hydroxycyclopent-2-en-1-one; 6. Guaiacol; 7. Cresol; 8. 2-Methoxy-4-vinylphenol; 9. 2, 6-Dimethoxyphenol; 10. Isoeugenol; 11. 1, 2, 4-trimethoxybenzene, 12. 3', 5'-Dimethoxyacetophenone, 13. Levoglucosan, 14. 4-Allyl-2, 6-dimethoxyphenol, 15. 3, 5-Dimethoxy-4-hydroxybenzaldehyde, 16. 3, 5-Dimethoxy-4-hydroxyphenylacetic acid).....	52
Figure 16 Molecular weight distribution of fresh bio-oil w/o HQ.....	54
Figure 17 Molecular weight distribution of aged bio-oil w/o HQ	54
Figure 18 Average molecular weights of bio-oils at different accelerated aging times	55
Figure 19 EPR spectra of lignin pyrolysis vapor condensed in solvent with or without HQ	55

LIST OF TABLES

	Page
Table 1 Composition of typical biomass materials.....	3
Table 2 Overall products distribution of co-pyrolysis lignin with sodium formate	26
Table 3 Overall products distribution of co-pyrolysis lignin with alkali salts (1 to 1).....	27
Table 4 Composition analysis of biomass pyrolysis vapors w/o hydroquinone solvent condensing.....	50

NOMENCLATURE

AMW	Average Molecular Weight
BCRF	Biocentury Research Farm
EPR	Genetically Modified
GC/MS	Hazardous Material
GPC	Gel Permeation Chromatography
HQ	Hydroquinone
LG	Levogluconan
PTFE	Polytetrafluoroethylene
RO	Red Oak

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ABSTRACT

With the rapid development of global economy, there is an ever-growing demand for energy. The excessive use of traditional fossil fuel exposes the human to multiple environmental issues. As a promising technology, thermochemical conversion of biomass is able to provide not only environmental-friendly substitute fuel, but also other value-added chemicals. However, the complex composition and poor quality of conversion products hinders industrial application of biomass in large scale. This study focuses on pyrolysis conversion of biomass and explores possible ways to improve bio-oil quality and stability.

First, sodium formate was selected as hydrogen donating agent and co-pyrolyzed with lignin in a micropyrolyzer. It was found that the presence of sodium formate promotes the production of simple and/or stable phenols such as phenol, syringol and ethylphenol, while reducing the yields of reactive vinylphenols. Among the pyrolysis products, acetic acid was eliminated by neutralization. As a result, the pyrolysis oil produced from co-pyrolysis of lignin and sodium formate contained an increased amount of phenolic monomers, and also had an improved thermal stability during aging tests compared to pyrolysis-oil of lignin. Deuterated sodium formate was also employed in the present study to investigate the mechanism of hydrogen transfer during lignin pyrolysis. The presence of hydrogen mainly affected depolymerization of lignin polymer through a series of reactions that involving both primary and secondary reactions to form alkylated phenols. Electrophilic substitution of hydrogen atoms in phenolic aromatic rings was observed.

Next, the effect of hydroquinone (HQ) on bio-oil storage stability was investigated as HQ is a well-known free radical scavenger. The addition of HQ in previously condensed bio-oil had no effect on bio-oil aging. In comparison, quenching pyrolysis vapors in HQ

containing solvent preserved more monomers after aging by suppressing bio-oil polymerization. The electro paramagnetic resonance (EPR) was used to analyze free radicals in the bio-oils condensed with or without HQ addition. The comparison of the EPR spectra of fresh and aged bio-oil samples showed that addition of HQ in the vapor quenching solvent effectively reduced the concentration of the free radicals in bio-oil. The study suggests that reactive free radicals present in both pyrolysis vapors and freshly condensed bio-oil. Eliminating these free radicals using capping reaction improves bio-oil stability.

CHAPTER 1

INTRODUCTION

With increasing industrialization and global population, especially with the economic development in emerging markets, the need for energy has been keep growing [1]. The most popular form of energy is fossil fuels, which include petroleum, coal and natural gas. In 2013, global energy consumption by the form of energy was petroleum 31.1%, coal 28.9% and natural gas 21.4% [2].

Fossil fuels are non-renewable energy resources and the consumption is irreversible. It has been reported that “total world proved oil reserves reached 1687.9 billion barrels at the end of 2013, sufficient to meet 53.3 years of global production” [3]. Pollution is another significant issue caused by the excessive consumption of fossil fuels. Greenhouse gases (carbon dioxide, methane, nitrous oxide and fluorinated gases, etc.) are primarily emitted from fossil fuel consumptions, creating serious environmental concerns. The average global temperature is expected to increase by 2°F to 11.5°F by 2100, depending on the level of future greenhouse gas emissions [4-6]. Aerosols stemming from particulate matter 2.5 micrometers or smaller in diameter are released from coal combustion and are adversely affecting human health [7-9]. The increasing concerns over world energy crisis and excessive pollutants emission have forced researchers to actively research for renewable alternatives of fossil fuels [10-14].

Biomass, the organic materials of recent biological origin, is a renewable energy resource that is abundantly available. The total heating value generated from combusting the biomass on the earth is approximately five times of the total heating value of the fossil fuel

consumption in the worldwide [15]. Biomass is also considered as carbon neutral energy source. Biomass absorbs carbon dioxide from atmosphere through photosynthesis and fixes the carbon in its structure as it grows. Therefore, biomass has been considered as the promising alternative of fossil fuels to resolve energy crisis and minimize environmental concerns.

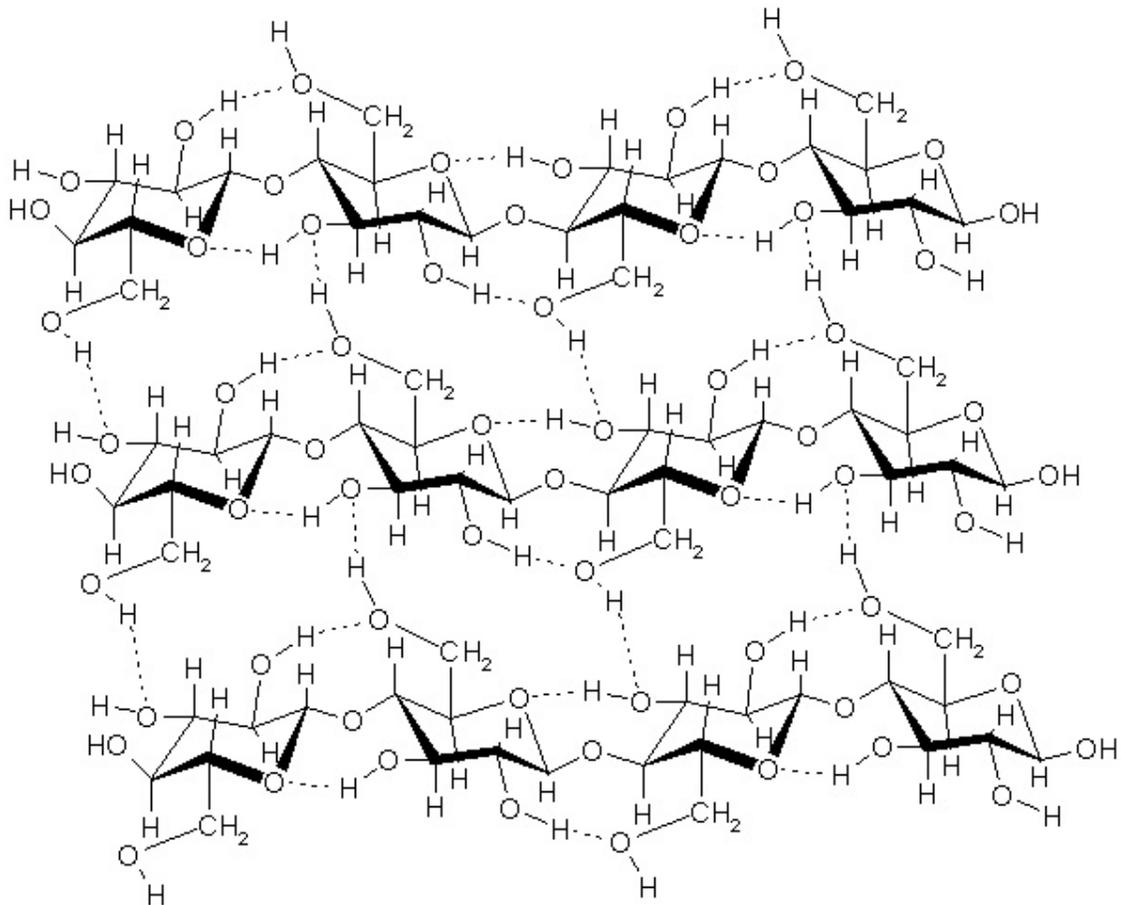
1. Overview of biomass

Biomass is the organic matter primarily presents in the form of grass, trees, crops residues and aquatic plants. Unlike traditional fossil fuels (i.e., coal, crude oil and natural gas) that are mainly consist of carbon and hydrogen, biomass contains a large amount of oxygen in its chemical structure in addition to carbon and hydrogen. The main compositions of lignocellulosic biomass are cellulose, hemicellulose and lignin. Biomass also contains small amounts of extractives and naturally occurring inorganic minerals. The ratios of cellulose, hemicellulose and lignin depend on biomass species. A summary of the compositions for typical biomass materials is listed in Table 1.

With a chemical formula $(C_6H_{10}O_5)_n$, cellulose is a high molecular weight polymer of repeating β -D-glucopyranose units bound by (1 \rightarrow 4)-glycosidic bonds, as shown in Figure. 1. Cellulose molecules are straight chain polymer with no coiling or branching in their structure. Bundles of cellulose molecules were hold side by side by multiple hydroxyl groups to form microfibrils, which enjoy highly tensile strength. These cellulose microfibrils build up into a polysaccharide matrix [18], [19].

Table 1. Composition of typical biomass materials [16]

Plant material	Lignocellulose Content (% of Dry Weight)		
	Lignin	Hemicellulose	Cellulose
Corn Stover	6.0	25.7	48.0
Wheat Straw	21.0	20.0	24.0
Rice Straw	14.2	40.0	34.0
Switchgrass	16.0	28	32.0
Orchard Grass	4.7	27.2	32.0
Oak	27.0	40.0	47.0
Birchwood	15.7	29.0	40.0

**Figure 1. Chemical Structure of Cellulose [17]**

Hemicellulose, also known as polyose, is another major composition within lignocellulosic biomass. It is embedded in the plant cell wall and binds with pectin to form cross-linked fibers. Although hemicellulose presents along with cellulose in almost all kinds of plant cell wall [20], hemicellulose has a different structure and property than cellulose, as shown in Figure 2. Unlike cellulose, which is homo-polysaccharide, hemicellulose is hetero-polysaccharide and is composed of different polymerized monosaccharides as shown in Figure 3. While cellulose consists of 7000-15000 glucose molecules, hemicellulose consists of much shorter chains, about 500-3000 sugar units [22]. In addition, hemicellulose is a branched polymer, contrary to cellulose which does not consist of braches. Cellulose and hemicellulose can be depolymerized biologically or thermochemically to provide monomeric sugars. The sugars are currently being upgraded to liquid fuels and chemicals [23-25].

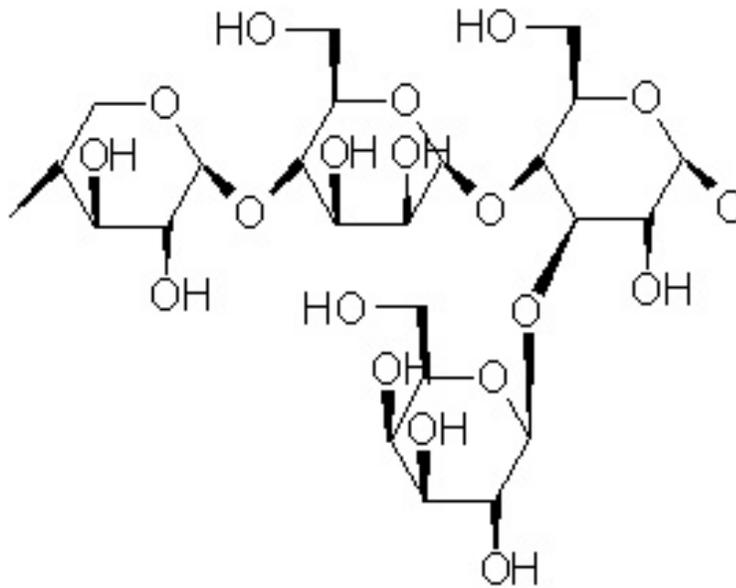


Figure 2. Chemical structure of hemicellulose [17]

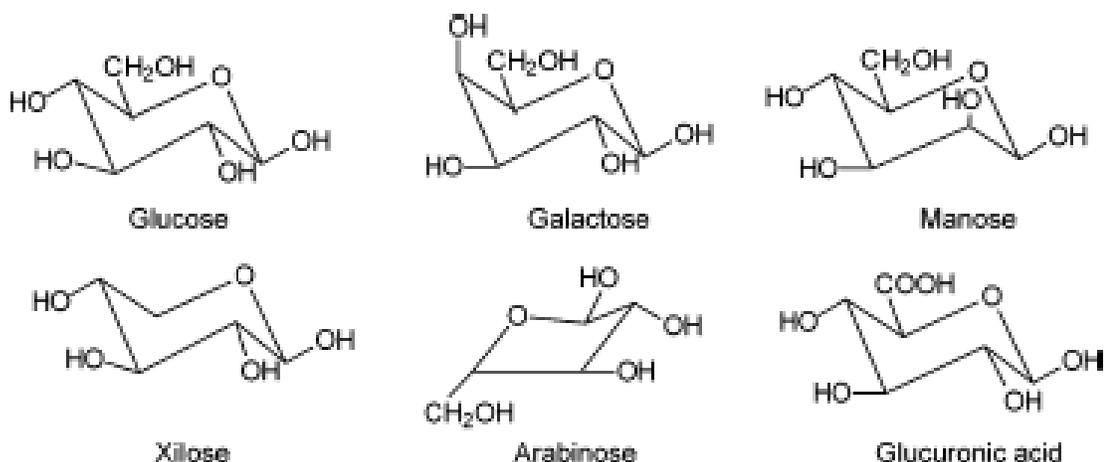


Figure 3. Main composition of hemicellulose [21]

Lignin accounts for up to 35% of biomass and is the most abundant renewable organic polymer next to cellulose [26, 27]. In plant, lignin provides mechanical strength for cell wall. Without the structure support provided by lignin, trees will not reach height out of 100 meters and would collapse on themselves [28]. Technical lignin is the lignin isolated from biomass by thermal and/or chemical processes and is readily available from industries as a byproduct. In paper industry, lignin is removed from biomass since it is responsible for paper yellowing with aging [29]. Lignin is also produced from cellulosic ethanol industry after cellulose is utilized for sugars and further to ethanol. [30]. As shown in Figure 4, lignin is a complex, three dimensional, cross-linked amorphous polymer made by random polymerization of its three primary precursor monomers: p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol [33, 34] shown in Figure 5. If depolymerized, the theoretical yields of benzene and phenol from lignin can be as high as 40% and 50%, respectively [35]. However, the complex and sturdy structure of lignin is recalcitrant for thermochemical or biological destruction, which hampers widespread application of lignin as the feedstock to produce high valued aromatic compounds [30, 36]. Majority of lignin is currently burned for

heat and power and only less than 5% of lignin is utilized for products, such as resin, binder, flavoring agent etc [37].

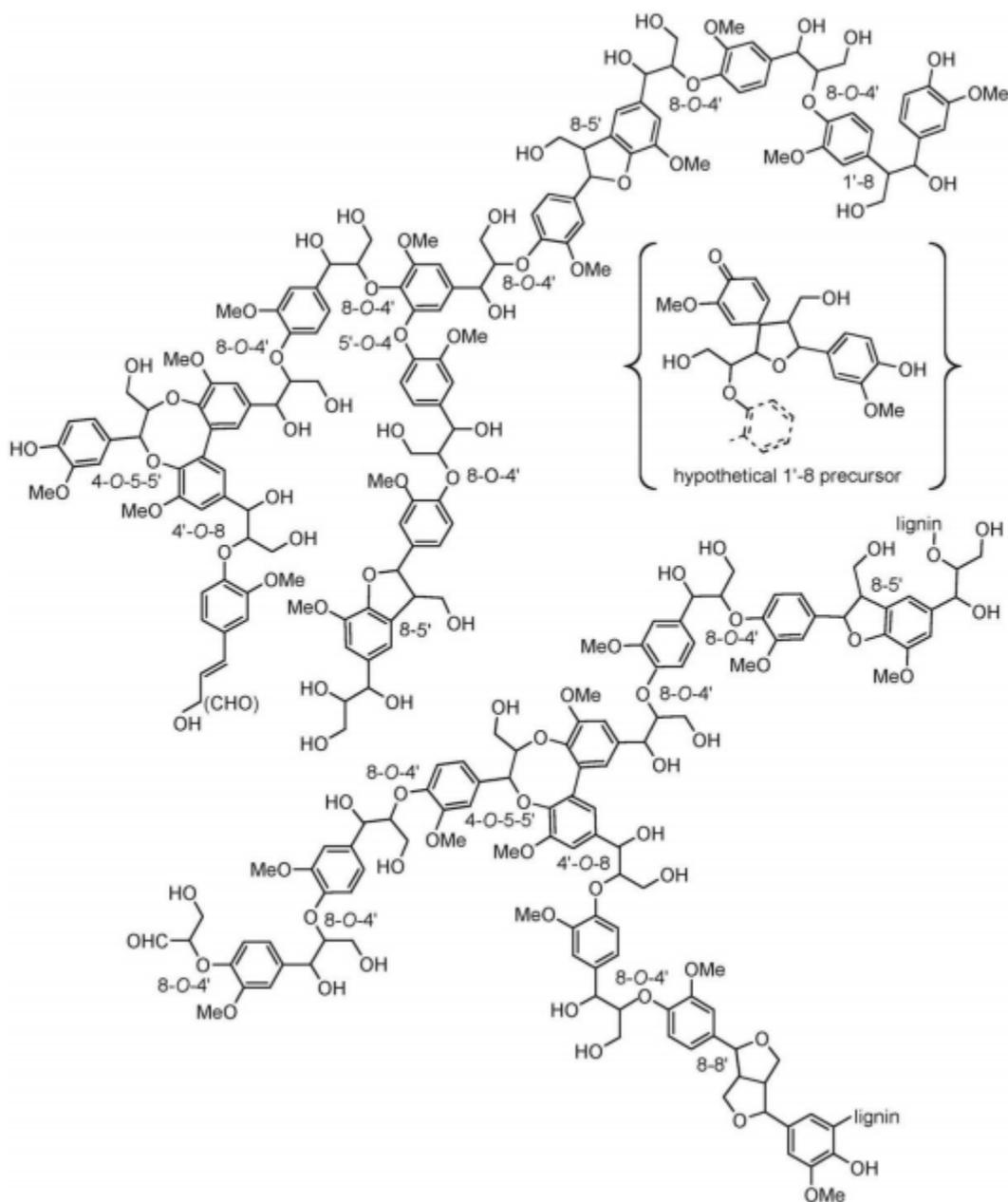


Figure 4. Lignin segment structure [31, 32]

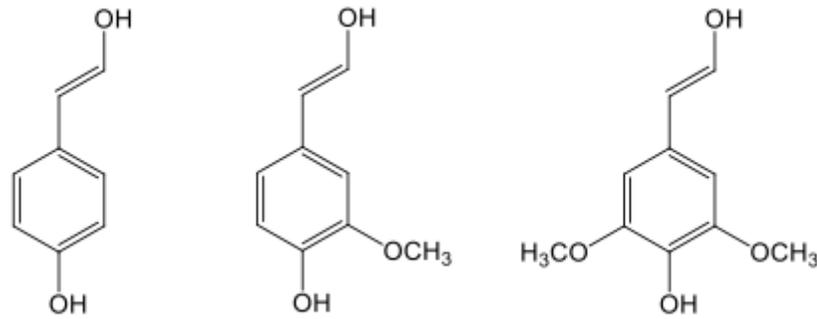


Figure 5. Three major precursor monomers build up lignin (From left to right, p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol) [21]

2. Overview of fast pyrolysis

Pyrolysis is a thermal treatment process that occurs in the absence of oxygen. Depending on the operational conditions employed, pyrolysis process can be defined as slow pyrolysis or fast pyrolysis. Fast pyrolysis is commonly used to convert biomass to liquid product, so called bio-oil. During fast pyrolysis, biomass is rapidly heated (heating rate > 100 C/s) and the arising vapor is quenched to produce bio-oil. The vapor residence time is usually less than 2 seconds in order to maximize bio-oil yield [38-41]. Bio-oil is the major pyrolysis product, accounting for 60-75 wt% of biomass [42, 43]. It is a complex mixture of oxygenated compounds produced from depolymerization of biomass [44]. These compounds could be further upgraded into transportation fuels and other value-added products. Pyrolysis products also include 10-20 wt% of gas and 15-25 wt% of char [42]. Biochar is a solid charcoal which is rich in carbon [45]. Biochar has an appreciable surface area due to its micropores and also contains various nutrient elements, such as N, S, P and K. Biochar can be used as soil amendment to increase soil fertility and improve agricultural production. When applied to soil, biochar fix carbon back to the ground to reduce greenhouse gas

emission. Biochar also has applications as activated carbon or solid fuel. The non-condensable gas products of fast pyrolysis are mainly carbon dioxide, carbon monoxide, methane and also smaller amounts of hydrogen and hydrocarbon gases. The pyrolysis gas can be flared off or recycled back into the process [22]. Therefore, there is nearly no waste produced by fast pyrolysis. Pyrolysis reactors usually have low capital and operation costs and also great flexibility in reactor design [22]. Thus, fast pyrolysis has been considered as one of the most promising approaches to utilize biomass for liquid transportation fuels and value-added chemicals.

3. Overview of bio-oil

Rapid quenching of the vapor after exposing biomass to intense heat was able to quickly trap depolymerized fragments of cellulose, hemicellulose and lignin in the form of bio-oil. Bio-oil is dark brown, free flowing liquid. It is composed of a number of highly oxygenated compounds, such as water, acids, alcohols, aldehydes, aromatics, furans, ketones, phenols and sugars [46-49]. Biomass-derived bio-oil is commended for its poor quality attributed to complex composition, high water content, corrosive nature and its reactivity. High oxygen content of bio-oil is crucial, as the heating value of bio-oil is only an half of traditional fossil fuels. Bio-oil contains over 300 different compounds [46] and many of them are very reactive [50]. Carboxylic acids in bio-oil do not only contribute to corrosiveness of bio-oil, but also act as catalyst to promote various reactions among phenols, sugars and aldehydes, for example polymerization, condensation and degradation [51]. Due to its high reactivity, bio-oil is thermally unstable during storage. Thermal instability of bio-oil increases viscosity of bio-oil and even causes phase separation.

Multiple approaches have been investigated in order to improve bio-oil stability. Polk et al. [52] added low viscosity solvents, such as water, methanol or acetone to reduce the viscosity of bio-oil. However, the effectiveness of the solvents on bio-oil stability and related reaction mechanism were not reported. Tiplady et al. [53] also added water to hardwood bio-oil and aged for four months at room temperature. They found that the viscosity of bio-oil decreased clearly with the increase of water addition. When adding 20 wt% water into bio-oil, the viscosity decrease is 3.3 cP/d. When adding 25 wt% water into bio-oil, the viscosity decrease is 0.9 cP/d. When adding 30 wt% water into bio-oil, the viscosity decrease is 0.05 cP/d. Diebold et al. [54] compared the effectiveness of multiple solvents, including methanol, ethanol, acetone, ethyl acetate, in stabilizing hardwood bio-oil. They concluded that methanol is the most effective solvent and recommended adding 10 % of methanol in bio-oil to improve stability.

Although lignin accounts for less than 30% of total biomass, phenolic oligomers derived from lignin are the major portion of high molecular weight compounds in bio-oil. It has been reported that repolymerization of phenolic oligomers during bio-oil storage is one of the main contributors of bio-oil instability and high viscosity of bio-oil [55]. The phenolic oligomers were thought be partly decomposed fragments of lignin that are thermally ejected [56-59]. On the other hand, recent studies showed that lignin initially depolymerizes to phenolic monomers and dimers, rather than large phenolic oligomers [60]. After pyrolysis, the phenolic monomers can rapidly repolymerize into oligomers through their reactive functionalities even in vapor phase [60]. Thus it has been hypothesized that reducing reactivity of phenolic monomers using capping reactions can prevent the formation of phenolic oligomers and improve stability of bio-oil.

In addition to the reactive functionalities, free radicals in pyrolysis products could also initiate polymerization through free radical initiation, propagation and termination reactions. Although the mechanism is still under debate, it is experimentally proven that lignin is the major source of free radicals in biomass [61, 62]. Thus, controlling free radicals among pyrolysis products could possibly reduce the polymerization reactions. However, it has also been noted that the reactive free radicals often have extremely short life times (less than milliseconds) [63]. For this reason, the free radicals that can be detected in condensed bio-oil are stable ones, which do not contribute to bio-oil aging [61, 62]. Nevertheless, the reactivity of the free radicals in pyrolysis vapor has not been fully understood.

The goal of this research is to improve bio-oil quality by increasing monomer yields and storage stability. In the present study, two types of capping reactions are explored in order to stabilize reactive species in bio-oil.

First, sodium formate is co-pyrolyzed with lignin as the hydrogen donor agent. Sodium salt could also potentially neutralize carboxylic acids in bio-oil to reduce the catalytic effects of the acids for polymerization. Deuterated sodium formate is also employed in order to investigate the mechanism of hydrogen capping reaction. Next, hydroquinone (HQ) is used as a free radical scavenger and introduced during biomass pyrolysis. Electro Paramagnetic Resonance (EPR) technology is used to investigate the free radicals capping mechanism of hydroquinone.

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CHAPTER 2

UNDERSTANDING HYDROGEN TRANSFER EFFECT DURING LIGNIN PYROLYSIS
FOR STABILIZED PYROLYTIC OIL USING DEUTERATED SODIUM FORMATE**Abstract**

With the rapid commercialization of cellulosic ethanol in recent years, utilization of lignin byproduct to produce value-added products has received increasing attention. Depolymerizing lignin into phenolic monomers could provide valuable aromatic precursors for biofuels and chemicals. Although fast pyrolysis process has the ability to thermally depolymerize lignin, it usually yields relatively small amount of phenolic monomers. Instead, lignin produces a large amount of phenolic oligomers that are difficult to upgrade. Repolymerization and condensation reactions occurring during pyrolysis increase the molecular weights of the products and cause thermal instability of bio-oil. Thus, it is hypothesized that providing hydrogen atoms during pyrolysis process could stabilize the reactive species and improve product stability. In the present study, sodium formate was selected as the hydrogen donating agent and co-pyrolyzed with lignin in a micro-pyrolyzer. It was found that the presence of sodium formate promotes the production of simple and/or stable phenols such as phenol, syringol and ethylphenol, while reducing the yield of reactive vinylphenols and acetic acid. The bio-oil produced from co-pyrolysis of lignin and sodium formate contained an increased amount of phenolic monomers, lower fraction of phenolic oligomers and a better thermal stability during aging tests compared to the bio-oil of lignin. Deuterated sodium formate was also employed in the present study to investigate the mechanism of hydrogen transfer during lignin pyrolysis. Hydrogen influences both primary

and secondary reactions of the depolymerization of lignin through a series of reactions to form alkylated phenols and simpler phenolic monomers during pyrolysis. Substitution of hydrogen atoms in phenolic aromatic rings was observed.

Keywords: Fast pyrolysis, sodium formate, bio-oil stability, deuterium

1. Introduction

Increasing concerns over greenhouse gas emission by fossil fuels and national energy security have forced researchers to pay more attention to renewable energy [1-4]. Biomass is an important source of renewable energy and it is the only alternative of fossil fuels for liquid transportation fuels and chemicals [5]. Lignocellulosic biomass consists of three basic components, which are cellulose, hemicellulose and lignin [6]. Upgrading of C5 or C6 sugars derived from cellulose and hemicellulose to ethanol, hydrocarbon fuels and various chemicals have been frequently reported [7-12]. Utilization of lignin for value-added products, however, has been known to be extremely challenging.

Lignin accounts for 10-35% of lignocellulosic biomass and it is the second most abundant biopolymer on the earth next to cellulose [13, 14]. In addition to plant biomass, technical lignin is also readily available in paper, pulping and cellulosic bio-refineries in large quantities as a byproduct [15, 16]. Lignin is a randomly cross-linked three dimensional polymer biosynthesized from three primary precursor monomers: p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol [17, 18]. Due to its molecular structure, lignin can be a potential source of renewable aromatics. However, only a very small percent of over 50 million tons of annually produced lignin has been utilized as products, such as resin, adhesive, flavoring agent, and over 95% of the lignin is used as boiler fuels for heat and power [16]. Lignin is difficult to be utilized either biologically or thermochemically, due to its complex chemical structure and recalcitrant for depolymerization [19]. An effective utilization of lignin would not only provide an alternative source of biofuels and chemicals, but also greatly improve the economic prospect of the lignin producing industries [20].

Fast pyrolysis of biomass is a rapid thermochemical decomposition process, mainly used to liquefy biomass into high-energy density liquid. Fast pyrolysis occurs at inert environment, moderate temperature (around 500 °C) and usually at atmospheric pressure [21]. During pyrolysis, dry biomass particles are heated at heating rates above 100 °C/s and the pyrolysis vapor is rapidly quenched to become bio-oil [22]. High heating rate, moderate pyrolysis temperature and short vapor-residence time are critical factors in maximizing bio-oil yield. The yield as much as 70% is achievable from fast pyrolysis [23]. Bio-oil derived from pyrolysis of lignocellulosic biomass is a mixture of decomposed carbohydrates and lignin, such as sugars, furans, acids, ketones, aldehydes, alcohols and phenols dispersed in water [24]. Although sometimes it is directly used as fuels in boilers, bio-oil is usually considered as an intermediate product and further upgraded. Due to its simplicity in the reactor design, low capital and operation costs, fast pyrolysis has been considered as one of the promising ways to convert biomass into building block chemicals for transportation fuels and other value-added products.

Despite the aforementioned advantages of fast pyrolysis, several significant technical barriers remain to be overcome in terms of producing fuels and chemicals from bio-oil in scale. The problems are associated with the intrinsic properties of bio-oil, which make it much poorer raw material compared to petroleum. Bio-oil is an acidic liquid that has high oxygen content. It also contains high percentage of water derived from both reaction product and original moisture [25]. Bio-oil is also a complex and thermally unstable mixture of hundreds of chemicals [26]. During storage, bio-oil subjects to aging reactions. The aging of bio-oil increases viscosity of bio-oil and even causes phase separation. Increasing average molecular weight of bio-oil and water content during bio-oil aging indicates polymerization,

condensation reactions occur during aging. Aging is highly undesired as it causes the fluidity and volatility of bio-oil to dramatically decrease. Bio-oil aging is a complex process, involving many different groups of compounds and series of reactions [27-31]. Among it, lignin-derived phenolic oligomers greatly contribute aging effect of bio-oil [32]. These high molecular weights, high viscosity compounds continue to increase their molecular weights due to the reactivity of various functionalities on phenolics.

Several strategies have been proposed by researchers, aiming to improve stability of bio-oil. Some examples include esterification, solvent addition and hydrodeoxygenation (HDO). Esterification converts carboxylic acids in bio-oil with alcohols in the presence of acidic catalyst [33-38]. Although the mechanisms is under discussion, adding solvents, such as methanol, ethanol, water, acetone and ethyl acetate into bio-oil has been experimentally proved effective to decrease bio-oil viscosity and aging rate[39-42]. HDO can effectively deoxygenates pyrolysis products to stabilize bio-oil, but it usually occurs in the presence of catalysts and/or under relatively higher pressures. [18, 43, 44].

It should be noted that these approaches target condensed bio-oil. Our previous study has shown that repolymerization could also occur in the vapor phase prior to the pyrolysis products condense [45]. Therefore, it is hypothesized that stabilizing the reactive species using capping agents as they formed could produce stable bio-oil. Capping reactions have been used in coal liquefaction processes to stabilize the reaction products [46]. Researchers proposed that the free radicals formed during coal liquefaction would be stabilized by donor hydrogen and thus prevent repolymerization reactions [46-43]. The examples of hydrogen donating agents are tetralin, naphthol and formic acid. It should be noted that capping reactions often occur at elevated pressures and extended reaction times [51]. It is unknown

whether capping reaction equally effective in fast pyrolysis. Therefore, in the present study, lignin is co-pyrolyzed with sodium formate as the capping agent. Deuterated sodium formate is also employed in the present study to investigate the reaction mechanism of hydrogen donor.

2. Materials and Methods

2.1 Materials

Organosolv lignin derived from corn stover was provided by Archer Daniels Midland (ADM) Company, Chicago, USA. Methanol, acetone and tetrahydrofuran were purchased from Fisher Scientific Company. Sodium formate, deuterium sodium formate and the rest of the compounds were purchased from Sigma-Aldrich Company.

2.2 Pyrolysis

Pyrolysis experiments were performed using a Frontier Lab Tandem μ -Reactor (Rx-3050TR) with an Auto-Shot sampler (AS-1020E) pyrolysis system. The reactor system has two reaction furnaces (1st and 2nd furnaces) and two independent interface sections arranged in tandem. Temperature of the furnaces and interfaces can be controlled independently from 40 to 900 °C with 1 °C interval. In the present study, the temperature of the 1st reactor was kept at 500 °C, and the 2nd reactor and both of the interface sections were set at 300 °C to prevent pyrolysis products from condensation. The 1st furnace was used for pyrolyzing samples and 2nd reactor was originally designed to hold a catalyst bed. However, no catalyst bed is used in the present study, the pyrolytic vapors just passed through the second reactor without any reaction in it. The pyrolysis vapor leaving the micropyrolyzer was swept into an

on-line Agilent 7890B/5977A GC/MSD system for instant identification and quantification of the products.

An alloy capillary column (Ultra Alloy-1701) for the GC is purchased from Frontier Laboratories LTD, Japan. The GC oven was heated from 40 °C to 280 °C at a heating rate of 6 °C/min and kept at the final temperature for additional 10 minutes. Three independent detectors, MS, FID and TCD, were connected with the end of the GC column and substances eluted from the column were separated into 3 parts and measured by the three detectors separately. Only MS and FID detector were employed in the present study. The MS signal was used to identify the reaction products, including deuterated phenolic compounds. Pyrolysis compounds were identified by NIST library, and quantified using authentic compounds. The FID signal was used to quantify all the volatile products.

For each test, about $500 \pm 10\mu\text{g}$ of lignin or phenolic model compound mixed with or without sodium formate was placed in a deactivated stainless sample cup for pyrolysis. The ratio of lignin to sodium formate ranged from 1:0.5 to 1:4.

2.3 Collection of pyrolysis vapor

Pyrolysis reactor system was detached from the GC/MS system and placed on the top of a solid framework with a hole in the middle. The reactor needle on the pyrolyzer was inserted into a sealed end of a U-shaped glass tube. The other end of the U-shaped tube was connected with a fume hood for releasing the non-condensable gas during vapor collection. The glass tube was filled with glass beads and immersed into a vessel filled with liquid nitrogen to quench the vapors. The glass beads were used to provide a large surface area to condense pyrolytic vapors.

To collect enough amounts of pyrolysis vapors, 10 cups of the sample were sequentially pyrolyzed. For each run, the reactor was purged for two minute to create an inert environment in micropyrolyzer. Then place the sample cup into the reactor for one minute before take it out of the pyrolyzer. After all ten cups of sample were pyrolyzed, the tube and the beads inside the tube were washed with 2.5 mL tetrahydrofuran or methanol to recover bio-oil. Generally, tetrahydrofuran was used for GPC analysis, while methanol for aging test.

2.4 Bio-oil aging test

The methanol dissolved bio-oil samples holding in GC vials were placed in fume hood with their cap open to evaporate methanol. After the methanol removed, re-tighten the GC vials and leave them aging for two weeks at room temperature. After aging, 2.5 ml of THF was added to the bio-oil for the following GPC analysis.

2.5 Gel Permeation Chromatography

Gel permeation chromatography (GPC) analysis of the fresh bio-oil or aged bio-oil was performed in Dionex ultimate 3000 High Performance Liquid Chromatography system, which equipped with a Shodex Refractive Index (RI) and a Diode Array Detector (DAD). The GPC system column was calibrated through 6 polystyrene standard samples. Each bio-oil sample was filtered by a 0.25 μ m Whatman PTFE filter before analysis.

3. Results and Discussion

3.1 Distribution of pyrolysis products

The distribution of pyrolysis vapor products is shown in Table 1. When lignin was co-pyrolyzed with sodium formate, the yields of ethyl and methyl phenols increased. These products include 4-ethylphenol, 2-methylphenol and 4-ethyl-2-methoxyphenol. On the other hand, the phenols with C=C bonds or carbonyl group, such as 4-vinyl-phenol, 2-methoxy-4-vinyl-phenol, trans-isoeugenol and vanillin decreased. Among other types of phenols, the phenols with long side chain decreased and simpler phenols, such as phenol, guaiacol, increased. As the ratio of sodium formate to lignin increased, the trend became more profound. Clearly, the presence of sodium formate promoted both saturation and cracking reactions. Another significance of co-pyrolyzing lignin and sodium formate was that it significantly reduces the yield of acetic acid, and higher sodium formate content in the sample decreased acetic acid even more (Figure 1). When lignin to sodium formate ratio was over 1 to 3, no acetic acids was found among the products.

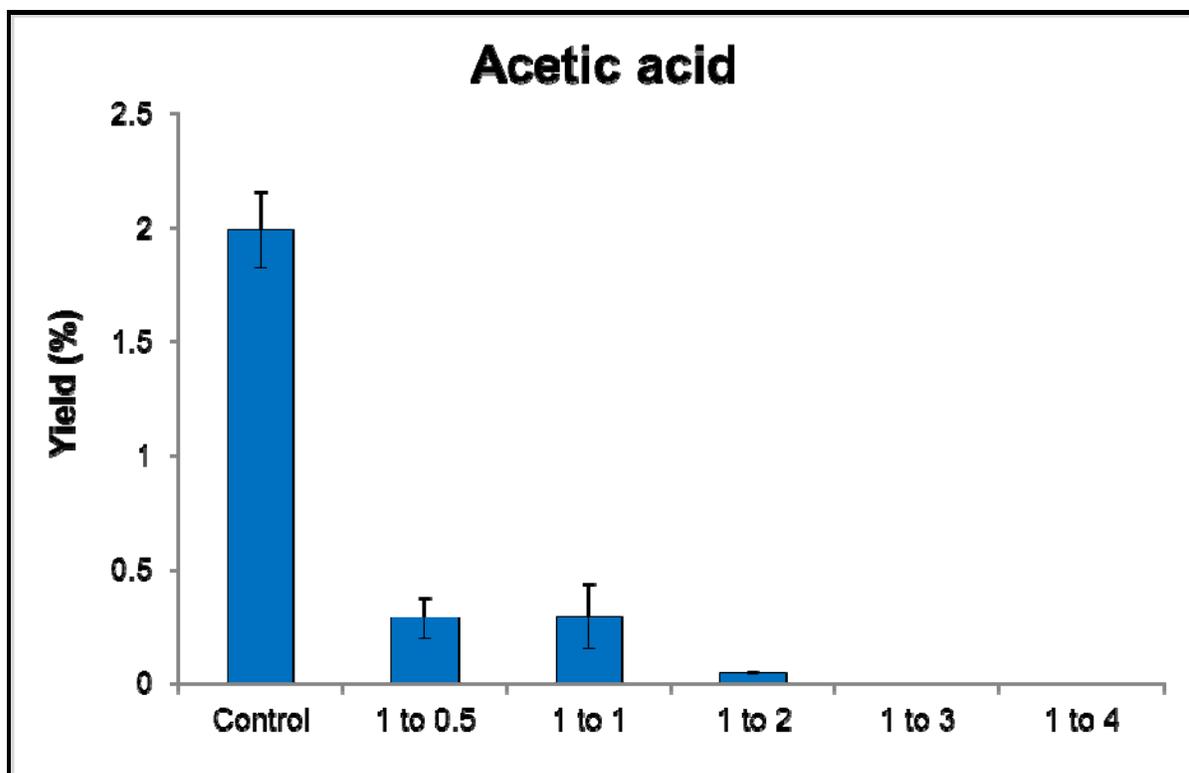


Figure 1. Acetic acid yields from lignin co-pyrolysis with sodium formate at different ratios

The two main phenolic monomers produced from corn stover-derived lignin are 4-vinylphenol and 2-methoxy-4-vinylphenol. These compounds are produced during co-pyrolysis, the yields of 4-vinylphenol and 2-methoxy-4-vinylphenol reduced remarkably, while the yield of 4-ethylphenol and 2-methoxy-4-ethylphenol increase. The unsaturated C=C bonds are likely saturated by hydrogen released from sodium formate. As a hydrogen donor, sodium formate decomposes at 330 °C into sodium carbonate, carbon monoxide and hydrogen. It has been previously reported that inorganic alkali salts can dramatically affect pyrolysis mechanism of cellulose to promote glycosidic-ring opening and gases formation [52, 53]. Since sodium carbonate is one of the decomposition products of sodium formate, it is unknown if sodium carbonate also affects lignin pyrolysis. Thus, lignin was also co-pyrolyzed with sodium carbonate and the pyrolysis products were examined. As shown in

Table 2, overall a reduced amount of volatiles was detected when co-pyrolysis lignin with sodium carbonate. The total volatiles yield reduced from 13.913% for pure lignin to 9.358% for 1:1 mixture of lignin and sodium carbonate. The yield of nearly every compound decreased, both vinylphenols, methyl and ethyl phenols. Comparing Table 1 with Table 2, we can find the decreasing trend of 2-methoxy-4-vinylphenol and 4-vinylphenol clearly moderate for co-pyrolysis lignin with sodium formate than with sodium carbonate, although the total yield reduced in both co-pyrolysis reactions. Besides, co-pyrolysis of lignin to sodium formate 1 to 3 case is a turning point and the yield of 2-methoxy-4-vinylphenol and 4-vinylphenol increase when the ratio of sodium formate to lignin is higher than this turning point. In addition, unlike co-pyrolysis lignin with sodium carbonate, for which decreasing is the overall trend, the yield of some compounds increase clearly, although some others decrease when co-pyrolysis lignin with sodium formate. All of these results indicate the hydrogen released from sodium formate rather than sodium carbonate had taken main effect during co-pyrolysis. And the presence of the hydrogen might have 2 functions in capping reactions. On one hand, it promotes the hydrocracking of lignin macromolecules, during which more amount of 2-methoxy-4-vinylphenol and 4-vinylphenol are created. On the other hand, excessive hydrogen will then saturate the unstable C=C and yield more 4-ethyl-2-methoxyphenol, 4-ethylphenol and other relatively stable compounds.

Table 1 Overall products distribution of co-pyrolysis lignin with sodium formate

No.	Compound name	Control	1 to 0.5	1 to 1	1 to 2	1 to 3	1 to 4
1	Benzene	0.028 ± 0.004	0.025 ± 0.002	0.027 ± 0.004	0.030 ± 0.002	0.033 ± 0.003	0.031 ± 0.002
2	Acetic acid	1.989 ± 0.166	0.286 ± 0.087	0.293 ± 0.142	0.043 ± 0.006	0.000 ± 0.000	0.000 ± 0.000
3	Toluene	0.063 ± 0.001	0.063 ± 0.000	0.071 ± 0.005	0.071 ± 0.002	0.076 ± 0.004	0.077 ± 0.003
	Sum of hydrocarbons (without acetic acid)	0.091 ± 0.005	0.088 ± 0.002	0.098 ± 0.009	0.101 ± 0.004	0.109 ± 0.007	0.108 ± 0.005
4	Phenol	0.578 ± 0.017	0.921 ± 0.019	0.970 ± 0.056	1.029 ± 0.003	1.067 ± 0.080	1.049 ± 0.032
5	2-methoxyphenol	0.540 ± 0.023	0.893 ± 0.023	0.949 ± 0.085	1.021 ± 0.001	1.028 ± 0.043	1.014 ± 0.049
6	2-methylphenol	0.053 ± 0.004	0.099 ± 0.000	0.107 ± 0.009	0.122 ± 0.007	0.135 ± 0.013	0.143 ± 0.006
7	4-methylphenol	0.328 ± 0.003	0.207 ± 0.001	0.229 ± 0.020	0.222 ± 0.011	0.223 ± 0.006	0.238 ± 0.008
8	2-methoxy-4-methylphenol	0.460 ± 0.017	0.238 ± 0.007	0.239 ± 0.022	0.212 ± 0.000	0.213 ± 0.003	0.217 ± 0.008
9	3,5-dimethylphenol,	0.043 ± 0.003	0.057 ± 0.001	0.062 ± 0.003	0.071 ± 0.006	0.080 ± 0.007	0.088 ± 0.005
10	4-ethylphenol	0.379 ± 0.016	0.459 ± 0.000	0.474 ± 0.021	0.493 ± 0.015	0.541 ± 0.041	0.542 ± 0.007
11	4-ethyl-2-methoxyphenol	0.240 ± 0.019	0.249 ± 0.004	0.261 ± 0.017	0.267 ± 0.006	0.270 ± 0.020	0.266 ± 0.003
12	4-vinylphenol	4.255 ± 0.107	4.159 ± 0.026	4.113 ± 0.090	4.013 ± 0.042	3.808 ± 0.302	3.844 ± 0.142
13	2-methoxy-4-vinylphenol	2.400 ± 0.032	2.405 ± 0.018	2.343 ± 0.023	2.295 ± 0.035	2.171 ± 0.194	2.188 ± 0.077
14	2,6-dimethoxyphenol	0.711 ± 0.031	1.006 ± 0.033	1.099 ± 0.094	1.191 ± 0.000	1.233 ± 0.040	1.186 ± 0.063
15	trans-Isoeugenol	0.133 ± 0.006	0.101 ± 0.005	0.103 ± 0.008	0.092 ± 0.000	0.085 ± 0.011	0.086 ± 0.003
16	1,2,4-Trimethoxybenzene	0.431 ± 0.018	0.195 ± 0.006	0.206 ± 0.024	0.176 ± 0.005	0.168 ± 0.012	0.171 ± 0.009
17	Vanillin	0.141 ± 0.015	0.090 ± 0.003	0.091 ± 0.012	0.080 ± 0.001	0.058 ± 0.020	0.054 ± 0.005
18	1,2,3-trimethoxy-5-methylbenzene	0.152 ± 0.007	0.156 ± 0.005	0.167 ± 0.008	0.178 ± 0.004	0.186 ± 0.009	0.181 ± 0.005
19	3',5'-Dimethoxyacetophenone	0.275 ± 0.004	0.281 ± 0.001	0.277 ± 0.005	0.271 ± 0.008	0.257 ± 0.037	0.271 ± 0.021
20	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	0.554 ± 0.014	0.461 ± 0.001	0.443 ± 0.032	0.416 ± 0.006	0.402 ± 0.045	0.404 ± 0.008
21	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	0.159 ± 0.007	0.094 ± 0.005	0.093 ± 0.010	0.072 ± 0.000	0.061 ± 0.015	0.063 ± 0.008
	Sum of phenolic compounds	13.822 ± 0.510	12.355 ± 0.245	12.521 ± 0.682	12.264 ± 0.158	11.986 ± 0.898	10.955 ± 0.427
	Total Yield	13.913 ± 0.515	12.443 ± 0.247	12.619 ± 0.691	12.365 ± 0.162	12.095 ± 0.905	11.063 ± 0.432

Table 2 Overall products distribution of co-pyrolysis lignin with alkali salts (1 to 1)

No.	Compound name	Control	w Na ₂ CO ₃
1	Benzene	0.028 ± 0.004	0.030 ± 0.001
2	Acetic acid	1.989 ± 0.166	0.000 ± 0.000
3	Toluene	0.063 ± 0.001	0.056 ± 0.006
4	Phenol	0.578 ± 0.017	0.629 ± 0.036
5	2-methoxyphenol	0.540 ± 0.023	0.525 ± 0.011
6	2-methylphenol	0.053 ± 0.004	0.059 ± 0.008
7	4-methylphenol	0.328 ± 0.003	0.251 ± 0.012
8	2-methoxy-4-methylphenol	0.460 ± 0.017	0.285 ± 0.005
9	3,5-dimethylphenol,	0.043 ± 0.003	0.041 ± 0.002
10	4-ethylphenol	0.379 ± 0.016	0.420 ± 0.067
11	4-ethyl-2-methoxyphenol	0.240 ± 0.019	0.186 ± 0.005
12	4-vinylphenol	4.255 ± 0.107	3.279 ± 0.109
13	2-methoxy-4-vinylphenol	2.400 ± 0.032	1.819 ± 0.110
14	2,6-dimethoxyphenol	0.711 ± 0.031	0.615 ± 0.011
15	trans-Isoeugenol	0.133 ± 0.006	0.092 ± 0.001
16	1,2,4-Trimethoxybenzene	0.431 ± 0.018	0.234 ± 0.005
17	Vanillin	0.141 ± 0.015	0.083 ± 0.001
18	1,2,3-trimethoxy-5-methylbenzene	0.152 ± 0.007	0.108 ± 0.001
19	3',5'-Dimethoxyacetophenone	0.275 ± 0.004	0.205 ± 0.001
20	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	0.554 ± 0.014	0.366 ± 0.001
21	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	0.159 ± 0.007	0.073 ± 0.000
	Total Yield	13.913 ± 0.515	9.358 ± 0.392

3.2 Stability of bio-oil

Phenolic oligomers in bio-oil are difficult to be detected by GC/MS. Thus, the molecular weight distribution of condensed pyrolysis vapor was analyzed by GPC. Figure 2 compared the molecular weight distributions of fresh bio-oils produced under various conditions. Compared to pyrolyzing lignin alone, there is a clear trend that the concentration of light molecular weight compounds increases, accompanied by decreasing concentration of the compounds with high molecular weight by the addition of sodium formate. The results

correspond to Table 1, indicating that the use of sodium formate as the capping agent effectively reduced the formation of phenolic oligomers and increased monomer formation.

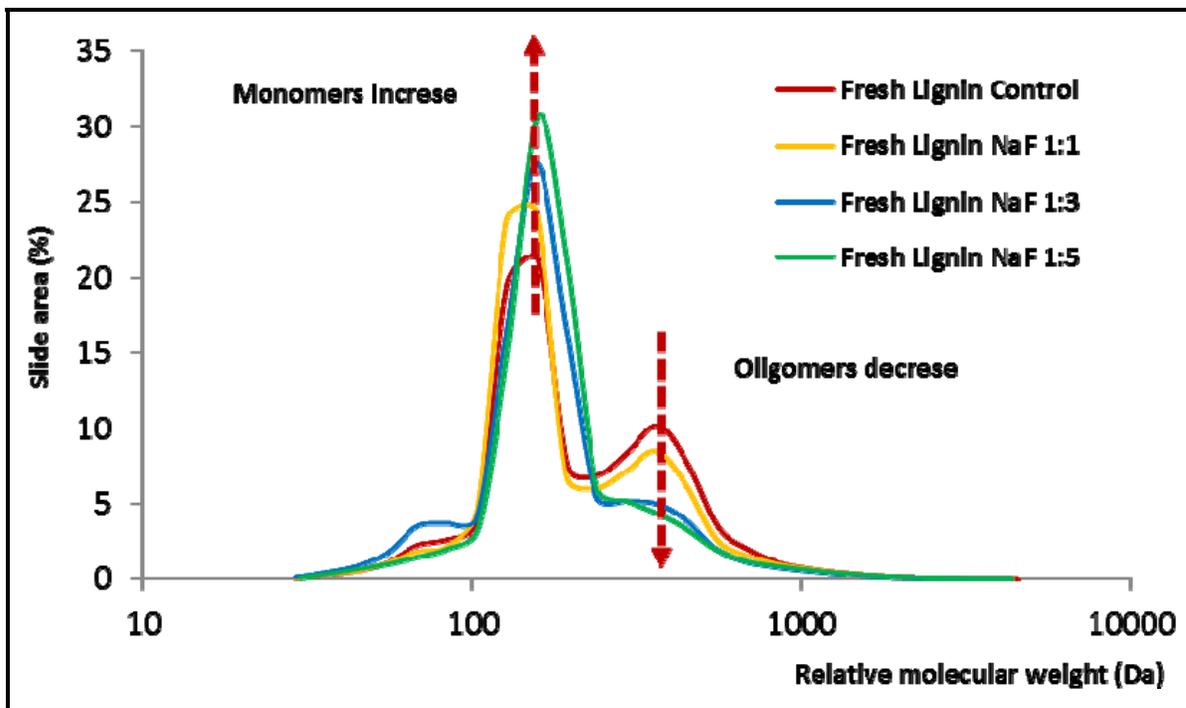
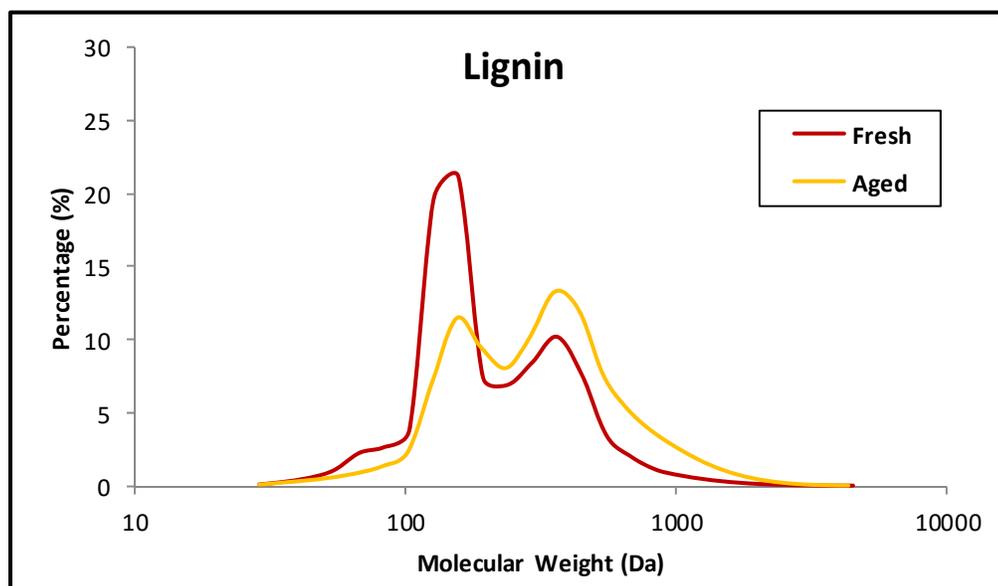


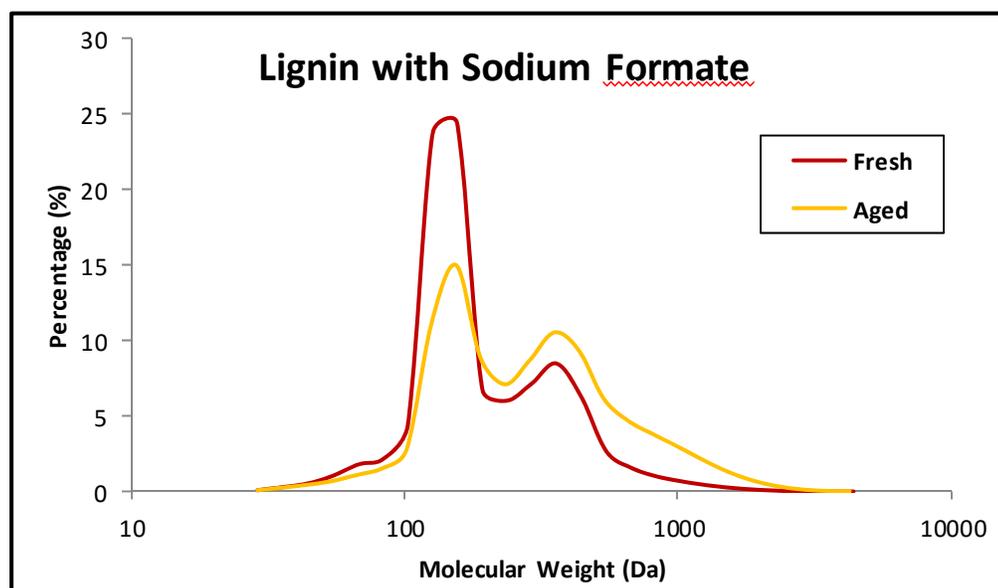
Figure 2. Fresh oils produced from pyrolysis of lignin and the mixture of lignin and sodium formate

Figure 3 (a) and (b) show the aging effect of the bio-oils derived from pyrolysis of lignin alone or the mixture of lignin and sodium formate with a ratio of 1 to 1 after 2 weeks storage at room temperature. In both cases, the shift in the molecular weight distribution to higher end was observed due to the polymerization of phenols to form oligomers. For the aged bio-oil of lignin, the right-side peak representing phenolic oligomers became the dominant peak. In comparison, this peak was still the minor peak in the aged bio-oil derived from co-pyrolysis of lignin and sodium formate. This GPC result indicates that co-pyrolysis of lignin and sodium formate produced bio-oil with an improved stability. Vinyl and carbonyl groups in phenols are known to be reactive for polymerization and carboxylic acids

can act as the catalyst. Co-pyrolysis with sodium formate suppressed the formation of the phenols with the reactive functional groups and also neutralized acetic acid in the pyrolysis products, which promoted stability of bio-oil.



(a)



(b)

Figure 3. Aging study of the oil products produced from (a) lignin and (b) the mixture of lignin and sodium formate

3.3 Deuterated MS data

Hydrogen induced capping reaction is essential in improving the quality of bio-oil. In order to investigate the mechanism of hydrogen transfer during pyrolysis, deuterated sodium formate was also employed in the present study. Deuterated (D form) sodium formate and natural sodium formate (H form) were co-pyrolyzed with lignin respectively and the mass spectrum for each pyrolysis product was compared individually.

The presence of deuterium in a phenolic compound can be determined by comparing with the masses (m/z value) of the compound between natural and deuterated sodium formate. From NIST database, taking 2-methylphenol as example, as shown in Figure 4, the molecular weight of 2-methylphenol is 108, it's represented by the parent peak, if there is one deuterium attached on this compound, it would add one peak line on the right side of the parent peak, if there are 2 deuteriums attached on this compound, there would be 2 more peak lines added on the right side of the parent peak. So, for 2-methylphenol, there are 5 more peak lines added besides the parent peak, which means for this compound it could be attached by as much as 5 hydrogen atoms during the copyrolysis.

The presence of deuterium atoms was found in nearly all the pyrolysis products of lignin indicate hydrogen had transferred from sodium formate to lignin during pyrolysis. However, different compounds show a different hydrogen attachment accessibility. The phenomenon that different numbers of deuterium atoms was embedded into different phenolic compounds was observed. As shown in Figure 4, alkylphenols (methylphenol and ethylphenol), taking 2-methylphenol as example, contained higher number of deuterium atoms. Phenol, as shown in Figure 5, contained up to five deuterium atoms, indicating all hydrogen atoms on benzene ring are substituted by deuterium. In comparison, fewer

deuterium atoms were found in the methoxyl group of phenols, such as 2, 6-dimethoxyphenol, as shown in Figure 6 and 3', 5'-Dimethoxyacetophenone. Hydrogen in methoxyl group of phenols was not substituted by deuterium possibly because hydrogen promotes the cleavage of methoxyl group from benzene ring and thus deuterium substitution was often observed at ortho position of benzene ring. The plausible structures of the phenolics after deuterium transfer are presented in Figure 7.

3.4 Pyrolysis of model compounds with sodium formate

To distinguish if capping reactions occur during thermal decomposition of lignin or secondary reaction of the primary pyrolysis products of lignin, phenolic compounds were also co-pyrolyzed with natural sodium formate and deuterium sodium formate respectively. Co-pyrolyzed natural sodium formate is used to examine product distribution change, while deuterium sodium formate was used to identify hydrogen transfer pathway. The GC/MS chromatograms of Figure 8 shows the product composition when 2-methoxy-4-vinylphenol (i.e., the main pyrolysis product of lignin) was pyrolyzed with or without sodium formate with a constant ratio of 1 to 1. Secondary reaction of the vinylphenol was significant during pyrolysis, indicated by the presence of several smaller peaks representing the phenols other than the starting material in the MS spectra. Among the secondary reaction products, simple and/or saturated phenolic compounds, such as phenol, guaiacol and 4-ethylphenol increased when the vinylphenol was co-pyrolyzed with sodium formate. When deuterated sodium formate was co-pyrolyzed, as the molecular structure plot shown in Figure 8, deuterium atoms were also found in the secondary reaction products. This result suggests that hydrogen transfer affects secondary reaction of primary pyrolysis products of lignin to produce saturated products and promote hydrocracking.

Other model compounds, such as phenol, cresol, benzene and guaiacol, were also co-pyrolyzed with sodium formate and deuterium sodium formate. Interestingly, these compounds were fairly stable during pyrolysis and deuterium substitution in these molecules was not found. The mass spectrums of phenol co-pyrolyzed with and without sodium formate are given in Figure 9 as an example. However, it is noteworthy that these compounds as the products of co-pyrolysis of lignin and sodium formate contained deuterium atoms. This suggests that the simpler aromatics (phenol, cresol, benzene and guaiacol) are generated either by primary lignin depolymerization through hydrocracking or by secondary reaction through the saturation or substitution reaction with the products of primary reaction. Based on these results, it is concluded that external hydrogen transfer affects thermal depolymerization of lignin as well as the secondary reactions of primary products by promoting hydrocracking, saturation and substitution reactions.

4. Conclusions

Co-pyrolysis of lignin and sodium formate was found to increase the yields of simpler phenolic monomers and alkylated phenols at the expense of the phenols with vinyl, carbonyl and other complex functionalities. The presence of sodium formate also dramatically reduced the yield of acetic acid by neutralization. GPC analysis shows that the bio-oil produced from co-pyrolysis of lignin and sodium formate was more stable during storage and contained a higher amount of total monomers than the oil produced from pyrolysis of lignin. Hydrogen transfer from sodium formate to lignin, as well as decreased catalytic effect of acetic acid suppressed polymerization of phenolic products and improved the quality of bio-oil. The mechanism of hydrogen transfer during lignin pyrolysis was studied using deuterated sodium

formate. It was found that external hydrogen mainly transfers to phenolic alkyl side chain as well as para and ortho positions of phenolic benzene ring. Pyrolysis of phenolic model compounds and sodium formate suggests that external hydrogen affects thermal decomposition of lignin polymer through a series of reactions occur in steps to form simpler and stable phenols.

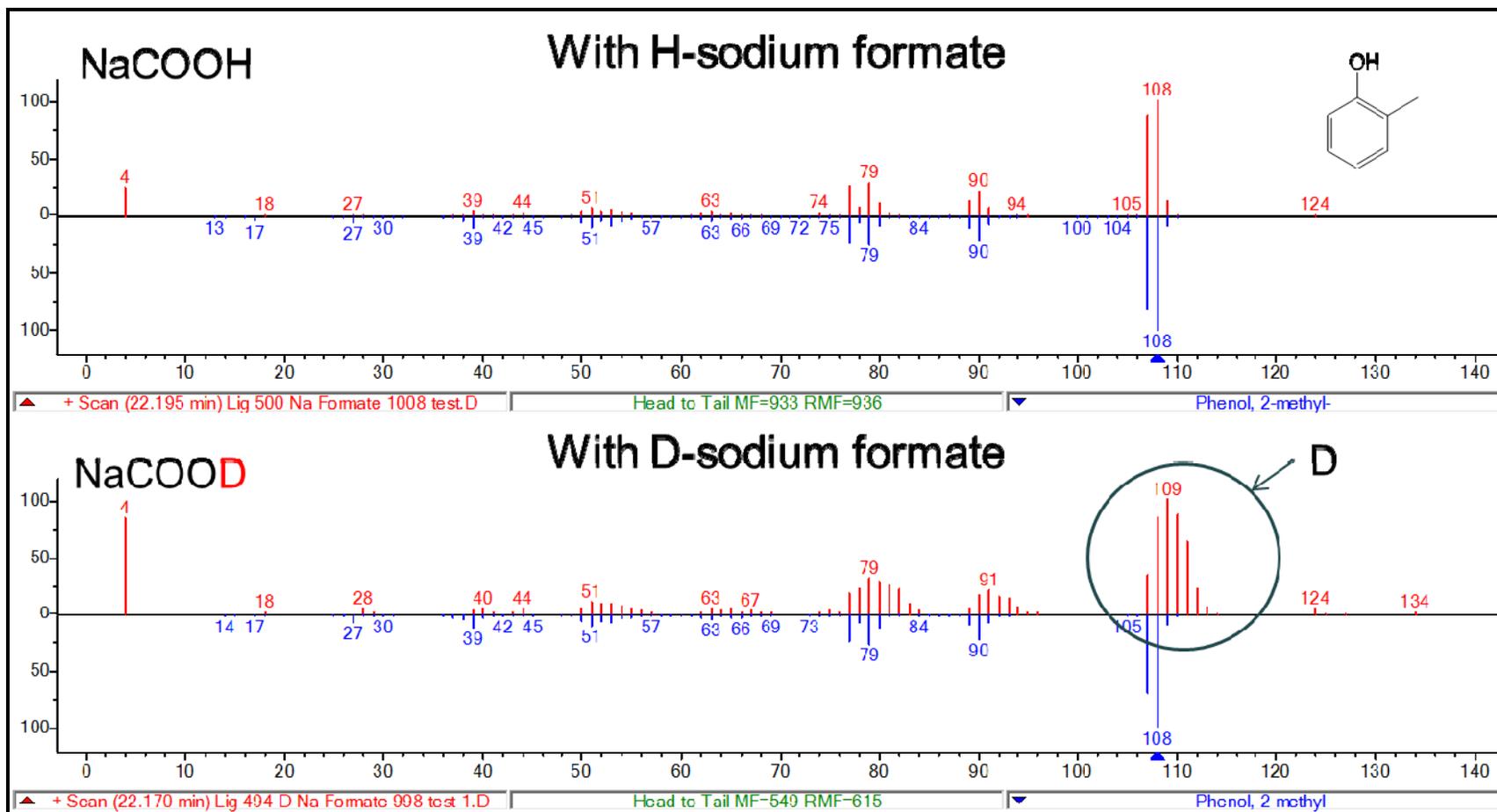


Figure 4. Presence of deuterium atoms in pyrolysis products of lignin (2-methylphenol)

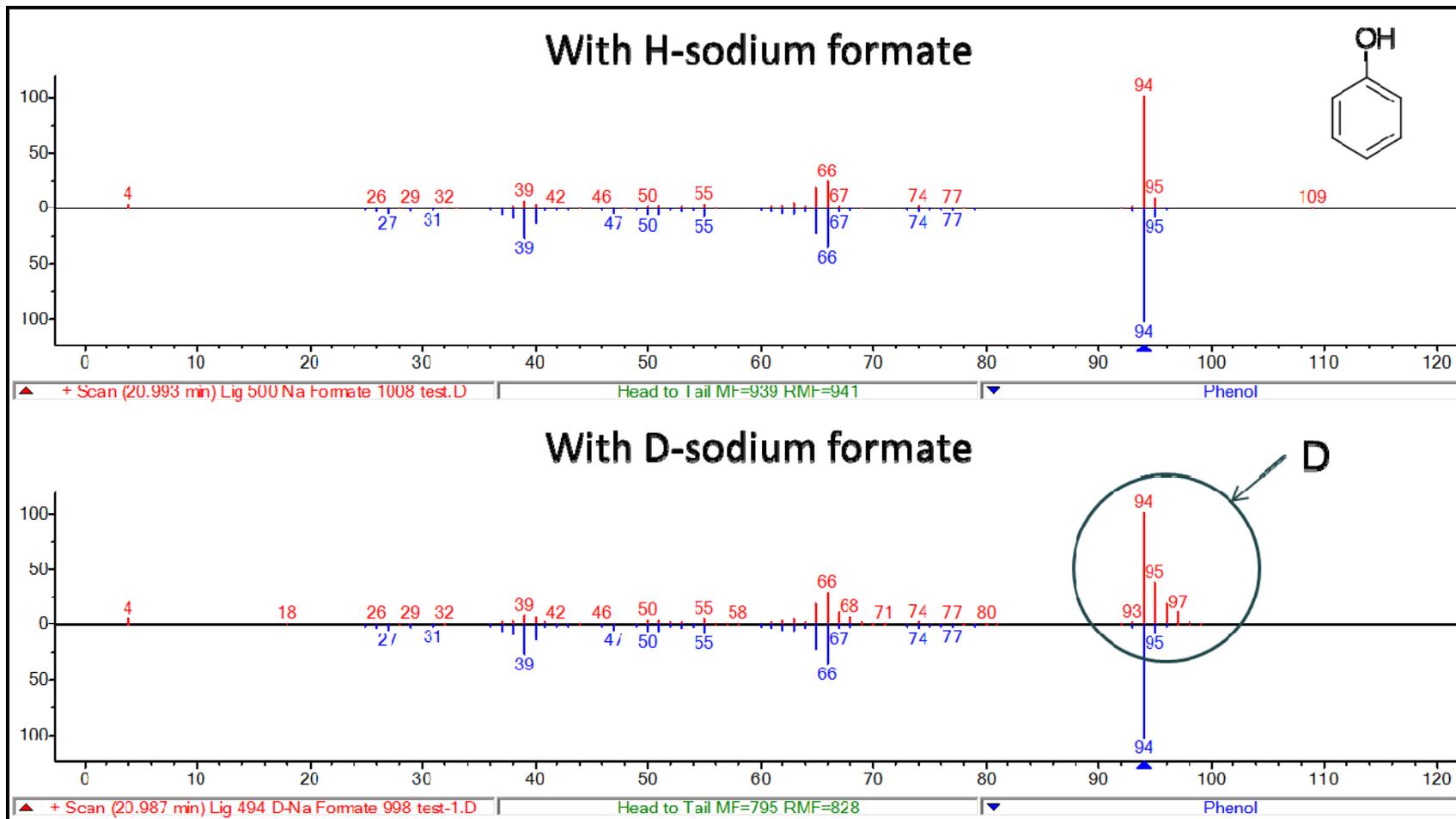


Figure 5. Presence of deuterium atoms in pyrolysis products of lignin (Phenol)

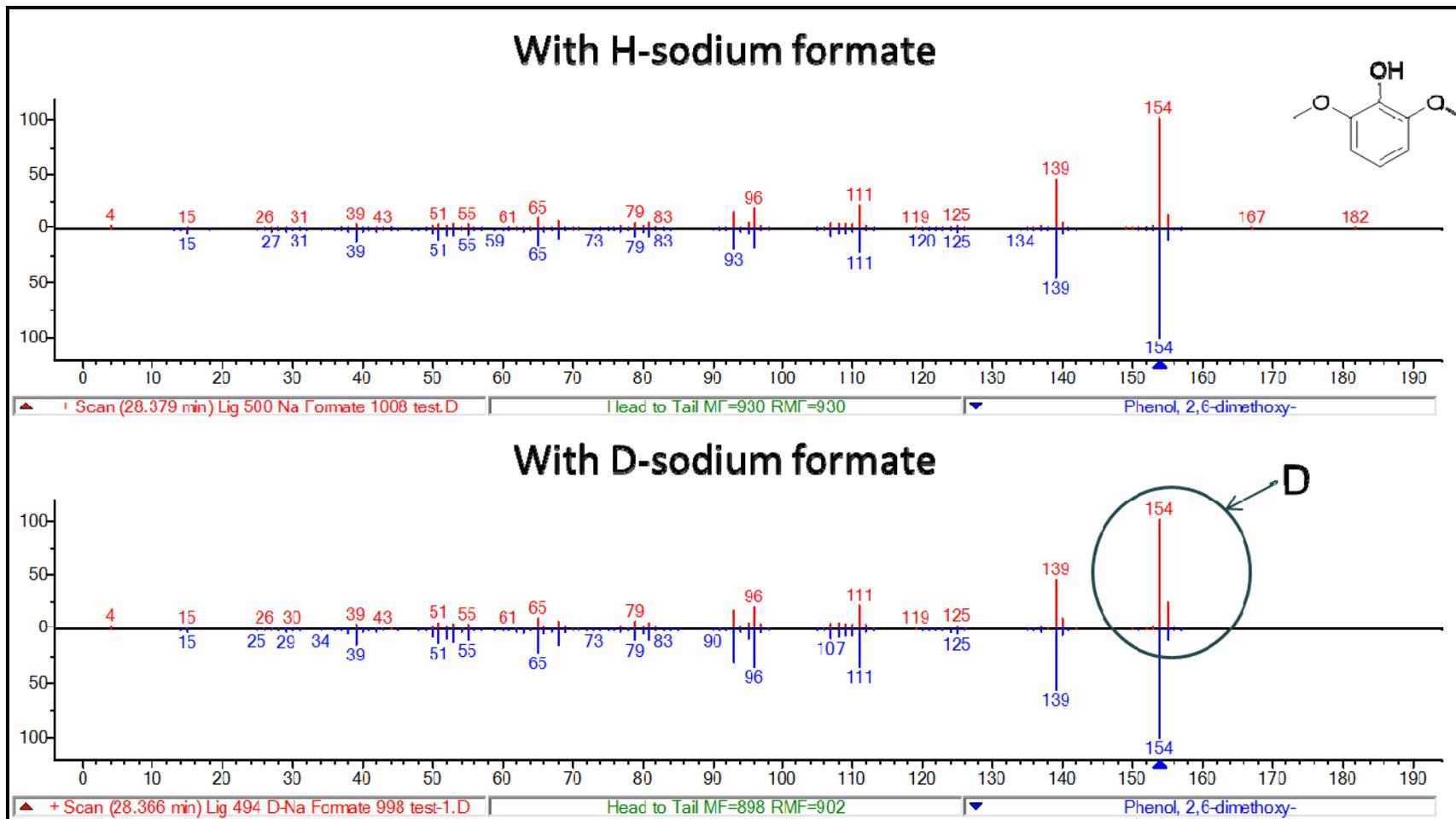


Figure 6. Presence of deuterium atoms in pyrolysis products of lignin (2, 6-dimethoxyphenol)

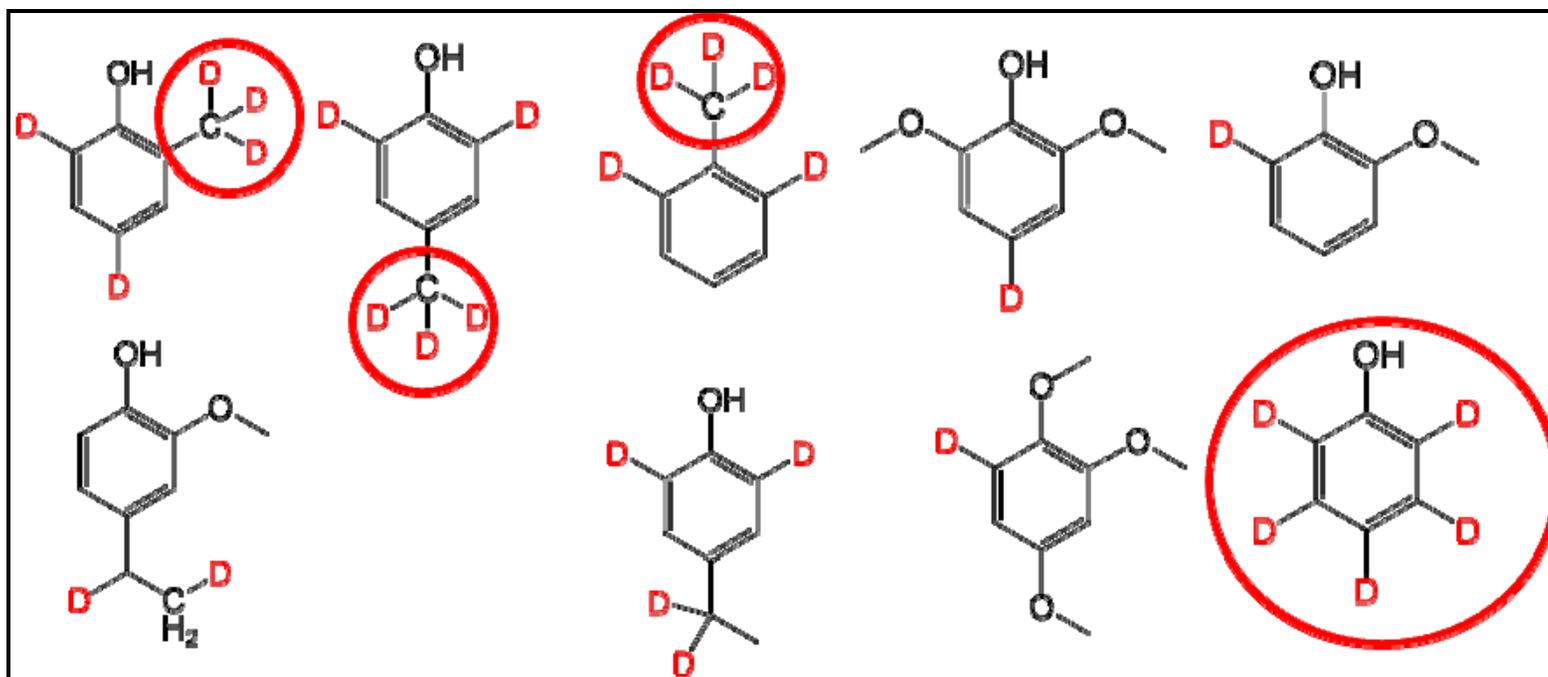


Figure 7. Hydrogen transfer in phenolic compounds during co-pyrolysis of lignin and sodium formate

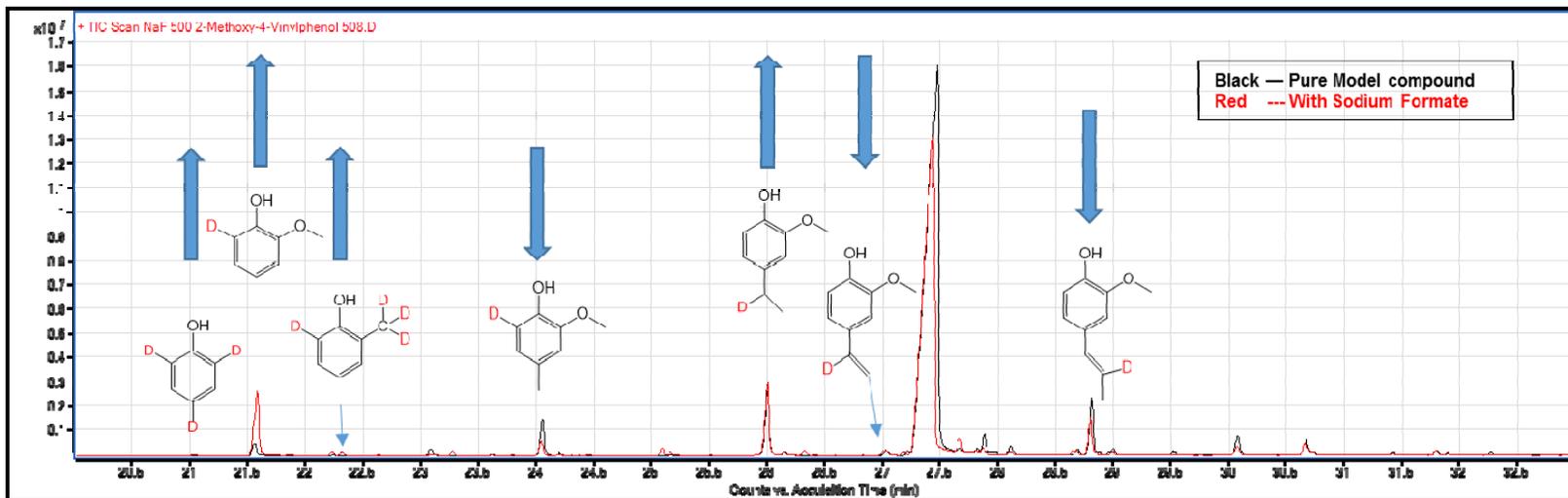


Figure 8. Pyrolysis-GC/MS chromatogram of 2-methoxy-4-vinylphenol w/o sodium formate

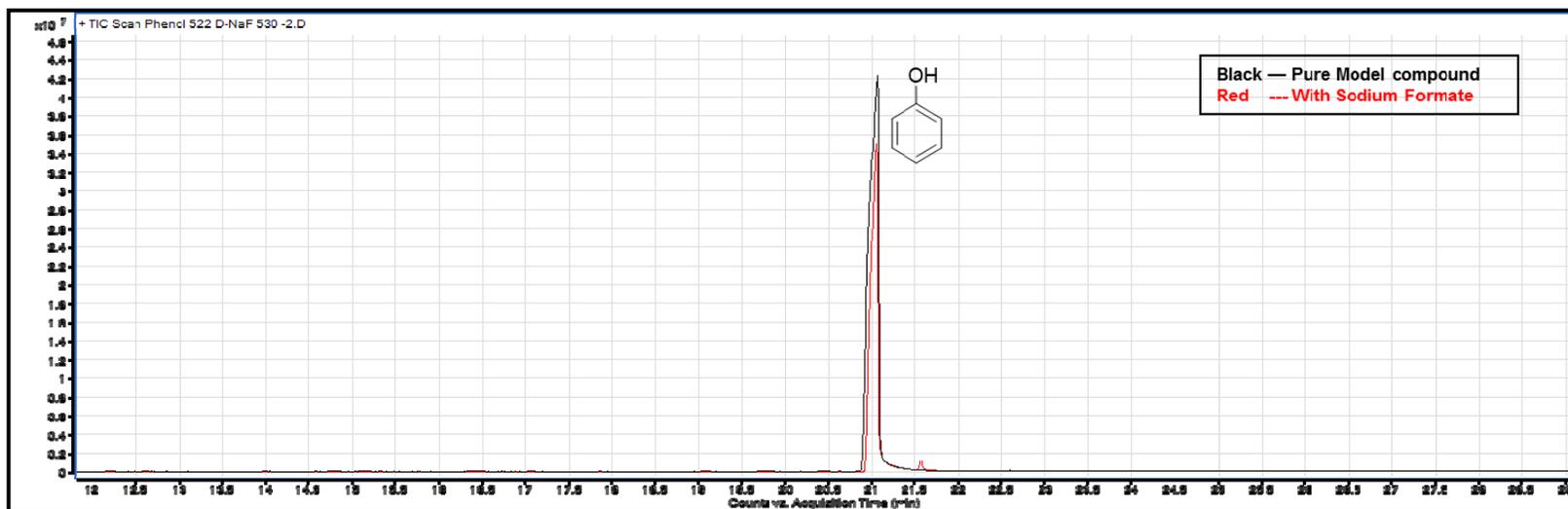


Figure 9. Pyrolysis-GC/MS chromatogram of phenol w/o sodium formate

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CHAPTER 3

THE EFFECT OF HYDROQUINONE TO IMPROVING BIO-OIL STORAGE STABILITY

Abstract

Bio-oil produced from pyrolysis of biomass is unstable during storage and upgrading process. Polymerization and condensation of bio-oil compounds catalyzed by carboxylic acids can cause increased molecular weight and viscosity of bio-oil. Water content of bio-oil also increases and phase separation is possible. The conventional approaches to improve bio-oil stability is either adding methanol to bio-oil or reducing carboxylic acid through catalytic esterification of condensed bio-oil. In the present study, the effect of hydroquinone (HQ) as the free radical scavenger related to bio-oil stability was examined. It was found that quenching pyrolysis vapors in HQ containing solvent can reduce polymerization of pyrolysis products and further improve bio-oil storage stability. However, adding HQ in already condensed bio-oil is found to be less effective. Electron paramagnetic resonance (EPR) was employed in the present study to investigate the mechanism of hydroquinone in stabilizing bio-oil.

Keywords: Biomass, pyrolysis, hydroquinone, bio-oil stability, free radicals

1. Introduction

Increasing energy consumption accompanied by the rapid development of global economy and population explosion, the global environment is experiencing increasingly serious problems caused by fossil fuels. Climate change due to greenhouse gas (i.e., carbon dioxide, methane, nitrous oxide, etc.) emission [1, 2], and human disease due to aerosol particulates generated from coal combustion are some of the examples [3-5]. Thus, developing green and renewable alternatives of fossil fuel become an urgent task. Among various green technologies, biomass is the only natural source that can provide liquid fuels and chemicals [6, 7]. Coming from plants, biomass is considered as a carbon neutral energy resource since there is no net carbon dioxide is emitted into the earth's atmosphere during the combustion of biomass based fuels [8-10]. Lignocellulosic biomass is also the most abundant resources to generate sustainable energy. The worldwide annual production of biomass is 1×10^{10} million tons [11]. The first generation bio-fuels, which are mainly produced from edible crops, are considered finite capability in replacing fossil fuel and alleviating the pressure of environmental issues since the competition for land and water. However, these concerns have been successfully solved by the second generation biofuel, lignocellulosic biofuel [12-14].

As a rapid thermochemical decomposition process of organic materials, fast pyrolysis is performed in the absence of oxygen to produce non-condensing gases, liquids, and char [15]. Fast pyrolysis is considered as one of the most promising conversion technologies due to its relatively low capital and operation costs, attributed by the moderate reaction temperatures and atmospheric pressure operation [16]. During fast pyrolysis, lignocellulosic biomass is depolymerized into building block chemicals through series of reactions, such as cracking, deoxygenation, dehydrogenation, decarboxylation and dehydration [17, 18]. The

moderate reaction temperature, high heating rate, and super short residence time of the vapor are the keys for obtaining high yield of liquid products from biomass by pyrolysis [19]. The liquids, so-called, bio-oil, is the major product of fast pyrolysis and it is composed of various chemical compounds, including sugars, furans, acids, ketones, aldehydes, alcohols and phenols [20]. Bio-oil is also an intermediate produce suitable for upgrading to transportation fuels and other value-added products [21].

Despite of obvious advantages in pyrolytic bio-oils, multiple significant technical barriers have to be overcome before fast pyrolysis process being considered for large scale industrial application. First of all, high oxygen content of pyrolysis oil is crucial, which contributes to a heating value as low as half of traditional fossil fuels [22]. Bio-oil is also a complicated mixture of a variety of chemicals and it is known that carboxylic acids in bio-oil can catalyze the polymerization and condensation reactions among different compounds [22, 23]. As a result, bio-oil is extremely unstable and has a poor quality. Thermal instability of bio-oil has to be addressed properly before bio-oil can be commercially used as transportation fuel, since it increases viscosity of bio-oil and even causes phase separation [24, 25].

The cause of bio-oil instability has been extensively investigated. Polymerization of phenolic compounds, reaction of aldehydes, esterification, sugar polymerization and degradation were found to contribute bio-oil aging [26-30]. Bio-oil also contains free radicals. Free radical is an atom, molecule, or ion that has unpaired valence electrons. Researchers have detected the presence of free radicals during the pyrolysis of biomass and its components [31-35] and lignin is the major source of free radicals among biomass composition [36-39]. Since reactive free radicals usually have very short lifetime, it has been

considered that the free radicals remaining in previously condensed bio-oil are stable and they do not contribute bio-oil instability [40]. However, the reactivity of free radicals in pyrolysis vapor is unknown and how they are correlated with bio-oil instability has never been investigated. Furthermore, it may be an effective way to improve bio-oil stability and quality by capping the free radicals while they are in pyrolysis vapor.

Hydroquinone has been commercially utilized as free radical traps to inhibit polymerization [41]. A slight amount of HQ can effectively prevent polymerization of monomers that initiated by free radical chain reaction [42, 43]. Therefore, it is hypothesized that HQ could possibly react with free radicals generated from pyrolysis of biomass and therefore prevent polymerization reactions and stabilize bio-oil. To test this hypothesis, HQ was either co-pyrolyzed with red oak or added to the vapor quenching solvent in a small quantity.

2. Materials and methods

2.1 Materials

Red oak powder

Red oak chips obtained from Wood Residuals Solutions was milled and sieved to a size about 250 - 400 μ m.

Red oak-derived lignin

A solvent mixture of ethanol and water (125 ml of ethanol and 125 ml of water) were used for lignin extraction. 15 g of biomass sample and 1.5 g sulfuric acid were added to the mixture. The solution was transferred into a 500 ml Parr reactor in Iowa State University BioCentury Research Farm, the reactor was heated up to 180°C and then cooled down. The

solution was filtered by filter paper (Whatman 42), the filtrate was precipitated in 750 ml water, and the solid residue was collected and dried at 50°C.

Chemical compounds

Methanol, tetrahydrofuran and sulfuric acid were purchased from Fisher Scientific Company. Hydroquinone and the other compounds employed in the present study were purchased from Sigma-Aldrich Company.

2.2 Pyrolysis test and vapor collection

A Frontier Lab Tandem micro-pyrolysis reactor system (Rx-3050TR) was employed to perform red oak biomass pyrolysis. The reactor system has two reaction furnaces (1st and 2nd furnaces) and two independent interface sections arranged in tandem, each of which is able to be independently temperature-controlled. The temperature can be controlled from 40 to 900 °C with 1 °C interval for both reactor and interface section. In the present study, to collecting pyrolytic vapors, only the first furnace and its interface section is employed. The temperature of reactor was set at 500 °C and interface section was set at 300 °C to prevent pyrolysis products from condensing inside the system.

Pyrolysis reactor system was fixed on a solid framework and the needle of 1st reactor was inserted into a Thermo Science GC glass vial filled with 1.5 mL solvent to condense pyrolysis vapor. The vial was placed in a container which filled with dry ice. The solvent can be either tetrahydrofuran or methanol, depending on analytical need. In the present study, pure tetrahydrofuran was used for GPC analysis, while pure methanol was for GC/MS, EPR analysis and aging tests. For each run, $4000 \pm 50\mu\text{g}$ of red oak biomass or red oak derived

lignin was weighed in a sample cup. In order to acquire enough concentration, ten samples were pyrolyzed sequentially and the vapors were collected in the same vial. When collecting pyrolytic vapors in HQ added solvent, a constant 5 wt% HQ solvent concentration was employed in the present study.

2.3 Bio-oil aging test

To preparing aging samples for GC/MS analysis, an accelerated aging test was accomplished at 80 °C for 12 hours. The GC vials with the methanol condensed bio-oil were placed inside a fume hood at room temperature to evaporate the solvent. After methanol evaporated, the vials were sealed and heated in a Fisher Scientific Isotemp Oven maintained at 80 °C for 12 hours.

As for aging test for already condensed bio-oil sample, red oak bio-oil produced in a pilot-scale pyrolysis unit in Iowa State University BioCentury Research Farm was employed. The bio-oil sample and the bio-oil with 10wt% of HQ were subjected for accelerated aging test at 80 °C for 0, 8, 16 and 24 hours, respectively. The average molecular weights of the bio-oils were determined by GPC analysis.

2.4 GC / MS analysis for bio-oil

An Agilent 7890B/5977A GC/MS system was employed for bio-oil composition analysis. A 1 μ L of bio-oil sample was injected into the GC column, which was an alloy capillary column (Ultra Alloy-1701). The column was contained in GC oven, which was heated from 40 °C to 280 °C at a heating rate of 6 °C per minute and kept at the final temperature for additional 10 minutes. In the column, volatile compounds were propelled by

helium gas and travelled through the column and eventually eluted at different times. Three independent detectors, MS, FID and TCD, were connected with the end of the GC column and substances eluted from the column were separated into 3 parts and measured by the three detectors separately. The MS signal and NIST mass spectral library were used to identify the reaction products. FID detector was used to quantify pyrolytic products and the TCD detector was not employed in the present study.

2.5 Gel Permeation Chromatography analysis

The molecular weight (MW) distribution of condensed bio-oil was determined by Gel Permeation Chromatography (GPC) through Dionex ultimate 3000 High Performance Liquid Chromatography (HPLC) system. The GPC system equipped a Shodex Refractive Index (RI) and a Diode Array Detector (DAD). The GPC system column was calibrated by six polystyrene standards. Each bio-oil sample was filtered by a Whatman 0.25 μ m polytetrafluoroethylene (PTFE) filter before analysis. The AMW and the molecular mass distribution were determined by Dionex – Chromeleon chromatograph data system software.

2.6 Electron Paramagnetic Resonance analysis

A 100 μ L of vapor condensed solution was transformed to a special EPR quartz tube for analysis. EPR spectra was acquired on a Bruker ELEXYS E580 FT-EPR spectrometer at the X-band microwave frequency 9.9 GHz with a magnetic field modulation of 100 KHz at room temperature, microwave power 6.289mW. EPR parameters: center field of 3510 G, sweep time of 20.9 s, sweep width of 200 G, number of scans=16, receiver gain of 50dB, and modulation amplitude of 1 G.

3. Results and discussion

3.1 Co-pyrolysis red oak with HQ

When HQ was co-pyrolyzed with red oak biomass, the thin reactor needle of micro-pyrolyzer was clogged almost instantly. This suggests that HQ, as free radical scavenger, strongly reacts with biomass-derived free radicals in the solid/liquid matrix to create non-volatile products. The condensation of the large MW products in the vapor clogs the passage of the pyrolytic vapors. Thus it is concluded that capping the free radicals in the vapor phase using HQ was unsuccessful probably due to thermal instability of HQ.

3.2. GC/MS analysis of HQ treated bio-oil

Then we tried to collect pyrolytic vapors into HQ added solvent and analyze the bio-oils composition using GC/MS. Table 1 compared the composition of fresh pyrolysis vapor of red oak with or without HQ treated. As shown, the bio-oils collected in HQ added quenching solvent have the similar concentrations of GC/MS detectable products compared to the bio-oils collected in the quenching solvent without HQ.

The GC/MS chromatograms of the aged bio-oils with and without HQ treatment were compared in Figure 1. As it can be seen, very few volatile compounds can be detected for the aged bio-oil samples without HQ treated due to their low concentrations in the bio-oils. On the other hand, multiple carbohydrate-derived and lignin-derived compounds were still detectable for the bio-oils with HQ treatment after aging.

**Table 1. Composition analysis of biomass pyrolysis vapors
w / o hydroquinone solvent condensing**

	Compounds (wt% per biomass)	W/O HQ	With HQ
1	Glycolaldehyde	2.34 ± 0.03	2.46 ± 0.05
2	Acetic acid	1.45 ± 0.14	1.61 ± 0.15
3	Acetol	0.67 ± 0.05	0.73 ± 0.05
4	Acetoxyacetic acid	0.13 ± 0.01	0.17 ± 0.01
5	Furfural	0.11 ± 0.00	0.09 ± 0.01
6	2-Hydroxycyclopent-2-en-1-one	0.02 ± 0.00	0.02 ± 0.00
7	Guaiacol	0.17 ± 0.03	0.18 ± 0.02
8	Creosol	0.08 ± 0.01	0.08 ± 0.00
9	2-Methoxy-4-vinylphenol	0.01 ± 0.00	0.01 ± 0.00
10	2,6-Dimethoxyphenol	0.09 ± 0.01	0.10 ± 0.01
11	Isoeugenol	0.09 ± 0.01	0.09 ± 0.01
12	1,2,4-Trimethoxybenzene	0.12 ± 0.00	0.13 ± 0.01
13	1,2,3-Trimethoxy-5-methylbenzene	0.26 ± 0.01	0.28 ± 0.02
14	3',5'-Dimethoxyacetophenone	0.10 ± 0.01	0.10 ± 0.01
15	Levoglucosan	0.20 ± 0.01	0.20 ± 0.02
16	2,6-Dimethoxy-4-allylphenol	0.20 ± 0.01	0.18 ± 0.02
17	3,5-Dimethoxy-4-hydroxybenzaldehyde	1.11 ± 0.14	0.93 ± 0.02
18	3,5-Dimethoxy-4-hydroxyphenylacetic acid	0.27 ± 0.01	0.28 ± 0.02
19	3',5'-Dimethoxy-4'-hydroxyacetophenone	0.10 ± 0.00	0.08 ± 0.00

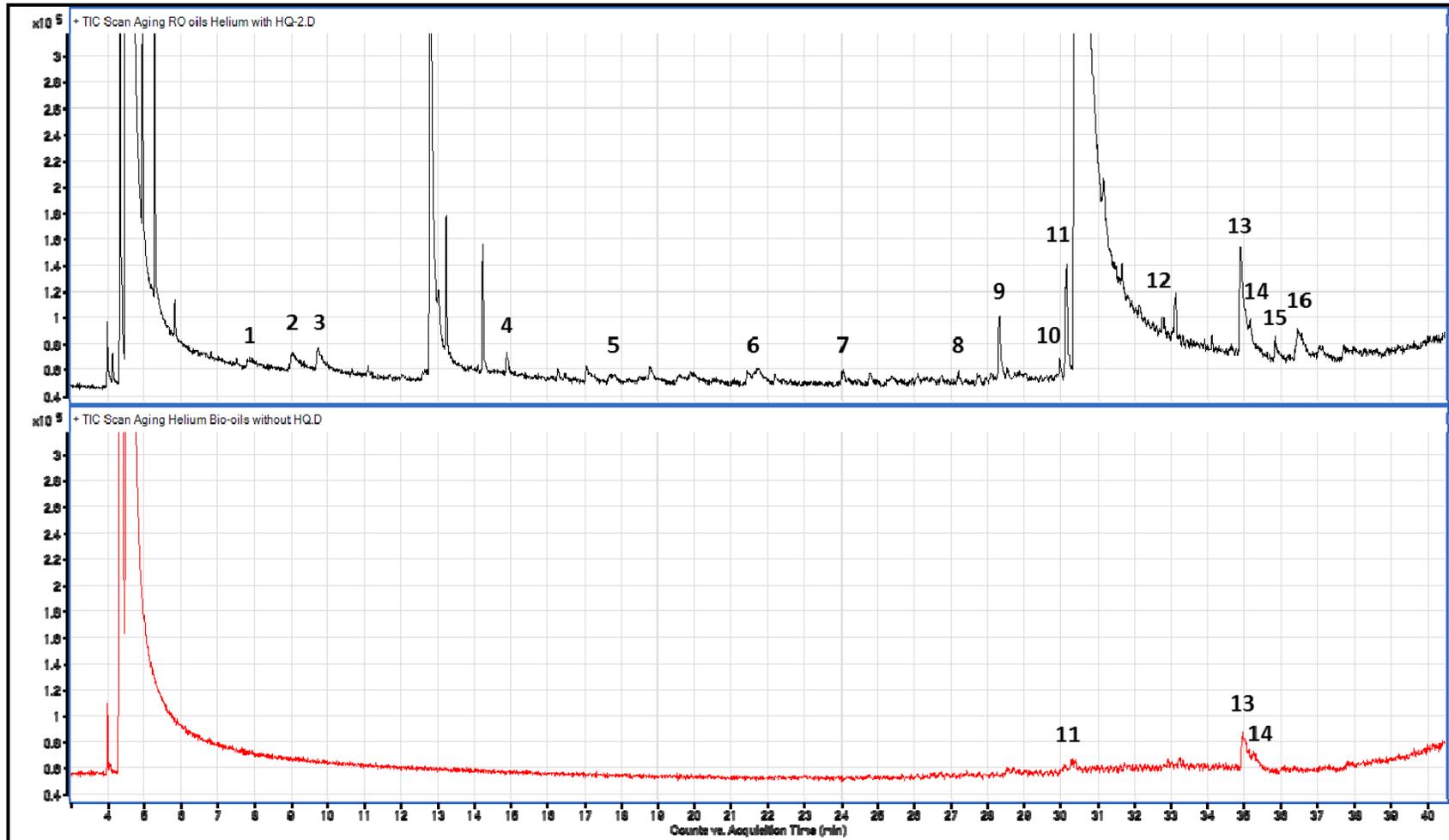


Figure 1. GC/MS chromatograms for aged red oak bio-oils collected in a solvent with no HQ and with HQ (1. Glycolaldehyde; 2. Acetic Acid; 3. Acetol; 4. Furfural; 5. 2-Hydroxycyclopent-2-en-1-one; 6. Guaiacol; 7. Cresol; 8. 2-Methoxy-4-vinylphenol; 9. 2, 6-Dimethoxyphenol; 10. Isoeugenol; 11. 1, 2, 4-trimethoxybenzene, 12. 3', 5'-Dimethoxyacetophenone, 13. Levoglucosan, 14. 4-Allyl-2, 6-dimethoxyphenol, 15. 3, 5-Dimethoxy-4-hydroxybenzaldehyde, 16. 3, 5-Dimethoxy-4-hydroxyphenylacetic acid)

3.3 GPC analysis of HQ treated bio-oil

For fresh condensed bio-oil samples, as shown in Figure 2, the MW distribution between with and without HQ treated were very similar. After aged for 12 hours, the bio-oils with HQ treated consisted of the compounds with both low molecular weights and high molecular weights after aging (Figure 3). On the other hand, the bio-oils without HQ treated mostly consisted of the compounds with only high molecular weights. For the fresh red oak bio-oil with and without hydroquinone solution condensing, the average molecular weight (AMW) were 287 Da and 307 Da. After aging, the AMWs of bio-oil samples increased to 442 Da and 567 Da. The results suggest that the presence of HQ was able to suppress polymerization of bio-oil and preserve more low MW compounds after aging. The GPC analysis results were in correspondent to the GC/MS chromatograms of the bio-oils since the oligomeric compounds with high molecular weights cannot be detected by GC/MS. Therefore, the bio-oils quenched in HQ containing solvent probably have lower tendency to polymerize thus containing higher concentration of GC/MS detectable low-molecular weight products after aging.

3.4 The effect of HQ addition to condensed oil

The AMWs of the bio-oils (i.e., condensed bio-oil, obtained from the BCRF pilot scale reactor) without and with HQ addition after aging test are compared in Figure 4. As shown, the addition of HQ to already condensed bio-oil did not have significant influence on the aging of bio-oil, as both types of the bio-oil aged in nearly identical pattern. The result is consistent with other researchers [38, 39], showing stable radicals in condensed bio-oil do

not contribute bio-oil aging and thus the addition of HQ has no effect to the already condensed bio-oil.

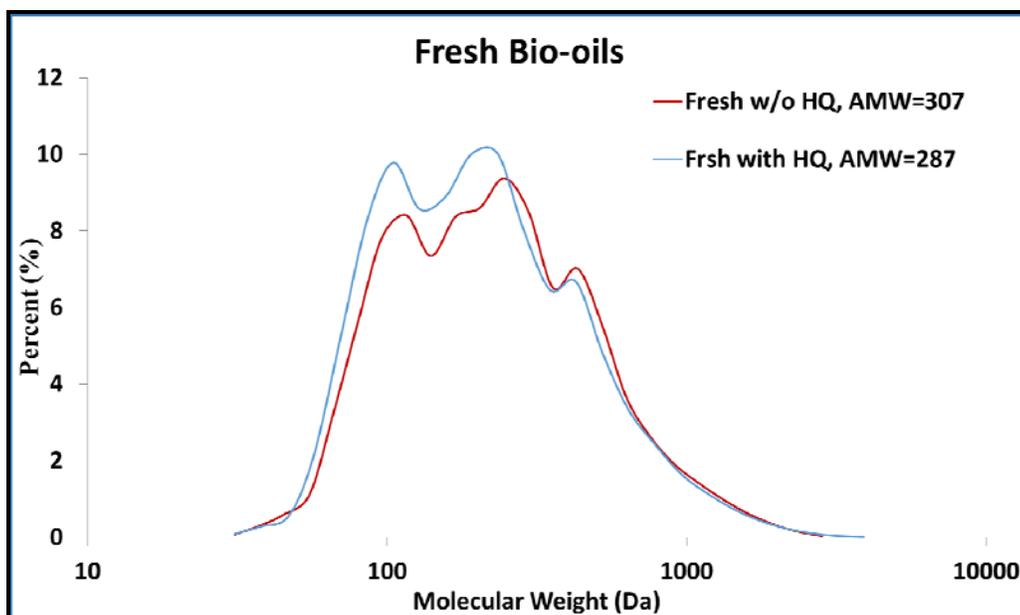


Figure 2. Molecular weight distribution of fresh bio-oil w/o HQ

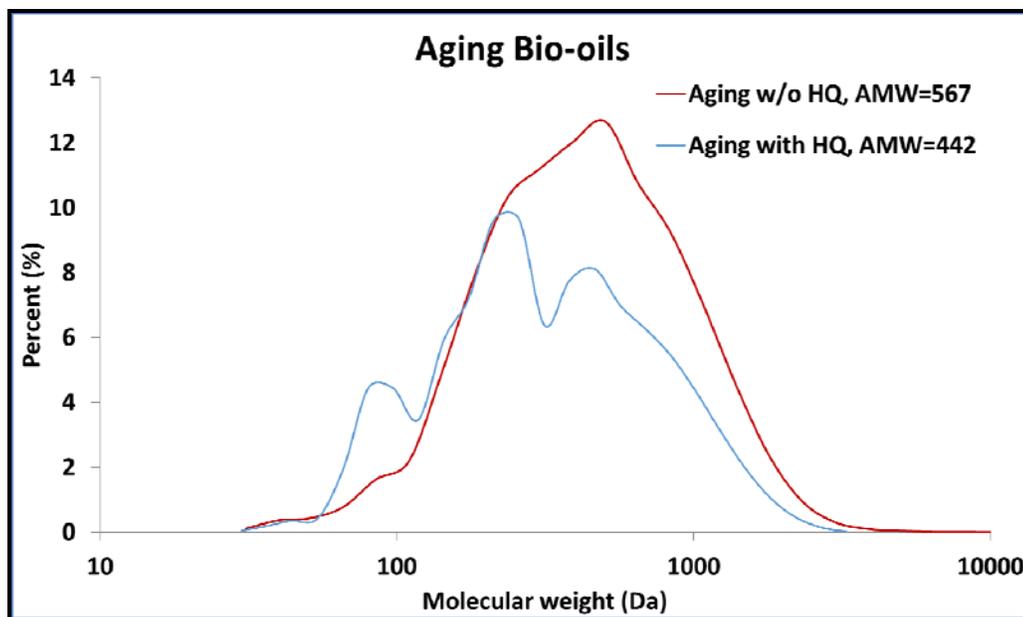


Figure 3. Molecular weight distribution of aged bio-oil w/o HQ

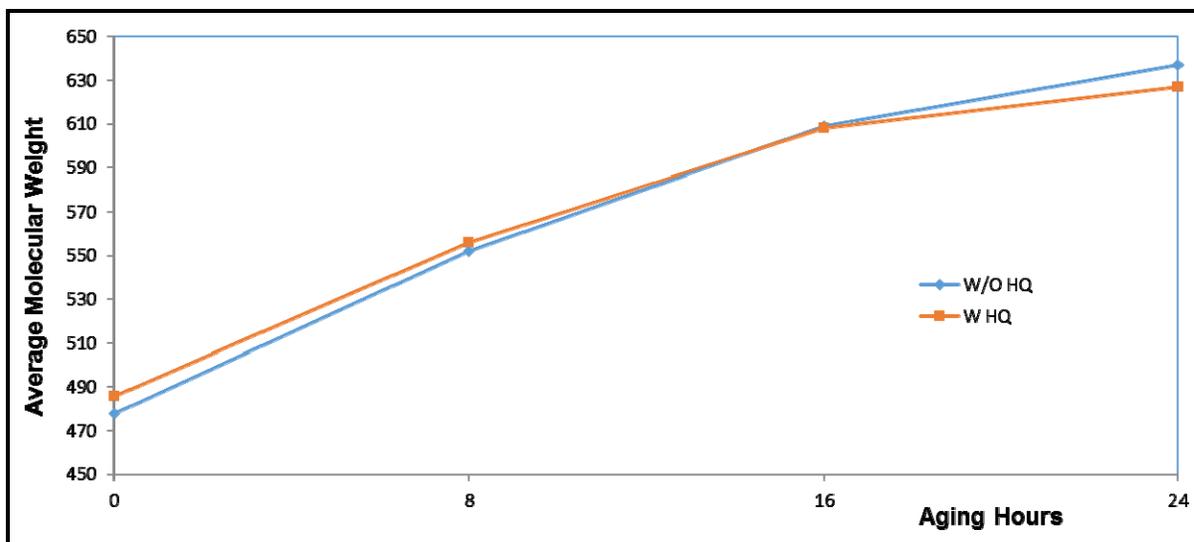


Figure 4. Average molecular weights of bio-oils at different accelerated aging times

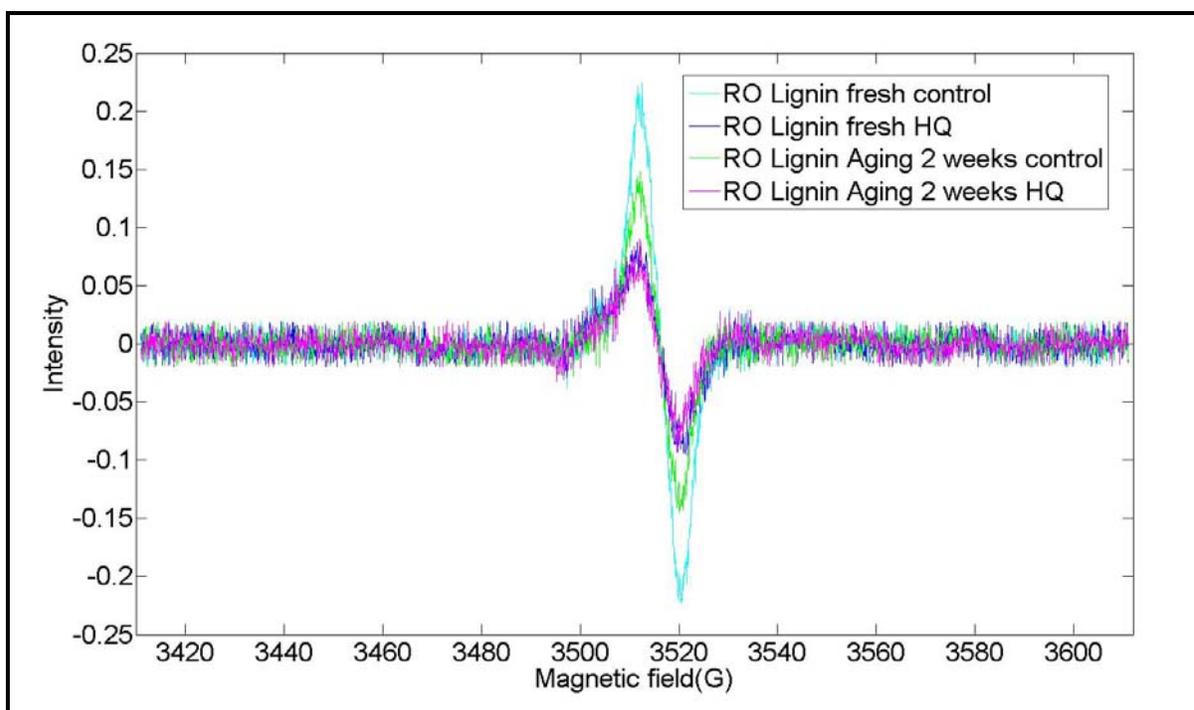


Figure 5. EPR spectra of lignin pyrolysis vapor condensed in solvent with or without HQ

3.5 EPR analysis of HQ treated bio-oil

As discussed above, the addition of HQ in already condensed bio-oil had no effect to bio-oil aging. In comparison, treating hot pyrolysis vapor with HQ was effective in decreasing bio-oil polymerization. This indicates that reactive free radicals is present in the pyrolysis vapor and HQ could act as a free radical scavenger. This speculation was further confirmed by measuring the free radicals in the bio-oil using EPR analysis technique.

Since lignin is the major source of free radicles, the EPR spectra compared the free radical signal of red oak lignin-derived bio-oils with or without HQ treatment. As shown in Figure 5. The signal of the fresh bio-oil without HQ treated was significantly stronger than the fresh bio-oil with HQ, which indicate that HQ might react with the free radicals in the hot vapors when they were condensed in the HQ added solvent. After aging, the bio-oil without HQ treated showed a clearly decrease in the concentration of free radicals, while the free radical concentration in the bio-oil with HQ treatment did not change after aging. This indicates that reactive free radicals present in freshly condensed bio-oil and HQ addition to the quenching solvent is able to stabilize reactive free radicals.

4. Conclusion

The reactivity of free radicals in pyrolysis vapor and its effect on bio-oil stability were investigated using HQ as the free radical scavenger.

1. Quenching pyrolysis vapors in HQ containing solvent can lower the tendency of polymerization and thus improve bio-oil storage stability.
2. The addition of HQ in already condensed bio-oil is less effective.

3. The EPR analysis of bio-oil indicates that the free radicals in pyrolysis vapors are reactive and contribute to bio-oil instability. HQ stabilized the reactive free radicals when the vapor condenses, thus prevented free radical initiated polymerization.

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CHAPTER 4

GENERAL CONCLUSIONS

In the present study, fast pyrolysis of biomass and its model compounds was investigated in order to understand reaction mechanisms and overcome the technical barriers that keep pyrolytic bio-oil from being produced for large scale application. Currently, the poor quality of bio-oil due to complex product composition, and thermal instability of bio-oil are among the important factors that impact industrial upgrading of bio-oil. Therefore, it is necessary to in-depth examine the reaction mechanism of biomass pyrolysis and the cause of bio-oil instability, and provide solutions to improve bio-oil quality and stability. First, sodium formate was used as a hydrogen donor capping agent to co-pyrolyze with lignin. It was found that sodium formate strongly affects the distribution of lignin pyrolysis products by increasing simpler phenolic monomers and alkylated phenols at the expense of the phenols with vinyl and carbonyl groups. The addition of sodium formate dramatically reduced the yield of acetic acid by neutralization. As a result, bio-oil produced from co-pyrolysis of lignin and sodium formate contained a higher amount of total monomers and a better thermal stability than the bio-oil produced from pyrolysis of lignin. The mechanism of hydrogen-transfer from sodium formate to lignin was studied using deuterated sodium formate. It was found that external hydrogen atoms mainly substitute phenolic alkyl-side chain and para-, ortho- positions of the benzene rings. Hydrogen was able to directly affect thermal decomposition of lignin polymer through a series of reactions involving hydrocracking, demethoxylation, saturation and substitution to produce simpler and stable phenols.

The free radical capping reaction was also investigated using hydroquinone (HQ) as the scavenger. It was found that quenching pyrolysis vapors in HQ containing solvent can lower the tendency of bio-oil polymerization and improve bio-oil storage stability. However, adding HQ in already condensed bio-oil was less effective since the condensed bio-oil contains stable free radicals, which do not contribute to bio-oil aging. The EPR analysis of bio-oil showed that reactive free radicals present in pyrolysis vapor and adding HQ in the vapor condensing solvent effectively cap the radicals and further improve bio-oil stability.