BIO-BASED PHENOLIC RESINS AND ADHESIVES DERIVED FROM FORESTRY RESIDUES/WASTES AND LIGNIN

(Spine title: Bio-based Phenolic Resins and Adhesives from Lignin)

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by

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ABSTRACT

The work presented here aims to produce bio-phenolic compounds from forestry biomass (residues, wastes and lignin), and substitute petroleum-based phenol with the bio-phenolic compounds to produce high quality bio-based phenol formaldehyde (PF) resins.

For the production of bio-phenolic compounds from biomass, alcohol (methanol or ethanol) and water showed synergistic effects on biomass direct liquefaction. 65 wt% of bio-oil and a biomass conversion at > 95% were obtained at 300 °C for 15 min in the 50%/50% (w/w) co-solvent of either methanol-water or ethanol-water. At a temperature higher than 300 °C, conversion of bio-oil to char was significant via re-polymerization reactions. The Fourier Transform Infrared Spectroscopy (FTIR) and Gas Chromatography-Mass Spectroscopy (GC-MS) analyses of the obtained bio-oils confirmed the presence of primarily phenolic compounds and their derivatives (such as benzenes), followed by aldehyde, long-chain (and cyclic) ketones and alcohols, ester, organic acid, and ether compounds. The Gel Permeation Chromatography (GPC) results suggested that hot-compressed ethanol as the liquefaction solvent favored lignin degradation into monomeric phenols. The X-ray Diffraction (XRD) patterns of Eastern White Pine (*Pinus strobus L.*) wood before and after the liquefaction displayed that the cellulosic structure of the feedstock was completely converted into amorphous carbon at around 300 °C, and into crystalline carbon at about 350 °C.

The bio-oil was successfully applied to synthesize bio-oil phenol formaldehyde (BPF) resins up to 75 wt% substitution for phenol. All the BPF resins showed similar physical-chemical properties, such as viscosity, pH value, free formaldehyde level, non-volatile contents, thermal behavior and thermal stability as the pure phenol-formaldehyde (PF) resin. Particularly for the bond strength (dry and wet tensile strength), all the BPF adhesives demonstrated similar or better strength than the PF adhesive. In order to further improve the reactivity of the bio-oil for production of higher quality phenolic resole resins based on the previous work, the bio-oil was methylolated by treating with formaldehyde before resinification. The results showed that the methylolation treatment improved the thermal stability and decreased curing temperature of the resins. But the treatment slightly increased the viscosity and slightly decreased the bond strength of the methylolated bio-oil PF (MBPF) resins, depending on the methylolated bio-oil ratio in the formula. Dry/wet bond strengths of MBPF resins at a phenol substitution ratio up to 60 wt% exceeded or were still comparable to those of the pure PF resin. Although the substitution ratio is lower than that for the BPF resin, it is still higher than that (< 50 wt%) reported by other researchers.

For the production of bio-phenolic compounds from alkali lignin (AL), 89% degraded lignin (DL) was achieved by hydrothermal treatment in 50/50 (v/v) water-ethanol at 300 ^{o}C under 5 MPa H_2. The relative molecular weights of the lignin were markedly reduced from its original M_w and M_n of 60,000 g/mol and 10,000 g/mol, respectively, to M_w: 1010 g/mol and M_n: 415 g/mol for the DL. The reaction time had little effects on the DL yields and properties. 300-325 ^{o}C and 400 ^{o}C appeared to be the optimal temperature for the process in 50/50 (v/v) water-ethanol and pure ethanol, respectively. The catalyst tested in this work did not significantly affect the yield of DLs, but slightly reduced the relative molecular weights of the DLs. For the production of bio-phenolic compounds from organosolv lignin (OL), 81 % of DL with very low relative molecular weights (M_n 181 g/mol and M_w 568 g/mol) was produced at 340 ^{o}C in 50/50 (v/v) water-ethanol with Ni10/AC catalyst. The reaction temperature had significant effects on the yield and molecular-weight distributions of the DL. Faster heating and stirring had a positive effect on the yield of DL, particularly the stirring. The bio-phenolic compounds derived from the OL were then used to replace phenol in the production of phenolic resole resins. All the degraded lignin-phenol-formaldehyde (DLPF) and the organosolv lignin-phenol-formaldehyde (OLPF) resole resins have similar physical-chemical properties as the pure PF resin. The plywood samples glued with the OLPF and DLPF adhesives with a phenol replacement ratio up to 75 wt% showed higher dry and wet tensile strengths than that of the PF resin. Although the OLPF adhesives have better bond strengths and thermal stability than DLPF adhesives, the DLPF resins have lower free formaldehyde content and a lower curing temperature.

In this study, formic acid that can act as a hydrogen donor at elevated temperatures was employed for degradation of AL and OL in the medium of sub-/super-critical 50/50 (v/v) water-ethanol. With formic acid, 77 % yield of DL with the relative molecular weights of M_n 295 g/mol and M_w 816 g/mol was obtained from the degradation treatment of AL at 300 ^oC. For the degradation treatment of OL, a high yield of DL (80 %) with low relative M_n 150 g/mol and M_w 464 g/mol was successfully achieved with formic acid at 350 ^oC. The use of formic acid was found to be effective for increasing the DL yields while suppressing the formation of solid residues compared with the use of gaseous hydrogen, likely because the in situ formed hydrogen from formic acid can prevent the recombination of reaction intermediates.

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LIST OF ABBREVIATIONS

AC – Active Carbon
AL – Alkali Lignin
AP – Aqueous Products
BET – Brunauer, Emmett and Teller
BPF – Bio-oil Phenol Formaldehyde
CAS – American Chemical Society
CHP – Cumene Hydroperoxide
DHMP – Dihydromethyl Phenol
DIN – Deutsches Institut für Normung’
DL – Degraded Lignin
DLPF – Degraded Lignin Phenol Formaldehyde
DMSO-d_6 – Dimethyl Sulfoxide-d_6
DSC – Differential Scanning Calorimetry
DTG – Derivative Thermogravimetry
FC – Fixed Carbon
FTIR – Fourier Transform Infrared Spectroscopy
GC-MS – Gas Chromatography-Mass Spectroscopy
GPC – Gel Permeation Chromatography
HPLC – High-Performance Liquid Chromatography
HMP – Hydromethylphenol
^{1}H NMR – Proton Nuclear Magnetic Resonance Spectrometry
IB – Internal Bond
LEL/UEL – Lower Explosive Limit/Uper Explosive Limit
MAK limit – Maximale Arbeitsplatz-Konzentration
MB – Methylolated Bio-oil
MBPF – Methylolated Bio-oil Phenol Formaldehyde
MC – Moisture Content
M_n – Number Average Molecular Weight
MOR – Modulus of Rupture

MOE – Modulus of Elasticity

Mt – Million Tons

M_w – Weight Average Molecular Weight

ND – Not Detectable

NMR – Nuclear Magnetic Resonance

NOHFC – Northern Ontario Heritage Fund Corporation

NREL – National Renewable Energy Laboratory

NSERC – Natural Sciences and Engineering Research Council

OL – Organosolv Lignin

OLPF – Organosolv Lignin Phenol Formaldehyde

OMAFRA – Ontario Ministry of Agriculture, Food and Rural Affairs

OSB – Oriented Strand Board

OSHA PEL – Occupational Safety and Health Administration Permissible Exposure Limit

PD – Polydispersity

PF – Phenol Formaldehyde

PJ – Peta Joule

PMDI – Polymeric Diphenylmethane Diisocyanate

RH – Relative Humidity

SR – Solid Residue

TCD – Thermal Conductivity Detector

TGA – Thermogravimetric Analysis

THMP – Trihydromethyl Phenol

THF – Tetrahydrofuran

TMS – Tetramethylsilane

TWA – Time Weighted Average

VM – Volatile Matters

WFP – Wood Failure Percentages

WSP – Water-soluble Products

XRD – X-ray Diffraction

CHAPTER 1. INTRODUCTION

1.1 Background

Phenol-formaldehyde (PF) resins are widely used as adhesives (Alma and Basturk, 2006; Wang et al., 2009 (a); Amen-Chen, et al., 2002 (a), 2002 (b)) in the wood products industry for the manufacture of plywood, oriented strand board (OSB), particleboard, fiberboard, other composite products, and molded products (Alma, 1996, 1997; Shiraishi et al., 1993) because of its high strength and moisture resistance. PF resin manufacturing is a $2.3 billion industry in North America. Phenol as the most costly feedstock for the synthesis of PF resins is primarily produced from petroleum-derived benzene by the cumene process (developed by Hock and Lang in 1944) (Hock and Lang, 1944). The production of PF resins consumes 35-40% of the phenol production in the USA. Due to the high and fluctuating price of petroleum-based phenol (currently at about $700-1200 per metric ton), the PF resin is very expensive (at about US$1000/t). The production of phenolic compounds from non-petroleum sources such as biomass is therefore of great interest. In recent decades, depleting petroleum resources combined with increasing demands for petroleum by developing economies, as well as political and environmental concerns over fossil-based resources has intensified the interest in researching and developing alternative renewable resources for both energy and chemical production. Biomass is the only sustainable source of organic carbon that provides approximately 14% of the world's energy needs, representing an alternative, and renewable, source of both bio-fuels and valuable chemical compounds.

Biomass is readily available and renewable; it contains negligible nitrogen and sulfur contents and does not affect the overall CO_2 concentration in the atmosphere because the carbon released during combustion was taken recently from the atmosphere by photosynthesis during biomass growth. It is thus widely accepted that biomass can be a promising alternative source for energy and a variety of chemicals such as phenols, organic acids and alcohols (Connor and Piskorz, 1994). The abundant forestry/lignin resources provide the potential renewable sources for energy and chemicals. For instance, forest trimmings (e.g. leaves and branches) account for 15% of the harvested biomass and 40% of harvested timbers are converted to sawmill co-products and wastes (e.g. wood chips, sawdust and bark) (Harms, 1998). Lignin (e.g., alkaline or kraft lignin, and lignosulfonates) is produced as a by-product in large quantities from chemical pulping processes in the pulp and paper industry, and the annual generation is estimated at 50 million tons worldwide (Kües, 2007). Currently, these forestry residues/lignin are primarily used for energy. The pulp and paper industry and the sawmill industry are the largest users of bioenergy in Canada, amounted to 513 PJ (513×10^{15}J, or equivalent 16.2 billion m^3 of natural gas), supplying 50% of their own energy needs. Although 70% of the residues are utilized as energy, the remaining 30% (more than 5 million bone-dried tons per annum) are not utilized in Canada (Groves, 1998). Biomass is a lignocellulosic material whose principal chemical components are cellulose, hemi-cellulose and lignin (Gani and Naruse, 2007; Bridgwater and Peacocke, 2000). Forestry residues/wastes contain 40-45% cellulose, 15-35% hemicellulose and 20-35% lignin. The composition of these three components in lignocellulosic materials varies with species as shown in Table 1-1.

Table 1-1. Compositions of some lignocellosic materials

<table>
<tr><th colspan="2">Lignocellosic material</th><th>Lignin (wt%)</th><th>Cellulose (wt%)</th><th>Hemicelluloses (wt%)</th><th>Reference</th></tr>
<tr><td colspan="2">Forestry residues/wastes</td><td>20-35</td><td>40-45</td><td>15-35</td><td rowspan="3">S′anchez, 2008</td></tr>
<tr><td colspan="2">Agricultural residues/wastes</td><td>10-20</td><td>34-39</td><td>20-25</td></tr>
<tr><td colspan="2">Newspaper and waste paper</td><td>8-18</td><td>62-75</td><td>12-20</td></tr>
<tr><td rowspan="2">Softwood</td><td>Wood</td><td>25-30</td><td colspan="2">66-72</td><td rowspan="4">USDA Forest Service Research Note, 1971</td></tr>
<tr><td>Bark</td><td>40-55</td><td colspan="2">30-48</td></tr>
<tr><td rowspan="2">Hardwood</td><td>Wood</td><td>18-25</td><td colspan="2">74-80</td></tr>
<tr><td>Bark</td><td>40-50</td><td colspan="2">32-45</td></tr>
<tr><td colspan="2">Eastern White Pine sawdust</td><td>28.4</td><td>40.2</td><td>21.9</td><td rowspan="2">This work</td></tr>
<tr><td colspan="2">Cornstalk</td><td>24.7</td><td>26.7</td><td>21.0</td></tr>
</table>

Lignin is an amorphous three-dimensional phenyl-propanol polymer of three phenyl-propanols i.e., p-coumaryl alcohol (p-hydroxyl-phenyl propanol), coniferyl-alcohol (guaiacyl-propanol) and sinapyl-alcohol (syringyl-propanol), as illustrated in Figure 1-1 (Desch and Dinwoodie, 1996; Tsoumis, 1991). The phenyl propanol units in lignin may be de-polymerized into phenolic chemicals by pyrolysis or direct liquefaction process. Therefore, the obtained bio-oil products from the processes can be used for preparing bio-phenolic compounds to replace petroleum based phenol in phenolic resins and adhesive (Shiraishi and Kishi, 1986, Maldas et al., 1997; Ono and Sudo, 1993; Pu et al., 1991; Alma et al., 1995(a); 1995(b)).

1.2 Substitution for Phenol with Bio-based Phenolic Compounds from Forestry Residues in the PF Resins

During the past several years, many attempts have been made to replace the petrochemical resins with bio-based phenolic products from biomass feedstock by thermochemical conversions (liquefaction process and pyrolysis process) (Ono and Sudo, 1993; Alma et al., 1995(a); Shiraishi and Kishi, 1986; Maldas and Shiraishi, 1997; Pu and Yoshioka, 1991).

The U.S. National Renewable Energy Laboratory (NREL) is actively exploiting phenolic compounds from sawdust and bark through a controlled pyrolysis technology. Research at the NREL has demonstrated that it is possible to produce phenolic resins from wood for about half the cost of those produced from fossil fuels (NREL, 2003). However, pyrolysis oil is a complex mixture of water (15-30 wt%) and organics of a high oxygen-content (45-50 wt%). This oxygen content distributes more than 300 identified compounds, which consist of hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids and phenolics (Effendi and Gerhauser, 2008). The majority of the phenolics are present as oligomers containing varying numbers of acidic, phenolic and carboxylic acid hydroxyl groups as well as aldehyde, alcohol and ether function. The molecular weights of the oligomers reside in several hundreds to 5000 or more depending on the operation conditions. Therefore, pyrolysis oils are unstable upon storage and require further upgrading, which will result in a high cost. This makes them less reactive in the PF resin synthesis reactions due to shortage of the reactive sites and the steric hindrance of large molecules. In order to produce practically useful bio-based PF resins, the substitution ratio for phenol with pyrolysis oil was normally below 30-50 wt% of phenol (Zhang et al., 2006; Roy et al., 2000; Lee, 2003).

Solvolytic liquefaction of biomass is more advantageous than pyrolysis processes in that it is conducted at much lower temperatures (~ 300 °C) in a suitable solvent such as alcohols (NREL, 2003; Xu and Etcheverry, 2008), ethylene glycol (Miller et al., 1999), cyclic carbonates (Rezzoug and Capart, 2003) or phenol/phenol derivatives (Yamada and Ono, 1999; Lee and Yoshika, 2000). As such, the solvolytic liquefaction technologies of lignocellulosic materials have attracted increasing interest for the production of bio-phenol precursors for synthesis of bio-based phenolic resins (Russell and Riemath, 1985; Alma et al., 1997; 2001). More recently, there has been a huge surge of interest in using hot-compressed and sub-/super-critical fluids for biomass liquefaction. Supercritical fluids have found applications for the chemical conversion of lignocellulosic materials due to their unique properties, e.g., they possess unique transport properties (gas-like diffusivity and liquid-like density), and supercritical fluids also have the ability to dissolve materials not normally soluble in either the liquid or gaseous phase of the solvent, and hence to promote the gasification/liquefaction reactions. Hot-compressed or sub-critical water has been used by many researchers for biomass liquefaction (Matsumura et al., 1999; Karagoz et al., 2004; 2005; Xu and Lad, 2008), while the main drawback of using water as the liquefaction solvent could be its lower yields of the water-insoluble oily product, compared with the liquefaction using sub-/super-critical alcohols or acetone (Xu and Etcheverry, 2008; Miller et al., 1999; Minami and Saka, 2005; Yamazaki et al., 2006; Liu and Zhang, 2008). Another advantage of using alcohols as the solvent for biomass liquefaction is that these alcohols were expected to readily dissolve relatively high molecular weight products derived from cellulose, hemicelluloses, and lignin due to their lower dielectric constants when compared with that of water (Yamazaki et al., 2006). Biomass solvolytic liquefaction was found to be highly affected by the solvent type (Liu and Zhang, 2008). Inspired by the above research on organosolv delignification of biomass, liquefaction of woody biomass in alcohol-water mixture at a higher temperature will be of interest for the production of bio-oil and phenolic feedstock for the synthesis of bio-based phenolic resins (Pasquini et al., 2005).

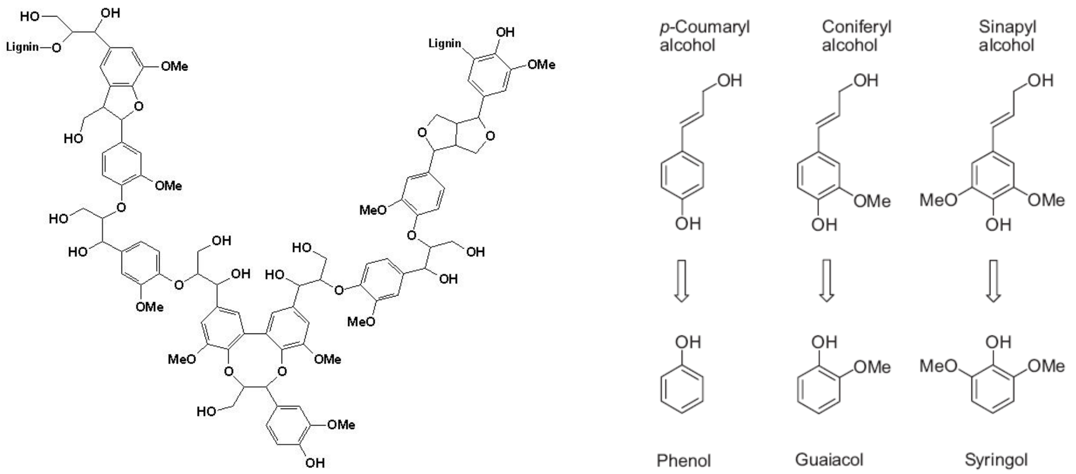


Figure 1-1. Chemical structure of a piece of lignin molecule, three monomers of lignin, and the respective direct degradation products (Desch and Dinwoodie, 1996; Tsoumis, 1991).

1.3 Substitution for Phenol with Bio-based Phenolic Compounds from Lignin in the PF Resins

Extensive studies have been conducted into the use of various lignins (Kraft, lignosulfonate, soda-anthraquinone, organosolv, and steam explosion) as a phenol substitute in the synthesis of lignin-modified phenol-formaldehyde resins (Benar, 1999). Lignin-modified resins, with up to 35% phenol replacement by lignin, have been widely used in the USA to bond fiberboard and plywood. Direct use of lignin as a substitute for phenol in PF resins is limited due to the lower reactivity of lignin as shown in Figure 1-2. There are three reactive sites of phenol, i.e., two ortho-positions and one para-position, as shown in Figure 1-2. Compared with pure phenol, most bio-phenolic compounds derived from lignin (Figure 1-1) are thus less reactive due to its fewer reactive sites and steric hindrance effects caused by its complex chemical structure (Alonso et al., 2004; Cetin and Ozmen, 2002), which has been the major challenge for substituting petroleum-based phenol with bio-phenolic compounds. Work is continuing to find ways to produce adhesive resins with 50% or greater replacement of petroleum-derived phenol with biomass derived phenolic compounds (Peng and Reidl, 1994).

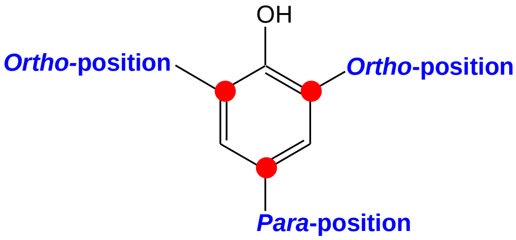


Figure 1-2. The reactive sites of phenol for the PF resin synthesis reactions.

A high level of phenol replacement may be achieved by chemical or biological modification/degradation of lignin to enhance its reactivity. Thermochemical processes were demonstrated to be effective for lignin degradation, e.g., pyrolysis (Jegers and Klein, 1985; Petrocelli and Klein, 1984), hydrocracking/hydrogenolysis (Windt et al., 2009; Kleinert and Barth, 2008), hydrolysis (Benigni and Goldstein, 1971; Fang et al., 2008) and oxidation reactions (Crestini et al., 2006; Hofrichter et al., 2002). However, pyrolysis oils were found to be less effective in substitution of phenol for the PF resin synthesis. The substation ratios were normally below 30-50 wt% of phenol (Roy et al., 2000; Zhang et al., 2006; Lee et al., 2003) in order to produce useful resins. Oxidative degradation of lignin in the presence of a catalyst such as a noble metal (Crestini et al., 2006) or peroxide (Hofrichter et al., 2002) and an oxidant (H_2O_2) usually produce a significant amount of benzaldehydes, ketones, and benzoic acids, which can be perfumes and pharmaceutical intermediates, but these compounds are not suitable for the synthesis of PF resins. Previous studies (Miller et al., 1999; Yuan et al., 2010; Minami et al., 1999) have demonstrated that hydrolysis or hydrocracking/hydrogenolysis of lignin in sub-/super-critical alcohol or aqueous alcohol solution with and without an appropriate catalyst could be an effective thermo-chemical approach to degrade lignin into aromatic and phenolic chemicals from lignocellulosic biomass and lignin. The application of an appropriate hydrogen donor (e.g., Tetralin, 9,10-dihydroanthracene (AnH_2) and its derivatives 1,4,5,8,9,10-hexahydroanthracene, formic acid, and isopropanol) that provided reactive hydrogen atoms could also be an effective solution.

1.4 Objectives

Long-term objective:

(1) Obtain a high substitution ratio (> 50 wt%) of phenol by bio-based phenolic compounds derived from forestry residues/lignin for the production of phenolic resole resins without compromising the properties (viscosity, non-volatile content, free formaldehyde level, thermal cure and stability, and bond strength) of the resin products.

Short-term objectives:

(1) Production of a high-yield and high-quality bio-oil from forestry residues and wastes via a hydrothermal liquefaction process and synthesis of bio-oil phenol formaldehyde (BPF) resole resins with a high bio-oil substitution ratio (> 50 wt%);

(2) Extraction of lignin from lignocellulosic forest biomass and production of a high-quality degraded lignin product from the lignin via a hydrothermal liquefaction process and synthesis of degraded lignin phenol formaldehyde (DLPF) resole resins with a high bio-phenol substitution ratio (> 50 wt%);

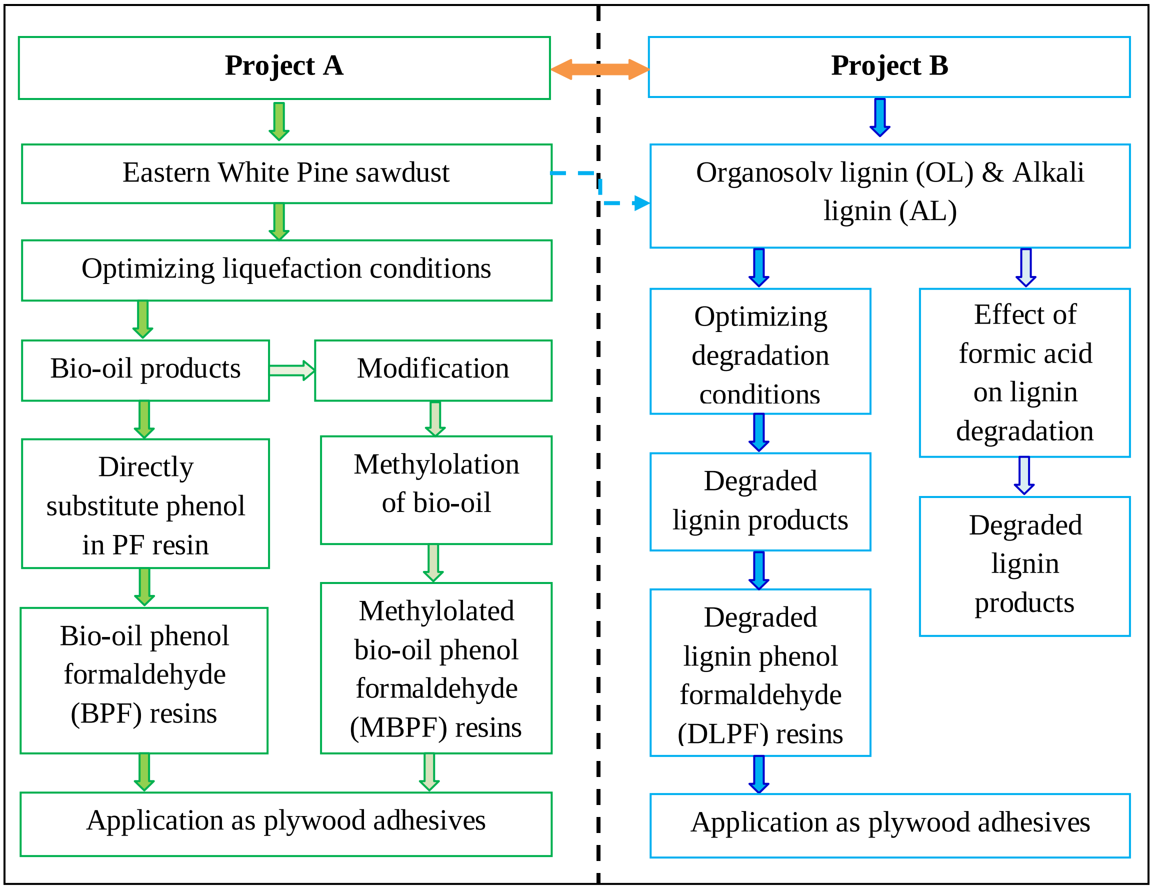
(3) Production of high quality BPF and DLPF resole resin adhesives with better or comparable properties to the petroleum based phenol formaldehyde resole resin adhesives.

1.5 Organization of the Thesis

This PhD thesis is organized to consist of 10 chapters. Chapter 1 is a general introduction on the background, motivations and objectives. Chapter 2 is a comprehensive literature review on the chemistry of traditional PF resin synthesis and the state-of-the-art the technologies to produce bio-based phenolic resole resins from renewable resources (biomass and lignin). This chapter also describes the advantages, disadvantages and challenges of each technology, and provides technical solutions to the production of high quality bio-based phenolic resins at a higher phenol substitution level.

This PhD research work was developed in accordance with two main projects (Project A and Project B) corresponding to the motivations and objectives as described in Scheme 1-1. Chapters 3 through 5 are three manuscripts derived from Project A (Solvolytic liquefaction of forestry residue/wastes into bio-oils and synthesis of bio-based phenolic resins). Chapter 3 presents the work aiming to obtain the optimal conditions for hydrothermal liquefaction of woody biomass (Eastern White Pine sawdust) for the production of a high-quality bio-oil product at a high yield; Chapter 4 focuses on producing high-quality bio-oil phenol formaldehyde (BPF) resole resins with the bio-oil product obtained from the work of Chapter 3; Chapter 5 describes the results of the effect of methylolation treatment on the reactivity of bio-oil, and the properties of methylolated bio-oil phenol formaldehyde (MBPF) resole resins.

Chapters 6 through 8 are three manuscripts resulted from Project B (Degradation of lignins into bio-phenolic compounds and synthesis of bio-based PF resins). Chapter 6 provided results on degradation of alkali lignin (AL) for the production of bio-phenolic compounds; Chapter 7 illustrates a study to degrade organosolv lignin (OL) into bio-phenolic compounds, and produce degraded lignin phenol formaldehyde (DLPF) resole resins; Chapter 8 presents a study to investigate the effects of formic acid on lignin degradation.



Scheme 1-1. Proposed approaches for the PhD research.

Chapter 9 summarizes the main contributions and novelties for the entire research work.

Chapter 10 proposes some future work for commercialization the bio-based phenolic resin products.

Chapters 3-8 have been either published or accepted to publish as peer-reviewed papers in journals, or are under review and in submission.

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CHAPTER 2. LITERATURE REVIEW

2.1 Chemistry of Phenol-Formaldehyde (PF) Resin Synthesis

PF resin was the first synthetic polymer commercialized (Pizzi and Walton, 1992). It has become one of the most widely utilized synthetic polymers since Baekeland developed a commercial manufacturing process in 1907 (Wendler and Frazier, 1995). The global production and consumption of PF resins in 2009 were approximately 3.0 Mt. It is expected an average growth of 3.9% per year from 2009 to 2014, and 2.9% per year from 2014 to 2019 (SRI consulting, 2010). The global PF resin market value is about $4.5-6 billion per year. PF resin manufacture is an important industry valued at approximately $10 billion globally, and $ 2.3 billion in North America.

By varying the type of catalyst and the molar ratio of formaldehyde (F) to phenol (P), two classes of PF resin can be synthesized: resoles (resols) and novolaks (novolacs). Resoles are synthesized under basic conditions with excess formaldehyde (i.e. F/P>1); novolacs are synthesized under acidic conditions with excess phenol (i.e. F/P<1) (Pizzi and Walton, 1992). Resoles and novolacs are inherently different: resoles are heat curable while novolacs require addition of a crosslinking agent such as hexamethylenetetramine (HMTA) to cure. For most novolacs, this additional step results in slower cure rates and lower crosslinking than resoles (Wendler and Frazier, 1996(a)).

PF resins were first introduced as binders for particleboard and plywood in the mid 1930's (Wendler and Frazier, 1996(b)). They have since become one of the most important thermosetting adhesives in the wood composites industry, especially for exterior applications. In 1998, PF resins comprised approximately 32 % of the total 1.78 million metric tons of resin solids consumed in the North American wood products industry (Niand Frazier, 1998). Almost all PF resins currently used in wood bonding applications are resoles. PF resoles are desirable for exterior applications due to their rigidity, weather resistance, chemical resistance and dimensional stability (Wendlerand Frazier, 1996(b)). PF resoles, in either a liquid or a spray-dried form, are currently used as binders for the manufacture of plywood and oriented strand board (OSB) (Wendlerand Frazier, 1996(a)). Compared to polymeric diphenylmethane diisocyanate (PMDI), the only other binder currently used in OSB manufacturing in North America, PF resoles have the advantage of low cost, good thermal stability and reasonably fast cure times.

2.1.1 Raw materials

Phenols

Phenol is the generic name for any molecule containing one or more hydroxyl groups connected to an aromatic ring at different positions as shown in Figure 2-1. The pure phenol is used in the largest quantity to make phenolic resins. In the United States, 35-40 % of phenol is used for the production of phenolic resins.

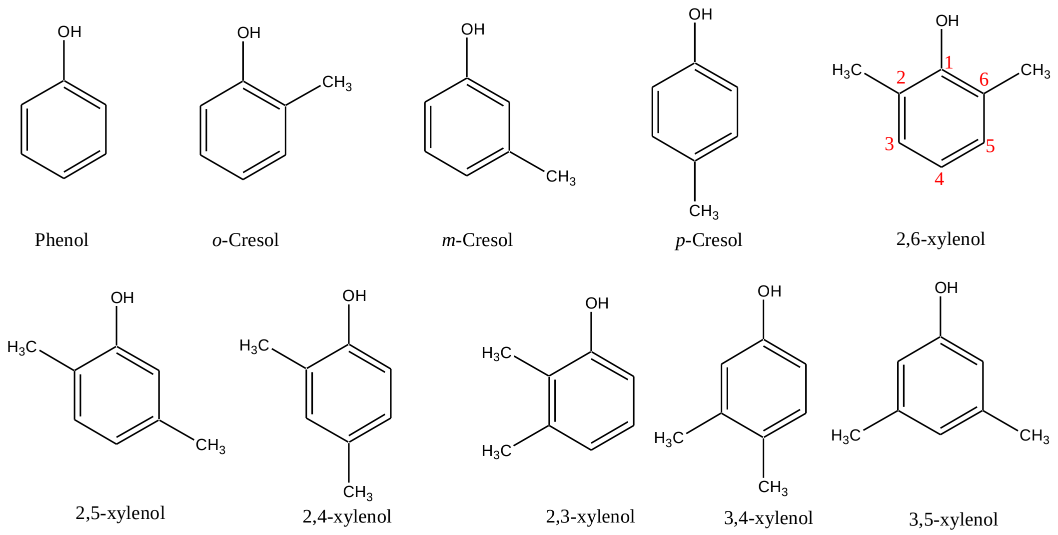

Figure 2-1. Typical phenols structure.

Some typical properties of pure phenol are summarized in Table 2-1 (Gardziella et al., 1999). The solid pure phenol is colorless and a weak acid. It will rapidly convert to pink quintones if it is exposed to air, or contains impurities, in particular copper or iron. It is thus usually stored under a nitrogen blanket. Pure phenol is generally handled in liquid state at 50-60 ^{o}C due to the low melting point. It is highly toxic, and the exposure limits must be strictly controlled.

Table 2-1. Some typical properties of pure phenol (Gardziella et al., 1999).

Properties	**Values**
CAS registration NO.	108-95-2
EG registration NO.	604-001-00-2
M_w (g/mol)	94.11
Melting Point/^{o}C	40.9
Boiling Point/^{o}C	181.7
Flash point (DIN 51758) /^{o}C	81
Ignition temperature (DIN 51794)/^{o}C	595
Relative density @ 20 ^{o}C	1.071
Vapor pressure @ 20 ^{o}C	0.02 kPa
Dissociation constant in water @ 20 ^{o}C	1.28×10^{-10}
Explosive limits LEL/UEL[1]	1.7%/8.6%
MAK limit[2]	19 mg/m^3/5 ppm
OSHA PEL[3]	TWA[4] 5 ppm

[1] LEL/UEL –Lower Explosive Limit/Uper Explosive Limit;

[2] MAK limit –Maximale Arbeitsplatz-Konzentration;

[3] OSHA PEL –Occupational Safety and Health Administration Permissible Exposure Limit;

[4] TWA –Time Weighted Average.

Phenol was found and isolated from coal tar and firstly named as carbolic acid in 1834 by Runge. The first synthetic phenol was produced commercially by the benzenesulfonate process, which is no longer employed for phenol production. The other classic process of hydrolysis of chlorobenzene with caustic soda is also no longer used for commercial production of phenol. The production of phenol grew with the commercialization of phenolic resins after World War I, bio-phenols after World War II and polycarbonates during the 1960s.

Presently, the main route, accounting for more than 95% of production (7.3 × 10^6 t in total in 2003) (Weber et al., 2004), for producing commercial phenol is the cumene oxidation process which was first reported by Hock and Lang (Hock and Lang, 1944) in 1944. Due to increasing demand for phenol, more interest has been put on developing new processes (Weber et al., 2004), such as direct oxidation of benzene to phenol, direct toluene oxidation, and phenol recovered from coal.

In terms of the cumene oxidation process, it comprises two steps: the oxidation of cumene to cumene hydroperoxide (CHP); and CHP is subsequently catalyzed by a strong acid, such as sulfuric acid, to cleave to phenol and a by-product of acetone as shown in Figure 2-2.

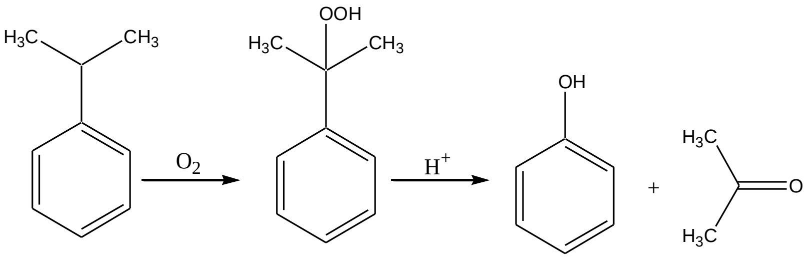

Figure 2-2. Mechanism of cumene process for the production of phenol.

Formaldehyde

Pure formaldehyde has a low boiling point –19.5 ^{o}C, which results in a gaseous product at room temperature. Gaseous formaldehyde is readily absorbed in water to form various forms as shown in Scheme 2-1. When the "n" is > 3, the formaldehyde will form solid products which can be prevented by adding a certain amount of methanol. A water solution containing 36-50% formaldehyde is a formalin solution. The water solution is the favorite form used for the production of phenolic resins. Formaldehyde is applied almost exclusively in the production of phenolic resins, despite the phenol type. It is frequently produced near the site of the resin plant by using methanol as the raw material:

silver catalyst process operated at 600-650 °C with byproducts of water and hydrogen, or a metal oxide process operated at 300-400 °C.

$$CH_2O + H_2O \rightleftharpoons HOCH_2OH$$

$$HOCH_2OH + CH_2O \rightleftharpoons HOCH_2OCH_2OH$$

$$HOCH_2OCH_2OH + CH_2O \rightleftharpoons HOCH_2O(CH_2O)_nH$$

Scheme 2-1. Polymerization process of formaldehyde water solution.

2.1.2 PF resole synthesis

Resole-type PF resins are generally synthesized with a molar ratio of F/P between 1.2:1 to 3.0:1 in an alkaline aqueous medium at 80-90 °C with a final pH ranging from 9 to 12 (Bao and Daunch, 1999; Rosthauser and Haider, 1997) and a final resin solids in the 40 wt% to 60 wt% range due to the presence of water solvent. Common alkaline catalysts are sodium hydroxide, calcium hydroxide and barium hydroxide (Kopf, 2002). In addition to the catalytic function, it may also enhance the solubility of PF resoles in aqueous solution, which allows resoles to be synthesized with a high degree of advancement for fast curing, while maintaining good processability (less viscous) (Robbins, 1971). It is generally agreed that the synthesis of PF resole is a two-step process: addition and condensation reactions. In the first addition reaction step, formaldehyde is added on phenolate anions to form hydroxyl methylated phenols, which subsequently leads to the condensation reaction as a result of the chain growth and crosslinking.

Formation of methylolated phenols

The mechanism of formaldehyde addition to phenol is still not completely understood. The most likely reaction pathway was described as follows: Water solutions of formaldehyde mainly composed of telomers of methylene glycol with < 100 ppm of the formaldehyde as CH_2O (Walker, 1974). In an alkaline medium, three resonance structures of a charged phenoxide anion are formed by delocalization of the negative charge to the ortho and para positions as shown in Figure 2-3. The electron rich ortho and para positions in phenoxide anions are susceptible to electrophilic aromatic substitution with methylene glycol to form mono-, di- and tri-substituted methylolated phenols under sodium hydroxide as shown in Figure 2-4 (Freeman and Lewis, 1954). It is an exothermic reaction. The reaction rate of dimethylol-substituted phenols with formaldehyde is two to four times faster than phenol. The unreacted phenol, thus, remains high in resole resins (5–15%) even though the molar ratio of formaldehyde/phenol is as high as 3:1 (Kopf, 2002).

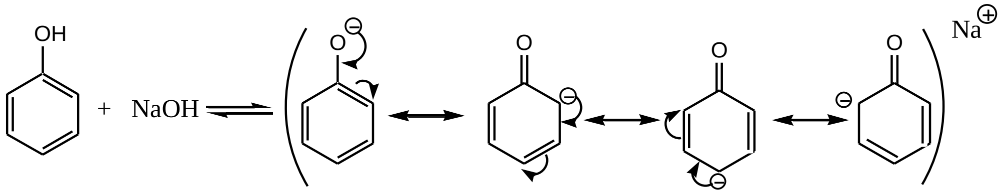

Figure 2-3. Resonance structures of the phenoxide anion under sodium hydroxide medium.

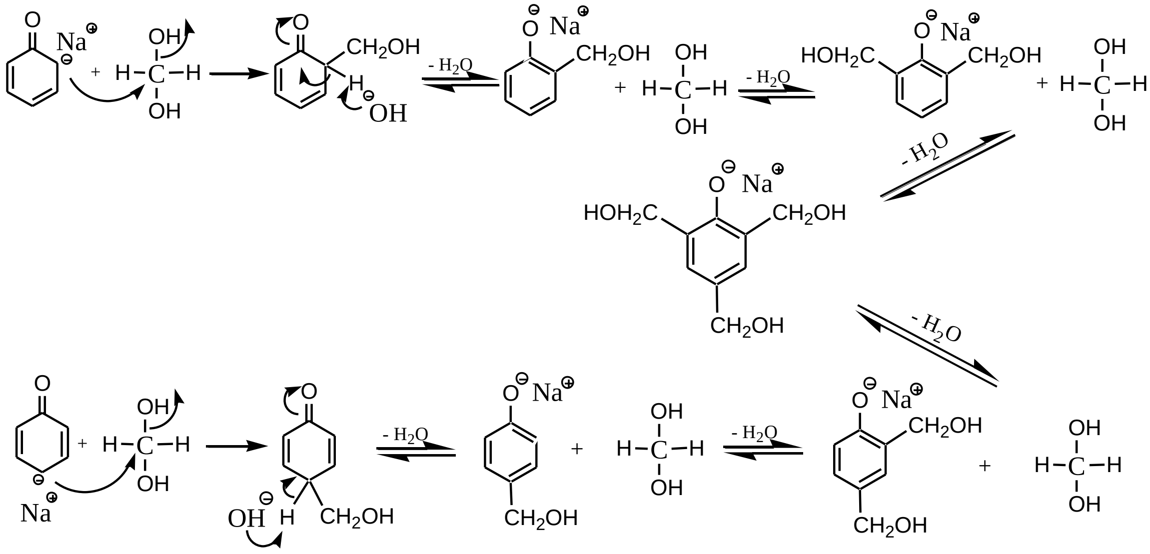

Figure 2-4. Formation of mono-, di- and tri-substituted methylolated phenols through addition reaction under sodium hydroxide.

The para position was reported to be more reactive than the ortho position (Zheng, 2002). In addition, the methylolation at the ortho positions was found to improve the reactivity of the para positions (Zhou and Frazier, 2001) due to the formation of stable intra-molecular H bonds as a result of a higher negative charge on the para position as shown in Figure 2-5 (Grenier-Loustalot et al., 1996). Aierbe and coworkers (2000) reported that the formation of 2,4-dihydromethyl phenol (2,4-DHMP) + 2,4,6-trihydromethyl phenol (2,4,6-THMP) is more favored than 2,6-DHMP due to the steric and chemical restrictions between the involved hydroxyl groups.

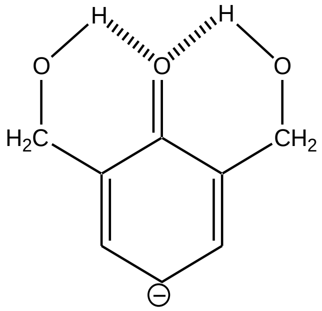

Figure 2-5. Formation of negative charge on the para position due to the formation of intra-molecular hydrogen bonds after ortho-substitutions. (Grenier-Loustalot et al., 1996)

Condensation reactions of methylolated phenols

It is generally agreed that the condensation of methylolated phenols occurs through quinone methide intermediates (Jones, 1946; Haider, 2000) (Figure 2-6) which are very reactive and unstable. However, the absorption peak of the structure of $C=CH_2$ at 1660 cm^{-1} proved the existence of quinone methide intermediates in phenolic resin. The quinone methide intermediates will react with other electron-rich phenoxides to form methylene bridges or dimethylene-ether bridges with releasing water as shown in Figure 2-7. It is also an exothermic reaction. Kopf (Kopf, 2002) reported that the formation of methylene bridges is favored above 150 ^{o}C and under strongly alkaline conditions; the formation of dimethylene-ether bridges are favored at lower temperatures and near neutral pH. The dimethylene-ether bridges are generally unstable and will further convert to more stable methylene bridges with eliminating formaldehydes (Figure 2-7) (Zhuang and Steiner, 1993; Kim and Watt, 1996). Furthermore, the formed methylene bridges are mainly para-para and ortho-para type while the ortho-ortho type is hardly formed due to the relative higher reactivity of para methylol. Similar results were also observed by Aierbe et al (2002). The remaining othro methylol group thus dominated crosslinking during the curing process.

Under alkaline conditions, the condensation of methylolated phenols can generally occur for three stages: initial resoles, resitols, and resite (Sellers, 1985). The initial resoles stage is mainly to form monomers and dimers where as the resite stage is the complete cured material stage (Marra, 1992). PF resole resin used for wood adhesives generally condenses to the resitols stage. The final PF resoles is thus a mixture of polymer molecules with different molecular weights, structure, and substitution ratios of methylol groups or methylene groups. The endpoint of the resitols stage can be achieved by monitoring the gel time, viscosity or molecular weights by gel permeation chromatography (GPC).

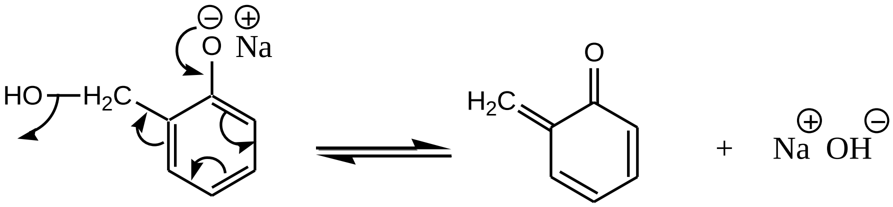

Figure 2-6. Formation of quinone methide intermediates under sodium hydroxide.

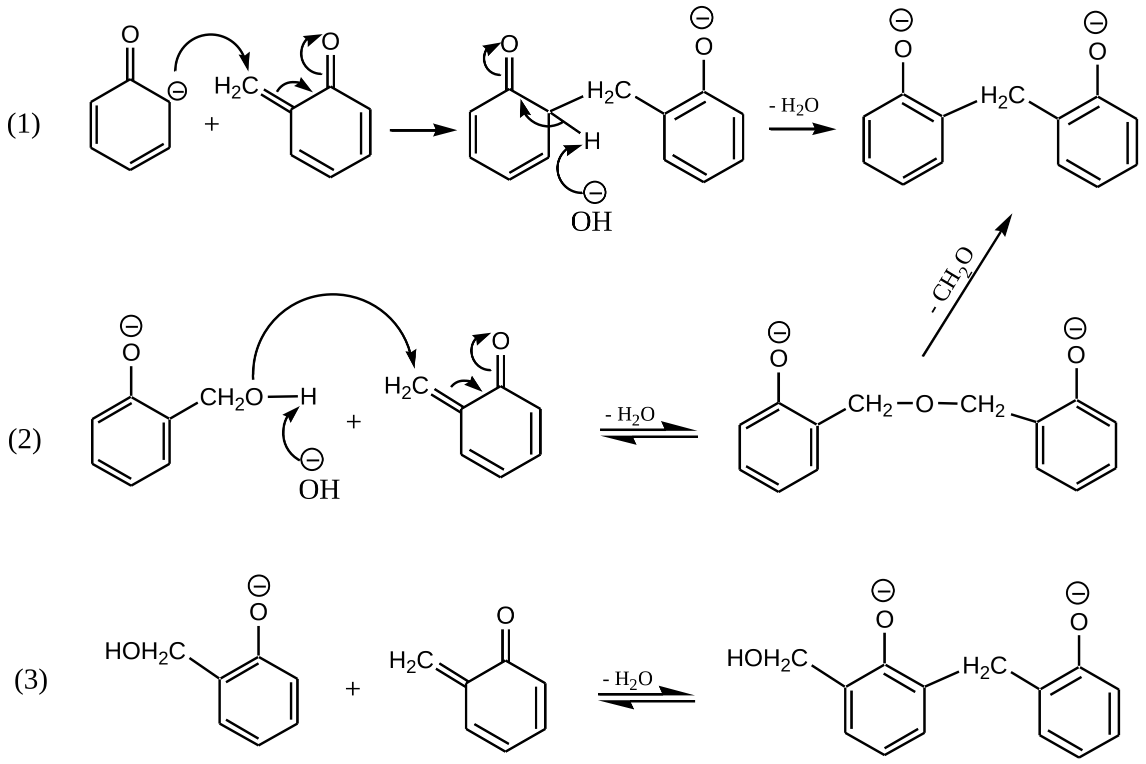

Figure 2-7. Three possible pathways of formation of diphenyl-methylene under alkaline condition.

2.1.3 PF resole resin curing chemistry

An understanding of the curing mechanism and thermal stability of PF resoles provides insight into the overall quality and durability of a glue line in wood products. In the wood products industry, the curing of PF resole adhesives is achieved without adding a curing agent under heating and pressure. Under alkaline condition, the resoles containing reactive methylol groups can ensure itself to cure upon heating. The curing process is essentially a further condensation stage to form methylene bridges through quinone methide intermediates (Zhuang and Steiner, 1993; Schaefer et al., 1977). Dimethylene ether bridges are rarely identified in the cured PF resoles (Zhuang and Steiner, 1993; Larsson, 1997; McBriertyand Packer, 1993). In addition to the methylene bridges for the cured resoles, Maciel and co-authors (Maciel et al., 1984) proposed additional cross-linking mechanisms which involve the reaction of hydroxymethyl moieties with the phenolic hydroxyl group and reaction of free formaldehyde and methylol groups with methylene carbons as shown in Figure 2-8.

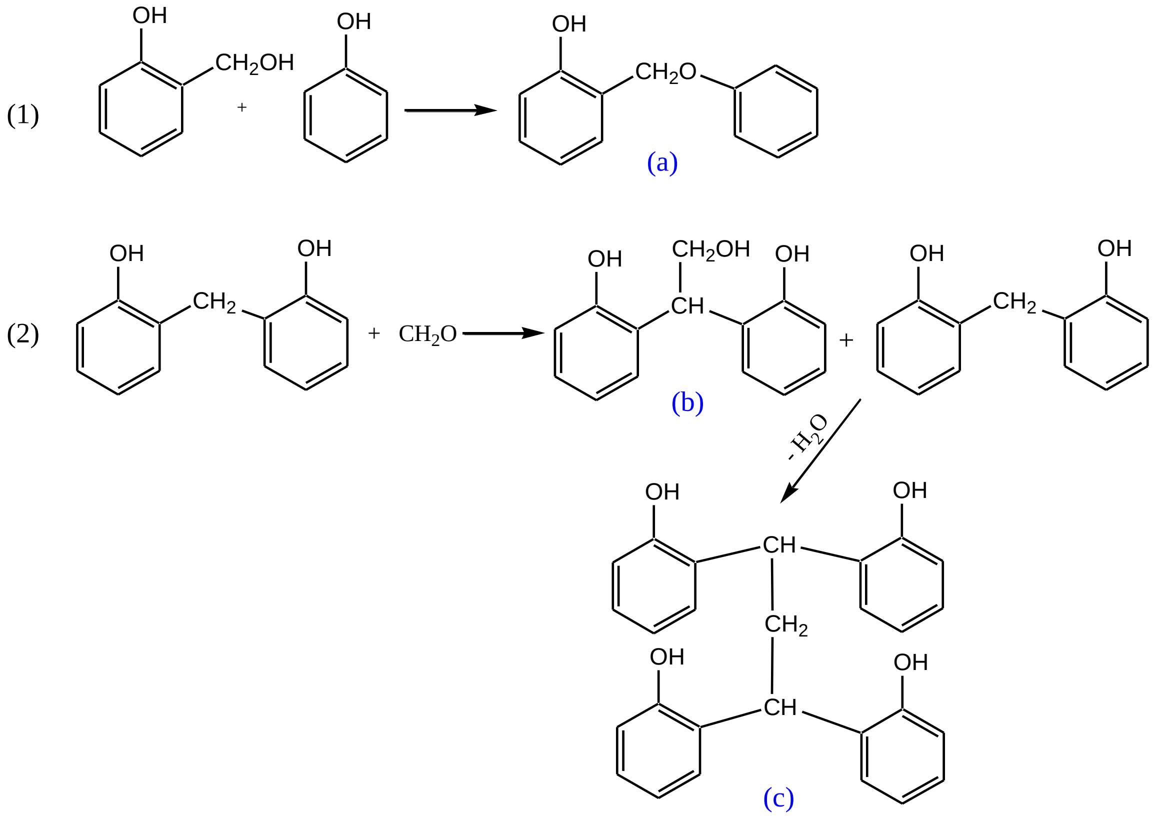

Figure 2-8. Three possible additional crosslinking (a, b, c) for cured resoles proposed by Maciel and the co-authors (Maciel et al., 1984).

2.1.4 Thermal stability of cured PF resoles

It is known that the decomposition of PF resoles has three major steps: post-curing, thermal reforming and ring stripping (Khan and Ashraf, 2007) as shown in Figure 2-9 (Cheng et al., 2011). PF resoles generally are very stable at temperatures below 220-250 ^{o}C depending on the synthesis parameters, such as pH value and molar ratio of F/P. Figure 2-9 shows the first event of the pure PF resin is observed in the range of 25-300 ^{o}C, which could be ascribed to the post-curing reactions of the resin (the removal of terminal groups and further crosslinking or condensation reactions); the second event is obtained from 365 to 500 ℃, which may be attributed to the thermal reforming to break the bridged methylene linkage; and the last event is detected in the range of 500 to 650 ℃ (the main mass loss region) due to the breakdown of the ring network.

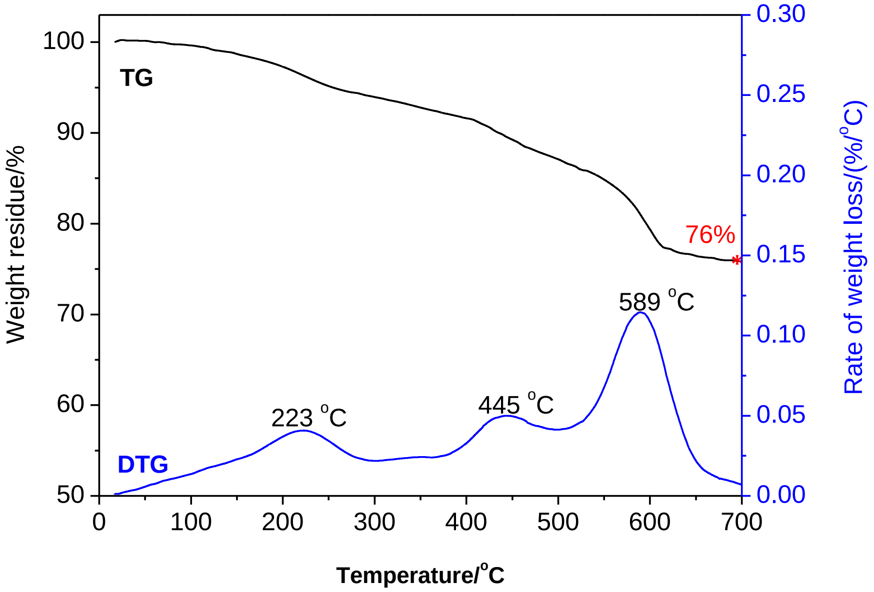

Figure 2-9. TG and DTG profiles of PF (pH: 10.5, molar ratio of F/P of 1.3, non-volatile content sample) resole from 25 to 700 °C with a heating rate of 10 °C/min under N_2 of 30 mL/min (Cheng et al., 2011).

2.1.5 Effects of synthesis parameters on properties of PF resoles

The properties, related to the prepolymer formation, and curing, structural and mechanical properties of the final products of the phenolic resole products, are affected by many synthesis parameters, such as the initial F/P molar ratio, type and amount of catalyst, pH value, reaction temperature, condensation viscosity, and other factors (reaction time and type of reactants). These effects are briefly summarized as follows.

Effect of initial molar ratio of F/P

Two types of PF resin can be synthesized by varying the molar ratio of F/P under different catalyst condition: resoles and novolacs, which were synthesized with excess formaldehyde (i.e. F/P>1) under basic conditions and with excess phenol (i.e. F/P<1) under acidic conditions (Pizzi and Walton, 1992), respectively. The following brief summaries will only focus on PF resole resins, which are the target product of this research.

The initial molar ratio of F/P is one of the most important factors for phenolic resole resin synthesis (Holopainen et al., 1997; 2004; Aierbe and coworkers (2000)), in terms of the final free formaldehyde and free phenol concentration, the structural properties, the gel time, molecular weights and viscosity of the final resin products. Aierbe and coworkers (2000) studied the effect of initial molar ratio of F/P (1.0 to 2.6) on the formation of PF resins catalyzed with amine. The results showed that the free formaldehyde concentrations increased with the initial amount of formaldehyde. There was an initial maximum F/P ratio around 1.8 for free phenol. When the ratio was over 1.8, the free phenol content was similar and very low. When the ratio was 1.0, the free phenol concentration was high and became stable after the first 60min; the F/P ratio for the maximum formation of 2-hydromethylphenol (2-HMP) was found to be 1.8-2.0; the formation of bonding bridges (methylene and ether) increased with F/P ratio as a result of the higher concentration of hydroxymethyl groups. Another effect of increasing the initial molar ratio of F/P will decrease the pH value due to the formation of water through condensation reactions, solid content of the resin solids and the amount of non-volatile material in the resin solution. Gel time of the resin decreases with increasing F/P due to the methylolation of free phenol resulting in a more reactive system. In other words, a higher F/P molar ratio results in higher methylolation. Thus, a higher F/P molar ratio makes the resin cure faster than a lower F/P molar ratio does. Molecular weight of the polymer will increase with F/P ratio due to the greater number of bonds formed between the substituted phenols increasing the amount of formaldehyde. This would also explain the polydispersity of the resin oligomers. Viscosity of the resins increases with F/P molar ratio as expected. A higher degree of methylolation results in the solution of more crosslinked and sterically hindered oligomers.

Effect of pH value and type of catalyst

The pH value of the resin is controlled by the basic content during resin synthesis. The common basic catalysts for PF resole resins as mentioned above are $Ba(OH)_2$, $Ca(OH)_2$, KOH, NaOH and Na_2O_3. There are some obvious effects of the basic content on resin synthesis as follows. With increasing the amount of basic content, gel time, molecular weights, resin pH, solid content and curing peak temperature increases. The activation energy, however, decreases with increasing the amount of basic content. The effect of the type of catalyst on addition reactions between phenol and formaldehyde was also investigated. Solonom and Rudin (1990) reported that the methylolation reaction at the para-position of the phenol ring increased in the order: $Ba(OH)_2 < NaOH < Na_2O_3$. Moreover, the cation of the alkaline catalyst and the pH was found to have an effect on the ratio of ortho-to-para substitution. K^+ and Na^+ ions and a higher pH promote para substitution. While ortho substitution was favored by divalent cations (e.g. Ba^{2+},Ca^{2+} and Mg^{2+}) and a lower pH (Peer, 1959; 1960). A chelate ring structure may be formed under calcium hydroxide as shown in Figure 2-10.

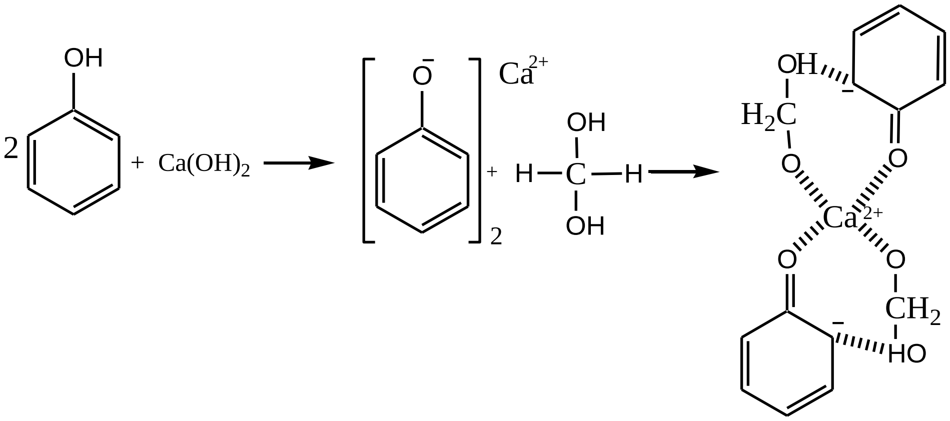

Figure 2-10. Formation of chelate ring structure under calcium hydroxide.

Effect of reaction temperature on the PF resins

Aierbe et al (2002) studied the influence of temperature (60, 80, 95 °C and reflux at 98-102 °C) on the formation of a phenolic resole resin catalyzed with amine and with an initial pH of 8.0 and F/P molar ratio of 1.8. The results showed that with increasing the reaction temperature, the reactant consumption rates and first addition products increased, but the condensation time decreased. The prepolymer formed at reflux temperature showed more ortho addition than that at the other temperatures. Furthermore, the free formaldehyde and phenol content and the amount of free ortho and para reactive sites on the phenol ring decreased with increasing reaction temperatures.

2.2 Biomass Pyrolysis and its Application in the Production of PF Resins

Depending on operating conditions, pyrolysis processes could be classified into two major types: fast pyrolysis and vacuum pyrolysis. Fast pyrolysis is so far the only industrially realized thermo-chemical process for biomass liquefaction. A fast pyrolysis process typically operates at > 500 °C in an inert atmosphere under a very high heating rate with a short vapor residence time of less than 2 seconds, producing a yield of liquid products (pyrolysis oil or bio-oil) as high as 70-80% (Bridgwater and Peacocke, 2000; Effendi et al., 2008). Compared to fast pyrolysis, vacuum pyrolysis, operating under reduced pressure with a much longer vapor residence time, produces a much lower liquid yield (Bridgwater, 2004).

Pyrolysis oil is a complex mixture of water (15-30 wt%) and organics of a high-oxygen-content (45-50 wt%). This oxygen content distributes more than 300 identified compounds, which consist of hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids and phenolics (Effendi and Gerhauser, 2008). The majority of the phenolics are present as oligomers containing varying numbers of acidic, phenolic and carboxylic acid hydroxyl groups as well as aldehyde, alcohol and ether function. The molecular weights of the oligomers resided in several hundreds to 5000 or more depending on the operation conditions. Therefore, pyrolysis oils are unstable upon storage and require further upgrading, which will result in a high cost. And they have so far mainly been used as an energy source by direct combustion. The liquid product from lignocellulosic materials pyrolysis can be separated into two fractions based on water solubility and density by decanting or more easily by solvent extraction: water-soluble fraction and water-insoluble fraction. The water-insoluble fraction that usually constitutes 25-30 wt% of the whole bio-oil is often called pyrolytic lignin because it is essentially composed of oligomeric fragments derived from thermal degradation of native lignin (Radlein and Piskorz, 1987; Meier and Scholze, 1997). Although without being commercialized so far, the use of pyrolytic lignin as a source of phenol in PF resins seems to be promising. Applications of bio-oil for the production of bio-based phenolic resins are briefly overviewed as follows.

2.2.1 Applications of fast pyrolysis oils in renewable PF resins

The reactive phenolic components and neutral fractions were fractionated from fast pyrolysis oil for resin synthesis. The bio-based resins were evaluated and tested for wood panel production. Chum and co-workers (Chum and Black, 1993; Chum and Diebold, 1989; Chum and Kreibich, 1992) synthesized resins of both novolac and resole types using fast pyrolysis bio-oils derived from softwood, hardwood and bark residue to partially substitute phenol. They found that the novolac resin prepared with a 50% phenol substitution had a shorter gel time than commercial plywood resins. Moreover, the reactive fraction separated from pyrolysis oil was found to mainly contain phenolic compounds and aldehyde groups. Accordingly, the reactive fraction was not only to replace phenol but also some of the formaldehyde used during the resin synthesis process. Himmelblau from Biocarbon Corporation patented a technology of producing PF resins using fast pyrolysis bio-oils from mixed hardwood (maple, birch, and beech) after the removal of the non-reactive fraction (Himmelblau, 1991; Himmelblau and Grozdits, 1999). The whole pyrolysis bio-oil from wood and bark was also investigated as a feedstock for phenolic resins (Nakos P, Tsiantzi, 2001). Although the wood adhesive properties of the bio-based resins were normally inferior to the commercial resins with pure petroleum-based phenol, higher phenol substitution was considered to be possible with a fraction enriched in reactive phenolics. Ensyn Group Inc. developed patented methods of preparing a natural resin by liquefying wood, bark, forestry residues and wood industry residues using a patented rapid pyrolysis process (Giroux and Freel, 2001; 2003). The natural resin components (containing up to 60 wt% phenolic compounds) were found to be suitable resin formulations without requiring any further extracting/fractionating procedures. It may partly replace phenol, or both phenol and formaldehyde in the manufacture of PF resins. The properties of wood adhesives using synthesized PF resin comprising up to 60 wt% of the natural resin precursor were demonstrated to be comparable to those of a commercial control.

2.2.2 Applications of vacuum pyrolysis oils in renewable PF resins

According to the study of Chan et al. (Chan et al., 2002), the chemical compositions of bio-oil products from vacuum pyrolysis of softwood bark residues is shown in Table 2-2. Such phenolic-rich vacuum pyrolysis oil could be used to replace 25-35 wt% of phenol in PF resin which was evaluated by applying to 3-layer boards (11.1mm thick). The mechanical properties (Modulus of Rupture (MOR), Modulus of Elasticity (MOE), and internal bond (IB) strength) were found to exceed the minimum requirements set by CSA 0437 Series 93, both in dry and wet (after boiling for 2hr) tests. A higher phenol substitution of 50 wt% in the bio-based resins reduced the performance of the bio-based phenolic resin in terms of cure kinetics and the extent of condensation (Amen-Chen et al., 2002(a)). The curing behavior of bio-based resins could be improved by addition of a small amount of polypropylene carbonate (at 0.5-1.5 wt%) while it did not have a significant effect on the mechanical properties of OSB glued by the resins (Amen-Chen et al., 2002(b)). Mourant et al. (2009) reported a vacuum pyrolysis process, performed at 450 °C and at a total pressure of 20 kPa, to produce vacuum pyrolysis bio-oil from a bark mixture (70 % balsam fir and 30 % white spruce), which was employed as a phenol replacement in PF resins at ratios of as high as 50-85 wt%.

Table 2-2. Typical chemical compositions of pyrolysis oils obtained from pyrolysis of softwood bark residues (Chan et al., 2002).

Family of compounds	**Concentration (wt%, d.b.)**
Hydrocarbons	3
Sugars	9
Low-molecular weight-acids	1.5
High-molecular weight-acids	10
Alcohols	2.5

Esters and ketones	4
Phenols	10
Steroids and triterpenoids	4
Lignin/tannin-based compounds	48
Labile compounds	8
Total	100

2.3 Biomass Solvolytic Liquefaction and its Applications in the Production of PF Resins

Direct liquefaction of lignocellulosic materials in a suitable solvent at relatively lower temperatures, known as solvolytic liquefaction, is more advantageous than the pyrolysis processes with respect to energy efficiency and the quality of the oily products. As such, the solvolytic liquefaction technologies of lignocellulosic materials have attracted increasing interest for the production of bio-phenol precursors for synthesis of bio-based phenolic resins and heavy oils (bio-crude) for bio-fuel production. In terms of the type of solvents and operating conditions in the liquefaction processes, typical solvolytic liquefaction processes may be grouped into two categories: (1) solvolysis under low temperatures and atmospheric pressure, and (2) solvolysis in a hot-compressed and sub-/super-critical fluid.

2.3.1 Solvolysis under low temperatures and atmospheric pressure

Lignocellulosic materials can be efficiently liquefied at a low temperature and atmospheric pressure in the presence of phenol with a proper catalyst such as an acid (hydrochloric acid, sulfuric acid, phosphoric acid, and oxalic acid) (Alma et al., 1995; Lin et al., 2000; Lin et al., 1994; Lin et al., 1995; Alma and Basturk, 2006; Alma et al., 1998; Alma and Kelley, 2000), or an alkaline solution or a metal salt (NaOH, $Cu(OH)_2$, $NaHCO_3$, NH_4Cl, $AlCl_3$, $CuSO_4$, $FeSO_4$, and NaH_2PO_4) (Maldas and Shiraishi, 1997(a), Maldas et al, 1997(b)). The resulting phenolated products were widely used as feedstocks for the synthesis of phenolic resins (Lin et al, 1995; Alma and Basturk, 2006; Alma and

Kelley, 2000; Maldas and Shiraishi, 1997(a)). Strong acids, such as concentrated sulfuric acid has been used widely as an effective catalyst in the phenolysis liquefaction of lignocellulosic materials, and the resulting liquefied products could be used as matrix resins with satisfactory mechanical properties (Alma and Basturk, 2006). However, disadvantages of the processes using strong acids include partial carbonization of biomass during liquefaction and corrosion of the equipment. Moreover, the use of phenol as the liquefaction solvent could yield some problems, such as the high cost of the solvent, and the difficulty in recycling of phenol from the liquefied products as well as some environmental concerns.

Other solvents instead of phenol, such as alcohols (Shiraishi et al, 1992; Hassan and Shukry, 2008) and cyclic carbonates (Yamada and Ono, 1999) and co-solvent (Pasquini et al, 2005) (e.g. alcohols and water) were tested as solvents for low-temperature liquefaction of biomass. These low boiling-point solvents could be recycled easily for reuse by distillation/evaporation after liquefaction and are much cheaper than phenol. Hassan and Shukry (2008) investigated the liquefaction of bagasse and cotton stalks by using polyhydric alcohols (polyethylene glycol and glycerin) in the presence of sulfuric acid as a catalyst at temperatures ranging from 140 to 170 °C under atmospheric pressure. The residue for both bagasse and cotton stalks were less than 10 wt%. In addition, ionic liquids (ILs) at or below 100 ℃ that are comprised entirely of cations and anions, have been developed over the past decades as green solvents with tunable solvation properties (Earle and Seddon, 2000). Recently, ionic liquids were employed as solvents to liquefy natural polymeric materials of cellulose and starch (Swatloski et al., 2002), and wood (Xie and Shi, 2006). Xie and Shi (2006) reported that Dawn Redwood (*Metasequoia glyptostroboides*) could be effectively liquefied at 120 °C for 25 min with imidazole-based ionic liquid as the liquefaction solvent, being more efficient than the conventional phenol/H_2SO_4 system. A major challenge for the application of ILs for biomass conversion may be the difficulty in recovering of the expensive ILs from the reaction products.

2.3.2 Solvolysis in a hot-compressed and sub-/super-critical fluid

The liquid bio-oil products, produced from the above mentioned low-temperature solvolytic processes using phenol or alcohols, are however less reactive than petroleum-based phenol in the synthesis of phenolic resins due to high molecular weights and their shortage of phenolic compounds with unoccupied ortho and para positions (Effendi et al., 2008). The liquid products from the low-temperature solvolytic processes are rich in large molecules of oligomers derived from lignin or cellulosic components. In this regard, liquefaction of lignocellulosic materials at a high temperature is preferable. Numerous studies have been reported on the liquefaction of biomass at relatively higher temperatures and under high pressure. For instance, agricultural residues, peat moss, sawdust and wood chips were liquefied at 290-350 °C and under 10-20 MPa pressure with water as the solvent and sodium carbonate or calcium carbonate as the catalyst. The extracted reactive phenolic contents were used for preparing phenolic resins (Russell and Riemath, 1985). The mechanical properties of birch plywood bonded by the bio-based phenol formaldehyde resins were found to be superior to that by a commercial control. Wood wastes (Monarch birch, *Betula maximowicziana Regel*) were liquefied with phenol in the presence of NaOH at 250 °C for 1hr in a pressure-proof tube placed in an oil bath (Alma et al., 1997; 2001). The obtained methanol-soluble liquid products were phenolic fractions, which were resinified with formaldehyde to produce resole-type resins which were applied as adhesives to the production of plywood, and the results indicated that almost all of these resin adhesives could meet the Japanese Industrial Standard as far as dry shear adhesive strength of plywood is concerned.

More recently, there has been a huge surge of interest in using hot-compressed and sub-/super-critical fluids for biomass liquefaction. Supercritical fluids have found applications for the chemical conversion of lignocellulosic materials due to their unique properties, e.g., unique transport properties (gas-like diffusivity and liquid-like density) and ability to dissolve materials not normally soluble in either liquid or gaseous phase of the solvent, and hence to promote the gasification/liquefaction reactions. Hot-compressed or sub-critical water has been used by many researchers for biomass liquefaction (Matsumura et al., 1999; Karagoz et al., 2004; 2005; Xu and Lad, 2008). Karagoz et al.

(2005) studied oil composition produced from pine sawdust, rice husk, lignin and cellulose liquefactions at 280 °C for 15 min in water solvent. The oil yields (ether extraction) were 8.6, 8.3, 3.9 and 3.2 wt%, respectively. The main compounds of bio-oils from pine sawdust and rice dusk were mainly phenolic compounds. While bio-oil derived from rice husk consisted of more benzenediols than that from pine sawdust. The main drawback of water solvent for biomass liquefaction is a lower yield of the water-insoluble oily product. Cornstalk powders (Wang et al, 2009) were effectively liquefied in a hot-compressed (around 350 °C) phenol-water medium (1/4 wt/wt). A high bio-oil yield up to 70 wt% was obtained. Phenolic resole resins were readily synthesized using the cornstalk-derived bio-oils with catalyst of sodium hydroxide. Tymchyshyn and Xu (2010) investigated hydrothermal liquefaction of lignocellulosic wastes (sawdust and cornstalks) and two model compounds (organosolv lignin and cellulose as references) in a hot-compressed water solvent at temperatures ranging from 250 °C to 350 °C with an initial pressure of 2 MPa H_2 with an aim of producing phenolic compounds suitable for the production of phenolic resins. The liquefaction operated at 250 °C for 60 min producing a bio-oil product yield of 53 wt%, 32 wt%, 32 wt% and 17 wt% for lignin, sawdust, cornstalk and cellulose, respectively. Significant quantities of phenolic compounds, such as 2-methoxy-phenol, 4-ethyl-2-methoxy-phenol, and 2,6-dimethoxy-phenol were present in the resulting bio-oils.

Sub-/super-critical phenol (Lee and Ohkita, 2003) was used for liquefaction of wood meal (Birch, *Betula maximomawiczii Regel*) in a pressure-proof autoclave. A very high yield (up to 95%) of liquid products was achieved within 2 min at 421 °C with a phenol/wood weight ratio of 3/1, where combined phenol content was about 75%. Generally, the properties of liquefied wood are dependent on the liquefaction conditions such as reaction temperature, time, and catalyst used (Lin et al., 1994; Alma et al., 1995; Alma et al., 1996). Sub-/super-critical alcohols have been tested for the liquefaction of lignocellulosic materials (Xu and Etcheverry, 2008; Miller et al., 1999). Since these alcohols have critical temperatures and pressures lower than water, more moderate reaction conditions can be employed. Another advantage of using alcohols as the solvent for biomass liquefaction is that these alcohols themselves are renewable. They can be readily produced from biomass. In addition, alcohols have a higher solubility for the liquid products derived from cellulose, hemicelluloses, and lignin due to their lower dielectric constants compared with that of water (Yamazaki et al., 2006). Xu and Etcheverry (2008) reported that a high yield of bio-crude (rich in phenolic compounds) up to 60 wt% was produced from the liquefaction of Jack Pine sawdust in sub-/super-critical ethanol at 200 °C to 350 °C under H_2 at a cold pressure of 2.0-10.0 MPa with and without iron-based catalysts (FeS or $FeSO_4$). Liu and Zhang (2008) compared the effect of various solvents (water, acetone and ethanol) on pinewood liquefaction for producing fuels and chemical feedstocks. Experiments were conducted in an autoclave at temperatures ranging from 250 °C to 450 °C for 20 min with a biomass-to-solvent ratio of 1/6 (wt/wt). The results showed that the yield and composition of the liquefaction products were greatly affected by the solvent type. The highest oil yield of 26.5 wt% was obtained in ethanol. Ethanol was favorable for the formation of (E)-2-methoxy-4-(1-propenyl)-phenol and 2-methoxy-4-methyl-phenol, while the composition of bio-oil from the liquefaction using water solvent was rich in 2-methoxy-phenol, organic acids and furans. Co-solvent of alcohol-water was found to be very effective in lignocellosic materials liquefaction at temperatures around 300 °C, as reported by Minami and Saka (2005). More than 95 wt% of Japanese beech (*Fagus crenata Blume*) wood was liquefied in water-methanol (10/90, v/v) at 350 °C in 5 min. Guaiacyl and syringyl lignins were decomposed to coniferyl alcohol-γ-methyl ethers and sinapyl alcohol-γ-methyl ethers, and further converted to isoeugenol and 2,6-dimethoxy-4-(1-propenyl)phenol after a long treatment, respectively.

2.4 Extraction, Modification and Degradation of Lignin, and Its Application in the Production of PF Resins

Crude lignin is generated as a by-product in large amounts in the pulp and paper industry. Lignin is currently utilized mainly by direct combustion in the recovery boilers for heat generation. Recently, efforts in replacing commercial phenol in phenol formaldehyde resins has gained increasing interest, although there is not much published research focused on obtaining phenols from lignin.

2.4.1 Lignin extraction

Two types of lignins have been produced from lignocellulosic materials: sulfur-containing lignins and sulfur-free lignins. The sulfur-containing lignins include Kraft lignin and lignosulfonates which are by-products existing in black liquor from the production of papermaking pulp. The sulfur-free lignins include soda, organosolv, and steam-explosion, oxygen delignification and hydrolysis lignins (mainly for bio-fuel production). The widely used kraft pulping process produces 80% of the available chemical pulping lignins (Mansouri and Salvado, 2006; Kirk-Othmer, 1999-2008). The experimental procedure for lignin extraction from black liquor proposed by Olivares et al. (1988) is briefly described as follows. The black liquor normally with pH >13 is first acidified using H_2SO_4 to pH 8-9.5 at temperatures between 75 °C and 85 °C and filtrated while hot. The filtrate was further acidified to pH 2, followed by final filtration, washing and drying to produce a highly pure lignin. This procedure is advantageous since it allows recycling of a solution rich in Na^+ and SO_4^{2-} to the kraft process. However, the kraft pulping process has long-standing problems with the air/water pollution and odour issues (Wegener, 1992).

A better method for removing lignin from lignocellulosic materials should show the following characteristics: without causing environmental pollution problems, low energy consumption, easy operation, easy solvent recovery and ease of product isolation. Many organic solvents have been tested for converting wood to its components: lignin and carbohydrates. These include alcohols (methanol, ethanol, propanol, etc.), alcohol-water, organic acids (formic acid, acetic acid, other organic acids and salts of organic acids), phenol and cresols, ethyl acetate, amines and amine oxides (ethylenediamine, hexamethylene diamine, methylamine, ethanolamine, amine oxides), ketones and diaxane, etc. (Muurinene, 2000). Aqueous ethanol (or ethanol-water mixture) could penetrate readily into the structure of wood resulting in uniform delignification (Kleinert, 1975). As reported by Li and Kiran (1988), red spruce was effectively de-lignified in ethanol-water mixture at 190 °C and 29 MPa. Pasquini et al. (2005) also described an effective organosolv delignification process at around 190 °C using ethanol-water mixture and CO_2 for *Pinus taeda* (loblolly pine) wood chips. In addition to alcohol-water mixtures, formic acid was also found to be a potentially good solvent for separating lignin and extractives from wood, and it could also result in the hydrolytic breakdown of wood polymers into smaller and more soluble molecules (Sundquist, 1996).

2.4.2 Lignin modification for PF resins production

Crude lignin has a much lower reactivity than pure phenol because it has less reactive sites for reacting with formaldehyde (Alonso et al, 2004; Clarke and Dolenko, 1978; Lee et al, 2000). Many researchers have attempted to modify lignin in order to improve its reactivity. There are three main methods: methylolation (Clarke and Dolenko, 1978; Lawson and Kleln, 1985), phenolation (Cetin and Ozmen, 2002(a); 2002(b)), and demethylation (Olivares et al, 1988; Narayamusti and George, 1954; Hayashi et al, 1967; Shashi et al, 1982). Clarke and Dolenko (1978) reported a highly cross linked methylolated kraft lignin was obtained by stirring a mixture of kraft lignin and formaldehyde with a pH value of 12-12.5 at room temperature for a period of at least three days. Then the methylolated kraft lignin (at least 5 wt% of total resin solids) and phenol-formaldehyde were combined to produce a lignin-phenol-formaldehyde (LPF) resin at a pH of 6-7 for a sufficient time. The LPF resin was applied as adhesive to 3-ply poplar plywood, which displayed a dry bond strength of 309 psi (wood failure 40%) and wet bond strength of 247 psi (wood failure 60%). Strengths were better than those of the LPF resin using unmethylolated kraft lignin (dry strength of 233 psi with 0% wood failure, and no wet strength). Cetin and Ozmen (2002(a); 2002(b)) described the production of LPF resin using phenolated organosolv lignin, and the properties of particleboard using this resin. In a first step, phenolated lignin was prepared by adding lignin into a mixture of phenol and industrial methylolated spirit (IMS) at desired weight ratios and stirring at 70 °C for a sufficient time. The IMS was removed in a rotary evaporator under vacuum at 40 °C to 50 °C. The remaining product was phenolation lignin, which was subsequently mixed with 35% formaldehyde water solution to synthesize LPF resoles in at pH 10.2 at 50 °C for 1 hr. The temperature was then increased up to 80 °C where the reaction was kept till the desired viscosity was achieved. The final viscosity (200-250 cP) of LPF resin was obtained by removing excess water under vacuum at 40 °C to 50 °C. The LPF resin was used for the production of particleboard whose physical and mechanical properties (including thickness swell, water absorption, IB strength, MOR, and MOE) were tested. The results showed that the physical and mechanical properties of phenolated-lignin-formaldehyde resins with 30% phenol replacement were comparable to those of a commercial PF resin. Lignin demethylation can be an effective measure to increase lignin reactivity, and the demethylation of lignin was achieved by reaction with potassium dichromate ($K_2Cr_2O_7$) (Narayamusti and George, 1954; Hayashi et al, 1967; Shashi et al., 1982). Shashi et al. (1982) used $K_2Cr_2O_7$ in the presence of acetic acid, decreasing the concentration of methoxyl groups from 11.9 to 2.8 %, and increasing the phenolic hydroxyl groups from 2.4 to 11.2 %. As per Olivares et al. (1988), for demethylation of 100 g of lignin, the lignin were dispersed in 2000 mL water in a reactor at 40 °C with moderate agitation; 750 mL of 0.033M $K_2Cr_2O_7$ together with 30 mL of acetic acid was added, in order to maintain a pH of 4. After 2 h, lignin was separated by precipitation at pH 2. As such, the lignin demethylation process using $K_2Cr_2O_7$ has challenges in wastewater disposal combined with the high acid consumption in the process.

2.4.3 Lignin degradation for PF resins production

Crude lignin has a much lower reactivity not only because it has less reactive sites compared with pure phenol for reacting with formaldehyde (Alonso et al., 2004; Clarke and Dolenko, 1978; Lee et al., 2000) as discussed above, but also the reactive positions of the macromolecules of lignin or its fragments have less accessibility to formaldehyde due to the steric interactions.

It is thus more advantageous to degrade/de-polymerize the lignin or its fragments into bio-phenolic compounds which are suitable for the synthesis of bio-based phenolic resins (Alma et al., 2001; Lee and Ohkita, 2003). Some model lignin compounds, such as, guaiacol, guaiacol-β-guaiacol, veratrote (or diphenyl ether), 2,6-dimethoxyphenol, and

1,2,3-trimethoxybenzen, biphenyl and 5-5, *β*-1, *β*-*O*-4, and *α*-*O*-4 types of dimeric lignin, were used as a probe into the liquefaction mechanism of lignin in supercritical fluid solvents such as water and methanol (Lawson and Kleln, 1985; Tsujino et al., 2003; Minami et al., 2003). The influence of supercritical water on guaiacol pyrolysis was examined at 383 °C. Neat guaiacol pyrolysis resulted in catechol and char as the major products, and a small amount of phenol and o-cresol. However, guaiacol hydrolysis leads to catechol and methanol, the selectivity to which is a continuous and increasing function of water density (Lawson and Kleln, 1985). Reaction behavior of lignin in supercritical methanol (250 °C to 270 °C, 24-27 MPa) was investigated by using lignin model compounds of guaiacol, veratrote, 2,6-dimethoxyphenol and 1,2,3-trimethoxybenzene, and 5-5, *β*-1, *β*-*O*-4, and *α*-*O*-4 types of dimeric lignin fragments (Tsujino et al., 2003; Minami et al., 2003). It was found that *β*-ether linkage in *β*-*O*-4 model compounds and *α*-ether linkage in *α*-*O*-4 model compounds could be easily cleaved, but 5-5 (biphenyl)-type and aromatic rings structures were more stable. Recombination of the obtained highly reactive radicals would be a major challenge for this approach.

Several chemical degradation processes have been developed to break down lignin polymers to lower molecular weight products. These include oxidative processes (with the presence of oxidants such as O_2 or H_2O_2), reductive processes (with the presence of reducing agents such as H_2 or formic acid), and acidic and basic hydrolytic processes.

Oxidative/reductive depolymerization

Oxidative degradation of lignin in the presence of an appropriate catalyst such as a noble metal (Crestini et al, 2006) or peroxide (Hofrichter, 2002) and an oxidant (H_2O_2) usually produces benzaldehydes, ketones, and benzoic acids which are not suitable for the synthesis of PF resins, but they can be used for perfumes and pharmaceutical intermediates.

In order to prevent the recombination, hydrogenation using hydrogen as a reductive agent could be a solution based on Kleinert's work (Kleinert and Barth, 2008 (a)), suggesting that hydrogenation led to a higher yield of monomeric phenols and less char formation. The reactive hydrogen could be obtained from gaseous hydrogen in combination with suitable catalysts or a solvent medium. Attempts have been made to hydro-treat lignin over alumina-supported NiMo and CoMo catalysts (Piskorz et al., 1989; Oasmaa et al, 1993; Thring et al, 2000). It was recently reported by Yan et al. (2008) that wood lignin (using pine and birch sawdust as the lignin source) could be effectively degraded into monomers of guaiacylpropane, guaiacylpropanol, syringylpropane and syringylpropanol in hot-compressed water at 200 °C for 4 h under 4MPa (cold pressure) H_2 with carbon-supported Pt or Ru catalysts, where the biomass-to-solvent ratio was fixed at about 1:15 (wt/wt). The yield of total mono-phenols was as high as 45 % of the total amount of C_9 units in the lignin when co-solvent of dioxane/H_2O (1:1 wt/wt) with 1 H_3PO_4 (1 wt% of the solvent) was used combined with Pt/C catalyst (5wt% of the sawdust). The application of hydrogen-donating solvents such as Tetralin, 9,10-dihydroanthracene (AnH_2) and its derivatives and 1,4,5,8,9,10-hexahydroanthracene, proved to be effective hydrogen donors for the liquefaction of coal (Shen and Iino, 1994; Li et al, 2003). It was found that the quantity of hydrogen transferred from the solvent to the coal had a significant effect on the liquefaction reactions. However, these solvents are relatively expensive and hard to recover. There is another family of solvents such as formic acid and 2-propanol, which are less thermally stable and will decompose to give hydrogen atom upon heating at elevated temperatures. For example, formic acid decomposes completely into hydrogen and carbon dioxide, and 2-propanol can be decomposed into hydrogen and acetone by heating. Recently, this type of hydrogen-donating solvent has found special applications in hydro-conversion of biomass and lignin. As reported by Kleinert et al. (Kleinert and Barth, 2008 (a), 2008 (b); Kleinert et al, 2009; Kleinert and Barth, 2008 (c); Kleinert and Barth, 2007 (a); 2007 (b)), formic acid and 2-propanol were used as hydrogen donators to de-polymerize and hydrogenate lignin. Kleinert and co-workers obtained a high yield (25-35 wt%) of phenolic fraction, exclusively composed of monoaromatic phenols with alkylation ranging from C_1–C_7 in the side chain(s), by one-step conversion of lignin to oxygen-depleted bio-fuels and phenols using a co-solvent of formic acid and ethanol at about 400 °C. The yield was 2 or 3 times that of earlier work by Dorrestijn et al. (1999) using AnH_2 for de-polymerization of wood lignin at 352 °C. There was also a three-step process developed (Zmierczak and Miller, 2008) for producing gasoline from lignin as shown in Figure 2-11, in which the first two steps can be adopted for the production of bio-phenols from lignin. Recent research by our research group demonstrated that at > 350 °C hot-compressed ethanol-formic acid solvent with a Pt or Ni catalyst could effectively de-polymerize lignin into low molecular weight phenols (M_n: 143 g/mol, M_w: 247 g/mol). The research work in this regard continues in the authors' research lab.

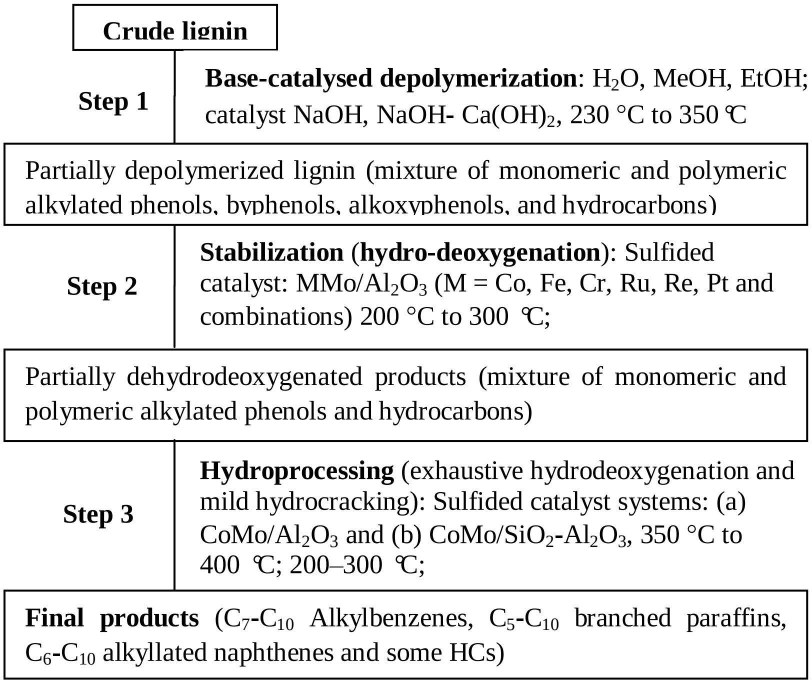

Figure 2-11. Three-step process for production of gasoline from lignin (Zmierczak and Miller, 2008)

Hydrolytic depolymerization (acidic and alkaline condition)

As a common process of biomass acid hydrolysis, hydrolytic degradation of lignin can be achieved using 72% sulfuric acid at 60°C to 80^{o}C (Matsushita and Yasuda, 2005) to produce sulfuric lignin. This lignin can then be used to synthesize ionic exchange resins. The main drawback of acidic hydrolysis includes unavoidable repolymerization between phenol reactive sites and the α-position of phenol propanol, and the waste disposal problem for sulfuric acid. To address the above problems of the acid hydrolysis, aqueous alkaline de-polymerization of lignin was carried out in a 5% NaOH solution at a temperature of 180 ℃ for 6 hr with anthraquinone as a co-catalyst (0.5 wt %) (Nenkova et al., 2008). A variety of monophenol and phenyl carbonyl compounds in the liquid products were identified by GC-MS. The de-polymerization of kraft- and organosolv-derived lignins by KOH in supercritical methanol or ethanol at 290 ^{o}C was studied in rapidly heated batch micro-reactors (Miller et al, 1999). High conversions were realized and the conversion was fast, reaching the maximum value within 10–15 min. The dominant de-polymerization route is the solvolysis of the ether linkages. A drawback of this method was its high yield (up to 7%) of solid residues due to re-polymerization and condensation of the reaction intermediates and the liquid products. The kraft process is also an alkaline de-polymerization process with re-polymerization occurring (Chakar and Ragauskas, 2004). Usually a capping agent such as sulfur or sulfite is used to react with degraded intermediates.

Current research by the authors' group (Yuan et al., 2010), found alkaline lignin of a very high molecular weight was successfully degraded into oligomers in a hot-compressed water-ethanol medium with NaOH as the catalyst and phenol as the capping agent at 220°C to 300^{o}C. Under the optimal reaction conditions, such as, 260 ^{o}C, 1 hr, and lignin/phenol ratio of 1:1 (wt/wt), almost complete degradation was achieved, producing <1% solid residue and negligible gas products. The obtained degraded lignin had a relative number-average molecular weight M_n and a relative weight-average molecular weight M_w of 450 g/mol and 1000 g/mol, respectively, significantly lower than the M_n and M_w of 10,000 g/mol and 60,000 g/mol, respectively, of the original lignin. A higher temperature and longer reaction time favored phenol combination, but increased the formation of solid residue due to the condensation reactions of the degradation intermediate/products. The degraded lignin products were soluble in organic solvents (such as Tetrahydrofuran (THF)), and were characterized by High-performance liquid chromatography (HPLC), Gel permeation chromatography (GPC), Infrared spectroscopy (IR) and Nuclear magnetic resonance (NMR). A possible mechanism for lignin hydrolytic degradation was also proposed in this study as shown in Figure 2-12.

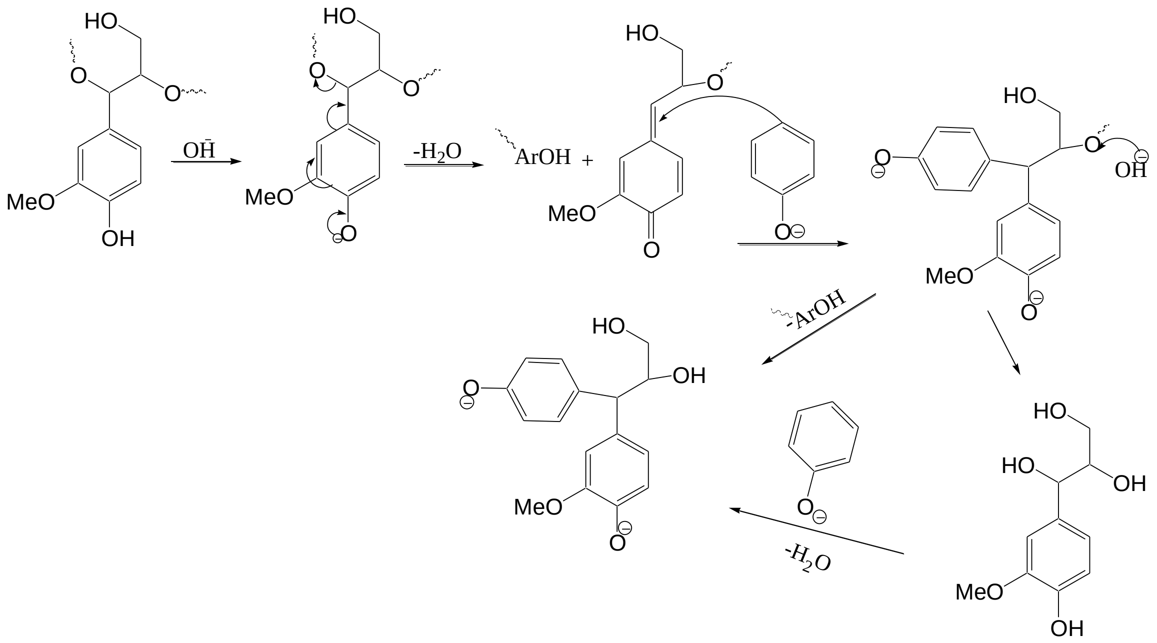

Figure 2-12. Possible hydrolytic degradation mechanisms of alkaline lignin catalyzed by NaOH (Yuan et al., 2010).

2.5 Concluding Remarks

In the field of forest residuals/lignin degradation, the main challenge is to prevent the recombination of reaction intermediates from forming larger molecules. There are also twin challenges in the synthesis of bio-phenol formaldehyde (BPF) resin: high substitution of phenol and satisfactory quality requirements. Based on the survey of the literature, solvolitic liquefaction under sub-/super-critical conditions is believed to be an effective solution for forest residuals/lignin degradation into high value-added bio-phenol products for replacing petroleum-based phenol in PF resins. Considering the cost, environment, and function concerns for production of bio-phenolic compounds, green co-solvent of water and alcohol could be a good choice for forest residuals/lignin degradation. As such, the related bio-based phenolic resins could have similar or comparable properties as pure PF resins, and meet the twin challenges.

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CHAPTER 3. HIGHLY EFFICIENT LIQUEFACTION OF WOODY BIOMASS IN HOT-COMPRESSED ALCOHOL-WATER CO-SOLVENTS

3.1 Abstract

There were synergistic effects of alcohol and water on biomass direct liquefaction, and a 50%/50% (wt/wt) co-solvent of either methanol-water or ethanol-water was found to be the most effective solvent for white pine sawdust liquefaction, producing roughly 66 wt% bio-oil yield and more than 95% biomass conversion at 300 °C for 15 min for a solvent to biomass ratio of 10 (wt/wt). At a temperature higher than 300 °C, conversion of bio-oil to char was significant by condensation and re-polymerization. The Fourier Transform Infrared Spectroscopy (FTIR) and Gas Chromatography-Mass Spectroscopy (GC-MS) analyses of the obtained bio-oils confirmed the presence of primarily phenolic compounds and their derivatives (such as benzenes), followed by aldehyde, long-chain (and cyclic) ketones and alcohols, ester, organic acid, and ether compounds. The Gel Permeation Chromatography **(**GPC) results suggest that hot-compressed ethanol as the liquefaction solvent favored lignin degradation into monomeric phenols. The X-ray Diffraction (XRD) patterns of white pine wood before and after the liquefaction displayed that the cellulosic structure of the feedstock was completely converted into amorphous carbon at around 300 °C, and into crystalline carbon at about 350 °C.

3.2 Introduction

As a potential renewable alternative to petroleum for the world’s energy and chemical production, biomass has attracted increasing interest in recently decades. Woody biomass primarily consists of natural polymers of hemi-cellulose (20-30%), cellulose (40-50%) and lignin (20-30%) (Panshin and DeZeeuw, 1980). Cellulose as the most abundant constituent of the plant-cell wall is a highly crystalline homo-polysaccharide of D-glucose with a degree of polymerization of up to 10,000 or higher. Hemi-celluloses are complex heterogeneous polysaccharides composed of D-glucose, D-galactose, D-mannose, D-xylose, and L-arabinose, etc (Willför et al., 2005(a); 2005(b)). The cellulosic components can be de-polymerized into monosaccharides by dilute acid hydrolysis and more economically by enzymatic hydrolysis. However, due to the high crystallinity of cellulose and the presence of lignin networks that shield the cellulose from enzymatic attack, hydrolysis of the cellulose and hemicellulose in woody biomass into monosaccharides has been a challenge for the production of secondary generation ethanol from forest biomass resources. For efficient and cost-effective efficient hydrolysis of cellulose into monosaccharides, expensive pre-treatment processes are needed to make biomass accessible by breaking the lignin seal, removing hemicellulose, or disrupting the crystalline structure of cellulose (Jørgensen et al., 2007; Fan et al., 1981). The cellulose/hemi-cellulose derived carbohydrates can be refined into various value-added products such as alcohols, esters and carboxylic acids through the so-called ‘sugar platform’ bio-refineries.

The lignin component in woody biomass is mainly utilized for process heat by direct combustion. However, lignin can be a promising source for such chemicals as phenols and aromatics. Lignin is a complex polymer of three main lignin building blocks, i.e., p-hydroxy-phenyl-propanol, guaiacyl-propanol and syringyl-propanol, linked mainly by two types of linkages: condensed linkages (e.g., 5-5 and β-1 linkages) and ether linkages (e.g., β-*O*-4 and α-*O*-4), while the ether linkages are the dominant linkages between the three main lignin building blocks. The phenyl propane units in lignin may be de-polymerized into phenolic chemicals by pyrolysis or direct liquefaction. Liquefied woody biomass can be used for preparing bio-fuels (Demirbas and Balat, 2006), phenolic resins and adhesive (Shiraishi and Kishi, 1986, Maldas et al., 1997; Ono and Sudo, 1993; Pu et al., 1991; Alma et al., 1995(a); 1995(b)), polyurethane foams (Alma and Shiralshi, 1998; Kurimoto et al., 1992), and carbon fiber (Shiraishi et al., 1993).

Wood and other lignocellulosic materials can be easily liquefied using low temperatures at atmospheric pressure (Lin et al., 2001(a); 2001(b)) in the presence of phenol with catalysts such as acids (sulfuric acid, hydrochloric acid, phosphoric acid, and oxalic acid)

(Alma et al., 1995(b); Lin et al., 1994; Lin et al., 1995 (a); 1995 (b); Yamata et al., (1996); Zhang et al., 2006), and alkali and metal salts (NaOH, $Cu(OH)_2$, $NaHCO_3$, NH_4Cl, $AlCl_3$, $CuSO_4$, $FeSO_4$, and NaH_2PO_4) (Zhang et al., 2006; Alma et al., 2001). A strong acid, such as concentrated sulfuric acid, has been used widely as an effective catalyst in the phenolysis liquefaction of woody biomass, and the resulted liquefied products could be used as matrix resins with satisfactory mechanical properties. However, disadvantages of the process using strong acids include partial carbonization of biomass during liquefaction and corrosion of the equipment. Thus, weaker acids such as hydrochloric acid and phosphoric acid may be more advantageous catalysts for the low-temperature biomass liquefaction by phenolysis. Zhang et al. (2006) compared the efficiency of four kinds of acid catalysts: hydrochloric acid (37 wt%), sulfuric acid (36 wt%), phosphoric acid (85 wt%), and oxalic acid (99.5 wt%), on liquefaction of Chinese fir and poplar in the presence of phenol. The results showed that phosphoric acid (85 wt%) and sulfuric acid (36 wt%) were more active catalysts, leading to solid residues as low as 3.2 wt% and 4.0 wt%, respectively, at 150 °C (Zhang et al., 2006). Maldas and Shiraishi reported the effects of various alkalies and salts on the liquefaction of a birch wood meal in phenol, and found that in comparison with acidic catalysts, alkalies or alkaline salts could produce a lower yield of solid residues, a lower ratio of combined phenol and hence a higher ratio of uncombined phenol (Alma et al., 2001).

However, the use of phenol as the liquefaction solvent could yield some problems, such as, high cost of the solvent, and recycling of phenol from the liquefied products as well as some environmental concerns. As a result, other organic solvents instead of phenol, such as alcohols and cyclic carbonates were tested as solvents for low-temperature liquefaction of biomass (Shiraishi et al., 1992; Hassan and Mun, 2002; Yamada and Ono, 1999). These solvents could be recycled by evaporation after liquefaction and are much cheaper than phenol. On the other hand, there is growing interest in producing phenol-formaldehyde resole resins and wood adhesives from renewable substances for the engineered wood industry, motivated by increasing phenol costs and depleting fossil fuel resources, as well as the vast availability of lignin-containing renewable feedstocks. In the past several years, considerable effort was made to replace the petroleum-based phenol partially with lignins, tannins, and liquefied biomass (Zhang et al., 2006; Roy et al., 2000; Lee, 2003). In the synthesis of a phenol-formaldehyde resin with an alkaline catalyst, phenols are deprotonated to form phenoxide ions, and the electron rich ortho- and para-positions in phenoxide ions are more susceptible to electrophilic aromatic substitution by the hydrated form of formaldehyde (often referred to as addition reaction) (Tonge et al., 2001). Lignin, tannins and the liquid products from the above mentioned low-temperature solvolytic processes using phenol or alcohols are however less reactive than phenol in the synthesis of phenolic resins due to their shortage of mono-phenolic compounds with unoccupied ortho- and para-positions (Effendi et al., 2008). The other reason is the liquid products from the low-temperature solvolytic processes are rich in large molecules of oligomers derived from lignin and cellulosic components. In this regard, liquefaction of lignocellulosic materials for application as a source of phenol derivatives at a high temperature is preferable.

Numerous studies have been reported on the liquefaction of biomass at a relatively higher temperature and under a high pressure. Appell et al. (1971) reported that woody biomass could be converted into 40%-50% liquid products in the presence of CO with aqueous sodium carbonate as catalyst under 28 MPa and 350 °C to 400 ^{o}C. Ogi and Yokoyama (1993) proved that woody biomass could be converted into bio-oil in a water medium with sodium carbonate as the catalyst under 10 MPa and 300 °C, but not in a reductive atmosphere of H_2 or CO. More recently, there has been a surge of interest in using hot-compressed and sub-/super-critical fluids for biomass liquefaction. Supercritical fluids have found applications for the chemical conversion of lignocellulosic materials due to their unique properties, e.g., they possess unique transport properties (gas-like diffusivity and liquid-like density), and supercritical fluids also have the ability to dissolve materials not normally soluble in either liquid or gaseous phase of the solvent, and hence promote the gasification/liquefaction reactions. Hot-compressed or sub-critical water has been used by many researchers for biomass liquefaction (Matsumura et al., 1999; Karagoz et al., 2004; 2005; Xu and Lad, 2008), while the main drawback of using water as the liquefaction solvent could be its lower yields of the water-insoluble oily product, compared with the liquefaction using sub-/super-critical alcohols or acetone

(Fuel, 1999; Minami and Saka, 2005; Xu and Etcheverry, 2008; Yamazaki et al., 2006; Liu and Zhang, 2008). Another advantage of using an alcohol as the solvent for biomass liquefaction is that these alcohols were expected to readily dissolve relatively high molecular weight products derived from cellulose, hemicelluloses, and lignin due to their lower dielectric constants when compared with that of water (Yamazaki et al., 2006). Biomass solvolytic liquefaction was greatly affected by the solvent type (Liu and Zhang, 2008). Lignin in woody biomass could be effectively extracted using a co-solvent of ethanol-water at 190 °C (i.e., the organosolv delignification process) (Li and Kiran, 1988; Pasquini et al., 2005).

Inspired by the above research work on organosolv delignification of biomass, liquefaction of woody biomass in alcohol-water mixture at a higher temperature will be of interest for the production of bio-oil and phenolic feedstock for the synthesis of bio-based phenolic resins (Pasquini et al., 2005). In the present study, hot-compressed methanol, ethanol and water, and their co-solvents were tested for direct liquefaction of white pine sawdust at 200 °C to 350 °C. Effects of co-solvent composition (methanol or ethanol content ranging from 0 to 100 wt%) and solvent-to-biomass ratio (ranging from 5-20 wt/wt) were examined.

3.3 Experimental Section

3.3.1 Materials

The biomass used in this study was Eastern White Pine (*Pinus strobus L.*) sawdust sieved to particles less than ca 20 mesh. The sawdust sample was dried in an oven at 105 °C for 24h before use. The proximate and ultimate analysis results of the sample and its structural compositions are given in Table 3-1. The solvents used in the liquefaction tests were distilled water and ACS reagent-grade chemicals (ethanol, methanol, acetone and ethyl acetate).

Table 3-1. Analyses of the pine sawdust used in the tests.

Proximate analysis, wt % (d.b.^{a})	
VM^b	84.5
FC^b	15.1
Ash	0.4
Ultimate analysis, wt % (d.a.f.$^{c)}$	
C	52.5
H	6.32
N	0.10
S	<0.05
O^d	40.6
Structural composition, wt% (d.b.)^e	
Total lignin	28.4
Cellulose	40.2
Hemicelluloses	21.9

Note: [a] On a dry basis; [b] Determined by thermogravimetric analysis (TGA) in N_2 at 10°C/min to 900°C; [c] On a dry and ash-free basis; [d] By difference; [e] The samples were extracted with acetone for the extractive-free test specimens, cellulose/hemicellulsoe were determined according to TAPPI test method T249cm-85, and the acid-soluble and acid-insoluble lignin were determined according to the TAPPI test method T222 om-88.

3.3.2 Liquefaction operation and product separation.

The liquefaction of pine sawdust was carried out in a 600 mL stainless steel autoclave reactor equipped with a stirrer and a water-cooling coil. In a typical run, the reactor was charged with 10g pine sawdust and 100g mono-solvent (water, methanol or ethanol) or methanol-water or ethanol-water co-solvent of various alcohol contents. The reactor was sealed, and the air inside the reactor was displaced by high-purity nitrogen. The reactor was subsequently pressurized to 2.0 MPa with nitrogen to prevent the reactive material from boiling during the course of the heating process. The reactor was heated to the desired temperature at 10 °C/min with stirring at a speed of 120-130 rpm and soaked at the temperature for 15 min of reaction before cooling down. Once the reactor was cooled down to room temperature using the water-cooling coil, the gaseous product inside the reactor was collected into a pre-vacuum fixed-volume (2800 mL) gas-collecting vessel. In each run, the gas vessel's pressure was adjusted to 1 atm (abs) using high-purity nitrogen make-up gas. The gas inside the vessel was analyzed using a Micro-GC equipped with Thermal Conductivity Detectors (TCD)s. The formation (moles) of gas species (H_2, CO, CO_2, CH_4, and C_2-C_3) was obtained. The liquid products and solid residue (SR) in the reactor were completely rinsed using acetone. The resulting suspension was filtered under reduced pressure through a pre-weighted Whatman No. 5 filter paper. The SR products and filter paper were dried at 105 °C for 4hr before weighing. The acetone and alcohol (ethanol or methanol) in the filtrate solution were then removed by rotary evaporation under vacuum at 40 °C, and the remaining liquid solution was extracted with ethyl acetate using a separatory funnel to separate bio-oil from aqueous soluble products. Ethyl acetate soluble phase was evaporated under a reduced pressure at 57 °C to remove ethyl acetate, and recover liquid oily products, denoted as bio-oil. Yields of bio-oil, SR and Gas (gaseous products) were calculated by the wt% of the mass of each product to the mass of the dry pine sawdust loaded into the reactor each run. The biomass conversion was simply calculated by (100 wt% − SR yield wt%). Being the common challenge for the biomass liquefaction studies, quantification of aqueous products (AP) was difficult not only because it is hard to separate the aqueous soluble products from water due to the high boiling of water and the complexity of the aqueous products (a mixture of carboxylic acids, carbohydrates, aldehydes, etc.). Since our major interest of this research was the bio-oil products, the aqueous products were not analyzed. For simplicity, the yield of aqueous products, AP including the pyrolytic water from the biomass was calculated by difference. Two or three duplicate runs were conducted for all the experimental conditions to minimize the experimental errors, which was mostly within 5%.

3.3.3 Characterization of the liquid and solid products

The obtained bio-oils were analyzed on an IR2000 spectrometer (Perkin-Elmer, US), and on a gas chromatography-mass spectrometry (GC-MS, Shimadzu QP2010S) with a SHRXI-5MS column (30m × 0.25mm × 0.25 um) and the temperature program of 40 °C (hold for 2 min) to 190 °C (12°C/min) –330 °C (8°C/min, hold for 20 min). Chemical compounds in the bio-oils were identified using the WILEY8 library based on the GC-MS chromatographs. Admittedly, the GC–MS analysis for the bio-oil products has a limitation in that the less/non-volatile compounds such as oligomers of the lignin-degraded products are not able to be detected as they are unable to pass through the GC column. The molecular weights and their distributions of the bio-oils were analyzed on a Waters Breeze Gel Permeation Chromatography (GPC) (1525 binary High-Performance Liquid Chromatography (HPLC) pump; UV detector at 270 nm; Waters Styragel HR1 column at 40 ^{o}C) using Tetrahydrofuran (THF) as eluent at a flow rate of 1 mL/min, and polystyrene standards were used for calibration. In addition, the crystalline forms of pine sawdust before and after liquefaction at different temperatures were examined by X-ray diffraction (XRD) using a PANalytical X'Pert PRO X-Ray diffractometer using Cu K_{α} radiation with a wavelength of 1.54187Ǻ.

3.4 Results and Discussion

3.4.1 Effects of solvent types and compositions

Figure 3-1 shows the yields of bio-oil, SR and Gas and AP from the liquefaction at 300 °C in different solvents while the solvent-to-biomass ratio was fixed at 10:1 (wt/wt). As shown in Figure 3-1, when mono-solvent was used, water was much more active than the other two alcohol solvents: the liquefaction with 100% water led to 70 wt% biomass conversion and 40 wt% bio-oil yield, compared with about 42 wt% biomass conversion and ~25 wt% bio-oil yield with either 100% methanol or 100% ethanol. Ethanol was slightly more reactive than methanol for biomass liquefaction. Hot-compressed water was demonstrated to be an effective solvent for biomass liquefaction by many previous studies on biomass hydrothermal liquefaction (Matsumura et al., 1999; Karagoz et al., 2004; 2005; Xu and Lad, 2008). The high activity of hot-compressed water for liquefying biomass may be ascribed to its unique roles in disassociation of the polymer structures of the lignocellulosic biomass by hydrolysis reactions. The high activity of hot-compressed water might also be related to many special properties of water in hot-compressed or sub-critical state, e.g., it has a lower dielectric constant, fewer and weaker hydrogen bonds, a higher isothermal compressibility and an enhanced solubility for organic compounds than ambient liquid water (Savage, 1999; Akiya and Savage, 2002). Moreover, hot-compressed water has been found to be very effective for promoting ionic, polar non-ionic and free-radical reactions (Akiya and Savage, 2002), which make it a promising reaction medium for biomass direct liquefaction. It is shown from Figure 3-1, the 50%/50% (wt/wt) co-solvent of either methanol-water (i.e., 50 wt% methanol solution) or ethanol-water (i.e., 50 wt% ethanol solution) was a much more effective solvent than any constituent mono-solvent. The liquefaction in the 50 wt% methanol solution or the 50 wt% ethanol solution led to conversion of biomass at 95 wt% or higher and a bio-oil yield as high as 65 wt% at 300 °C. Again the co-solvent of ethanol-water was found to be slightly more reactive than the co-solvent of methanol-water. These results strongly suggest synergistic effects on biomass direct liquefaction were observed when the association of the alcohol and water produced a higher yield of bio-oil and better conversion compared with a mono-solvent of alcohol or water. The synergy between water and alcohol has also been reported previously in organosolv delignification of woody biomass at 190 °C, where 50 wt% methanol-water solution or 50 wt% ethanol-water solution were found to be very effective for wood delignification (Li and Kiran, 1988; Pasquini et al., 2005). Although a methanol-water co-solvent is as active as an ethanol-water co-solvent for bio-oil production and biomass conversion, co-solvent of ethanol-water has attracted more interest, simply because ethanol is a renewable resource which can be obtained readily by fermentation of sugars. Furthermore, methanol is a poisonous chemical in the synthesis of bio-based phenolic resins using bio-oil to substitute phenol (Chen and Chen, 1988). Consequently, co-solvent of ethanol-water was selected as the medium of interest in this study, and more tests were carried out on biomass direct liquefaction in ethanol-water co-solvent.

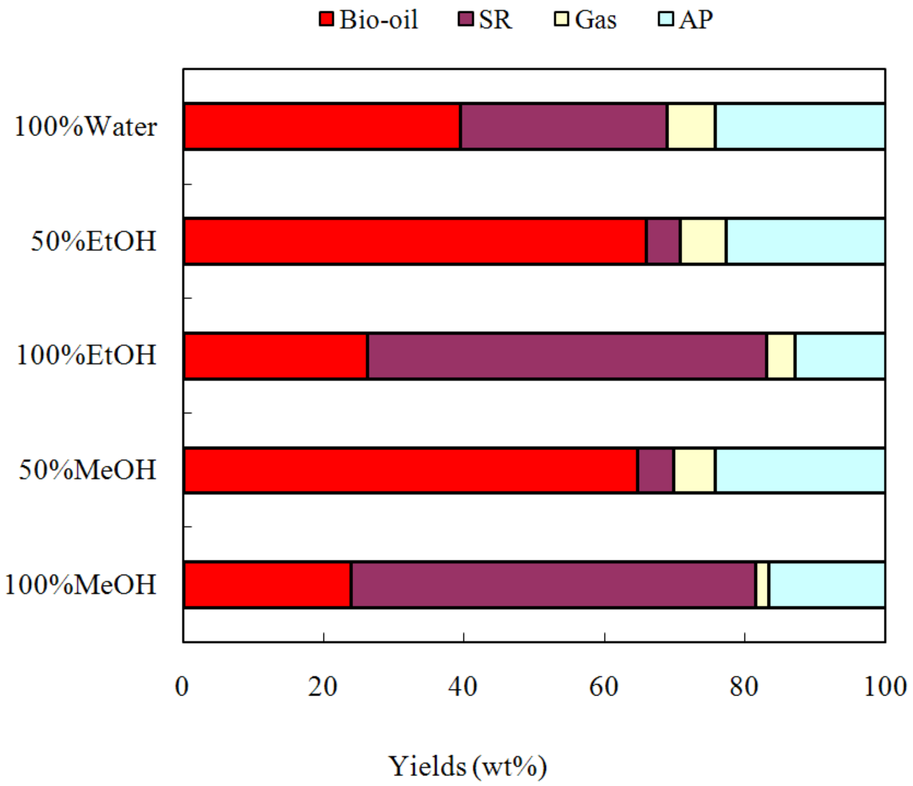

Figure 3-1. Yields of bio-oil, SR and Gas and AP from liquefaction of pine sawdust at 300 °C in different solvents.

In order to determine the optimal composition of the alcohol-water co-solvent for direct liquefaction, the sawdust sample was liquefied with co-solvents of ethanol-water of different ethanol contents varying from 0 to 100 wt% at 300 ^{o}C for 15 min. The yields of bio-oil, SR, Gas and AP are shown in Figure 3-2. The yields of gaseous products (mainly CO_2 and CH_4) almost in all runs were about 5 wt%, hence the formation of gaseous products in the process was negligible. As already shown in the previous Figure 3-1, Figure 3-2 revealed that a mono-solvent of either pure ethanol or pure water was less effective for biomass conversion or bio-oil yields, compared with the ethanol-water co-solvent consisting of < 50 wt% ethanol. The bio-oil yield and biomass conversion (referring to the SR yield) peaked with the 50 wt% ethanol solution, but interestingly both the bio-oil-yield and biomass conversion were greatly reduced as the ethanol content in the ethanol-water co-solvent increased to 75 wt%. The influence of ethanol content in the co-solvent system on the yield of Gas or AP was not significant, although generally the yields declined slightly as the ethanol content increased from 0 to 100 wt%, likely due to the suppression of the hydrolysis and gasification reactions.

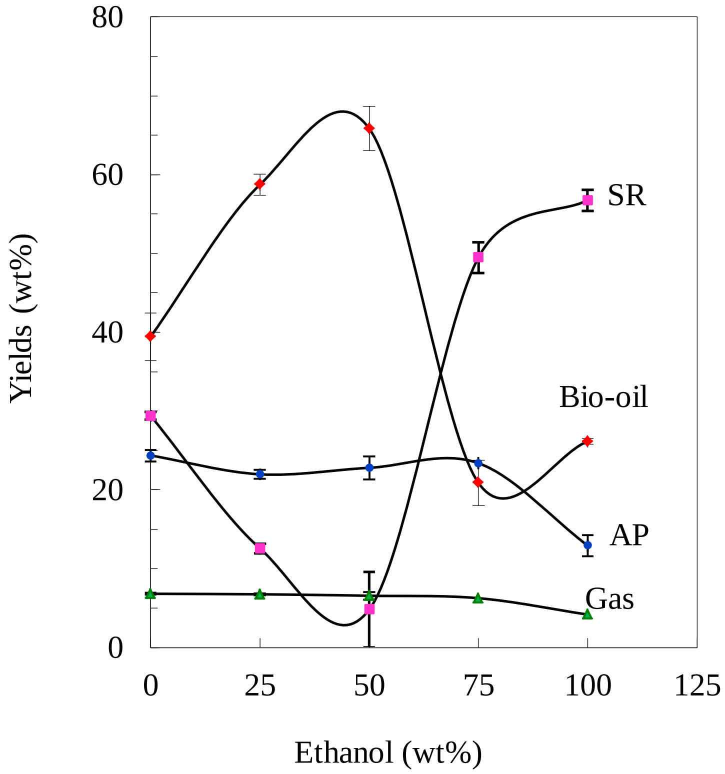

Figure 3-2. Yields of Bio-oil, SR, Gas and AP from the liquefaction at 300 °C in a co-solvent of ethanol-water of varying ethanol content.

The role of the constituent solvents in the co-solvent system for biomass direct liquefaction shall be discussed. For the biomass solvolytic liquefaction process at an elevated temperature in a closed system, ionic and radical reactions including nucleophilic, electrophilic, hydrolysis, thermal cracking/pyrolysis reactions would occur (Kabyemela et al., 1997; Antal et al., 1991). Alcohols are slightly weaker acids than water, and as mentioned before, the water in hot-compressed and sub-critical state has many special properties compared with ambient liquid water (Savage, 1999; Akiya and Savage, 2002). As a result, the lower activity of the 100 wt% ethanol for biomass liquefaction than that of 100% water may be predicted, because of the limited hydrolysis reactions in the system with 100% ethanol. The addition of water as a co-solvent into ethanol would thus enhance the solvolytic liquefaction of biomass, as evidenced by the results shown in Figure 3-2, as similarly observed by Pasquini et al. in organosolv delignification of biomass using ethanol-water co-solvents (Pasquini et al., 2005).

3.4.2 Effects of reaction temperature

In this study, slightly higher temperatures from 200 °C to 350 °C were tested for biomass direct liquefaction for the production of bio-oils. As shown previously in Figures 3-1 and 3-2, the gas yields in the process were negligibly low (about 5 wt%). The formation of gaseous and aqueous products was here with lumped into (Gas + AP). The effects of reaction temperature (200 °C to 350 °C) on the yields of bio-oil, SR and (Gas+AP) from the liquefaction with the 50 wt% ethanol solution are shown in Figure 3-3. The results clearly displayed that the yields of bio-oil increased continuously from 25 wt% to 66 wt% as the reaction temperature increased from 200 °C to 300 °C, while the solid residue decreased greatly from 70 wt% (at 200 °C) to 5 wt% (at 300 °C). However, the oil yield dropped markedly to below 35 wt% if the temperature was further increased to 350 °C, accompanied by significant increases in the yields of SR and (Gas+AP), suggesting conversion of bio-oil to char and gaseous/aqueous products at a temperature higher than 300 °C. The greatly reduced bio-oil at temperatures > 300 °C may be explained by formation of char through condensation reactions of the liquid bio-oil products, and by formation of hydrocarbon gases through cracking reactions of the bio-oil. Both types of reactions are thermodynamically favorable at high temperatures. Similar observations were reported previously in direct liquefaction of biomass in hot-compressed water (Qu et al., 2003) or ethanol (Xu and Etcheverry, 2008). We thus conclude that 300 °C appears to be the best temperature for direct liquefaction of pine sawdust to produce bio-oil using hot-compressed co-solvent of ethanol-water (50%/50%, wt/wt).

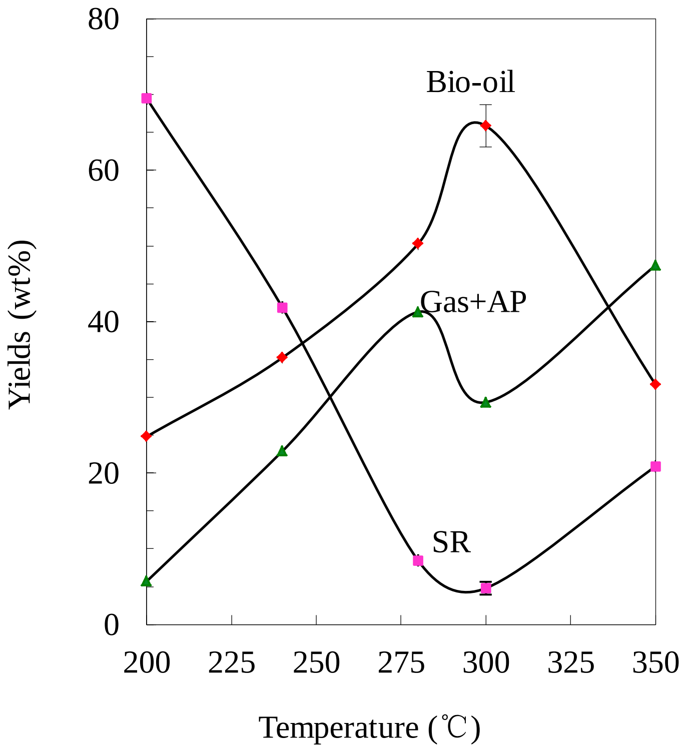

Figure 3-3. Yields of Bio-oil, SR and (Gas+AP) from the liquefaction with co-solvent of ethanol-water (50%/50%, wt/wt) at various reaction temperatures.

3.4.3 Effects of solvent-to-biomass ratio

Effects of solvent-to-biomass ratio were investigated by conducting the liquefaction tests for 15 min at 300 °C using the co-solvent of ethanol-water (50%/50%, wt/wt) at various initial solvent-to-biomass ratios ranging from 5 to 20. The results of liquefaction product yields are illustrated in Figure 3-4. Solvent-to-biomass ratio has been reported as an important factor to influence biomass liquefaction in hot-compressed or supercritical water (Xu and Donald, 2008; Xu and Lancaster, 2008), where interestingly a decreased water-to-biomass ratio generally led to increased yields of heavy oil and char but a decreased yield of aqueous products. For the operations with a smaller water-to-biomass ratio, a higher biomass concentration or a lower water concentration prevailed throughout the whole process, which might then restrict the solvolysis/hydrolysis/hydration of the lignocellulosic solids, leading to a smaller yield of aqueous products and a higher yield of solid residue or char. On the other hand, it is likely that a high biomass concentration or a low water concentration promoted the dehydration reactions of the aqueous intermediates/products leading to a greater yield of heavy oil. For the biomass liquefaction operations in this study employing a co-solvent of ethanol-water, different results from the previous work (using water) were obtained as illustrated in Figure 3-4. As clearly shown from the Figure, an increased solvent-to-biomass ratio up to 10 (wt/wt) led to a higher bio-oil yield and a lower SR. The low bio-oil yield at a low solvent-to-biomass ratio was likely caused by the fact that at a low solvent-to-biomass ratio (such as 5) the biomass could not form a well-mixed suspension in the reactor due to the limited amount of the solvent. This would result in unfavorable mass and heat transfer conditions inside the reactor, retarding the liquefaction and solvolysis reactions and hence reducing the bio-oil yield. Another possible reason could be the formation of char by condensation reactions of bio-oil intermediates/products at a low solvent-to-biomass ratio (Liu and Zhang, 2008). However, the yields of both bio-oil and SR leveled off at the solvent-to-biomass ratio of 10, suggesting that the solvent-to-biomass ratio greater than 10 (wt/wt) negatively affect the direct liquefaction process using the hot-compressed co-solvent of ethanol-water (50%/50%, wt/wt), likely due to the markedly enhanced formation of AP (as shown in Figure 3-4).

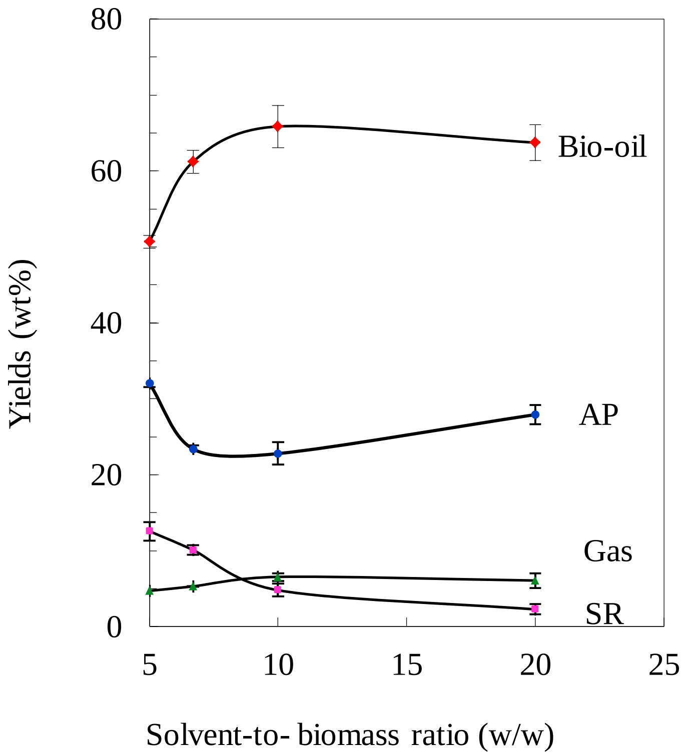

Figure 3-4. Yields of Bio-oil, SR, Gas and AP from the liquefaction with co-solvent of ethanol-water (50%/50%, wt/wt) at 300 °C at different solvent-biomass ratios.

3.4.4 Characterizations of liquefaction products

The FTIR spectra for the bio-oils from the liquefaction using different solvents are illustrated in Figure 3-5. All of the bio-oils displayed similar IR adsorption profiles, suggesting similar chemical structures. They all had the typical hydroxyl groups absorption at 3402 cm^{-1} which was caused by the combination and overlap of aliphatic and aromatic O-H stretching from the phenolic compounds as well as from the moisture inevitably contained in the samples, and the adsorption between 1715 cm^{-1} and 1738 cm^{-1} may be ascribed to the C=O stretching from ketone, aldehyde and ester groups (Serrano et al., 1996). The presence of both O-H and C=O stretching vibrations may also indicate the present of carboxylic acids and their derivatives. Absorption between 2845 cm^{-1} and 2945 cm^{-1} could be attributed to symmetrical and asymmetrical C-H stretching vibration of methyl group and methylene group. The band at 1379 cm^{-1} was attributed to C-H bending. The C-H stretching vibration and C-H bending indicate alkane groups in the bio-oil. Bands from 1447 cm^{-1} to 1612 cm^{-1} belonged to the aryl groups, and the adsorption band at 1612 cm^{-1} was likely by benzene backbone vibration. The absorption peaks between 1000 $cm^{-1}$and 1300 cm^{-1} were attributed to the C-O stretching and O-H deformation vibrations which described the present of primary, secondary and tertiary alcohols, phenols, ethers and esters (Das et al., 2004; Islam et al., 2005). The broad absorption peaks at 1250 cm^{-1} were likely attributed to methoxyl group. Meanwhile, the bands between 690 cm^{-1} and 950 cm^{-1} indicated the presence of single, polycyclic and substituted aromatic groups (Serrano et al., 1996).

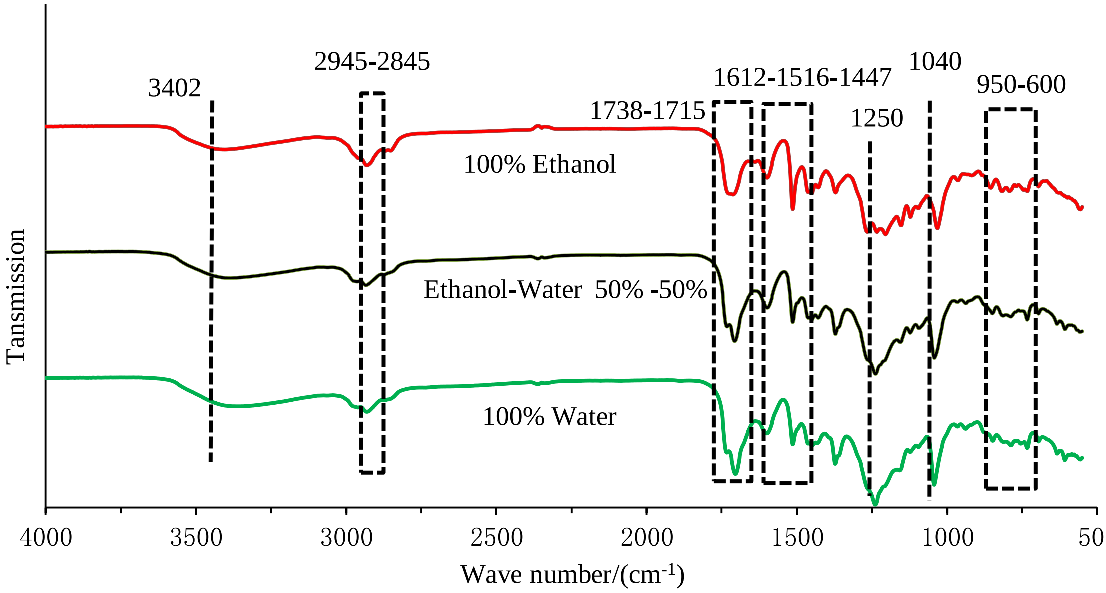

Figure 3-5. FTIR spectra of the bio-oil from liquefaction of pine sawdust with hot-compressed co-solvent of ethanol-water (50%/50%, wt/wt) at 300 °C (solvent-to-biomass ratio of 10, w/w).

The presence of the phenolic/aromatic compounds, ketones, aldehydes and carboxylic acids, as revealed by the IR analysis could be confirmed by the GC-MS analytical results as provided in Table 3-2.

Table 3-2. GC-MS analysis results for the bio-oils from the liquefaction of pine sawdust in mono-solvent of ethanol and water, and the co-solvent of ethanol-water (50%/50%, wt/wt) at 300 °C for 15 min with a solvent-to-biomass ratio of 10:1 (wt/wt).

Peak No.	Retention time /min	[1]Relative composition by area %			Compound name
		100% Ethanol	100% Water	50% Ethanol	
1	3.042	4.47	-	-	Ethyl 2-hydroxypropanoate
2	3.516	4.24	-		2-Furanmethanol
3	4.016	-	-	2.38	Benzene, methyl-
4	4.208	2.89	-	-	Butanoic acid, 2-hydroxy-, ethyl ester
5	4.228	-	-	2.47	1-propanol, 2-ethoxy-
6	4.392	2.8	-	-	Ethanol, 2-(ethenyloxy)-
7	4.505	2.27	-	-	Benzene, (1-methylethyl)-
8	4.75	-	-	13.02	Propanoic acid, 2-hydroxy-, ethyl ester
9	5.047	-	15	2.21	2-Furancarboxaldehyde
10	5.231	3.02	-	-	Oxiranemethanol
11	5.725	2.77	-	-	Piperazine
12	6.000	2.94	-	-	2-heptanamine, 5-methyl-
13	6.240	-	-	3.65	4-[(2-methoxyethoxy)methoxy]-1-Cyclopentene
14	6.467	-	-	2.53	Propanoic acid, 2-hydroxy-, methyl ester
15	6.525	-	-	2.05	Benzene, (1-methylethyl)-
16	6.549	-	5.77	-	2,5-hexanedione
17	6.586	2.2	-	-	Acetamide, n-(1-methylpropyl)-
18	6.583	-	-	2.34	2,5-hexanedione
19	6.656	3.06	-	-	Butanoic anhydride
20	6.828	6.79	-	-	Phenol, 2-methoxy-
21	7.104	-	10.74	3.26	2-furancarboxaldehyde, 5-methyl-
22	7.343	-	4.05	-	Phenol
23	8.209	4.79	-	-	1-hydroxy-2-methoxy-4-methylbenzene
24	8.033	-	6.27	6.64	3-methyl-1,2-cyclopentanedione
25	8.191	-	2.27	-	Ethanone, 1-(5-methyl-2-furanyl)-
26	8.516	-	-	6.62	Pentanoic acid, 4-oxo-, ethyl ester
27	8.783		-	3.75	2-furanmethanol, tetrahydro-
28	8.872	3.64	-	-	4-nonanol, 4-methyl-
29	8.947	-	17.62	9.00	Phenol, 2-methoxy-
30	9.290	6.5	-	-	Guaiacol, 4-ethyl-
31	9.458	5.57	-	-	Formamide, n,n-dimethyl-
32	9.713	2.62	-	-	2-methoxy-4-vinylphenol
34	9.842	2.92	-	-	2-amino-3-(2-amino-2-carboxy-ethyldisulfanyl)-propionic acid
35	10.22	4.44	-	-	Phenol, 2-methoxy-4-(2-propenyl)-
36	10.32	-	3.25	3.13	1-hydroxy-2-methoxy-4-methylbenzene
37	10.33	2.97	-	-	Guaiacol, 4-propyl-
38	10.72	-	-	3.71	2-furancarboxaldehyde, 5-(ethoxymethyl)-
39	11.25	21.01	-	-	Phenol, 2-methoxy-4-(2-propenyl)-

40	11.39	-	3.49	5.1	Guaiacol, 4-ethyl-
41	11.76	-	-	2.4	2-propyl-tetrahydro-pyran-3-ol
42	12.79	-	5.46	4.6	Benzaldehyde, 4-hydroxy-3-methoxy-
43	13.18	-	-	2.02	Benzenemethanol, 4-hydroxy-.alpha.-[(methylamino)methyl]-
44	13.34	-	-	5.77	Phenol, 2-methoxy-4-(2-propenyl)-
45	13.74	-	2.33	-	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-
46	14.20	-	2.82	-	2-propanone, (4-hydroxy-3-methoxyphenyl)-
47	15.38	-	3.18	-	3-benzofuranmethanol, 2,3-dihydro-2-(4-hydroxy-3-methoxyphenyl)-5-(3-hydroxy-1-propenyl)-7-methoxy-
48	16.30	-	2.55	-	1-(4-isopropylphenyl)-2-methylpropyl acetate
Total area/%		91.91	84.77	86.65	

[1] Not including the small peaks with an area less than 2% of the total area

Table 3-2 presents the chemical compounds in the obtained bio-oils from the liquefaction of pine sawdust in mono-solvent of ethanol and water, and the co-solvent of ethanol-water (50%/50%, wt/wt) at 300 °C for 15 min with the solvent-to-biomass ratio of 10:1 (wt/wt). The chemical compounds were identified using the WILEY8 library based on the GC-MS chromatographs. The relative area % for each compound identified (defined by percentage of the compound's chromatographic area out of the total area) and the total area% for all the identified compounds are shown in the Table. It should be noted that the area% values that are presented here show only the relative concentration of each compound in the fraction of the bio-oil, which can be vaporized and pass through the GC column. As shown in Table 3-2, the major compounds identified in the three bio-oil products were phenolic compounds and their derivatives (such as benzenes aromatics), aldehyde, long-chain (and cyclic) ketones and alcohols, ester, carboxylic acids and ether compounds. The liquefaction in ethanol produced a bio-oil rich in 2-methoxy-4-(2-propenyl)-phenol (21.01%), 2-methoxy- phenol (6.79%), other phenolic compounds (16.5%) and their derivatives benzenoid aromatic compound (7.1%), alcohol (10.9%), and ester (7.4%). Small amounts of compounds containing nitrogen and sulfur were also detected, such as piperazine, n-(1-methylpropyl)-acetamide, n-dimethyl-formamide, 2-amino-3-(2-amino-2-carboxy- ethyldisulfanyl)-propionic acid. The reason was attributed to the raw material of white pine sawdust containing a little amount of nitrogen and sulfur according to its ultimate analysis as shown in Table 3-1. In the bio-oil product from liquefaction in water, the major compounds identified were various aldehydes (31.2%) such as substituted furfural (25.7%) and benzaldehyde (5.5%), phenolic compounds (25.2%) and their derivatives (3.3%), and substituded ketones (13.86%). For the bio-oil produced with the co-solvent of ethanol-water, the detected compounds were mainly phenolic (19.9%) and benzenoid aromatic compounds (7.6%), various esters (22.2%), substituted aldehydes (13.8%) including furfural and benzaldehyde. The phenolic compounds, in particular the guaiacols, were apparently derived from the lignin in the pine sawdust. The bio-oil from the liquefaction in the mono-solvent of ethanol appeared to contain a larger amount of phenolic than that from water or the water-ethanol co-solvent. This suggests that hot-compressed alcohol would facilitate lignin degradation, as also observed in the literature (Miller et al., 1999; Minami and Saka, 2005; Xu and Etcheverry, 2008).

As mentioned before, GC-MS analysis for bio-oils has limitations due to the fact that less/non-volatile compounds in the bio-oil such as oligomers of the lignin-degraded products were unable to pass through the GC column, hence they were not able to be detected by GC-MS. According to our TGA analysis of the bio-oil with the co-solvent of ethanol-water (50%/50%, wt/wt) in nitrogen up to 800 °C, < 10 wt% of the bio-oil was vaporized at 280 °C, the same temperature as at the injection port of the GC-MS. Therefore, more than 90 wt% fraction of the bio-oil was not evaporated and hence the majority of the oil was unable to be detected by GC-MS. To address this problem, GPC analysis was performed to examine the molecular weight distribution of the bio-oils derived from the pine wood liquefaction in different solvents: mono-solvents of ethanol, methanol or water, and co-solvents of ethanol- or methanol-water (50%/50%, wt/wt). The GPC analytical results are shown in Figure 3-6. As clearly shown in the Figure, all the obtained bio-oils exhibited a broad molecular weight distribution, and contained a lot of oligomers derived from partial decomposition of lignin, cellulose or hemicelluloses. The bio-oil from the liquefaction in water has the largest M_w value (1373 g/mol) and M_n (630 g/mol) and the lowest polydispersity (M_w/M_n, 2.18), compared to the bio-oils obtained with other alcohol containing solvents. The liquefaction in 100% ethanol led to a bio-oil product with greatly reduced molecular weights (M_w = 760 g/mol and M_n = 235 g/mol), about or more than half of those for the bio-oil obtained with 100% water. More interestingly, as indicated by the sharp peaks at a retention time of about 17 min, the GPC results in Figure 3-6 clearly evidence the presence of phenol or monomeric phenolic compounds in all bio-oil samples. Again, the monomeric phenol peak was strongest for bio-oil obtained with 100% ethanol. These results suggested that ethanol was the best solvent among those tested with respect to lignin degradation into monomeric phenols.

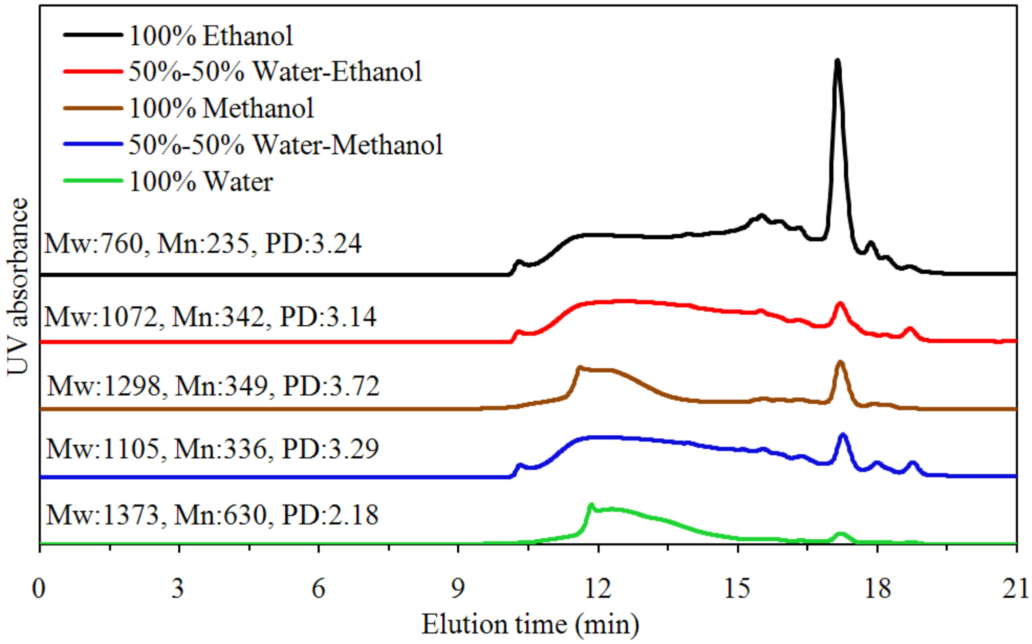

Figure 3-6. GPC results for the bio-oils derived from the pine wood liquefaction in various solvents at 300°C for 15 min with the solvent-to-biomass ratio of 10 (w/w). PD (polydispersity) = M_w/M_n

Figure 3-7 shows the XRD patterns of cellulose and crude pine sawdust and the solid residues, SR, after the liquefaction at various temperatures (200 °C, 240 °C, 300 °C and 350 °C) for 15 min in the co-solvent of ethanol-water (50%/50%, wt/wt) and at the solvent-to-biomass ratio of 10 (wt/wt). For reference, the XRD profile of pure cellulose (from Sigma Aldrich) was also obtained and shown in Figure 3-7. Compared with that for the crude pine sawdust, no significant evolution in XRD patterns was noticeable in the SR from the liquefaction at a temperature up to 240 °C. Four characteristic peaks at $2\theta = 14.6^\circ$, 16.5°, 22.4° and 34.6° from diffraction on the cellulose I's 110,$1\bar{1}0$, 002 and 040 planes (Zhang and Kamdem, 2000; Borysiak and Doczekalska, 2005; Nishio and Manley, 1988) were clearly observable in the pure cellulose sample, the crude pine sawdust and the SRs obtained at 200 °C and 240 °C. In contrast, all four peaks derived from cellulose I disappeared in the SR at 300 °C, instead broad signals at 2θ of around 24°, typical of amorphous carbon, were observed. As clearly shown in Figure 3-7, if temperature was further increased to 350 °C, there were strong X-ray diffraction lines at 2θ between 24° and 26° dominating the spectrum. These XRD signals can be attributed to the C(002) diffraction lines of amorphous carbon (2θ = 24.4) and turbostratic carbon (2θ = 26.2). This suggests the formation of partially crystallized coke/carbon from the pyrolysis of lignocellulosic matrix or condensation of liquid intermediates/bio-oils, as evidenced by a rapid decrease in bio-oil yield when increasing the liquefaction temperature from 300 °C to 350 °C (Figure 3-3). Similar observations on carbon crystallization were reported in some previous biomass liquefaction studies with hot-compressed water or methanol (Xu and Lad, 2008; Yang et al., 2009). The XRD results suggest that the cellulosic crystalline structures in the pine sawdust could remain with little change in the co-solvent of ethanol-water at a temperature up to 240 °C, while they would completely decompose to form amorphous carbon at 300 °C.

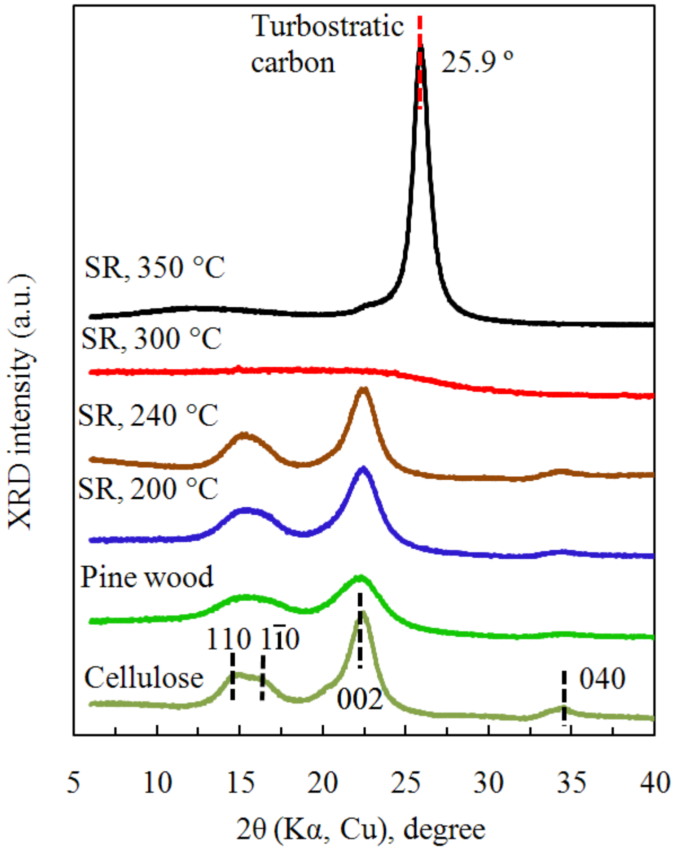

Figure 3-7. X-ray diffraction patterns of cellulose and white pine wood before and after liquefaction at different temperatures for 15min.

3.5 Conclusions

In this study, white pine sawdust was effectively liquefied with hot-compressed mono-solvents of water, methanol and ethanol, and co-solvents of alcohol (methanol- or ethanol) and water at a temperature from 200 °C to 350 °C. Some key conclusions are summarized below:

(1) There were synergistic effects for the combination of alcohol (methanol or ethanol) and water on pine sawdust direct liquefaction compared to mono-solvent of alcohol or water. Higher bio-oil yields (65 wt%) and better biomass conversion (95 wt%) at 300 °C for 15 min were obtained from liquefaction in co-solvent of 50 wt% aqueous alcohol than in mono-solvent of alcohol (~ 25 wt% bio-oil yield, and ~ 42 wt%

biomass conversion) or water (40 wt% bio-oil yield, and 70 wt% biomass conversion).

(2) The yields of bio-oil increased continuously from 25 wt% to 66 wt% as the reaction temperature increased from 200 °C to 300 °C, but the oil yield dropped markedly to below 35 wt% if the temperature was further increased to 350°C, accompanied by a significant increase in solid residue. These results suggested severe conversion of bio-oil to char by condensation reactions of the liquid bio-oil products at > 300°C, which was evidenced by the XRD measurements on the solid residues from the liquefaction.

(3) The solvent-to-biomass ratio of 10 (wt/wt) was found to be an optimal condition for direct liquefaction of pine sawdust to produce bio-oil using hot-compressed co-solvent of ethanol-water (50%/50%, wt/wt).

(4) The FTIR and GC-MS analyses of the obtained bio-oils revealed the presence of high contents of oxygen-containing chemical compounds such as phenolic compounds, aldehydes, long-chain (and cyclic) alcohols and ketones, ethers and esters and carboxylic acids, etc.

(5) All the obtained bio-oils exhibited a broad molecular weight distribution, and contained a lot of oligomers derived from the lignocellulosic feedstock. The bio-oil’s molecular weight distribution was strongly dependent on the solvent type. Among all solvents tested, ethanol was the most effective solvent for the degradation of lignin into monomeric phenols.

(6) The XRD measurements for solid residues after the liquefaction demonstrated that the cellulosic crystalline structures in the pine sawdust could remain with little change in the co-solvent of ethanol-water at a temperature up to 240 °C, while they would completely decompose to form amorphous carbon at 300 °C.

3.6 Acknowledgements

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CHAPTER 4. USING BIO-CRUDE DERIVED FROM WOODY BIOMASS TO SUBSTITUTE PHENOL AT A HIGH SUBSTITUTION LEVEL FOR PRODUCTION OF BIO-BASED PHENOLIC RESOLE RESINS

4.1 Abstract

Phenolic bio-oil produced by direct liquefaction of Eastern White Pine (*Pinus strobus L.*) sawdust in a hot-compressed ethanol-water (1:1 wt/wt) medium at 300 ^{o}C was used to substitute phenol for the synthesis of bio-oil phenol formaldehyde (BPF) resole resins. The addition of bio-oil to substitute phenol at high levels (up to 75 wt%) to produce bio-based resole resins could be used for plywood adhesives, ascribing to the low molecular weights found for phenolic bio-oil (with an relative M_w of 1072 g/mol and an M_n of 342 g/mol). The properties of the BPF resole resins were analyzed by Differential Scanning Calorimetry (DSC), Fourier Transform Infrared Spectroscopy (FTIR), Gel Permeation Chromatography (GPC) and Thermogravimetric Analysis (TGA). All experimental BPF resins possessed broad molecular weight distributions, but had similar chemical/thermal properties when compared with a conventional phenol formaldehyde (PF) resole resin (or 0 wt% BPF resin) reference. The BPFs exhibited typical properties of a thermosetting PF resin, e.g., an exothermic curing temperature of 140 °C to 150 ^{o}C, and an acceptable residual carbon yield of 48-72 wt% of non-volatile content at 700 ^{o}C. The experimental BPFs were applied as adhesives in the assembly of plywood and then the dry/wet tensile strengths evaluated. The tensile strengths of the dry plywood samples bonded with the BPF resins up to a high value of 75 wt% bio-oil ratio exceeded or were comparable to that of the conventional pure PF resin adhesive. All the BPF resin-bonded plywood samples gave comparable wet tensile strengths to those of the conventional PF adhesive.

4.2 Introduction

Phenol formaldehyde (PF) resins are the most widely used as wood adhesives in the manufacturing of engineered wood products such as plywood, laminated veneer lumber, particle boards, Oriented Strand Board (OSB) and fiberboards. Phenol formaldehyde (PF) resins are also used in different industrial products such as insulation, coated abrasives, paper saturation, and floral foam. In today's society where petroleum prices are high, petroleum resources are depleted coupled together with an increased demand for petroleum from the developing economies provides a dire situation. There are also political and environmental concerns over the fossil-based resources which have intensified interest in researching and developing alternative renewable (non-petroleum) resources to substitute phenol in the manufacture of PF-type adhesives.

Forest/agricultural biomass or residues are lignocellulosic materials containing about 10-35 wt% lignin, 35-45 wt% cellulose and 15-35 wt% hemicelluloses (Gani and Naruse, 2007; Bridgwater and Peacocke, 2000; S′anchez, 2009; USDA Forest Service Research Note, 1971). Lignin is the second most abundant polymer found in nature and a major waste product of the paper industry (50 million tons produced per year). Lignin is an amorphous macromolecule comprised of three phenyl-propanols i.e., p-hydroxyl-phenyl propanol, guaiacyl-propanol and syringyl-propanol, linked together by condensed linkages (e.g., *α*-1, *β*-5, 5-5 and *β*-1 linkages) and ether linkages (e.g., *5*-O-4, *α*-*O*-4 and *β*-*O*-4). This macromolecule can be decomposed/de-graded into the oligomeric and monomeric phenolic compounds through thermochemical technologies such as hydrolysis, pyrolysis and direct liquefaction (Kleinert et al., 2009; Wang et al., 2009; Liu and Zhang, 2008; Bridgwater, 2004; Amen-Amen et al., 2002). In this regard, lignocellulosic biomass can be a potential source of bio-phenolic compounds to replace petroleum-based phenol in the production of PF resins. In the past decade, considerable efforts have focused on replacing the petroleum-based phenol partially with lignins, tannins, and liquefied biomass such as pyrolysis oil and bio-crude from direct liquefaction processes (Zhang et al., 2006; Roy et al., 2000; Lee, 2003). Pyrolysis oils are a complex mixture of water (15-35 wt%) and organics with high oxygen-contents (45-50 wt%). This oxygen content is distributed throughout hundreds of compounds such as hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids and phenolics (Bridgwater, 2004). Pyrolysis oils are thus unstable for storage. Additionally, the phenolic compounds in pyrolysis oils are mainly fragments of lignin from large molecular weights molecules. This makes them less reactive in the PF resin synthesis reactions due to shortage of the reactive sites and the steric hindrance of large molecules. In the synthesis of a phenol-formaldehyde resin with an alkaline catalyst, phenols are deprotonated to form phenoxide ions, and the electron rich ortho- and para-positions in phenoxide ions are more susceptible to electrophilic aromatic substitution by the hydrated form of formaldehyde (often referred to as addition reaction). Therefore, pyrolysis oils were found to be less effective in substitution of phenol for the PF resin synthesis. In order to produce practically useful bio-based PF resins, the ratios were normally below 30-50 wt% of phenol (Zhang et al., 2006; Roy et al., 2000; Lee, 2003).

Biomass direct liquefaction or solvolytic liquefaction technologies have attracted increasing interest for the production of bio-phenol precursors to substitute phenol in the synthesis of bio-based phenolic resins (Russell and Riemath, 1985; Alma et al., 1997; 2001). Direct liquefaction processes are generally more advantageous than the pyrolysis processes with respect to energy efficiency and quality (e.g., molecular weights) of the liquid products. However, bio-oils from many low-temperature solvolytic processes using phenol or ethylene glycol catalyzed by H_2SO_4 are still of much lower reactivity than pure phenol in the synthesis of phenolic resins. This is due to their shortage of mono-phenolic compounds with unoccupied ortho- and para-positions (Effendi et al., 2008), and since the liquid products from the low-temperature solvolytic processes are rich in large molecules of oligomers derived from lignin and cellulosic components. In a recent study by the authors (Cheng et al., 2010), a high-temperature direct liquefaction process was investigated using co-solvents of water and ethanol. White pine sawdust was effectively liquefied in 50 wt% ethanol-water medium, producing approximately 66 wt% bio-oil and a biomass conversion > 95% at 300 °C for 15min (Cheng et al., 2010). The obtained bio-oil had M_w of 1373 g/mol and M_n of 630 g/mol, much lower than those of pyrolysis oils. As such, the bio-oil could be a promising bio-phenol precursor to substitute phenol at a higher substitution level for the production of bio-oil PF resins and adhesives.

In the present research, phenolic bio-oil produced by direct liquefaction of Eastern White Pine (*Pinus strobus L.*) sawdust in a hot-compressed ethanol-water (1:1 wt/wt) medium at 300^oC was used to partially substitute phenol to a high level (up to 75 wt%) for the synthesis of bio-oil phenol formaldehyde (BPF) resole resins. The experimental BPFs were characterized by Differential Scanning Calorimetry (DSC), Fourier Transform Infrared Spectroscopy (FTIR), Gel Permeation Chromatography (GPC) and Thermogravimetric Analysis (TGA). The obtained BPFs were applied as adhesives to the aseembly of plywood. The dry/wet tensile strengths of plywood samples bonded with the BPF resins were compared and evaluated against the conventional pure PF resins.

4.3 Materials and Methods

4.3.1 Materials

The woody biomass used in this study was Eastern White Pine sawdust obtained from a local sawmill in Thunder Bay. The woody biomass sample was subject to compositional analysis for its contents of cellulose, hemicelluloses and lignin. The tests were done in accordance to the TAPPI test method T249cm-85 (for cellulose and hemi-cellulose) and the TAPPI test method T222 om-88 method (for acid-soluble and acid-insoluble lignin). From the analysis it was found that the white pine sawdust contained 28.4 wt% lignin, 40.2 wt% cellulose and 21.9 wt% hemicellulose. The sawdust sample was oven dried at 105 ^oC for a period of 24h before use. The solvents and chemicals used in this study were distilled water, ACS reagent-grade ethanol (Fisher Scientific, Batesville, IN), acetone (Fisher Scientific, Fair Lawn, NJ) solid phenol crystal (99%, J. T. Baker, Phillipsburg, NJ), a sodium hydroxide solution (ca 50%, Ricca Chemical Co., Arlington, TX), and formaldehyde (ca 37%, Anachemia, Montreal, QC). In the GPC analysis for the liquid products, High Performance Liquid Chromatography (HPLC) grade solvent tetrahydrofuran (THF, Malinckrodt Baker, Phillipsburg, NJ) containing 0.03 wt% stabilizer of 2,6-di-t-butyl-4-methyl phenol and ACS reagent-grade pyridine and acetic anhydride (Sigma-Aldrich, St. Louis, MO) were used.

4.3.2 Preparation of phenolic bio-oil from woody biomass by direct liquefaction

The details of the liquefaction process can be found in the authors' previously published work (Cheng et al., 2010). In brief, the liquefaction of pine sawdust was carried out in a 1000 mL stainless steel autoclave reactor equipped with a stirrer and a water-cooling coil. In a typical run, the reactor was charged with 50g pine sawdust and 500g ethanol-water (1:1 w/w) co-solvent. The reactor was sealed, and the air inside the reactor was displaced by high-purity nitrogen. The reactor was subsequently pressurized to 2.0 MPa with nitrogen to prevent the reactive material from boiling during the course of heating. The reactor was heated to the desired temperature at a steady rate of 10 °C/min and soaked at the reaction temperature for 15 min before cooling down. Once the reactor was cooled to room temperature using the water-cooling coil, the gaseous products inside the reactor were vented. The liquid products and solid residue (SR) in the reactor were filtered and separated using acetone. The ethanol and acetone in the filtrate solution were then removed by rotary evaporation under vacuum at 40 °C while the remaining liquid solution was extracted with ethyl acetate using a separatory funnel. Under a reduced pressure at 57 °C ethyl acetate was removed to recover the liquid oily products, denoted as bio-oil. Bio-oil was used as the bio-phenol precursors to substitute phenol for the synthesis of BPF resole resins. The obtained bio-oil had relative M_w of 1072 g/mol and M_n of 342 g/mol, determined by GPC analysis.

4.3.3 Synthesis of BPF resole resins using woody biomass derived bio-oil

Various bio-oil-phenol-formaldehyde (BPF) resole resins with different bio-oil ratios (25, 50, 75 wt%) were synthesized in a 100 mL three-neck flask equipped with a pressure equalizing addition funnel, thermometer, cooling condenser and a water bath with a magnetic stirrer. These bio-based resole resins were denoted as 25% BPF, 50% BPF, and 75% BPF. A control reference sample using pure phenol, 0 wt% bio-oil, denoted as PF resin, was also prepared. In a typical run, 10g of bio-oil/phenol, 4g of water, 2g of 50 wt% sodium hydroxide solution (10 wt% of phenolic feed) and 10mL of ethanol were charged into the flask. The mixture was heated to 80 ˚C and maintained at this temperature for 2hr under stirring to maintain a homogeneous solution. Following this, 11.2 g formaldehyde (ca 37 wt%) was added dropwise to the flask through a pressure equalizing addition funnel. If the bio-oil was identified as containing phenols, the added formaldehyde was added correspondingly to the molar ratio of formaldehyde to phenols 1.3. After condensation for 2hr, the reaction was stopped by rapidly cooling in a water bath until room temperature was reached.

4.3.4 Characterization of the BPF and PF resole resins

The viscosity of all phenolic resins was measured at 50^{o}C by Brookfield CAP 2000+ viscometer (Brookfield Engineering Laboratories, Middleboro, MA), according to the standard of ASTM D1084-97. The non-volatile contents of resole resins were determined at 125 ^{o}C for 105min in accordance with ASTM standard D4426-01(2006). The free formaldehyde levels in the resins were determined using a modified Walker's hydroxylamine hydrochloride method (Walker, 1975). Approximately 2g of resin were diluted with 25mL of water, and pH was adjusted to 4.0 using 0.1 M HCl. Thirty milliliters of hydroxylamine hydrochloride (0.5 M, pH = 4.0) was added to the resin solution, and the mixture was stirred for 10 min. Free formaldehyde was determined by back titration to pH 4.0 using 0.1 M aqueous sodium hydroxide. The remained free phenol in the resins was detected by HPLC (1525 binary HPLC pump; Bio-RAD HPX-87H column at 65 ^{o}C) using 0.01M H_2SO_4 water solution as the eluent at a flow rate of 0.8 mL/min. The thermal curing properties of the resins were evaluated with a differential scanning calorimetry (DSC 1, Mettler-Toledo, Schwerzenbach, Switzerland) under (50-60) ml/min N_2 at four different heating rates (5, 10, 15 and 20 ^{o}C/min) between 40 °C and 250 ^{o}C in a sealed aluminum crucible. The thermal stability of the resins was determined on the TGA Instruments (TGA 1000i, Instrument Specialists Inc, Twin lakes, WI) from 25 °C to 700 ^{o}C. The non-volatile resin sample (~10 mg) was heated on a platinum pan at a heating rate of 10 ^{o}C/min under 30mL/min N_2.

The infrared spectroscopy of the resins was recorded on IR2000 spectrometer (PerkinElmer, Waltham, MA) in the range of 500-4000 cm^{-1} with a resolution of 4cm^{-1}.

GPC analysis was performed using Waters Breeze GPC (Waters, Milford, MA, 1525 binary HPLC pump; UV detector at 270 nm; Waters Styragel HR1 column at 40^{o}C) using THF as the eluent at a flow rate of 1 mL/min, and polystyrene was used as the calibration standard. In order to improve the resin's solubility in THF solvent, all the resin samples were subjected to acetylation by dissolving 0.5g resin into 10 mL of a mixture (1:1, v/v) of pyridine and acetic acid followed by magnetic stirring at room temperature for 24hr. Acetylated products were obtained by precipitation in ice-cooled 1.0 wt% HCl solution and then filtered, rinsed thoroughly with distilled water and vacuum dried at room temperature.

4.4.5 Evaluation of tensile strength of plywood samples bonded with BPF resins

All the synthesized phenolic resole resins were further tested as adhesives for manufacture of three-layer plywood. 11×11×1/16 inch yellow birch veneers were conditioned at 20^{o}C and 60% relative humidity (RH) to reach 10~12% moisture content (MC). The resin mixed with wheat flour (15wt% of the resin) was applied with a brush to the inside surface of the two face veneers at a spread rate of 250 g/m^2 per single glueline. Following this, the two face surface veneers were kept at room temperature for about 1h to remove any moisture content in the adhesives before hot pressing. The face and center veneer were bonded perpendicular to each other using a hot press at 140 ^{o}C under 2500 psi pressure for 4 min. To obtain better statistic significance in regards to the measurements, two panels were manufactured for each sample. In accordance with ASTM D906-98 (2004), twenty specimens were cut from each panel for tensile strength testing in such a way as to ensure that for half the specimens, lathe checks were pulled in the open direction; for the other half, lathe checks were pulled in the closed direction. Half the specimens of each sample including 10 in open direction and 10 in closed direction were tested after conditioning (to get 10~12% MC). In addition, 20 specimens were boiled for 3hr before testing to investigate wet tensile strength and water resistance for all the resins. The specimens were tested for shear stress by tension loading until failure with a Benchtop Universal Testing Machine (Model H10K-T UTM, Tinus Olsen Material Testing Machine Co. Horsham, PA) at a loading rate of 10 mm/min. The percentage of wood failure in the bonding area for each specimen was assessed visually.

4.4 Results and Discussion

4.4.1 Resin characterization

The pH value, non-volatile contents, viscosity, free formaldehyde levels and free phenol remaining of all the resins were measured and are presented in Table 4-1. The pH values of all the resins range from 9.5 to 10.5. The non-volatile contents of all the bio-based resins are very close and are slightly higher than pure PF resin. The lower non-volatile content of pure PF resins might be caused by the low molar ratio of F/P of 1.3 employed during the synthesis, which resulted in excessive phenol (6.2 wt% as shown in Table 4-1) that was not consumed with formaldehyde in the reaction. The un-reacted phenol evaporated during the heating period, led to a lower non-volatile content for the pure PF resin. As expected, the free phenol remaining of BPF resole resins would be very low, such as 50% BPF (< 0.1 wt%). The reason could be that phenol has the priority to react with formaldehyde compared to bio-oil. In this regard, the free phenol in 25% BPF and 75% BPF would also be very low. Thereby, they were not detected considering the time consuming. The viscosities of BPFs increase with increasing bio-oil ratio, most likely due to the much larger molecular weights and the complex molecular structures of the bio-phenolic compounds in the bio-oil than those of phenol (Cheng et al., 2010). The free formaldehyde content was not detected for the pure PF resin, while it was detected in all the BPF resins, and the content increases with increasing bio-oil ratio, suggesting the lower reactivity of bio-oil over phenol.

Table 4-1. Physical properties of the BPF and PF resole resins.

Type of resole resins	pH values	Non-volatile contents[a] /wt%	Free phenol /wt%	Viscosity [b] /cp	Free formaldehyde[c] / wt%
Pure PF	10.5	35.4 (±1.2)	6.2	18.4 (±0.03)	ND [d]

25% BPF	9.6	37.7 (±0.2)	-	19.5 (±0.01)	0.19 (±0.003)
50% BPF	10.0	38.3 (±0.3)	< 0.1	21.0 (±0.01)	0.51 (±0.01)
75% BPF	9.5	38.1 (±0.2)	-	29.5 (±0.01)	0.67 (±0.01)

[a, b] Each value represents an average of 3 samples; [c]Each value represents an average of 2 samples. [d] ND: not detected.

DSC thermograms were obtained under dynamic conditions at different heat rates (5, 10, 15 and 20 ℃/min) to study the kinetics of the curing reactions. DSC profiles of various BPF and the PF resole resins at 10 ℃/min are displayed in Figure 4-1. The DSC thermograms of all BPF resins exhibited an exothermic peak between 145 °C and 155 ℃, depending on the amount of bio-oil present in the formula. The main exothermic peak could generally be attributed to the condensation of phenol or bio-oil with methylol groups (-CH_2OH) to form a methylene bridge and the condensation of two methylol groups to form dibenzyl ether bridges (Christiansen and Gollob, 2003; Gabilondo et al., 2007; Wang et al., 2009). The DSC profiles of BPFs also displayed as shoulder peaks between 130 °C and 140 ℃, which might be caused by the addition of free formaldehyde (as was detected and shown in Table 4-1) to form phenolic rings (Christiansen and Gollob, 2003; Wang et al., 2009; Alonso et al., 2004). As is displayed in Figure 4-1, the pure PF resin exhibited two distinct peaks at 140 ℃ and 150 ℃. The first peak could be attributed to the condensation to form methylene and dibenzyl ether bridges and the second peak at the higher temperature might be related to the subsequent reactions, e.g. breakage of dimethylene ether linkages and re-condensation through the methylene bridges (Gabilondo et al., 2007; Wang et al., 2009; Vázquez et al., 2002). The DSC results of the main exothermic peak of BPF and PF resole resins at a heating rate of 10^{o}C/min is summarized and displayed in Table 4-2. Interestingly from Table 4-2, at a low bio-oil ratio ≤ 50 wt%, the curing temperatures were lower than the pure PF resin. This result suggests that the presence of bio-oil could promote the curing reactions of the BPFs, which is consistent with the results reported previously (Wang et al., 2009; Vázquez et al., 2002; Khan et al., 2004) where the addition of a small amount of bio-phenol materials in PF resin (e.g. tannin and lignin) reduced the curing temperature. The resins containing bio-oil more than 50 wt% (i.e., the 75 wt% BPF), however, displayed a higher curing temperature than the pure PF resin as similarly observed by the authors' group previously (Wang et al., 2009). These results suggest that the presence of bio-oil in a BPF resin could play two adverse roles in the process of curing depending on the amount of bio-oil in the BPF resins. For a BPF resin with a low bio-oil ratio, a small amount of bio-oil would favor the thermal cure reaction, governed by phenol. For a BPF resin with a high bio-oil ratio, the bio-oil becomes the majority component in the resin, and the thermal cure reactions are retarded by the low reactivity of bio-oil.

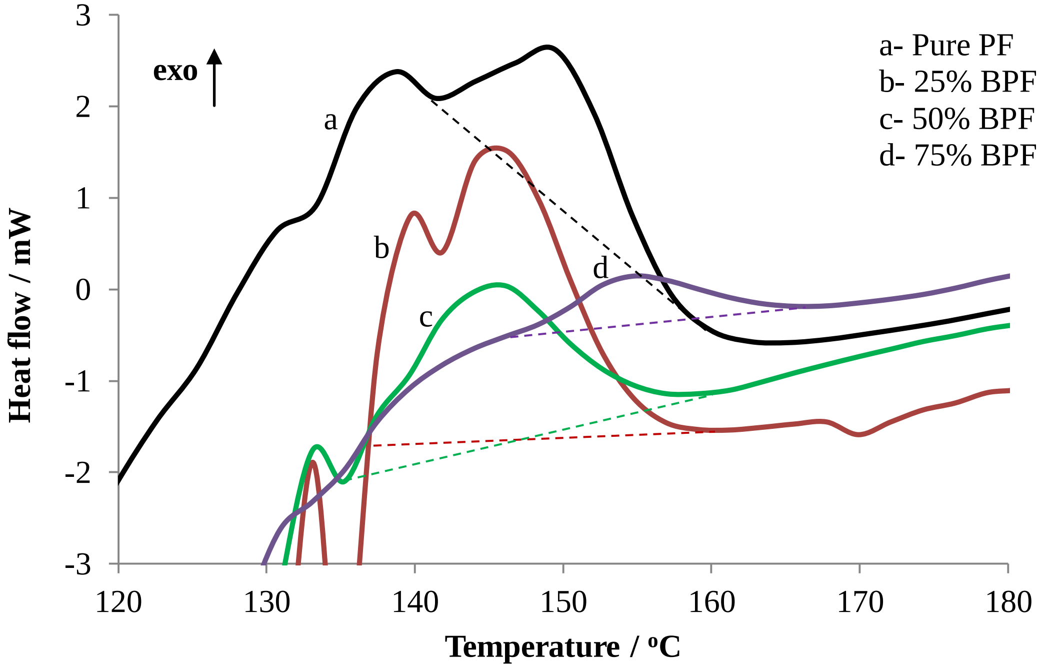


Figure 4-1. DSC profiles of various BPF and the PF resole resins at 10 ℃/min.

Table 4-2. DSC results of the main exothermic peak of BPF and PF resole resins at a heating rate of 10 ^{o}C/min.

Type of resole resins	PF resin	25% BPF	50% BPF	75% BPF
Onset Temp. (^{o}C)	142.3	136.6	135.2	148.3
Peak Temp. (^{o}C)	149.5	145.4	145.5	154.8
End Temp. (^{o}C)	162.6	156.9	156.9	165.7

The non-isothermal DSC scanning methods have been widely used for investigating the curing kinetics of thermosetting phenolic resins (Gabilondo et al., 2007; Wang et al., 2009; Want et al., 2005; Park et al., 1999). Since the results from a single heating rate may be inconsistent (Vázquez et al., 2002; Park et al., 1999), the multiple-heating rate method was employed with four different heating rates varying from 5 °C/min to 20 °C/min. Assuming that the cure reaction pathway does not change with the heating rate, the curing kinetic parameters of the curing reaction of a resin can be calculated by the Kissinger equation and Crane equation (Kissinger, 1957; Crane et al., 1973).

Kissinger Equation: $$\frac{d\ln(\beta/T_p^{2})}{d\ln(1/T_p)} = -\frac{E}{R} \quad (1)$$

Crane Equation: $$\frac{d\ln(\beta)}{d(1/T_p)} = -\frac{E}{nR} \quad (2)$$

Where β is the heating rate (^{o}C/min), T_p is the maximum exothermic temperature in the DSC profile (K), E is the activation energy (kJ/mol), and R is the gas constant (= 8.314 J/mol/K). The activation energy E and reaction order n can be calculated from the slope of the regression line of plots of $\ln(\beta/T_p^{2})$ and $\ln(\beta)$ vs. $1/T_p$, respectively. The working plots are displayed in Figure 4-2, and the calculated results listed in Table 4-3. The curing reaction for all the resole resins is approximately 1st order (n = 0.94~0.95), as was observed previously (Wang et al., 2009). The value of E is the lowest for 25% BPF, but increases with increasing the bio-oil ratio in the BPF resins. As indicated in Table 4-3, the activation energies of all BPFs are lower than that of the pure PF resin, which might be explained by two reasons. Firstly, bio-oil contains lignin-derived oligomers that can readily crosslink and cure. Secondly, the addition of a small amount of bio-oil in PF resins could promote the curing reaction more as the bio-oil could act as a highly efficient crosslinking reagent (with multiple un-occupied reactive sites on the bio-oil molecules) (Wang et al., 2009; Tymchyshyn and Xu, 2009). However, at a high bio-oil ratio in the BPFs (> 50 wt%) the curing activation energy would increase due to the lower reactivity of bio-oil than of phenol.

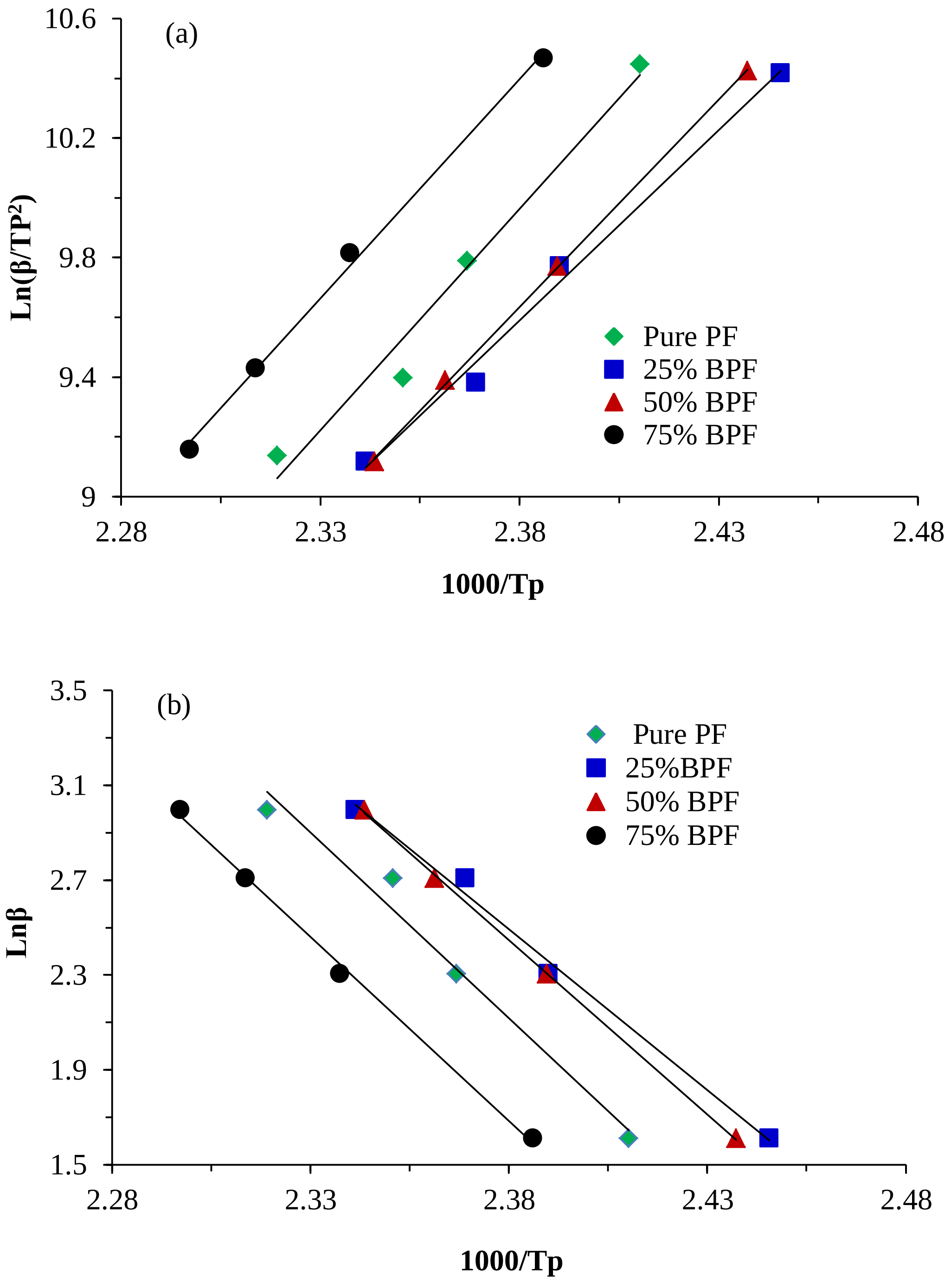


Figure 4-2. Plots of DSC kinetics analysis by the Kissinger equation (a) and the Crane equation (b).

Table 4-3. Thermal curing kinetics parameters calculated from Figure 2 for the BPF and PF resins.

Type of resole resins	DSC results		Curing characteristic peak temp.at 0 °C/min [a] (°C)	E^b (kJ/mol)	Reaction order n^c (-)
	Heating flow (°C/min)	Peak temp. T_p(°C)			
Pure PF	5	141.9	138.1	123.2	0.95
	10	149.5			
	15	152.4			
	20	158.2			
25% BPF	5	135.9	131.6	105.9	0.94
	10	145.4			
	15	149.1			
	20	154.1			
50% BPF	5	137.3	133.2	115.3	0.94
	10	145.5			
	15	150.5			
	20	153.7			
75% BPF	5	146.1	142.4	122.0	0.95
	10	154.8			
	15	159.2			
	20	162.3			

[a] By linear extrapolation; [b] Based on the Kissinger equation; [c] Based on the Crane equation.

The thermal stability of the non-volatile contents of the BPF and PF resole resins were also evaluated by TGA technique. Figure 4-3 contains the TG-DTG results of the resole resins between 25 °C and 700 ℃. The decomposition temperatures and mass loss values of the thermal events, and mass residue at 700 ℃ are listed in Table 4-4. As shown in Figure 4-3, all BPFs and the PF resin present similar thermal decomposition patterns, showing three major thermal events. It is known that the degradation of phenolic resins has three steps: post-curing, thermal reforming and ring stripping (Khan and Ashraf, 2007). The first event of the pure PF resin was observed in the range of 70 °C to 300 ℃ (6% mass loss), which could be ascribed to the post-curing reactions of the resin (the removal of terminal groups and further crosslinking or condensation reactions); the second event was obtained from 365 °C to 500 ℃ (5% mass loss), which could be attributed to the thermal reforming to break the bridged methylene linkage; and the last event was detected in the range of 500 °C to 650 ℃ (the main mass loss region, 11% mass loss) due to the breakdown of the ring network. When the ratio of bio-oil substitution in phenolic resole resins was lower than 50 wt%, the three decomposition ranges were 150 °C to 300 ℃ (around 5% mass loss), 300°C to 450 ℃ (9% mass loss), and 450 °C to 650 ℃ (the main mass loss region, 13% mass loss for the 25% BPF, and 23% mass loss for the 50% BPF). The ranges of the thermal events of 75% BPF, however, were transferred to higher temperatures, i.e., 150 °C to 300 ℃ (7% mass loss), 300 °C to 600 ℃ (the main loss region, 37% mass loss) and 600 °C to 700 ℃ (8% mass loss). As discussed previously in the DSC analysis, substituting phenol with bio-oil at a ratio larger than 50 wt% would lead to a BPF resin whose properties are governed by the less reactive bio-oil. Thereby, the large mass loss (37%) for the 75% BPF 300 °C to 600 ℃ could be explained by the degradation of side chains presented in the bio-oil molecules, and the breakdown of the methylene linkage, as was similarly observed by Wang et. al (2009). From the TG profiles, all the bio-oil derived resole resins possessed slightly superior thermal stability in terms of the residual carbon content below 240 ℃, but became significantly inferior above this temperature, especially for the BPFs with a high bio-oil ratio. As shown in Table 4-4, the residual carbon contents at 700 ℃ were 76, 72, 61 and 48% for the pure PF, 25% BPF, 50% BPF and 75% for the BPF resin, respectively. The decrease in the carbon residue for a BPF resin at an increased bio-oil ratio was likely caused by the loss of numerous side chains from the bio-oil molecules. In summary, the BPF resins with up to 50 wt% bio-oil displayed comparable thermal resistance to the pure PF resole resin.

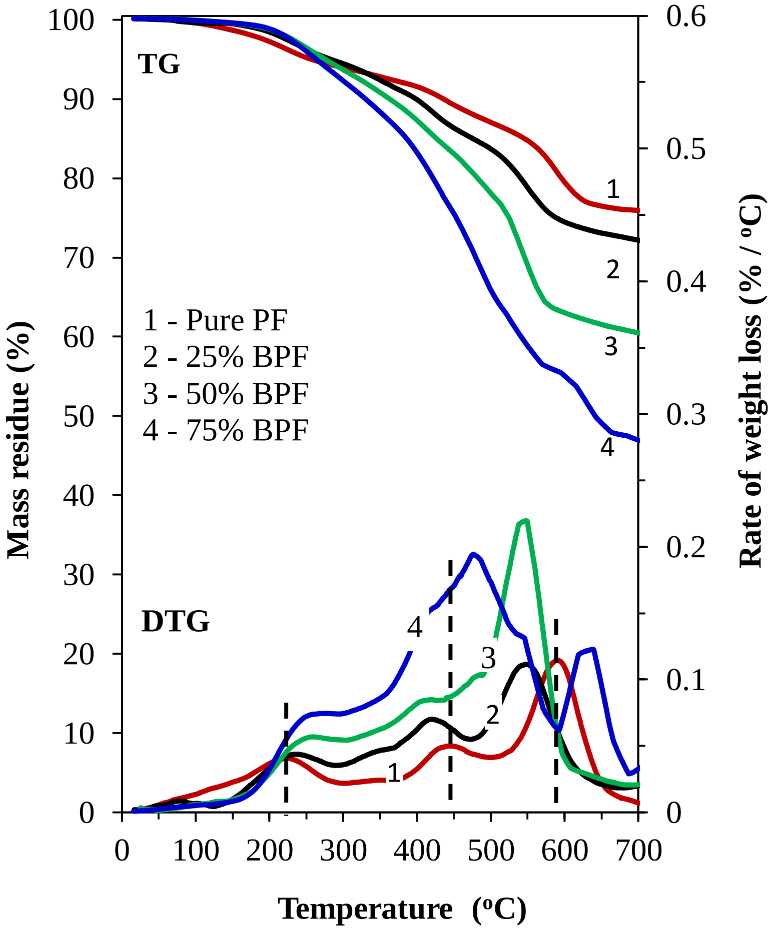


Figure 4-3. TG and DTG profiles of the BPF and PF resole resins.

Table 4-4. TG and DTG results of the BPF and PF resole resins.

Type of resole resins	DTG results			TG results
	First thermal Event $T_o/T_p/T_e$/ °C [a]	Second thermal event $T_o/T_p/T_e$/ °C	Third thermal event $T_o/T_p/T_e$/ °C	Mass residue at 700 °C[b] /%
Pure PF	70/223/300(6%)	365/445/500(5%)	500/589/650(11%)	76 (±0.1)
25% BPF	150/236/300(5%)	300/418/460(9%)	460/548/650(13%)	72 (±0.05)
50% BPF	150/240/300(6%)	300/393/430(9%)	430/535/650(23%)	61 (±0.2)
75% BPF	150/240/300(7%)	300/466/600(37%)	600/616/680 (8%)	48 (±0.9)

[a] T_o: Onset temperature; T_p: Peak temperature; T_e: Endset temperature; [b] An average of 2 samples.

Figure 4-4 shows the infrared spectra of the BPF resins compared with that of the reference pure PF resin. All BPFs displayed similar IR absorption profiles to that of the pure PF resole, indicating that the BPFs have similar chemical structure to the PF resole resins. All resins have typical hydroxyl group absorption between 3400 cm^{-1} and 3387 cm^{-1}, C-H stretching between 2980 cm^{-1} and 2875 cm^{-1}, and C–O stretching between 1000 cm^{-1} and 1030 cm^{-1}. However, some difference can also be observed among these spectra. For example, the signal between 1668 cm^{-1} and 1715 cm^{-1} (attributed to the C=O stretching from ketone, aldehyde, and ester groups) became stronger for a BPF resin with a higher bio-oil content. This could be accounted for by the high contents of ketone, aldehyde and ester groups in bio-oil as was reported in previous research (Cheng et al., 2010). As expected, the characteristic peaks of phenolic/aromatic structure compounds (Cheng et al., 2010, Serrano et al., 1996) at 1605cm^{-1}, 1500cm^{-1}, 1450cm^{-1}, 1248cm^{-1}, 835cm^{-1}, 758cm^{-1}, and 694cm^{-1} diminished with increasing the bio-oil content in the BPFs.

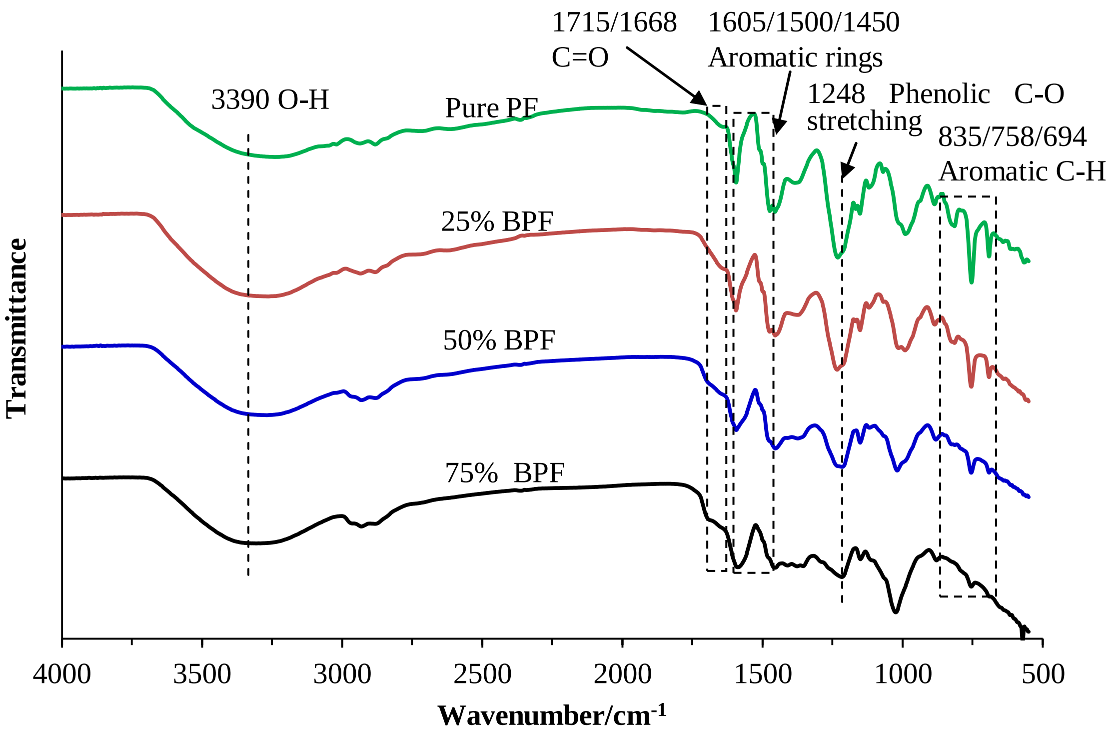
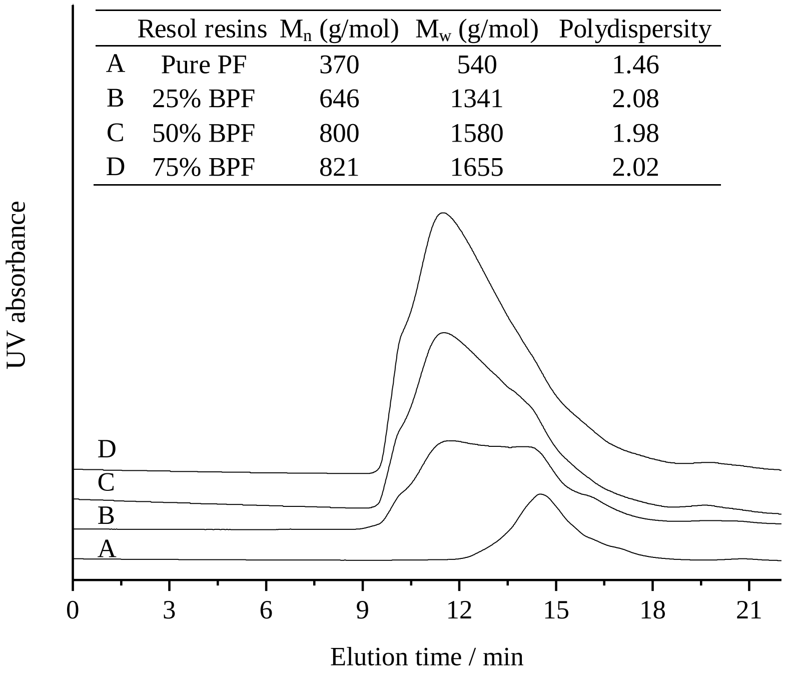


Figure 4-4. Infrared spectra of various types of BPFs and PF resole resins.

The molecular weight distribution of all resole resins can be obtained by the GPC chromatograms illustrated in Figure 4-5. The GPC profiles of all BPFs displayed a broader molecular weight distribution than that of the reference PF resin, leading to a higher M_w and M_n. The values of M_w and M_n increased gradually with increasing the bio-oil ratio in the BPFs, which could be explained by the large molecular weight of bio-oil and its broad molecular weight distribution (M_w: 1072 g/mol, M_n: 342 g/mol, Polydispersity: 3.13).



	Resol resins	M_n (g/mol)	M_w (g/mol)	Polydispersity
A	Pure PF	370	540	1.46
B	25% BPF	646	1341	2.08
C	50% BPF	800	1580	1.98
D	75% BPF	821	1655	2.02

Figure 4-5. GPC chromatograms of the acetylated BPF and PF resole resins (using THF as the eluent at 1 mL/min, UV detector at 270 nm, polystyrene standards).

4.4.2 Evaluation of adhesive bonds

Tensile strength (under both dry and wet conditions) of plywood specimens prepared with various BPF and PF resole resins as adhesives were evaluated and illustrated in Figure 4-6. Under dry conditions, the BPFs of a bio-oil ratio up to 50 wt% performed better than the reference PF resin. For the 75% BPF, the dry tensile strength was lower than that of the 50% BPF, but it was still comparable to the reference PF resin. All BPFs surpassed the minimum requirement of the tension shear strength specified in the JIS

K-6852 standard (i.e., 1.2 MPa) for resole-type adhesives. These results are superior to the results of previous studies where phenol was substituted with starch/tannin or Kraft lignin at a ratio less than 50wt% (Moubarik et al., 2009; Danielson and Simonson, 1998). The addition of bio-oil to substitute phenol at a high level (up to 75 wt%) could still produce bio-based resole resins useful as plywood adhesives, likely due to the low molecular weights of the obtained phenolic bio-oil (with M_w of 1072 g/mol and M_n of 342 g/mol). Under the wet conditions after boiling for 3hr, as expected, all specimens bonded with PF and BPFs gave a decreased tensile strength. Surprisingly, however, there was no significant difference among these resins, and all values exceeded the minimum value (1.0 MPa) of wet strength and even the minimum value of dry strength required in accordance to the same JIS standard mentioned above. Table 4-5 presents the wood failure of both dry and wet plywood specimens bonded with PF and various BPFs after the tensile strength testing. The wood failure of the dry specimens displayed a similar trend as was observed for the dry tensile strength, i.e., the specimen with a BPF resole at a bio-oil ratio up to 50 wt% produced a higher or similar wood failure to that of the pure PF resin-bonded specimen. All samples meet the wood failure requirement (85%) for exterior-grade plywood. However, the wood failure decreased as the bio-oil ratio further increased from 50 wt% to 75 wt% substitution. For example, the wood failure dropped from 87% (for the 50% BPF) to 22% (for the 75% BPF).

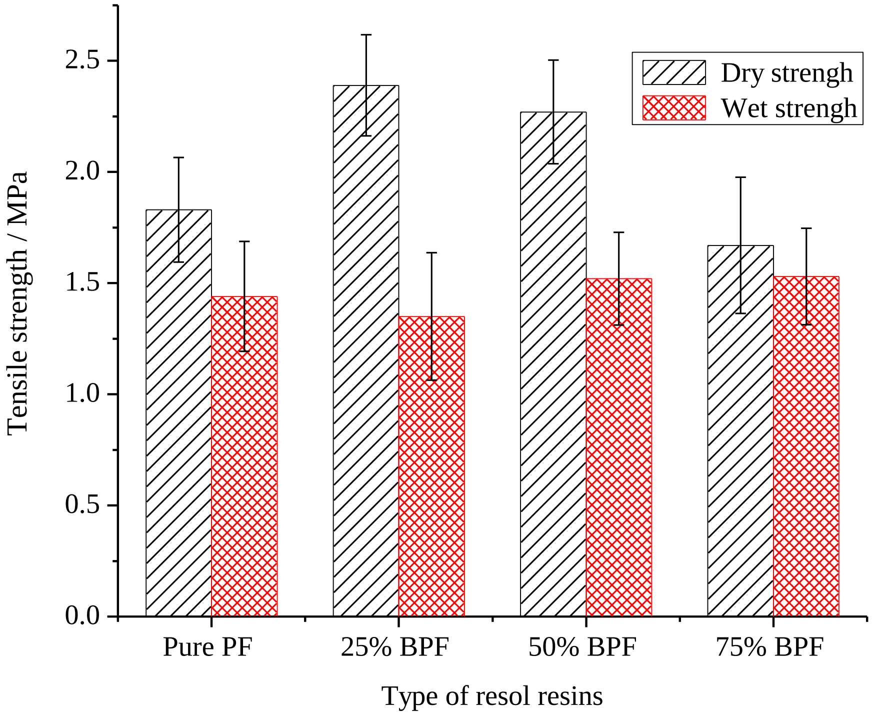


Figure 4-6. Tensile strength of the plywood samples bonded with the BPF and PF resole resins (Dry strength: test after conditioning; Wet strength: test after boiling in water for 3h).

Table 4-5. Wood failure of the plywood samples bonded with the BPF and PF resole resins.

Test conditions	Pure PF	25% BPF	50% BPF	75% BPF
	Wood failure[a] (%) (Standard deviation)			
Dry[b]	89 (±19)	97 (±13)	87 (±36)	22 (±33)
Wet[c]	65 (±43)	33 (±42)	35 (±41)	15 (±31)

[a]An average of 20 specimens; [b]Test after conditioning; [c] Test after boiling in water for 3hr.

4.5 Conclusions

(1) Phenolic bio-oil with a low molecular weight (M_w = 1072 g/mol and M_n = 342 g/mol) from direct liquefaction of Eastern white pine (*Pinus strobus L.*) sawdust in a hot-compressed ethanol-water (1:1 wt/wt) medium at 300 ^{o}C was successfully used to

partially substitute phenol at a high substitution level (up to 75 wt%) in the synthesis of bio-oil phenol formaldehyde resole resins (BPFs).

(2) All the BPFs displayed similar physical/chemical properties (non-volatile content, pH value, IR adsorption, etc.) to the reference pure phenol formaldehyde (PF) resole resin, while the viscosities, free formaldehyde levels and molecular weights of BPFs were all greater than those of the pure PF resin, as was expected.

(3) All BPFs were curable at a temperature of 130 ^{o}C to 160 ^{o}C. The resins containing bio-oil more than 50 wt% (i.e., the 75 wt% BPF), displayed a higher curing temperature than the pure PF resin. At a low bio-oil ratio ≤ 50 wt%, however, the curing temperatures were lower than the pure PF resin, suggesting that the presence of bio-oil could promote the curing reactions of the BPFs. The curing reaction for all the resole resins proved to be approximately 1st order, and the activation energies of all BPFs are lower than that of the pure PF resin.

(4) The residual carbon contents at 700 ℃ for the BPFs (25 ~ 75 wt% bio-oil ratios) are in the range of 72~48 %.

(5) The addition of bio-oil to substitute for phenol at a high level (up to 75 wt%) produced useful bio-based resole resins useful as plywood adhesives and had comparable or better dry/wet bond strengths than the reference pure PF resin.

4.6 Acknowledgements

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CHAPTER 5. SYNTHESIS OF BIO-BASED PHENOLIC RESINS/ADHESIVES USING METHYLOLATED WOOD-DERIVED BIO-OIL

5.1 Abstract

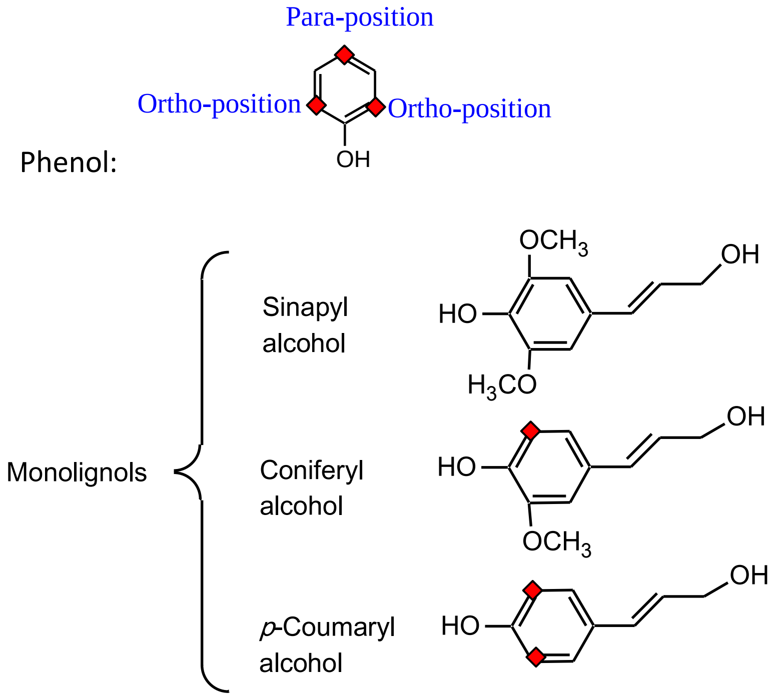
Bio-oil from hydrothermal liquefaction of Eastern white pine (*Pinus strobus L.*) sawdust was methylolated using formaldehyde in the presence of sodium hydroxide. The obtained methylolated bio-oil (MB) was used to synthesize methylolated bio-oil-phenol-formaldehyde (MBPF) resole resins with a phenol substitution ratio up to 75 wt%. All the resins were used as a wood adhesive for the production of three-layer plywood. The MBPF resole resins were comprehensively characterized for their physical, chemical, thermal and mechanical properties, e.g., viscosities, non-volatile contents, shelf life, free formaldehyde levels, molecular weight and distribution, curing temperatures, and bond strength when used as plywood adhesives. All MBPF resins contain similar non-volatile contents as a reference pure phenol formaldehyde (PF) resin, but have a higher viscosity and shorter shelf life, depending on the amount of MB in the MBPF. All MBPF resins displayed a lower curing temperature than the reference PF resin, with a main curing peak around 140 ^{o}C, similar to that of the pure PF resin. According to Thermogravimetric Analysis (TGA) analysis, methylolation treatment of bio-oil improved the thermal stability of the MBPF resins when compared to bio-oil-phenol-formaldehyde (BPF) resole resins using untreated bio-oil. Dry/wet bond strengths of plywood specimens glued with MBPF resole resins with up to 60 wt% phenol substitution exceeded or were comparable to those of the conventional PF resole resin.

5.2 Introduction

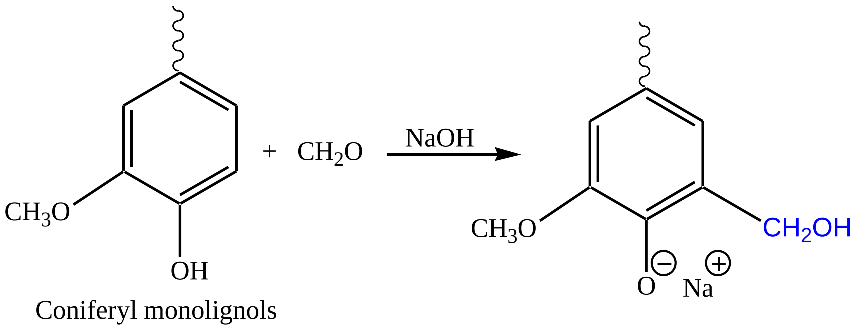
Lignin and bio-oil derived from lignocellulosic biomass have been employed as a potential source of bio-phenolic compounds to replace phenol in the production of phenol formaldehyde (PF) resins. However, substituting phenol with lignin or bio-oil at a high substitution ratio (e.g., >50%) without affecting the final product quality is very challenging (Alma and Basturk, 2006; Wang et al., 2009(a), Amen-Amen et al., 2002(a); 2002(b); Cheng et al., 2011) due to the much lower reactivity of these bio-feedstocks in reacting with formaldehyde. As shown in Scheme 5-1, the monolignols are less reactive than phenol due to the presence of steric hindrance of large molecules and less reactive sites for reacting with formaldehyde (Alonso et al., 2004; Clarke and Dolenko, 1978; Lee et al., 2000).

To improve the reactivity of lignin in the production of lignin phenol formaldehyde resins, many researchers have attempted to modify lignin by methylolation (Clarke and Dolenko, 1978; Lawson and Kleln, 1985), phenolation (Cetin andOzmen, 2002(a); 2002(b)), and demethylation (Olivares et al., 1988; Narayamusti and George, 1954; Hayashi et al., 1967; Shashi et al., 1982). For example, Cetin and Ozmen (2002(a); 2002(b)) demonstrated that the level of phenolated-lignin for phenol in phenolated-lignin phenol formaldehyde resole resins had to be controlled at < 30 wt% to achieve comparable strength as traditional phenol formaldehyde resole resin. Methylolation treatment of lignin proved to be effective for increasing the lignin substitution level while maintaining the strength of the resins. This was due to the introduction of methylol groups at a C_5 position of guaiacyl units (via the Lederer Manasse's Reaction), and that the methylol groups can condense with phenols (including bio-phenol) molecules or the pre-polymer of PF resin can be introduced. Olivares et al. (1988) reported that methylolated-lignin PF resin with a phenol substitution level of 40 wt% demonstrated a higher bond strength than the traditional PF resins as well as the lignin PF resins with 40 wt% unmodified lignin and demethylolated-lignin.

As an exciting achievement, the authors' group demonstrated that a low molecular weight bio-crude produced from hydrothermal liquefaction of sawdust could replace phenol to 75 wt% in the synthesis of bio-oil phenol formaldehyde (BPF) resole resins (Cheng et al., 2011). The obtained BPF resole resins were found to be comparable to the conventional pure PF resin with respect to the physical, chemical, and mechanical (bond strength) properties, while the BPF resole resins have a slightly deteriorated thermal property (carbon residue at elevated temperatures) (Cheng et al., 2011). Moreover, the BPF resole resins at a high substitution ratio (>50 wt%) did exhibit slightly inferior properties in terms of wet strength and wood failure in plywood bonding (Cheng et al., 2011). As described above, methylolation treatment of lignin proved to be effective for increasing the lignin substitution level while maintaining the strength of the resins. Accordingly, the reactivity of bio-oil would also be improved through methylolation to introduce methylol groups. So far, no research on methylolation treatment of bio-oil has been reported in this regard. As shown in Scheme 5-1, the main monolignol component of pine (softwood) lignin is coniferyl alcohol with one reactive site where one methylol group can be introduced as illustrated in Scheme 5-2.



Scheme 5-1. Reactive sites in phenol and three monolignols for PF resin synthesis reactions.



Scheme 5-2. Methylolation reaction mechanism of bio-oil with formaldehyde.

In this study, in order to obtain high-quality bio-oil PF resole resins with a high phenol substitution level, the pine wood-derived bio-oil was first treated with formaldehyde to introduce methylol groups, and then co-polymerized with phenol and formaldehyde in the presence of sodium hydroxide as the catalyst to prepare methylolated bio-oil-phenol-formaldehdye (MBPF) resole resins. The degree of methylolation reaction of bio-oil with formaldehyde was analyzed with proton nuclear magnetic resonance spectrometry (^{1}H NMR). The methylolated bio-oil (MB) was also analyzed with gel permeation chromatography (GPC), and the amount of un-reacted formaldehyde in MB was also determined. Physicochemical properties of the experimental MBPF resins were characterized with respect to their viscosities, non-volatile content, shelf life, free formaldehyde level, molecular weight and distribution, curing temperature, and thermal stability. The MBPF resole resins were also employed as plywood adhesives whose dry and wet tensile strengths were evaluated.

5.3. Materials and Methods

5.3.1 Materials

The bio-oil used in this study as a phenol substitute was derived from Eastern white pine sawdust by hydrothermal liquefaction at 300 ℃ in 50%/50% (v/v) ethanol-water medium. The main compositions of the pine sawdust are cellulose (40.2 wt%), hemicelluloses (21.9 wt%) and lignin (28.4 wt%) determined in accordance to TAPPI test method

T249cm-85 (for cellulose and hemi-cellulose) and the TAPPI test method T222 om-88 method (for acid-soluble and acid-insoluble lignin). The detailed procedure for the production of hydrothermal bio-oil can be found in the authors' previous work (Cheng et al., 2010). Other raw materials used in the synthesis of bio-oil-based phenol-formaldehyde resole resins include ACS reagent grade chemicals, i.e., ethanol (Fisher Scientific), acetone (Fisher Scientific), solid phenol crystal (99%, J.T. Baker), sodium hydroxide solution (ca 50%, Ricca Chemical Company), and formaldehyde (ca 37%, Anachemia).

For GPC analysis, High-Performance Liquid Chromatography (HPLC) grade solvent tetrahydrofuran (THF) containing 0.03 wt% stabilizer of 2, 6-di-*t*-butyl-4-methyl-phenol, and ACS reagent grade pyridine and acetic anhydride (Sigma-Aldrich) were used. In the ^{1}H NMR analysis for the methylolated bio-oil, ACS reagent grade chloroform-*d* (99.8 atom % D) containing 0.1% tetramethylsilane (TMS) was used as the solvent.

5.3.2 Preparation of methylolated bio-oil

The methylol groups were introduced to the bio-oil according to the reaction mechanism shown in Scheme 5-2, whose procedure is described briefly as follows. In a typical run, the bio-oil was first mixed in a three-neck flask with formaldehyde (F) at an F/bio-oil weight ratio of 0.37 and sodium hydroxide at a NaOH/bio-oil weight ratio of 0.1, and ethanol at an ethanol/bio-oil weight of 1.0 (Vázquez et al., 1997). Distilled water was also added to obtain the solids content of the reaction mixture of 29.4 wt%. All the materials were then reacted in the three-neck flask in a water bath at 50 ℃ under continuous stirring for 1hr to get a homogenous solution. Then, the temperature of the water bath was raised to 80 °C, and the reaction was continued for another 2hr before cooling the reactor down to room temperature.

5.3.3 Preparation of MBPF resole resins

Various MBPF resole resins with different phenol substitution ratios were synthesized in a 250 mL three-neck flask equipped with a pressure equalizing addition funnel, thermometer, water-cooled condenser and a water bath with a magnetic stirrer. The MBPF resole resin pH value was controlled at around 10 with a NaOH solution. In a typical run taking the synthesis of 50% MBPF resole resin as an example, 10.0 g phenol were added to 10.0 g methylolated bio-oil with 2.0 g of 50 wt% aqueous solution of sodium hydroxide (10 wt% of the phenolic feed). The mixture was mixed at 80 ^{o}C for 2hr under magnetic stirring to ensure a homogenous solution. Then 11.2g of aqueous solution of formaldehyde (F) [*ca* 37 wt%, F/P=1.3 (molar ratio)] was added dropwise into the flask through a cylindrical separatory funnel. After the addition of formaldehyde, the flask was held at 80 ^{o}C for 3hr of resinification reaction. The mixture was then cooled down to 40 ^{o}C to 50 ^{o}C. Some of the resin product was sampled for viscosity measurement using a Brookfield viscometer. The resin was collected in a sealed plastic bottle and stored at 4 ^{o}C. By varying the amount of MB in the reaction mixture, a series of MBPF resins with phenol substitution ranging from 0-75 wt% (i.e., 0, 25, 50, 60, 75 wt%) were prepared. The as synthesized MBPF resole resins were designated as PF, 25% MBPF, 50% MBPF, 60% MBPF and 75% MBPF.

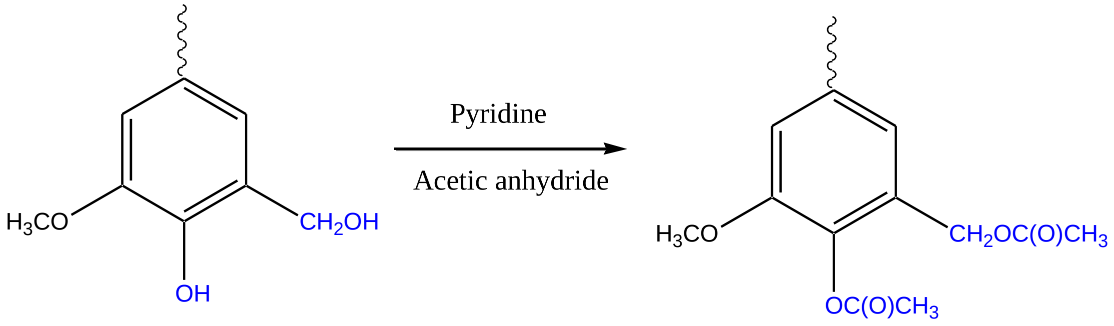
5.3.4 Characterizations of MB and MBPF resins

Free formaldehyde levels

The free formaldehyde levels in the MB and MBPF resins were determined with the modified Walker's hydroxylamine hydrochloric method (Walker, 1975). Approximately 2.0 g of MB or MBPF sample was diluted with 25 mL of water, and pH was adjusted to 4.0 using 0.1 M HCl, followed by addition of 30 mL of hydroxylamine hydrochloride (0.5 M, pH = 4.0). The mixture was stirred for 10 min at room temperature with a magnetic stirrer. The un-reacted formaldehyde was determined by back titration to pH 4.0 using 0.1 M of aqueous sodium hydroxide.

^{1}H NMR and GPC

Before the analyses of ^{1}H NMR and GPC, bio-oil samples were subjected to acetylation in order to improve the solubility in organic solvents. The acetylation pre-treatment was to substitute all the hydroxylic functions with acetyl groups, as illustrated in Scheme 5-3. The bio-oils (with and without methylolation) were acetylated using pyridine and acetic anhydride. The bio-oil or MB (0.5 g) was treated at room temperature for 48 hr with a 1:1 (v/v) mixture of pyridine (10 mL) and acetic anhydride (10 mL). The mixture was added into 100 mL of ice-cold 1 % HCl, and the precipitated solid product was separated by filtration with a Whatman No. 5 filter paper, and rinsed with deionized water until the filtrate attained a neutral pH. The acetylated bio-oils were vacuum dried at room temperature overnight before being subject to ^{1}H NMR and GPC analyses.



Scheme 5-3. Acetylation reaction of methylolated bio-oil.

The degree of methylolation of the bio-oil was determined by ^{1}H NMR. ^{1}H NMR spectra was obtained on a 500 MHz Unity Inova NMR instrument at room temperature where $CDCl_3$ containing 0.1% TMS as internal standard was used as the solvent to dissolve the acetylated bio-oil samples. For the preparation of samples, 25.0 mg of acetylated raw bio-oil or MB was dissolved in 1.0 mL of $CDCl_3$. The number of phenolic acetate and aliphatic acetate protons were detected, relative to the number of methoxyl protons, by integration of the corresponding ^{1}H NMR signals. The relative molecular weights and their distribution of acetylated bio-oil and MB were analyzed through a THF-eluted Waters Breeze GPC (1525 binary HPLC pump; UV detector at 270 nm; Waters Styragel

HR1 column at 40 ^{o}C) at a flow rate of 1 mL/min, and polystyrene standards were used for calibration.

Characterizations of MBPF resins

The viscosity of the as-synthesized resins was measured at 50 ^{o}C with a Brookfield CAP 2000+ viscometer according to the standard of ASTM D1084-97. The non-volatile content of the resins was determined at 125 ^{o}C for 105 min in accordance with ASTM standard D4426-01(2006). The thermal behavior of the resins was evaluated by DSC (DSC 1, Mettler-Toledo, Switzerland), where the sample was heated at 10^{o}C/min from 40 ^{o}C to 250 ^{o}C in a sealed aluminum crucible under 50 mL/min of N_2 flow. GPC analyses were performed to evaluate the average relative molecular weights of the resins. Thermal stability of the resins was determined on a TGA Instrument (TGA 1000i, Instrument Specialists Inc, USA) from 25 ^{o}C to 700 ^{o}C with ~10 mg non-volatile resin sample heated at a 10^{o}C/min under 30mL/min of N_2.

Dry/wet bond strengths of plywood specimens glued with MBPF resole resins

The detailed procedure can be seen elsewhere (Cheng et al., 2011). Simply, three ply laboratory plywood panels of rough dimension 11×11×3/16 inch were prepared from 1/16 inch yellow birch veneers using the conventional PF resole resin or the MBPF resole resins as the adhesives. The resin was mixed with wheat flour (15wt% of the resin) and uniformly applied with a brush to the two surfaces of the center veneers at a spread rate of 250 g/m^2 per single glueline. The hot pressing was carried out at 140 ^{o}C under 2500 psi pressure for 4 min on the three ply plywood panels with two face veneers and a center veneer aligned in a perpendicular direction. According to ASTM D906-98 (2004), 40 specimens were prepared for tensile strength testing. 20 specimens were used to test dry tensile strength after conditioning. The other 20 specimens were boiled in water for 3hr before testing for wet tensile strength to evaluate water resistance of all the resins. The specimens were tested for shear stress by tension loading until failure with a Benchtop Universal Testing Machine (Model H10K-T UTM, Tinius Olsen Material Testing

Machine Company) at a loading rate of 10 mm/min. Percentage of wood failure in the bonding area for each specimen was assessed visually.

5.4. Results and Discussion

5.4.1 Characterizations of the raw bio-oil and the methylolated bio-oil

^{1}H NMR spectra

Scheme 5-3 shows the acetylation reaction scheme of MB. As shown in the scheme, the groups of $–CH_2OH$ and –OH in bio-oil molecules would form ester groups $–CH_2OC(O)CH_3$ and $–OC(O)CH_3$ after acetylation, respectively. Figure 5-1 shows the ^{1}H NMR spectra of the acetylated raw bio-oil and the acetylated methylolated bio-oil. Table 5-1 lists the integrals of ^{1}H NMR signals of aliphatic acetate groups ($–CH_2OC(O)CH_3$) and $–OCH_3$ groups in the acetylated bio-oils at 1.85-2.25 ppm and 3.4-4.2 ppm, respectively. The values are normalized relative to the integrals of the $–OCH_3$ group. The signals of aliphatic acetate became stronger after methylolation as expected, from 0.760 to 0.943. It suggested that a certain amount of $–CH_2OH$ groups were introduced to bio-oil through methylolation reaction.

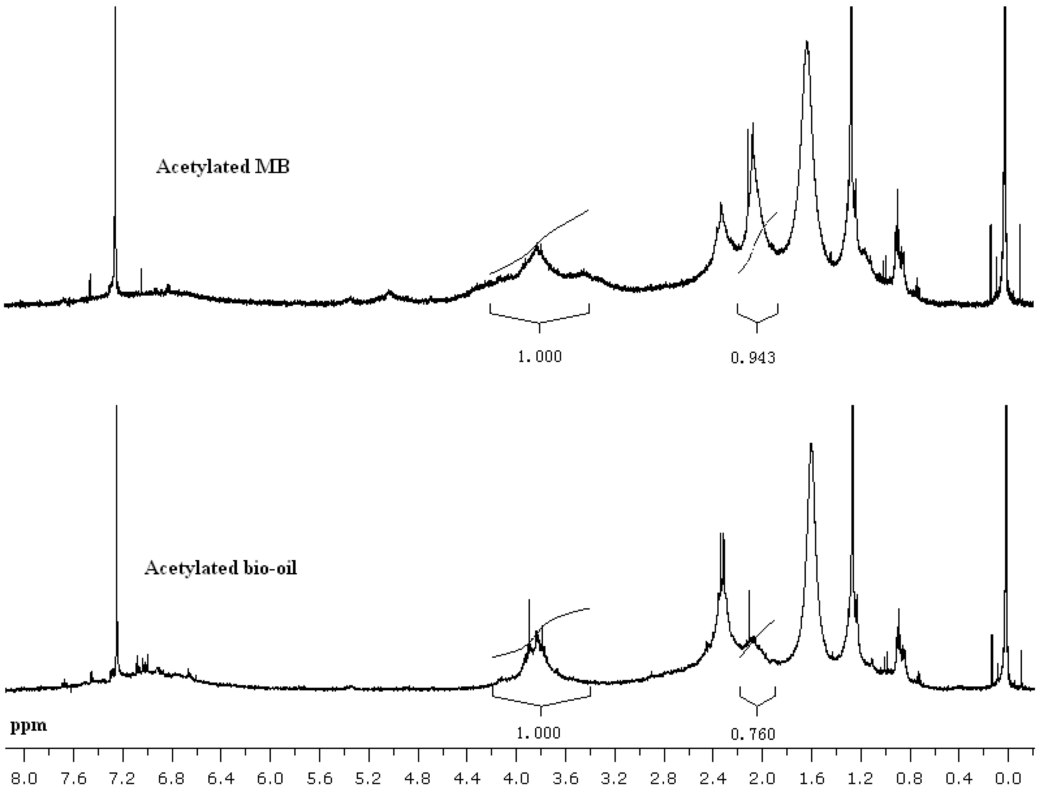


Figure 5-1. ^{1}H NMR spectrum of the acetylated raw bio-oil and the acetylated methylolated bio-oil. Peak at 7.26 and 1.6 ppm are the solvent and water, respectively.

Table 5-1. Integrals of ^{1}H NMR signals in the acetylated raw bio-oil and the methylolated bio-oil (values are normalized relative to the integrals of the $–OCH_3$ signal).

Acetylated bio-oils	$-OCH_3$ 3.4-4.2ppm	R-Acetate 1.85-2.25ppm
Raw bio-oil	1.00	0.760
Methylolated bio-oil	1.00	0.943

GPC analysis

The average relative molecular weights and their distribution of the raw bio-oil and the MB after acetylation were determined with GPC, and the obtained GPC spectra are displayed in Figure 5-2. Both samples displayed a wide molecular-weight distribution.

The peaks of acetylated bio-oil shifted to a higher molecular weight position (M_n from 490 g/mol to 592 g/mol, and M_w from 1120 g/mol to 1563 g/mol) after the methylolation treatment. The value of M_w increased more than M_n, suggesting a wider molecular weight distribution for the MB. As shown in the curve of MB, there were two split peaks. The small peak at lower retention time was possibly derived from the oligomerization reactions of MB during the methylolation treatment, which is possible due to the presence of NaOH catalyst in the process. The increases in M_n and M_w may also imply the introduction of the methylol groups during the methylolation treatment. The increase of PD value of MB suggested a broader distribution.

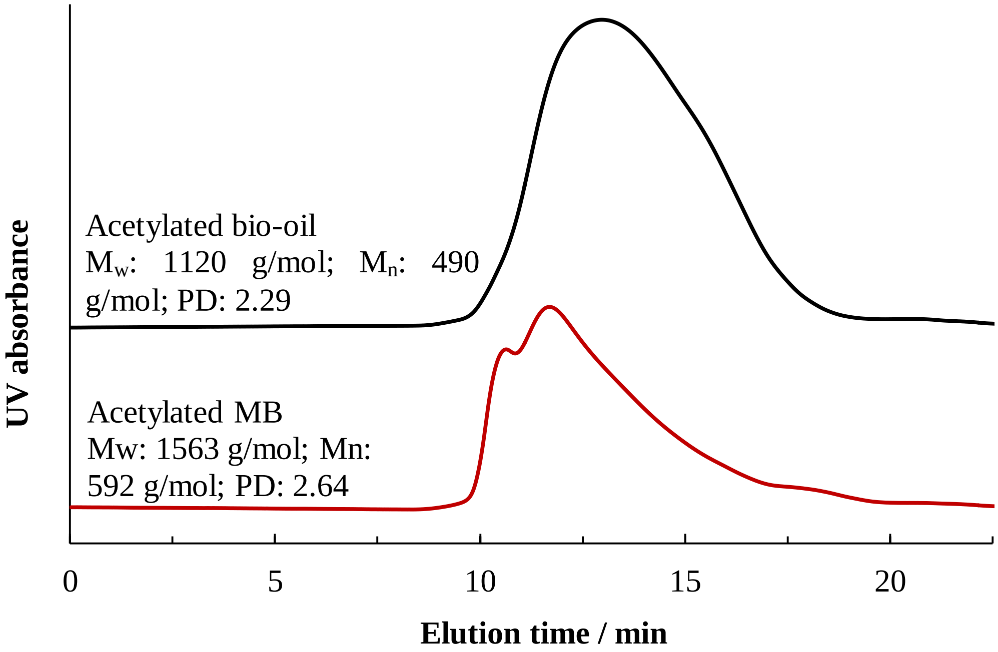


Figure 5-2. GPC spectra of the raw bio-oil and the MB after acetylation (PD = M_w/M_n: Polydispersity).

Free formaldehyde levels

The free formaldehyde levels of MBs collected at various reaction stages during the methylolation treatment were measured and are shown in Figure 5-3. Samples were collected at various reaction stages: i.e., sample "*b*" (at 50 ^{o}C for 1 hr), sample "*c*" (after 50 ^{o}C for 1 hr and further at 80 ^{o}C for 1 hr) and sample "*d*" (after 50 ^{o}C for 1 hr and at 80

^{o}C for 2 hr). Before the methylolation reaction, 10.5 % of initial formaldehyde (sample "*a"*) was present in the reactor. As shown in Figure 5-3, the majority of formaldehyde was consumed after reaction at 50 ^{o}C for 1 hr. The percentage of free formaldehyde was further reduced to a level as low as 0.57 % (sample "c") from 2.14 % (sample "*b"*) when the temperature was further increased to 80 ^{o}C for 1 hr. After methylolation reaction at 80 ^{o}C for 2 hr, only 0.35% of un-reacted formaldehyde content was detected. It appears that the free formaldehyde level would become relatively stable with the reaction continuing. The almost complete consumption of the formaldehyde suggested that the raw bio-oil was successfully methylolated during the methylolation treatment and the possible resinification reaction between formaldehyde and phenolic compounds in the bio-oil.

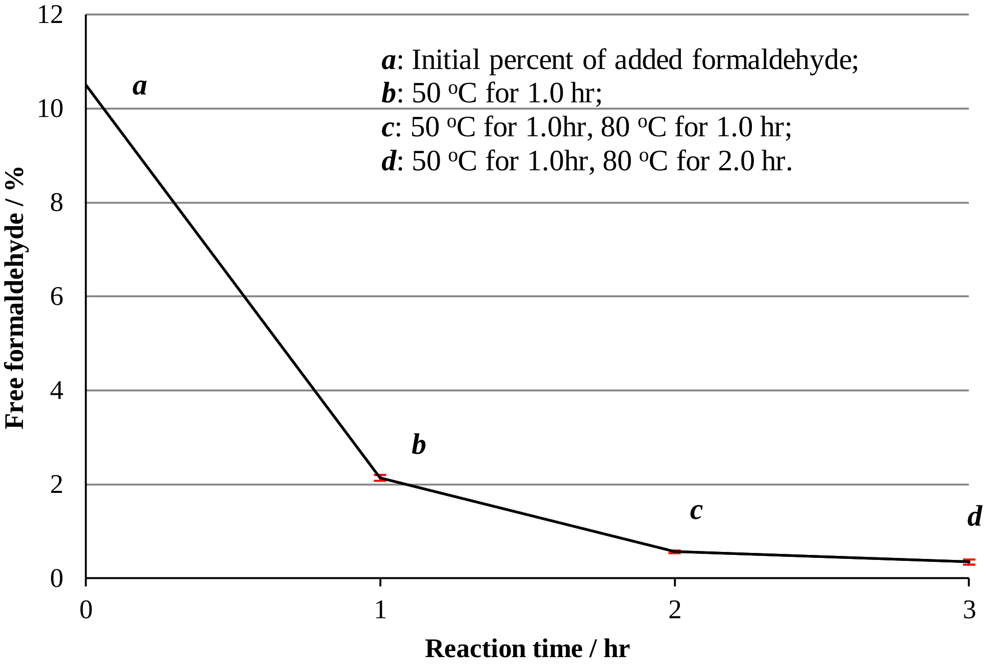


Figure 5-3. Free formaldehyde levels during the process of methylolation treatment.

5.4.2 Characterizations of the MBPF resole resins

Physical properties

All MBPF resins had a dark color with the odor of bio-oil. The measured viscosities and non-volatile contents and shelf life of various MBPF resins, compared with MB, the reference PF resole resin and various BPF resins, are summarized in Table 5-2. As shown in this Table, all MBPF and BPF resins exhibited a higher viscosity than the reference PF resin. Similar observations were reported previously by the authors (Cheng et al., 2011) and by Ferreiraetal (2008). The GC-MS analysis of the bio-oil in our previous work (Cheng et al., 2011) demonstrated that the bio-oil was a highly complex mixture of aldehyde, phenolic compounds, long-chain ketones and alcohols, ester, carboxylic acids, and ether compounds. These compounds might participate in the polymerization or condensation reactions with formaldehyde to form complicated large molecules, increasing the viscosities of the final products. Meanwhile, it is clearly shown that the viscosity of the MBPF resins increases with increasing MB value in the resin. Especially for the 75% MBPF, the viscosity drastically increased to 124.2 cp. Thus, the properties of the MBPF at high phenol substitution with MB would be governed by those of the MB as similarly reported in a previous study by the authors' group (Wang et al., 2009(b)). The amount of MB also had a significant effect on the shelf life of a MBPF resin at low temperatures (4 ^{o}C). Interestingly from Table 5-2, the MBPF resin at 25%MB ratio has a similar shelf life as the reference PF resole resin. After 3 months of storage at 4 ^{o}C, the resin was still in a fluid form. The MBPF resins containing MB of higher than 25%, however, precipitated in about a week. This shorter shelf life could be due to the lower solubility of bio-oil products in water at low temperature. The precipitated MBPF resins can become uniform liquid again by heating. And their shelf life could also be improved by adding more water before storage. Therefore, such appear-to-be shorter shelf lives for the MBPF resins due to precipitation would not affect the applications of MBPF resins. Wang et al. (2009(b)) also reported that a lignin phenolic resin with 60% phenol substitution precipitated in about a week. In contrast, all the BPF resins exhibited a shelf life longer than 3 months. This implies that the methylolation treatment of bio-oil caused a reduced shelf life of MBPF resins due to the enhanced precipitation effects at low temperatures. The free formaldehyde could not be detected in the reference PF resole. Negligible or very low levels of free formaldehyde (<1 wt%) was detected in all the

MBPF and BPF resins. The non-volatile contents of all MBPF resins were very similar to that of PF or BPF resins, in the range of 34 to 38 wt%.

Table 5-2. Physical properties of MB, PF, MBPF and BPF resole resins.

MB & Resins	Viscosity[a] /cps	Shelf life[b] /day	Free formaldehyde[d] / wt%	Non-volatile content[a]/ wt%
MB	38.2 (±0.03)	~7	0.35 (±0.06)	29.4 (±0.1)
PF	16.4 (±0.03)	>90[c]	[e]ND	34.4 (±0.1)
25% MBPF	18.2 (±0.02)	>90[c]	-	35.4 (±0.1)
50% MBPF	26.2 (±0.02)	~ 7	0.37 (±0.03)	36.8 (±0.1)
60% MBPF	35.7 (±0.06)	~ 7	-	35.2 (±0.1)
75% MBPF	124.2 (±0.13)	~1	-	32.9 (±0.1)
25% BPF	19.5 (±0.01)	>90[c]	0.19 (±0.003)	37.7 (±0.2)
50% BPF	21.0 (±0.01)	>90[c]	0.51(±0.01)	38.3 (±0.3)
75% BPF	29.5 (±0.01)	>90[c]	0.67(±0.01)	38.1 (±0.2)

[a] Each value represents an average of 3 samples; [b] At 4 °C; [c] The sample was still fluid after 3 months; [d]The value represents an average of 2 samples; [e] Not detectable.

GPC analysis

Figure 5-4 illustrates gel permeation chromatograms of PF and MBPF resins. As shown in the Figure, all MBPF resins presented much higher values of M_n and M_w and wider distributions than the PF resin due to the high molecular weights of MB (M_w 1563 g/mol and M_n 592 g/mol) than those of phenol. This suggests that MBPF resins, particularly those with high fraction of MB such as 75% MB, were mainly governed by the properties of bio-oil, causing the peak of the GPC chromatogram for a MBPF resin to shift to a higher position. Furthermore, from the GPC curve of 25 % MBPF (Figure 5-4), it can be separated into two parts A and B. The first part A displays a shorter retention time which was caused by the MB-based resin. Part B at longer retention time resulted from the pure phenol-based resin. With increasing the MB ratio, the peak of PF resin polymer gradually decreased which led to the molecular weights shifting to higher values as expected. Most of the reported literature has obtained similar results (Cheng et al., 2011; Wang et al., 2009(b)). Furthermore, another phenomenon observed was two split peaks in part A shown in all MBPFs. Peak-1 was likely attributed to the menthyolated bio-oil reacted with formaldehyde. Peak-2 might be derived from the oligomerization of peak-1 components through the menthylolation reaction between bio-oil molecules. The higher the level of bio-oil substitution, the higher chance of oligomerization, as shown in the GPC curves.

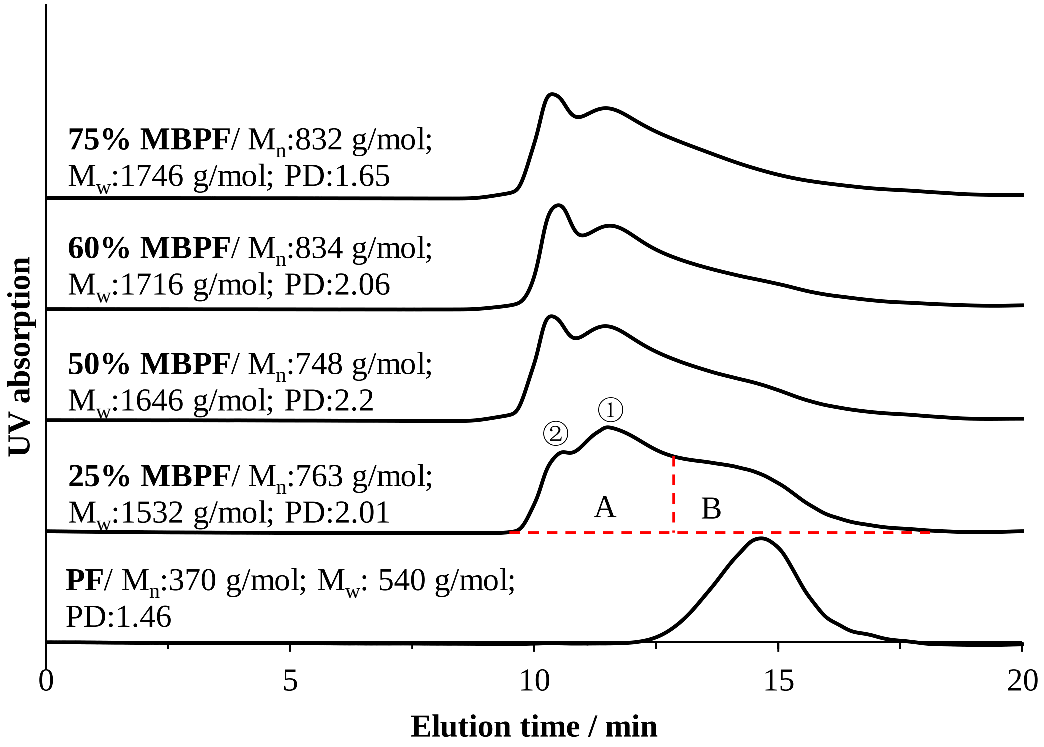


Figure 5-4. GPC chromatograms of MB and MBPF resins.

Thermal cure behaviors

DSC analysis as a popular technique to examine the curing process of thermosetting resins (Amen-Chen et al., 2002(b); Gabilondo et al., 2007; Holopainen et al., 1997), was employed to determine the thermal behavior of MBPF resins. Figure 5-5 shows the DSC curves of different resins obtained from 40 ^{o}C to 250 ^{o}C at a heating rate of 5 ^{o}C/min in an N_2 atmosphere. Table 5-3 summarizes the characteristic curing temperatures of these resins. Again, in order to examine the effects of methylolation treatment of bio-oil on the thermal behavior of the bio-resins, the DSC results for BPF resins are also listed in Table 5-3. As shown in Figure 5-5, more than one exothermic peak was detected for resins containing bio-oil of < 60%. All the DSC curves show distinct exothermic signals (peak 2) at the temperature around 140 °C, which could be ascribed to the main exothermic peak of phenolic resole resin. All MBPF and BPF resins (containing bio-oil of < 75 wt%) displayed peak 2 at a lower temperature than PF, suggesting a reduced curing temperature, as similarly reported in many previous studies (Amen-Chen et al., 2002(b); V ázquez et al., 2002; Khan et al., 2004) on synthesis of bio-based PF resins using phenol substitutes such as tannin and lignin. It is an interesting finding that, as shown in Table 5-3, the curing temperature of 75% MBPF (139.6 °C) is lower than that of 75% BPF (146.2 °C). The main curing peak (peak 2) can be attributed to the condensation of phenol or bio-oil with methylol groups ($–CH_2OH$) to form a methylene bridge and the condensation of methylol groups with phenolic compounds to form dibenzyl ether bridges (Wang et al., 2009(b); Gabilondo et al., 2007; V ázquez et al., 2002; Christiansen and Gollob, 2003). The curve of PF produced a large and well-split peak at a lower temperature of 133.3 °C. The DSC curves for 25% MBPF, 50% MBPF and 60% MBPF show the shoulder exothermic signals (peak 1) at a lower temperature of around 133°C, which could be due to the additional reactions of un-reacted free formaldehyde with bio-oil and phenol, as well as the methylolated phenolic components (Monni et al., 2007). It can be observed from Figure 5-5 that 50% MBPF and 60% MBPF show small signals (peak 3) at around 150 °C, which might be due to the subsequent radical coupling reactions, e.g. condensation reaction between side chains and bio-oil to form ether bridges (Ralph, 1999) and breakage of dimethylene ether linkages and re-condensation through the methylene bridges (Wang et al., 2009(b); Gabilondo et al., 2007; V ázquez et al., 2002). Interestingly, only one very weak exothermic peak was observed for 75% MBPF. As discussed above, the properties of MBPF resins with high phenol substitution with bio-oil are governed by MB, while the MB contains much fewer active sites for cross-linking.

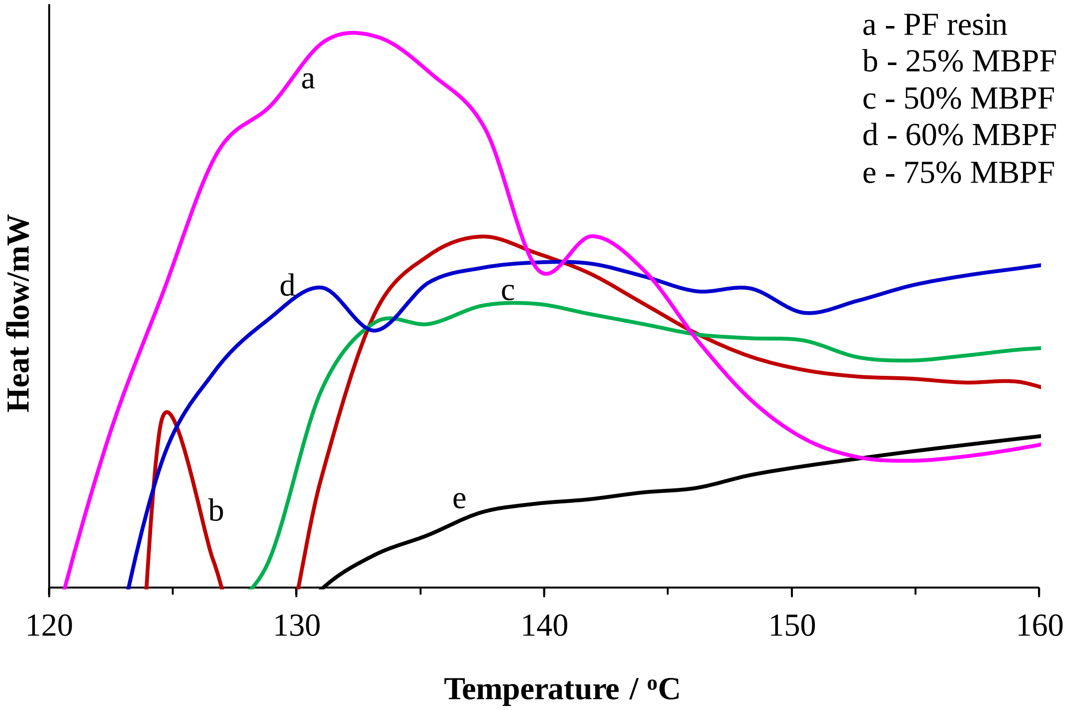


Figure 5-5. DSC curves for different resin systems obtained at a heating rate of 5 °C/min from 40 °C to 250 °C with 50 mL/min of N_2.

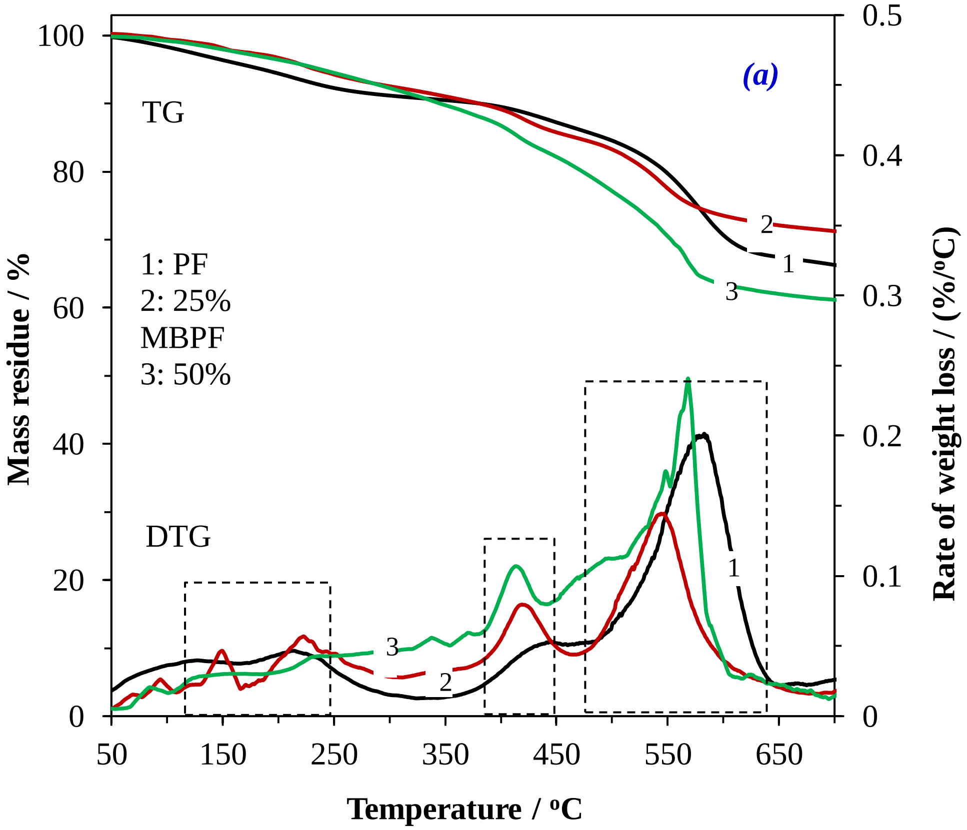
Table 5-3. Characteristic curing temperatures of PF, MBPF and BPF resins.

Type of resins	Characteristic curing temperatures / °C		
	Peak1	Peak 2	Peak 3
PF	133.3	141.9	-
25% MBPF	135.3	137.5	-
50% MBPF	133.1	139.6	150.5
60% MBPF	135.3	139.6	148.3
75% MBPF	-	139.6	-
25% BPF	133.2	135.4	-
50% BPF	131.0	137.5	-
75% BPF	-	146.2	-

Thermal stability

The thermal stability of MBPF resins was investigated with TGA by heating the sample from 25 °C to 700 °C in an N_2 atmosphere. The corresponding TG and derivative of TG (DTG) results are shown in Figures 5-6 ("*a*" and "*b*"). The decomposition temperatures for various thermal events and mass residue at 700 °C are summarized in Table 5-4. As shown in Figure 5-6a, the DTG curves for all resins showed similarly three thermal-decomposition events, which reflects the three step degradation of phenolic resins: post-curing, thermal reforming and ring stripping (Vázquez et al., 2002; Khan and Ashraf, 2007). In this regard, for the pure PF resin, the first maximum thermal event at 214 °C could be attributed to the post-curing reactions of the resin involving the removal of moisture and terminal groups and further crosslinking or condensation reactions, the transformation of ether bridges to methylene bridges with simultaneous release of formaldehyde (Khan et al., 2004); the second event in the range from 300 °C to 460 °C could be ascribed to the thermal reforming to break the bridged methylene linkage; and the third event in the range of 460 °C to 650 °C is the main mass loss event due to the breakdown of the ring network. MBPF resins with ≤ 50% phenol substitution exhibited very similar DTG profiles as the pure PF resin, as reported previously BPF resins using untreated bio-oil (Cheng et al., 2011) with three thermal-decomposition events at 70 °C to 300 °C, 300 °C to 450 °C and 450 °C to 650 °C. However, with the MB amount of > 50%, the MBPF resins exhibited similar DTG profiles as MB especially for 75% MBPF. As displayed in Figure 6b, the first of thermal event of MB occurred approximately between 160 °C and 330 °C which was larger than others, mostly due to the loss of free formaldehyde and the release of formaldehyde from the breakage of ether bridges to methylene, and the second event due to the breakdown of side chains of bio-oil and the bridged methylene linkage in the bio-oils. Similarly, the third event at the higher temperature could be caused by the breakdown of the ring network of the MB.

As for the carbon residues of these resins, the 25% MBPF resin has a slightly higher carbon residue (71%) at 700 °C than the pure PF (66%). These results suggest that the addition of a small amount of MB could improve the thermal stability of the resole-type phenolic resin. Even for the MBPF resins with a higher phenol substitution > 25%, the carbon residues (59-61%) are still comparable with that of the pure PF resin. The BPF resins with a lower bio-oil content (≤ 50%) have similar carbon residues as those of MBPF resins as shown in Table 3, but interestingly, the 75% MBPF has higher carbon residue at 700°C (59%) than that of 75% BPF (48%), suggesting that the thermal stability of bio-oil phenolic resins could be improved by methylolation treatment of the bio-oil before resinification.



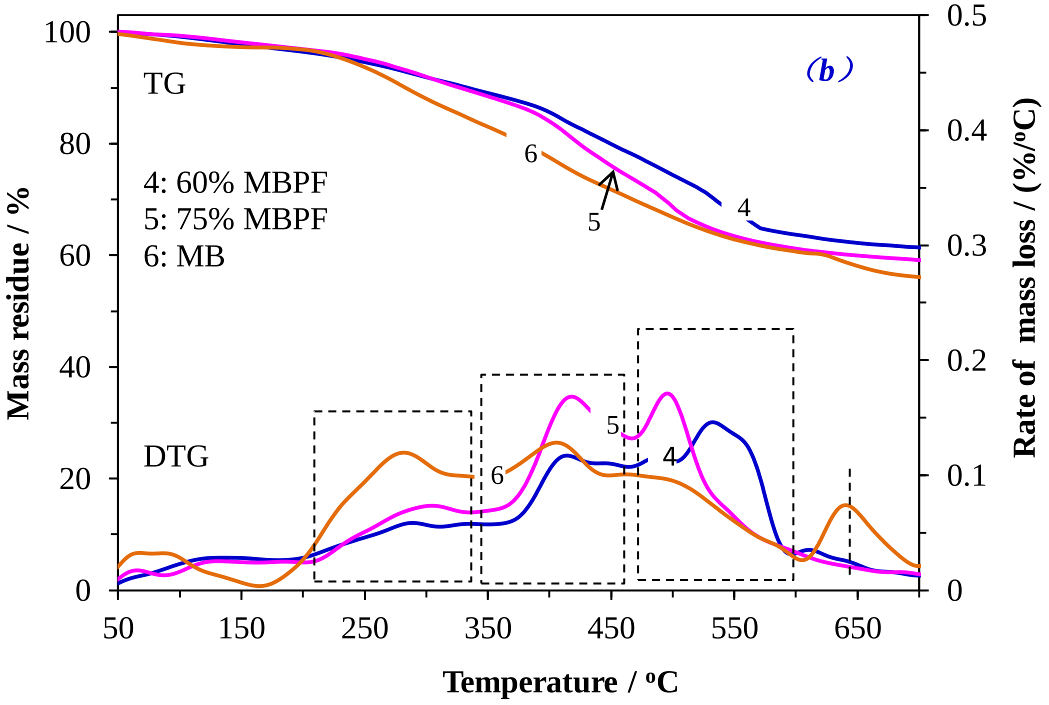


Figure 5-6. TG and DTG profiles of various MBPF resins obtained by heating from 25 to 700 °C in 30 mL/min of N_2 atmosphere.

Table 5-4. TG and DTG results of MBPF resins and MB observed from Figures 5-6.

Resins	DTG results			TG results
	First thermal event T_p/ °C[a]	Second thermal event T_p/ °C	Third thermal event T_p/ °C	Carbon residue @ 700 °C / %
PF	214	432	585	66
25% MBPF	222	422	541	71
50% MBPF	224	414	548	61
60% MBPF	289	414	532	61
75% MBPF	304	418	496	59
25% BPF	236	418	548	72
50% BPF	240	393	535	61
75% BPF	240	466	616	48
MB	281	405	461	56

[a] T_p: Peak temperature

5.4.3 Evaluation of bond strength of plywood samples glued with MBPF resins

Various MBPF resins and the reference PF resin were used as adhesives for plywood. Dry and wet tensile strength of plywood specimens were measured and compared in Figure 5-7. The dry and wet wood failure percentages (WFP) of all plywood specimens were also observed after the tensile strength testing and reported in Table 5-5. As shown in Figure 5-7, both dry and wet strength for the MBPF resins (with up to 60% bio-oil) are comparable to those of PF. Under dry conditions, all plywood specimens with MBPF adhesives possess better or very similar tensile strength compared to the reference PF adhesive. All MBPF adhesives surpassed the minimum requirement of dry tension shear strength (i.e., 1.2 MPa) in accordance to the JIS K-6852 standard for resole-type plywood adhesives. The wet tensile strength of all the MBPF resins also exceeds the minimum requirement of wet strength (i.e., 1.0 MPa). The above results suggest that it is practically feasible to produce MBPF resins as plywood adhesives with 60% phenol replacement with MB, without compromising the bond strength of the PF adhesives.

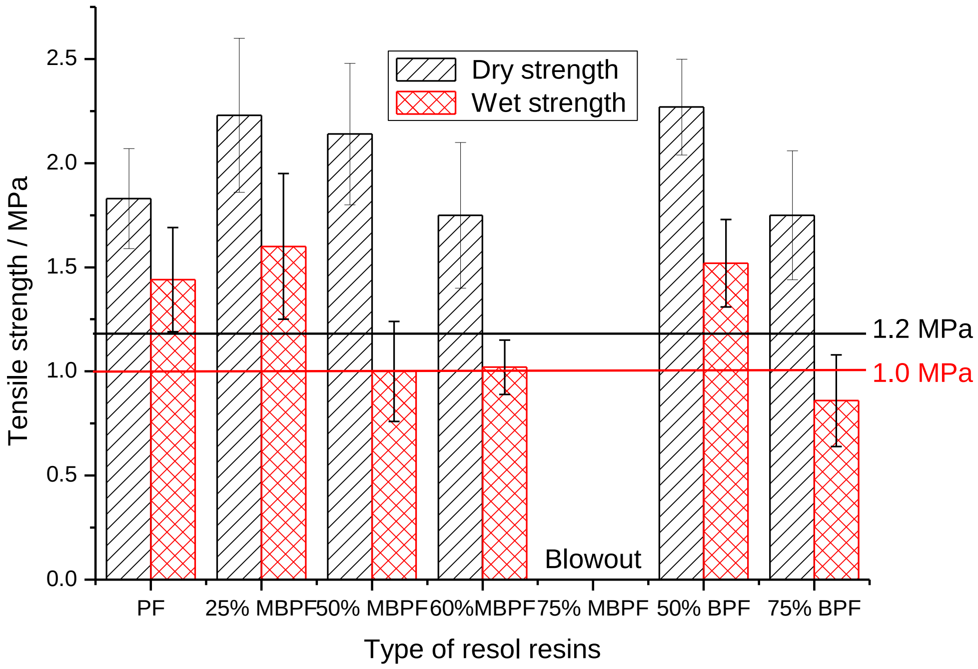


Figure 5-7. Tensile strength (dry and wet) of the plywood specimens bonded with MBPF and PF adhesives.

Table 5-5 lists the WFPs from the above bond strength tests. Under the dry condition, it was found that only the specimen with the adhesive of 25% MBPF performed comparably to that of the PF adhesive, which meets the minimum requirement of WFP (> 85%) for exterior-grade plywood products in accordance to U.S. plywood Product Standard PS 1–83. However, for the adhesives of MBPF containing MB of 50 % or 60%, the corresponding WFP dropped drastically to lower than 10%. In contrast, the specimens glued with adhesives of BPF resins showed much better WFP than the adhesives of MBPF resins under either dry or wet conditions. These results revealed that the MBPF adhesives are more sensitive to water than the PF and BPF adhesives. They could be used as adhesives for the production of interior wood products.

Table 5-5. WFPs of plywood glued with various resole-type PF, MBPF and BPF adhesives under dry and wet conditions.

Test conditions	Pure PF	25 % MBPF	50% MBPF	60% MBPF	25% BPF	50% BPF	75% BPF
	Wood failure percentage (WFP)[1] (%) (Standard deviation)						
Dry[2]	89 (±19)	86 (±24)	8 (±12)	2 (±5)	97 (±13)	87 (±36)	22 (±33)
Wet[3]	65 (±43)	8 (±12)	0 (0)	0 (0)	33 (±42)	35 (±41)	15 (±31)

1: Each value represents an average of 20 specimens. 2: Test after conditioning. 3: Test after boiling in water for 3.0 hr.

The plywood glued with adhesive of 75% MBPF suffered from blowouts immediately after hot pressing as displayed in Figure 5-8. In this Figure, the wide dark area represents a blowout of the upper glueline. As reported in our previous work (Cheng et al., 2011), plywood specimens boned with BPF adhesives with up to 75 wt% phenol substitution had comparable dry and wet tensile strengths to the PF adhesive. Thus, the results indicated that the methylolation treatment of bio-oil reduces the bond strength of the bio-oil PF adhesives, especially for the resins with a high phenol substitution. This could be explained by re-condensation of bio-oil via the methylol group in the process of the methylolation, resulting in fewer linking sites, as evidenced by the average higher molecular weight of MB (Figure 5-2), the high viscosity (Table 5-2) and the small thermal cure peak (Figure 5-5) for the 75% MBPF.

As shown in the manuscript, bio-oil/methylolated bio-oil based phenolic resins with a high substitution of phenol up to 75%/60% demonstrated similar or comparable properties as pure phenol-formaldehyde resin. The phenol substitution ratio is higher than that in others work using lignin. It can be explained from the effect of thermal conversion processes. Lots of studies (Roy et al., 2000; Amen-Chen et al., 2002; Himmelblau and Grozdits, 1999) on production bio-phenolic resin with pyrolysis oil showed that it is only feasible if the phenol substitution level is below 50 % in the resin synthesis, otherwise the properties of resin will be significantly affected. To our knowledge, pyrolysis oil is a highly complex mixture, which has been reported to contain hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids and phenolics. The molecular weights of pyrolysis oil reside in the range several hundreds to 5000 or more depending on the conditions (Mohan et al., 2006). It may cause the low reactivity and the low substitution. In contrast, solvolytic liquefaction processes were performed in an organic solvent, such as water, alcohol, acetone or co-solvents, which produce a uniform and high-quality bio-oil with more phenolic compounds of lower molecular weights. In this study, bio-oil was derived from a solvolytic liquefaction process, which was carried out in 50/50 (v/v) water-ethanol at 300 ^{o}C. A high yield of bio-oil (68 %) with low molecular weights (M_n 342 g/mol and M_w 1072 g/mol) was produced. Therefore, the high reactivity of the bio-oil used in this study may contribute to the higher phenol substitution ratio.

5.5 Conclusions

The ^{1}H NMR analysis of the bio-oil before and after methylolation demonstrated that the methylolation treatment could increase the methylol groups. The GPC analysis of bio-oil and MB suggested that condensation reactions occurred to the bio-oil during the methylolation treatment. All MBPF resins showed similar non-volatile contents as the pure PF. Although MBPF resins containing MB of higher than 25% precipitated in about a week at 4 °C, the resins could become liquid again by re-heating.

The experimental MBPF resole resins could be cured in the range from 128 °C to 155 °C. All MBPF resole resins exhibited a lower curing temperature, and better or comparable thermal stability than the PF resin. Interestingly, the 75% MBPF showed a higher carbon residue at 700 °C (59%) than the 75% BPF (48%). This suggests that the methylolation treatment of bio-oil could improve the thermal stability of bio-phenolic resins. When used as plywood adhesives, MBPF resins with 60% substitution for phenol proved to be possible without compromising the bond strength (dry and wet tensile strength) of the plywood specimens. However, the MBPF adhesives were more sensitive to water than the PF and BPF adhesive.

5.6 Acknowledgements

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CHAPTER 6. HYDROTHERMAL DEGRADATION OF ALKALI LIGNIN TO BIO-PHENOLIC COMPOUNDS IN SUB-/SUPER-CRITICAL ETHANOL AND WATER-ETHANOL CO-SOLVENT

6.1 Abstract

This work aimed to degrade alkali lignin for the production of bio-phenols. Effective degradation of alkali lignin (AL) was achieved by hydrothermal treatment in 50/50 (v/v) ethanol-water at 200 ^{o}C to 450 ^{o}C under 5 MPa H_2 with or without catalyst. The treatment at 300 ^{o}C for 2hr led to a yield of degraded lignin (DL, acetone-methanol soluble fraction) close to 90%. Molecular weights of the lignin were markedly reduced from its original M_w and M_n of 60,000 g/mol and 10,000 g/mol, respectively to (M_n 415 g/mol, M_w 1010 g/mol) for the DL. Compared with that in 50/50 (v/v) ethanol-water, treatment in pure ethanol led to a much lower yield of DL (< 15%) but the DL products have much smaller molecular weights (M_n 260 g/mol and M_w 631 g/mol from 300 ^{o}C treatment). Moreover, the DLs from pure ethanol treatment are completely soluble in THF, compared with only ~30% solubility in tetrahydrofuran (THF) for the DLs from 50/50 (v/v) ethanol-water treatment. While reaction time has negligible effects on the DL yields and properties, reaction temperature drastically influenced the product yields and properties: 300 ^{o}C to 350 ^{o}C and 400 ^{o}C appeared to be the optimal temperature for the process with 50/50 (v/v) ethanol-water and pure ethanol, respectively. In both solvent-systems, generally the use of alumina or activated carbon supported metal catalysts (Pt, Ru, Ni) did not affect the yields of DL, but it could slightly reduce the molecular weights of the DLs and greatly increased the solubility of DLs in THF, particularly in the process with 50/50 (v/v) ethanol-water.

6.2 Introduction

Lignin is a natural phenolic polymer with high molecular weights (600-15,000 kDa), which accounts for 20-35 wt% in woody biomass (40-50 wt% in bark) and 10-20 wt% in agricultural materials. Lignin is produced in large quantities as a by-product (e.g., alkaline or kraft lignin, and lignosulfonates) from the chemical pulping processes in the pulp/paper industry, and the annual generation is estimated at 50 million tons worldwide (Kües, 2007). Crude lignin is also generated as a waste stream in the organosolv delignification process and the steam explosion process for cellulosic ethanol production. Lignin is used predominantly as a solid fuel at a value of ~$ 200/t for heat generation in the recovery boilers in pulp/paper mills (Stewart, 2008). However, for 60-70% of North American Kraft mills the capacity of the recovery boilers is the bottleneck for the whole process, which means that precipitating and valorization of lignin for other value-added products can not only enhance the mill capacity but also greatly improve the mill economy.

Lignin is an amorphous macromolecule comprised of three phenyl-propanols i.e., p-hydroxyl-phenyl propanol, guaiacyl-propanol and syringyl-propanol, linked together by condensed linkages (e.g., 5-5, β-β, β-5 and β-1 linkages) and ether linkages (e.g., α-O-4, 5-O-4 and β-O-4). Thus, lignin could be de-polymerized/degraded into phenolic chemicals. One practical industrial application of lignin is to substitute petroleum-derived phenol for the synthesis of phenol-formaldehyde (PF) resin. Direct use of lignin as a replacement for phenol in PF resins is however limited due to its fewer reactive sites and steric hindrance effects caused by its complex chemical structure (Alonso et al, 2004; Çetin and Özmen, 2002). In this regard, an effective way to improve the reactivity of lignin for replacing the petroleum-based phenol in the synthesis of bio-based phenolic resins could be via de-polymerization of lignin into phenolic compounds with lower molecular weights.

Liquefaction of lignin or biomass in sub-/super-critical fluids such as water (Lawson and Kleln, 1985; Benigni and Goldstein, 1971), methanol (Tsujino et al., 2003; Minami et al., 2003), and ethanol (Miller et al., 1999) has been studied by many researchers to obtain bio-oil products or phenolic chemicals with low molecular weights. Miller and co-workers (Miller et al., 1999) showed that supercritical ethanol was more reactive than methanol in the de-polymerization of lignin and model compounds in a batch micro-reactor with base catalysts, resulting in less solid residual products. Our previous work (Cheng et al. 2010) also demonstrated that sub/supercritical ethanol was more reactive than methanol for liquefying woody biomass into biocrude products. The higher reactivity of ethanol than methanol might be owing to the slightly lower dielectric constant of ethanol (24.3 %) than that of methanol (33 %). As a result, ethanol in particular at its supercritical state may be expected to more readily dissolve and stabilize the relatively high molecular weight liquid products/intermediates derived from lignocellulosic biomass during the liquefaction/de-polymerization process. Furthermore, our previous work (Cheng et al. 2010) also showed that co-solvent of 50/50 (v/v) water-ethanol is much more reactive then either pure ethanol or water, leading to much higher biomass conversion and biocrude yields (up to 65 wt%). It is thus of great interest to investigate on degradation of lignin in sub-/super-critical 50/50 (v/v) water-ethanol co-solvent for the production of phenolic chemicals.

The objective of this research is to comprehensively investigate on degradation of alkali lignin (AL) in sub-/super-critical fluids of 50/50 (v/v) water-ethanol and pure ethanol under varying reaction conditions of reaction temperature, reaction time and catalyst. Metallic catalysts (e.g., Pt, Ru, and Ni) supported on γ-Al_2O_3 and carbon has been used for hydrogenolysis/hydrocracking of lignin (carbohydrate) (Pepper and Lee, 1969; Pepper and Steck, 1963; Duan and Savage, 2011). In this research, γ-Al_2O_3 and active carbon (AC) supported metallic (Pt, Ru, and Ni) catalysts were prepared, and hydrogen atmosphere was employed to prevent oxidation of the catalysts. The degraded lignin products were characterized using gas chromatography-mass spectrometry (GC-MS), and gel permeation chromatography (GPC) and proton nuclear magnetic resonance (^1H NMR).

6.3. Materials and Methods

6.3.1 Materials

AL was purchased from Sigma-Aldrich. The average molecular weights M_w and M_n of AL are 60,000 g/mol and 10,000 g/mol, respectively. All samples were vacuum dried overnight at room temperature before use. Proximate and ultimate analysis results of AL sample are listed in Table 6-1. In this study, ACS reagent grade solvents and chemicals, including ethanol, acetone, methanol, dimethyl sulfoxide-d_6 (DMSO-d_6), nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$), chloroplantinic acid ($H_2PtCl_6 \cdot 6H_2O$) (8 wt% solution in water), and ruthenium nitrosyl nitrate in dilute nitric acid ($HN_4O_{10}Ru$) were purchased from Fisher Scientific or Sigma-Aldrich. These materials were used as received. In the GPC analysis for the liquid products, HPLC grade solvent of tetrahydrofuran (THF) was used, which contained 0.03 wt% stabilizer of 2, 6-di-*t*-butyl-4-methyl-phenol.

Table 6-1. Proximate and ultimate analyses of the original alkali lignin (AL) sample.

Proximate analysis (wt %, d.b.) [a,b]			Ultimate analysis (wt %, d.a,f) [c]			
VM[d]	FC[e,h]	Ash	C	H	N	(S &O)[h]
72.6	17.9	9.5	49.0	4.4	0	46.6

[a] On a dry basis; [b] Determined by thermogravimetric analysis (TGA) in N_2 at 10 °C/min to 900 °C, and 900 °C in air for 15 min; [c] On a dry and ash free basis; [d] VM: Volatile matters; [e] FC: Fixed carbon; [h] By difference.

6.3.2 Catalyst preparation

All the catalysts were prepared by incipient wetness impregnation method using aqueous metal salt solutions of $Ni(NO_3)_2 \cdot 6H_2O$, $H_2PtCl_6 \cdot 6H_2O$ and $HN_4O_{10}Ru$. γ-Al_2O_3 (Inframat Advanced Materials) and a self-prepared AC were used as the catalyst support materials. The AC was derived from pine wood sawdust (850-2000 µm) activated using H_3PO_4 according to the procedure as detailed elsewhere (Zhang et al., 2011). The metal loading on each supported catalyst was fixed at 10 wt%. The γ-Al_2O_3-supported catalysts were calcined in air at 550 °C for 6.5 hr followed by 2 hr reduction in hydrogen at the same temperature. Similar calcination and reduction procedures were adopted for the AC-supported catalysts, except that the carbon-based catalysts were calcined in N_2 at 550 °C for 6.5 hr to prevent burn-out of the carbon material. All catalysts were then crushed and sieved to particles less than 300 μm for the experimental use in this study. The Al_2O_3-supported metallic catalysts have a BET surface area of ~70 m^2/g and a total pore volume of ~0.3 cm^3/g with an average pore diameter of ~10 nm (mesopores). The AC-supported metallic catalysts have a BET surface area of ~800 m^2/g and a total pore volume of ~0.5 cm^3/g with an average pore diameter of < 2 nm (micropores).

6.3.3 Lignin degradation experiments

The lignin degradation experiments were primarily carried out in a 14 mL microreactor (SS 316L) for all the tests at a lower temperature from 200 ^oC to 325 ^oC. In a typical run, the micro-reactor was charged with 1.0 g lignin, 10.0 mL water-ethanol co-solvents (or pure ethanol) and 0.1 g catalyst (if needed), and sonicated in an ultra-sonic bath for 20 min to ensure a uniform mixture. The reactor was securely sealed and purged with high-purity nitrogen for three purging-vacuum evacuation cycles, and finally pressurized to 5.0 MPa using hydrogen. The reactor was mounted on a mechanical shaker at 100 rpm and heated up rapidly in a fluidized sand bath at the desired reaction temperature. Assisted by shaking, the micro-reactor can reach the specific reaction temperature rapidly within 1-2 min. The reactor was kept at the temperature for a desired reaction time, which was measured from the time when the reactor was put into the sand bath. After the treatment was finished, the reactor was quenched, by submerging it in a cold-water bath. During each run the reaction pressure and temperature were recorded in every 10 min. Two or three duplicate runs were carried out for each condition to ensure the maximum relative error of the yield of degraded lignin within ±5 %.

Due to the pressure limit of the micro-reactor, the tests at a reaction temperature higher than 350 ℃ were performed in a 75 mL Parr high-pressure reactor. This reactor is constructed of Hastelloy alloy, with maximum working pressure of 41 MPa at 600 ℃. The experimental procedure was similar to that in the experiments with the micro-reactor as described above, except that the reactor was heated through an electric heater without shaking or stirring. The reaction time was measured from the time when the reactor reached the desired temperature.

6.3.4 Products separation

When the reactor was cooled to room temperature, the obtained gaseous product was collected into a pre-vacuumed gas cylinder, and then analyzed using a Micro-GC equipped with thermal conductivity detectors (TCDs). The formation (in moles) of gas species (H_2, CO, CO_2, CH_4, and C_2-C_3) was determined. The liquid and solid residue products in the reactor were completely rinsed out with acetone and methanol. The mixture was filtered with the Buchner funnel through a pre-weighed Ahlstrom Glass microfiber filter paper (1.1 μm Particle retention). Organic solvents (ethanol, acetone and methanol) in the filtrate were removed with an evaporator under reduced pressure at 40 ^{o}C and water was further evaporated at 60 ^{o}C. The remained oily product was vacuum dried at room temperature overnight to remove the residual water before weighing and was defined as degraded lignin (DL, acetone-methanol soluble fraction). A small amount of low boiling point ingredients might be evaporated in the drying process, which was ignored in this study. The obtained solid residue (SR) was oven dried at 105 ^{o}C overnight before weighing and was denoted as SR_1. Then SR_1 was completely rinsed with distilled water to separate water-soluble products (WSP), and the resulted solid yield was denoted as SR_2 (acetone-methanol-water insoluble faction). The weight of WSP was obtained from the weight difference between SR_1 and SR_2. Our major interest of this work was DL products. Therefore the chemical compositions of WSP were not analyzed. Yields of DL, SR_2, WSP and gas (gaseous products) were calculated by the weight percentage of the mass of each product to the mass of dry AL loaded into the reactor in each run. It should be noted that water was a by-product from the lignin degradation reactions via hydrogenolysis and dehydration reactions. The produced water was not analyzed in this study.

6.3.5 Characterizations of DL

Volatile compositions of the obtained DL products were detected using a GC-MS (Shimazu QP2010S) with an SHRXI-5MS column (30 m × 0.25 mm × 0.25 um) and the temperature program of 50 °C to 280 °C (10 °C/min, hold for 20 min). The chemical structure of the DL products was also characterized with a 500 MHz proton nuclear magnetic resonance (^{1}H NMR) (Inova NMR instrument) at room temperature in DMSO-d_6 solvent. And all the ^{1}H NMR spectra were calibrated to the signal of DMSO-d_6 of 2.50 ppm. The molecular weights and their distributions of the DL products were analyzed on a Waters Breeze GPC (1525 binary HPLC pump; UV detector at 270 nm; Waters Styragel HR1 column at 40 °C) using THF as eluent at a flow rate of 1 mL/min. Polystyrene standards were used for calibration. It is worth to mention that the GPC results reported in this study were obtained with the THF-soluble fraction of DL. The DL samples were only partially soluble in THF due to the presence of high-polar groups such as hydroxyl groups and carboxyl groups that are THF-insoluble. The solubility of DL in THF may be improved by complex acetylation treatment using pyridine and acetic anhydride which would result in a slight increase in the molecular weight analysis results. For example, the molecular weights of DL obtained with Ni10/AC at 300 °C increased from (M_n 356 g/mol and M_w 846 g/mol) to (M_n 684 g/mol and M_w 1381 g/mol) after the acetylation treatment. However, compared with the original molecular weights of the lignin (M_n 10,000 g/mol and M_w 60,000 g/mol), such difference in molecular weights was not significant. In this study, the complex acetylation treatment process was not performed for all the DLs, and the reported molecular weights were from the THF soluble fraction of DL.

6.4 Results and Discussion

6.4.1 Effects of solvent composition

Figure 6-1 shows the effects of ethanol concentration in the water-ethanol co-solvent on the yields of DL, WSP, SR_2 and gas products. All the reactions were performed at 300 °C for 4 h. All the collected DL products were in a solid powder form at room temperature except that the DL with pure ethanol was in an oily form. As clearly shown in the Figure, 50/50 (v/v) water-ethanol co-solvent produced the highest DL yield accompanied with the lowest SR_2 yield (2 wt%). Compared to 50/50 (v/v) water-ethanol co-solvent, the mono-solvent either pure ethanol or water produced a lower yield of DL and a higher yield of SR_2. The yield of DL was higher in pure water medium than in pure ethanol. As well known, the process of lignin/biomass hydrothermal de-gradation at an elevated temperature in hot-compressed water involves both ionic and radical reactions such as nucleophilic/electrophilic hydrolysis and thermal cracking/pyrolysis reactions (Kabyemela et al., 1997; Antal et al., 1991; Yuan et al., 2010). The lower DL yield in pure ethanol than in water might be due to the limited hydrolysis reactions. The addition of water as a co-solvent into ethanol would thus enhance the solvolytic/hydrolytic degradation of the lignin as markedly shown in Figure 6-1. Similar results were obtained in some previous works (Pasquini et al., 2005; Li and Kiran, 1988) and in a recent study from the authors' research group (Cheng et al., 2010) for delignification and hydrothermal liquefaction of biomass with aqueous ethanol. The total yield of gas products was lower than 5 wt% in all tests, and the gas product mainly contained CO_2, CH_4, C_2H_6, and C_2H_4 as expected.

Therefore, the 50/50 (v/v) water-ethanol solvent was found to be the most effective solvent for degradation of AL in terms of the DL yield. The DL produced from pure ethanol appeared to be of a higher quality due to its oily appearance (implying lower molecular weights). The DL samples from the treatment in 50/50 (v/v) water-ethanol solvent are only partially soluble in THF due to the presence of high-polar groups such as hydroxyl groups and carboxyl groups that are THF-insoluble, while the DL products from the treatment in pure ethanol are completely soluble in THF. As such, both solvent systems, i.e., 50/50(v/v) water-ethanol and pure ethanol were selected for further studies as discussed below.

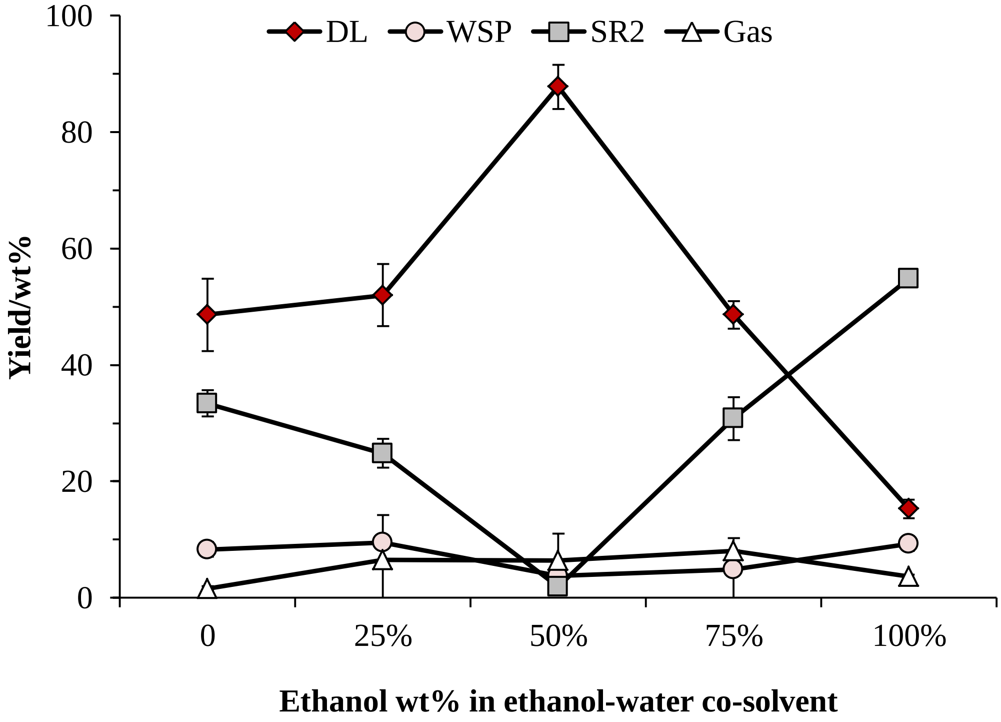
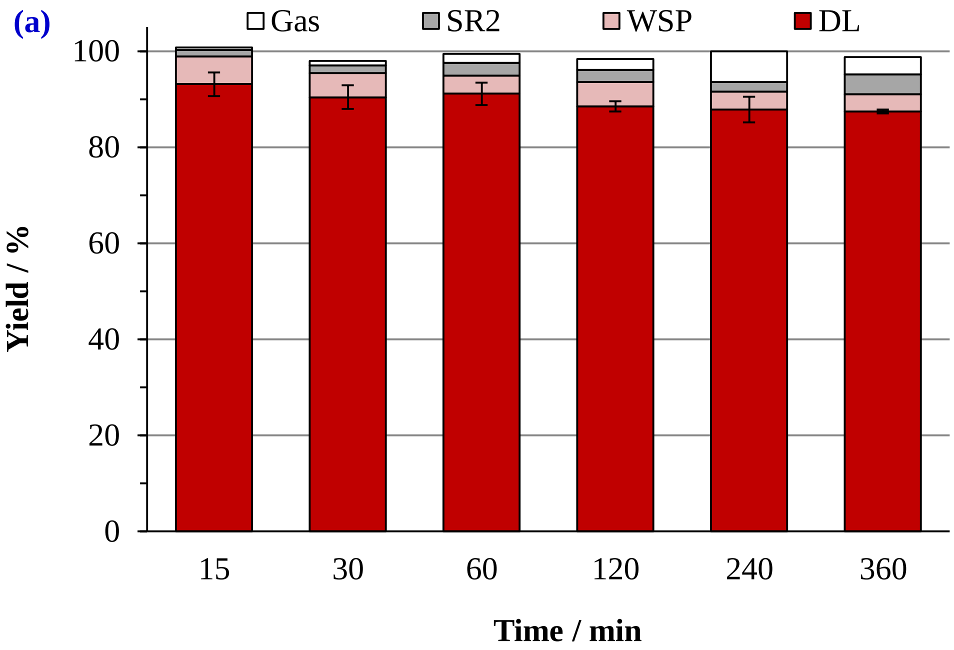


Figure 6-1. Effects of ethanol concentration on the yields of DL, WSP, SR_2 and Gas obtained at 300 ^{o}C for 4 hr in a 14 mL micro reactor.

6.4.2 Effects of reaction time

Batch experiments in two different mediums, i.e., 50/50 (v/v) water-ethanol and pure ethanol were carried out with the micro reactor at 300 ^{o}C for a reaction time ranging from 15 min to 360 min. The product yields from these two medium systems are displayed in Figure 6-2a and Figure 6-2b, respectively. As shown from the Figure, the yields and distributions of the degraded products were not significantly influenced by the reaction time, as similarly observed by Meier et al., (1992). For example, while the reaction time ranged from 15 min to 360 min, the yields of DL with the 50/50 (v/v) water-ethanol and pure ethanol solvent were within a narrow range of 90-95 wt% and 10-15 wt%, respectively. Comparing the average molecular weights and distribution of the DL products as given in Table 6-2, the reaction time between 1 hr and 2 hr appears to be optimal for both solvents. For a reaction time of 1 hr to 2 hr, the M_n of the obtained DL was in the range of 415-445 g/mol and 260-275 g/mol with the reaction medium of 50/50 (v/v) water-ethanol and pure ethanol, respectively. As such, the DL with pure ethanol (although with a lower yield) has a better quality than that with 50/50 (v/v) water-ethanol, in terms of molecular weights (M_n and M_w). A longer reaction time could lead to the formation of larger-molecular-weights components in DL due to re-condensation or cross-linking reactions between alcoholic groups and phenol rings of the lignin degradation intermediates (Yuan et al., 2010; Li and Kiran, 1988). It should however be noted that the GPC results reported in Table 6-2 were obtained with the THF-soluble fraction of the DL. While the DL products from the treatment in pure ethanol are completely soluble in THF, the DL from the treatment in 50/50 (v/v) water-ethanol solvent is partially soluble in THF (~30 % solubility for the DL obtained at 300 °C for 2 hr).



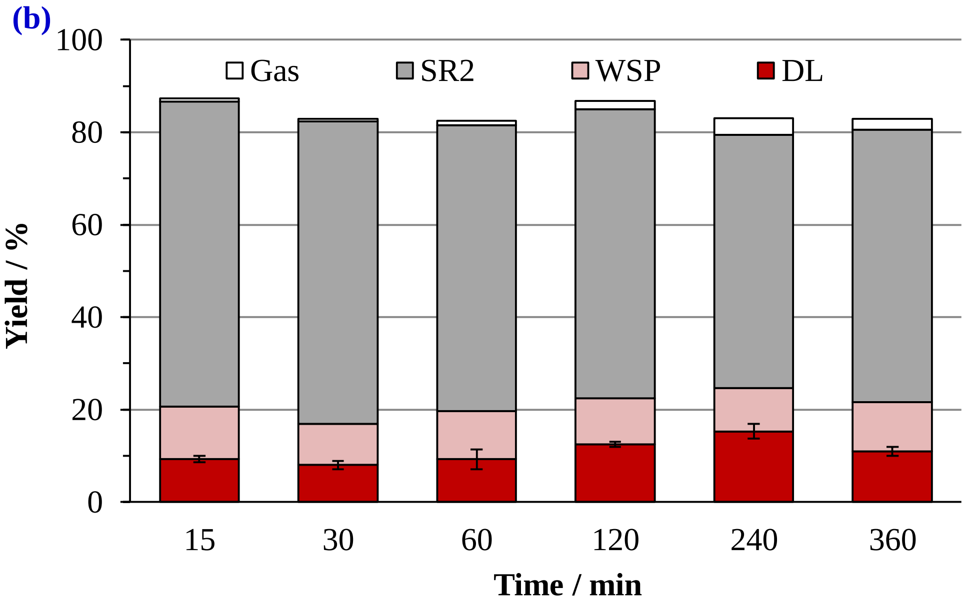


Figure 6-2. Effects of reaction time on yields and distribution of the lignin degradation products in 50/50 (v/v) water-ethanol (a) and in pure ethanol (b) at 300 °C in a 14 mL micro reactor.

Table 6-2. GPC results of DL (the THF soluble fraction) obtained at 300 °C for different reaction times.

Time / min	DL with 50/50 (v/v) water-ethanol			DL with pure ethanol		
	M_n	M_w	PD[1]	M_n	M_w	PD
15	ND[2]	ND	-	272	575	2.04
30	ND	ND	-	240	486	2.03
60	445	974	2.19	275	640	2.32
120	415	1010	1.95	260	631	2.43
240	566	1453	2.57	344	821	2.39
360	521	1199	2.30	303	800	2.64

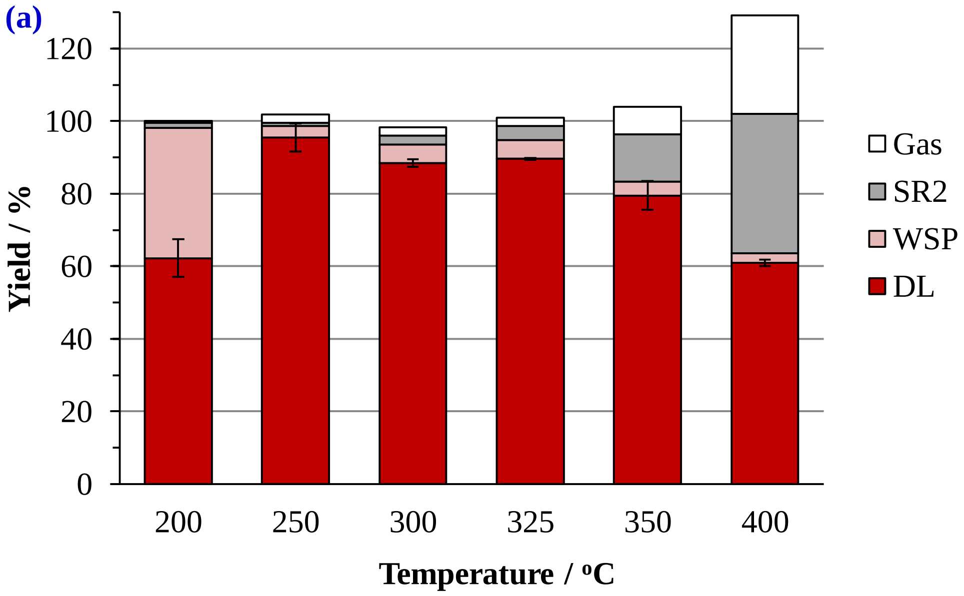
[1] Polydispersity (= M_w/M_n); [2] ND: Not detectable.

6.4.3 Effects of reaction temperature

The effects of reaction temperature on the yields of DL, WSP, SR_2 and gas products in 50/50 (v/v) water-ethanol and pure ethanol are displayed in Figures 3a and 3b, respectively. The average molecular weights and distribution of the DL products obtained at various temperatures with two different reaction medias are listed in Table 6-3.

When 50/50 (v/v) water-ethanol was used, as shown in Figure 6-3a, a lower reaction temperature (200 ^oC) produced a lower yield of DL (62 wt%) but a very high yield of WSP (36 wt%). As the reaction temperature increased to 250 ^oC, a very high DL yield (96 wt%) was obtained likely due to the fact that de-polymerization reactions are endothermic, thermodynamically favorable at a higher temperature. The DL yield seemed to level off at 250 ^oC, and it decreased if further increasing the reaction temperature to above 325 ^oC. For example, the DL yield dropped to 61 wt% at 400 ^oC, accompanied by a high yield of SR_2 (~40 wt%) indicating greatly enhanced condensation reactions to form char at a high temperature, as commonly observed in hydrothermal liquefaction of biomass (Cheng et al., 2010). The lignin hydrothermal degradation process in water-ethanol in the presence of hydrogen also involves hydrolysis and hydrogenolysis reactions that cause cleavage of the ether linkages (α-*O*-4, 5-O-4, β-*O*-4) of lignin to form monomeric or dimeric or oligomeric phenolic intermediates with reactive sites and alcohol side chains. As the reaction temperature increases, the reactive intermediates could be prone to condensation resulting in carbon-carbon linkages to form char. Table 6-3 displays the molecular weights and distribution of the DL products obtained at various temperatures. Taking into account both DL yield and molecular weights, 300 ^oC to 325 ^oC appears to be the optimal temperature for the lignin degradation in 50/50 (v/v) water-ethanol. For example, at 325 ^oC, the yield of DL (M_n: 510 g/mol and M_w: 1101 g/mol) was as high as ~90 wt%. In contrast, although the DL yield was the highest at 250 ^oC, the DL was almost THF insoluble. It is also worth mentioning that at 400 ^oC a large yield (> 20 wt%) of gas product was observed (Figure 6-3a), containing mainly of CO_2, C_2H_6, C_3H_8, C_2H_4, C_3H_6 (69.1, 17.3, 7.6, 4.2 and 1.5 vol%, respectively) which were likely derived from ethanol in the solvent and from the lignin side chains via decomposition and gasification reactions.

As shown in Figure 6-3b, degradation of AL in pure ethanol produced char (SR_2) as the dominating product. The overall yield of DL generally increased with increasing the reaction temperature up to 400 ^{o}C (40 wt%) then it slightly leveled off at 450 ^{o}C thereafter. All yields of DL were markedly lower than those in the 50/50 (v/v) water-ethanol medium, which could be due to the low solubility of lignin in pure ethanol. In general, the yield of WSP was around 10 wt% in pure ethanol at all temperatures. As shown in Table 6-3, the molecular weights of DL monotonically decreased with increasing temperature at 250 ^{o}C to 450 ^{o}C. The value of M_n and M_w for the DL (100 % soluble in THF) at 450 ^{o}C were as low as only 166 g/mol and 291 g/mol, respectively. The above results suggest that the degradation process in pure ethanol is favorable at a higher temperature. Figure 6-3b also clearly presents that the gas yield in pure ethanol was much larger, particularly at a temperature higher than 400 ^{o}C. For example, the gas yield increased drastically from ~50 wt% at 400 ^{o}C to ~200 wt% at 450 ^{o}C. The gas at 450 ^{o}C was mainly composed of CO_2, C_2H_6, C_3H_6, C_3H_8 and C_2H_4 (52, 36, 6, 4, and 3 vol%, respectively), implying decomposition/gasification of the ethanol solvent.



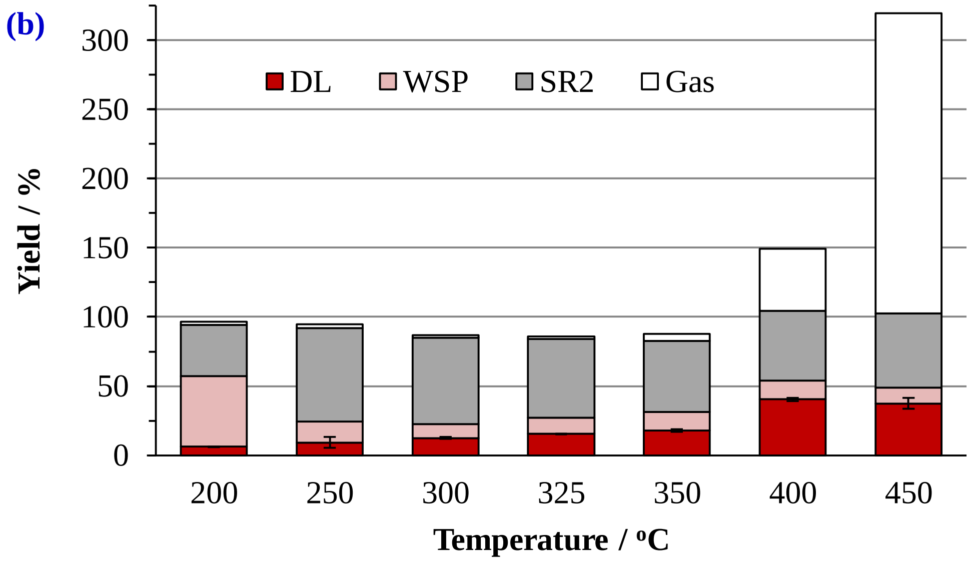


Figure 6-3. Effects of reaction temperature on the yields of DL, WSP, SR_2 and gas products obtained in 50/50 (v/v) water-ethanol (a) and in pure ethanol (b) for 2 hr.

Table 6-3. GPC results of DLs (the THF soluble fraction) obtained at different reaction temperatures for 2 hr.

Temp. / °C	DL with 50/50 (v/v) water-ethanol				DL with pure ethanol			
	M_n	M_w	PD[1]	Solubility in THF / %	M_n	M_w	PD[1]	Solubility in THF / %
200	ND[2]	ND	ND	0	276	597	2.17	~80
250	ND	ND	ND	0	334	740	2.22	~85
300	415	1010	1.95	~30	260	631	2.43	100
325	510	1101	2.16	~30	286	667	2.33	100
350	434	949	2.19	~95	278	683	2.49	100
400	260	530	2.04	100	230	468	2.03	100
450	-	-	-	-	166	291	1.75	100

[1] PD: Polydispersity (= M_w/M_n); [2] ND: not detectable.

It may be concluded from the above results that reaction temperature can drastically influence the products yield and distribution, as well as the molecular weights of the DL products. Taking into account both the yield and quality of the DL product, 300 ^{o}C to 325 ^{o}C and 400 ^{o}C appears to be the optimal temperature for the lignin degradation process in the medium of 50/50 (v/v) water-ethanol and pure ethanol, respectively.

6.4.4 Effects of catalyst

Table 6-4 shows yields of DL, SR_2, and Gas products obtained from catalytic degradation of AL with various heterogeneous catalysts in 50/50 (v/v) water-ethanol at 300 °C for 2 hr, and the GPC results of the DL products (THF-soluble fraction). As presented in Table 6-4, the degradation without catalyst produced 88.5 % yield of DL and 2.5 % yield of solid residue. Compared with the treatment without catalyst, the following three conclusions could be drawn from the results as listed in Table 6-4: (1) The metallic catalysts did not have a significant effect on the product yields, which might be due to the fact that the DL yields with and without catalyst are close to the upper limit for the AL that contains ~10 wt% ash. The presence of alumina-supported Ni/Ru catalysts even decreased the DL yield (from 89 % to < 70 %) and produced more SR_2 (the solid residue yield was up from 3 % to 22 %); (2) The treatment with catalyst of Ru10/AC or Ni10/AC yielded slightly higher or comparable DL when comparing with the treatment without catalyst. (3) The application of catalysts in lignin degradation generally lowered the molecular weights and improved the DL products' solubility in THF, particularly in the treatment with 50/50 (v/v) water-ethanol. For instance, the THF solubility of the DL products obtained with the catalyst of Ni10/Al_2O_3 or Ru10/Al_2O_3 increased to 70-90 %.

Table 6-4. Product yields from AL degradation at 300 °C for 2 hr in 50/50 (v/v) water-ethanol at with and without catalyst, and GPC results of the DL products (the THF soluble fraction).

Catalyst	Yield/%			GPC results of DLs			
	DL	[1]SR_2	Gas	M_n g/mol	M_w g/mol	[2]PD	[3]Solubility in THF/%

None	88.5 (±1.0)	2.5 (± 0.4)	2.3 (±0.4)	415	1010	1.95	~ 30
Ni10/Al_2O_3	62.5 (±0.9)	22.6 (±3.0)	3.5 (±0.1)	318	739	2.33	~ 70
Ru10/Al_2O_3	66.3 (±0.4)	22.1 (±0.6)	1.1 (±0.3)	370	869	2.35	~ 90
Pt10/AC	77.1 (±4.4)	12.2 (±3.2)	2.7 (±0.3)	418	944	2.26	~ 70
Ru10/AC	89.4 (±1.9)	6.1 (±1.6)	3.9 (±0.9)	396	927	2.34	~ 70
Ni10/AC	84.1 (±5.7)	8.8 (±1.3)	1.5 (±0.5)	356	846	2.38	~ 70

[1] SR_1=SR_2 for all the catalytic runs. There was no WSP detected in SR_1; [2] PD: Polydispersity; [3]By vision.

Table 6-5 presents product yields from AL degradation in pure ethanol at 300 °C with and without catalyst for 2 hr, and GPC results of the DL products (the THF soluble fraction). The treatment of lignin in pure ethanol with or without a catalyst produced oily DL products with low molecular weights ($M_n < 300$ g/mol) and 100 % solubility in THF, while the DL yield was low (10-15 %) and a very high yield of solid residue (66-82 %). While the effects of various catalysts on the DL yield varied, the use of a catalyst generally led to a decrease in the molecular weights (M_n and M_w). As also clearly shown in Table 6-5, in pure ethanol the AC-supported catalysts are more active than the alumina-supported counterparts for degradation of AL. Some possible reasons may be discussed as follows. (1) The AC-supported catalysts have a much higher surface area and porosity than the Al_2O_3-supported catalysts, which might account for their higher activity in the lignin degradation process. For instance, the Ni10/AC has a BET surface area of 777 m^2/g and a total pore volume of 0.5 cm^3/g, while the Ru10/Al_2O_3 has a BET surface area of 66 m^2/g and a total pore volume of 0.3 cm^3/g. Wildschut and the co-authors (Meier et al., 1992) found the carbon support performed much better than alumina in hydrotreatment of pyrolysis-oil, which was believed to be due to the higher specific surface area of active carbon than that of Al_2O_3; (2) The alumina-supported catalysts were known to be susceptible to attack of acidic water at elevated temperature to form a boehmite phase via the re-crystallization of the Al_2O_3. The re-crystallization reaction could cause deactivation of the Al_2O_3 supported catalysts (Wildschut et al., 2009; Laurent E and Delmon, 1994; 1993).

Table 6-5. Product yields from AL degradation in pure ethanol at 300 °C for 2 h with and without catalyst, and GPC results of the DL products (the THF soluble fraction).

Catalyst	Yield/%			GPC results of DLs			
	DL	[1]SR_2	Gas	M_n g/mol	M_w g/mol	PD[2]	Solubility[3] in THF/%
None	12.5 (±0.6)	62.6 (± 0.35)	1.9 (±0.3)	260	631	2.43	100
Ni10/Al_2O_3	10.4 (±0.7)	68.9 (±0.8)	0.7 (±0.1)	221	515	2.33	100
Ru10/Al_2O_3[4]	10.1	81.7	0.7	204	466	2.29	100
Pt10/AC	14.8 (±0.9)	66.2 (±0.8)	1.2 (±0.1)	203	448	2.21	100

[1] SR_1=SR_2 for all the catalytic runs. There was no WSP detected in SR_1; [2] PD: Polydispersity; [3] By vision. [4] Duplicate runs were not operated.

6.4.5 Characterizations of DLs

GC-MS analysis

The GC-MS spectra for DL products obtained with and without catalysts at 300 ^{o}C, particular in the 50/50 (v/v) water-ethanol co-solvent, had very few compounds detectable. This implies that the de-polymerized product at a relatively lower temperature was composed mostly of large molecules with a high boiling-point, as evidenced by the GPC results presented in Table 6-3. The GC-MS spectra of two typical DL products obtained at 400 ^{o}C for 2 hr in pure ethanol and 50/50 (v/v) water-ethanol are displayed in Figure 6-4a and Figure 6-4b, respectively. The detected compounds and their relative area % for the major compounds are summarized in Table 6-6. The relative area % for each compound was defined by the percentage of the chromatographic area of the specific compound out of the total area of 50 largest identified peaks. It should be pointed out that the area % value presented here shows only the relative concentration of the specific compound among the volatile fraction of the DL that could pass through the GC column. As shown in Table 6-6, only monomers and a few dimers were detectable in both DLs. Oligomeric products were not detected due to their low-volatility. The compositions of the DLs are significantly different: The DL from the treatment with pure ethanol (Figure 6-4a) is rich in esters (total relative area percentage of ~44 %), phenolic derivatives (total relative area percentage of ~19 %), and alcohols (total relative area percentage of ~10 %). The detected esters mainly consist of ethyl esters with carboxylic acids (C_6 - C_{10}), e.g. hexanoic acid, 2-ethyl-hexanoic acid, nonanoic acid, octanoic acid, and decanoic acid. The esters might be generated by esterification between ethanol and some lignin-derived intermediates, as similarly observed by Tang et al. (2010) in catalytic hydrocracking of pyrolytic lignin to liquid fuel in supercritical ethanol. The subsequent major groups were monomeric phenolic compounds and derivatives including phenolic groups with short-chain alkane substitutes such as –methyl, –ethyl, –methylethyl, and propyl groups, which can be ascribed to the cleavage of C_α/C_β, or C_β/C_γ, or reductive cleavage of *α-O*-4 and *β-O*-4 linkages of AL in supercritical ethanol at a high temperature. It is noted that no guaiacol or syringl units were detected, which might be a result of reductive cleavage of methoxyl groups. The alcohols and furanone, such as 1-octanol, 1-dectanol and, dihydro-4,5-dimethyl-(3H)-furanone, could be generated by both of the cleavage of ether linkages and the lignin side chains.

However, in the DL from the treatment with 50/50 (v/v) water-ethanol, as shown in Figure 6-4b and Table 6-6, the major identified compounds are almost exclusively monomeric phenolic and derivatives compounds (total relative area percentage of ~65 %) with alkyl substituents mainly –methyl, –ethyl, and –methylethyl groups, and a few propyl and butyl groups. Typical compounds are 2-ethyl-5-propyl-phenol, diethyl-phenol, 2-ethyl-6-methylphenol, 2,6-bis(1-methylethyl)-phenol, and 1-isopropyl-2-methoxy-4-methylbenzen. Only a small amount of methoxy groups were detected, which implies reduction of methoxy groups at a high temperature under hydrogen (reducing) atmosphere. The small amount of the oxygen-containing compounds in the DL products may suggest that the obtained DL could be a good feedstock for biofuels. Acid compounds were detected at a significant content (total relative area percentage of 9.4 %) in the DL from the treatment with 50/50 (v/v) water-ethanol, possibly resulted from hydrolysis of the ester linkages of AL, as observed previously by Cheng et al. (2008).

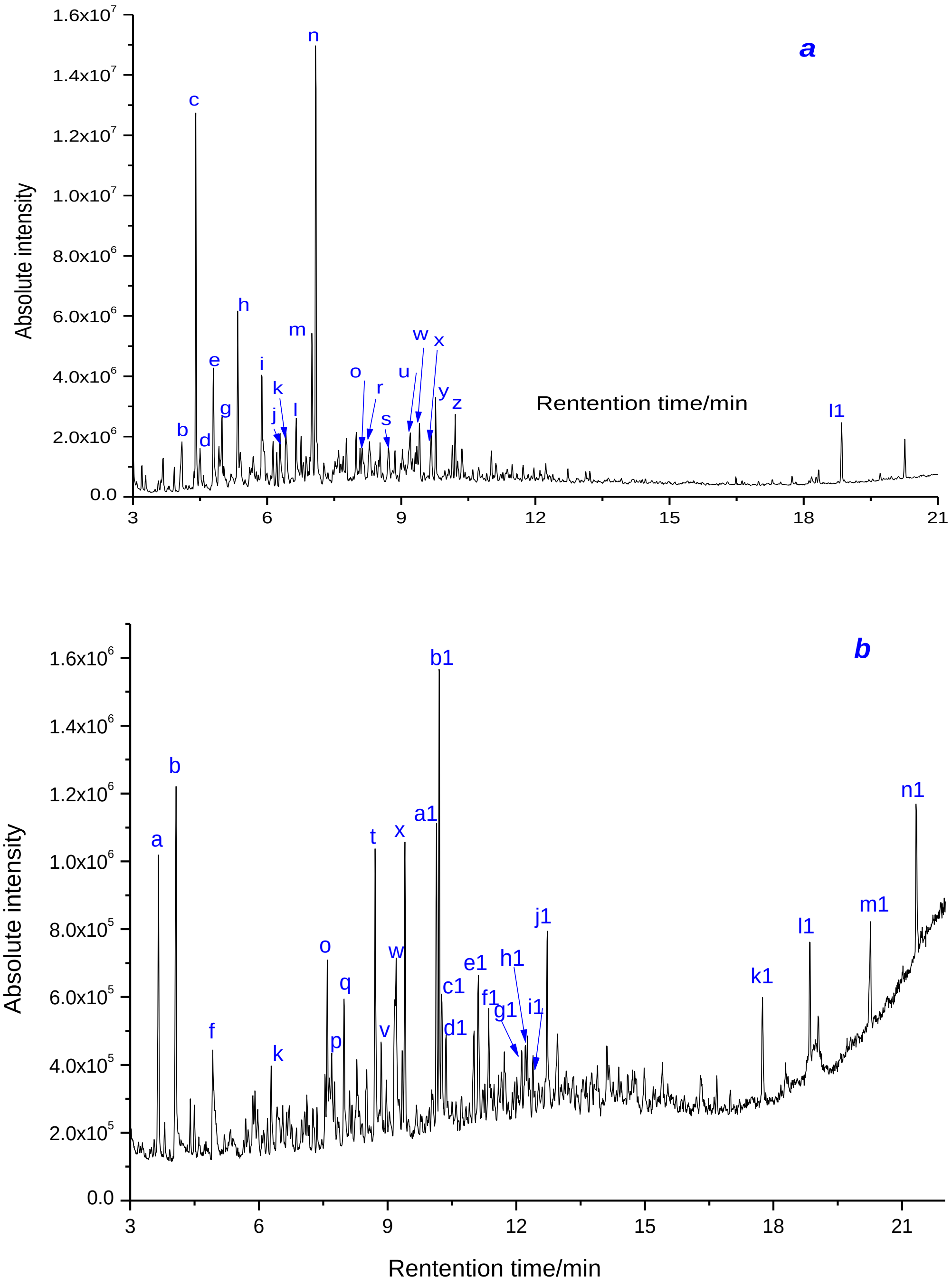


Figure 6-4. Typical GC–MS chromatograms of the DL products obtained at 400 ^{o}C for 2 hr using the 75 mL Parr High-Pressure reactor in pure ethanol (a) and 50/50 (v/v) water-ethanol (b).

Table 6-6. GC-MS detectable compounds in the DL products.

NO.	Ret. Time /min	Relative composition by area % [1]		Compound name
		50/50 (v/v) water-ethanol	pure ethanol	
a	3.660	4.10	-[2]	pentanoic acid, 3-methyl-
b	4.067	5.30	2.10	hexanoic acid
c	4.405	-	9.74	hexanoic acid, ethyl ester
d	4.501	-	1.56	2 (3H)-, dihydro- 4,5-dimethyl-furanone
e	4.798	-	3.54	1-hexanol, 2-ethyl-
f	4.925	3.13	-	benzenemethanol
g	4.989	-	2.30	2-hexensaeure, ethyl ester
h	5.343	-	4.55	1-octanol
i	5.879	-	5.98	hexanoic acid, 2-ethyl-, ethyl ester
j	6.288	-	2.40	phenol, 2,6-dimethyl-
k	6.426	1.87	2.78	benzenemethanol, 2-methyl-
l	6.649	-	3.34	nonanoic acid, ethyl ester
m	7.002	-	5.79	hexanoic acid, butyl ester
n	7.086	-	13.07	octanoic acid, ethyl ester
o	7.596	2.78	-	phenol, 3-ethyl-5-methyl-
p	7.700	1.67	-	phenol, 2-ethyl-5-methyl-
q	7.986	2.50	-	2-ethyl-6-methylphenol
r	8.127	-	1.63	1-decanol
s	8.289	-	2.19	phenol, 2-methyl-5-(1-methylethyl)
t	8.710	4.57	-	phenol, diethyl-
u	8.714	-	1.77	2-ethyl-4,5-dimethylphenol
v	8.854	1.78	-	phenol, 2,3,5,6-tetramethyl
w	9.200	6.68	4.11	phenol, 2-ethyl-5-propyl-
x	9.409	3.6	1.90	2-methoxy-4-(1-methylethyl) toluene
y	9.673	-	1.83	butyl octanoate
z	9.768	-	2.06	decanoic acid, ethyl ester
a1	10.142	3.86	-	1-isopropyl-2-methoxy-4-methylbenzene
b1	10.204	5.71	1.61	phenol, 2,6-bis(1-methylethyl)-
c1	10.261	4.39	-	1,3-cyclohexadiene, 1,3,5,5,6,6-hexamethyl
d1	11.014	1.54	-	2-tert-butyl-1-methoxy-4-methylbenzene
e1	11.115	2.63	-	phenol, 3,5-bis(1-methylethyl)-
f1	11.358	2.16	-	2-methoxy-4-ethyl-6-methylphenol
g1	12.128	1.51	-	benzene, 1,2,4-triethyl-5-methyl

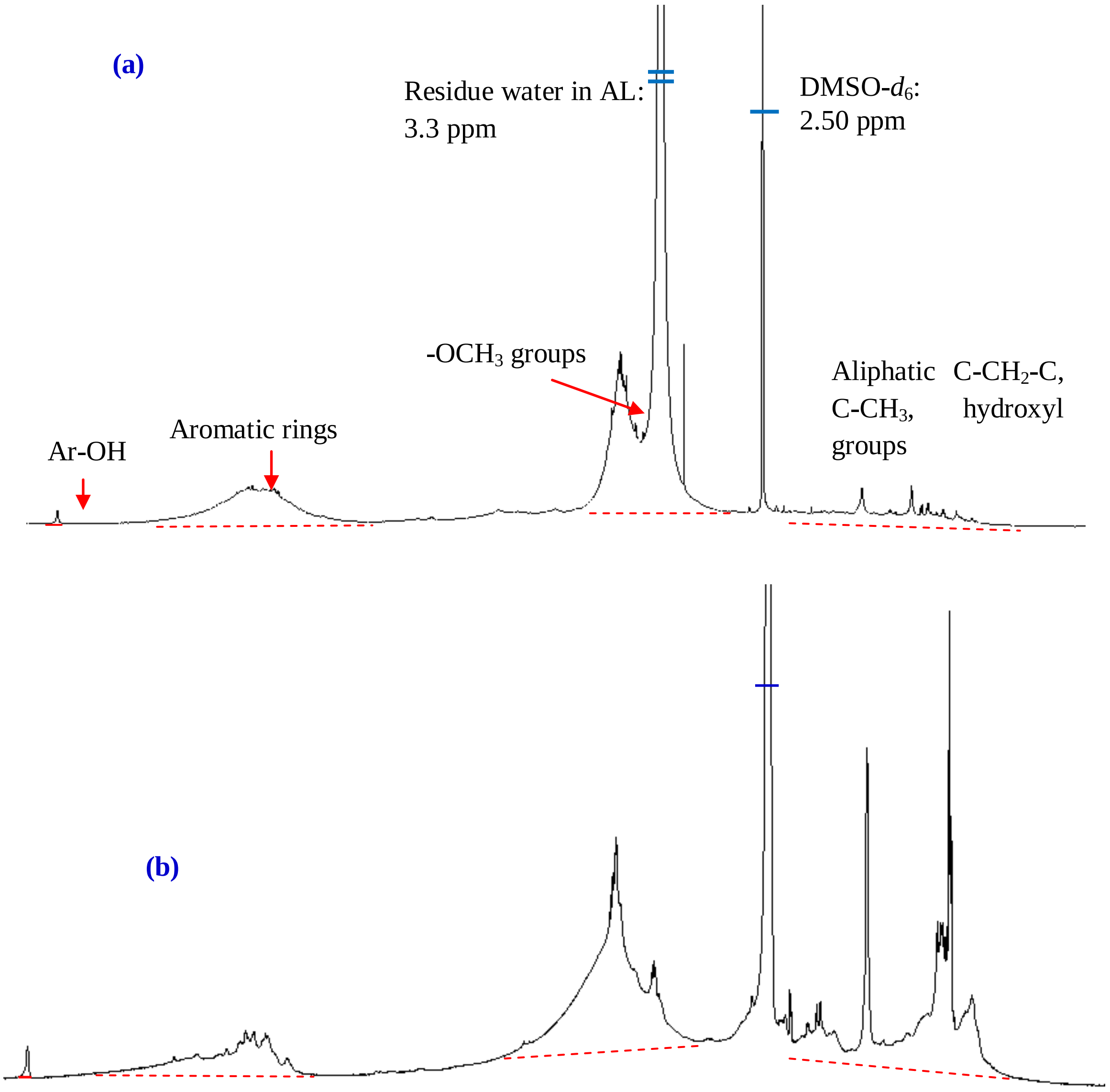
h1	12.213	1.57	-	3,4,5,6-tetraethyl-2h-pyran-2-one
i1	12.722	3.50	-	benzene, 1,4-dimethoxy-2,3,5,6-tetramethyl-
g1	12.962	1.93	-	benzene, 1,3,5-tris(1-methylethyl)-
k1	17.741	1.65	-	1,1,3,3-tetramethyl-5,6-benz-2-indanone
l1	18.846	1.64	1.79	phenanthrene, 2,4,5,7-tetramethyl-
m1	20.260	1.87	-	dehydroabietic acid
n1	21.328	2.38	-	1,2-benzendicarboxylic acid, dioctyl ester
Total area/%		74.32	76.04	-

[1] Total area was obtained based on the integration of 50 major peaks, without including the small peaks with an area % < 1.5%; [2]Not detectable.

From the above results it may be concluded that a large amount of monomeric phenolic compounds with C_1-C_4 short alky substituents are presented in the DL products from AL degradation in 50/50 (v/v) water-ethanol. However, a large amount of ether compounds were produced in pure ethanol.

^{1}H NMR analysis of DL

^{1}H NMR spectra for the original AL and the DL products obtained at 300 ^{o}C in 50/50 (v/v) water-ethanol for 2 hr without and with Ni10/AC catalyst are comparatively shown in Figure 6-5a, 6-5b and 6-5c, respectively. Broad peaks were observed in the AL's ^{1}H NMR spectrum of (Figure 6-5a), typical of the protons of high molecular weight polymers with long relaxation times (Yuan et al., 2010). Compared with that of AL, the ^{1}H NMR spectra of both DLs obtained without and with Ni10/AC show more sharper signals, as displayed in Figure 6-5b and Figure 6-5c, respectively. This suggests that the hydrothermal treatment had a significant effect on modifying the lignin structure. The most distinct difference between the ^{1}H NMR spectrum of a DL and that of the original lignin was the significantly strengthened signals at 0.8-2.5 ppm. Furthermore, the relative larger peak at 8.5 ppm in DLs was also found. It indicated the hydrolysis or hydrogenolytic cleavage of aryl-O-aryl and aryl-O-aliphatic linkages occurred. The two DL products showed similar DL structure. The difference was that the peaks at 1.0 and 1.8 ppm, which were the characteristic peaks of methylene (Duan and Savage, 2011) and aliphatic hydroxyl group, respectively were relatively stronger in DL without catalyst (Figure 6-5b) than that in DL with catalyst (Figure 6-5c), particularly the peak at 1.0 ppm. This indicates that the solvent of 50/50 (v/v) water-ethanol was more effective for the hydrogenolytic cleavage than the catalyst. However, DL with catalyst showed relative stronger signals of phenolic hydroxyl at 8.5 ppm and signals of aliphatic hydroxyl at 2.3 ppm. The result suggests that the hydrolysis cleavage of aryl-O-aryl and aryl-O-aliphatic linkages was more prone to take place with the catalyst.



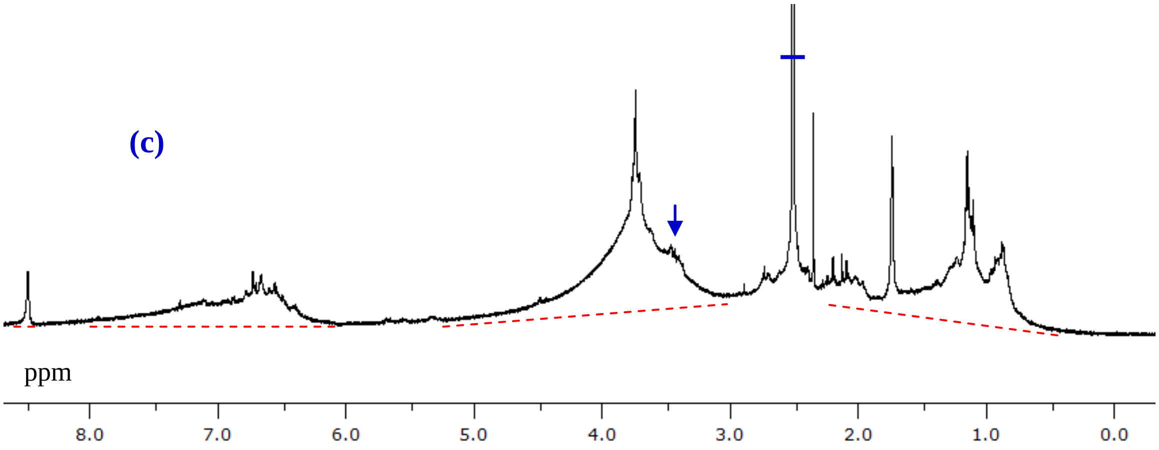


Figure 6-5. ^{1}H NMR spectra of the original AL (a) and the DL obtained at 300 ^{o}C in 50/50 (v/v) water-ethanol for 2 hr without (b) and with Ni10/AC catalyst (c). The big peak at 2.5 ppm and 3.3 ppm is derived from the solvent and residual moisture in the AL, respectively.

6.4.6 Alkali lignin degradation mechanism in sub-/super-critical water-ethanol

Lignin is an aromatic polymer comprised of three phenyl-propanols i.e., p-hydroxyl-phenyl propanol, guaiacyl-propanol and syringyl-propanol, connected both by carbon-carbon linkages and ether linkages. Ether bonds (α-O-4, β-O-4, and 5-O-4) (60-62 % in spruce, and 74.5-76.5 % in birch) are the major bonds in which the β-O-4 bond (50 % in spruce, and 62 % in birch) is the most abundant ether bond (Alder, 1977). Lots of studies (Minami et al., 2003; Yuan et al., 2010; Tang et al., 2010; Cheng et al., 2008) on lignin/lignin-model compounds have shown that the β-O-4 bond is readily to break at temperature from 200 ^{o}C to 300 ^{o}C in different solvents. The aryl-aryl ether bonds, however, are more stable which can only be cleaved when an appropriate catalyst was added at a higher temperature (e.g., 400 ^{o}C) (Robert, 2008). Furthermore, the cleavage of carbon-carbon bonds needs severer condition. The possible hydrothermal degradation mechanisms for lignin in sub-/super-critical water-ethanol may be proposed and illustrated in Figure 6-6. Under sub-/super-critical water-ethanol, hydrogenolysis and hydrolysis occurred at ether bonds to form aryl hydroxyl groups and alcohol hydroxyl groups and alkyl groups. A fraction of degraded products/intermediates will undergo further hydrocracking to form low-molecular-weight products, such as monophenols, benzen and alcohols as shown in Table 6-6. Simultaneously, addition and condensation reactions among the degraded products/intermediates may take place to form oligomers, char and coke. The addition and condensation reactions of the highly reactive lignin degradation intermediates would explain that the yield of SR increased at a higher temperature than 325 ^{o}C in 50/50 (v/v) water-ethanol.

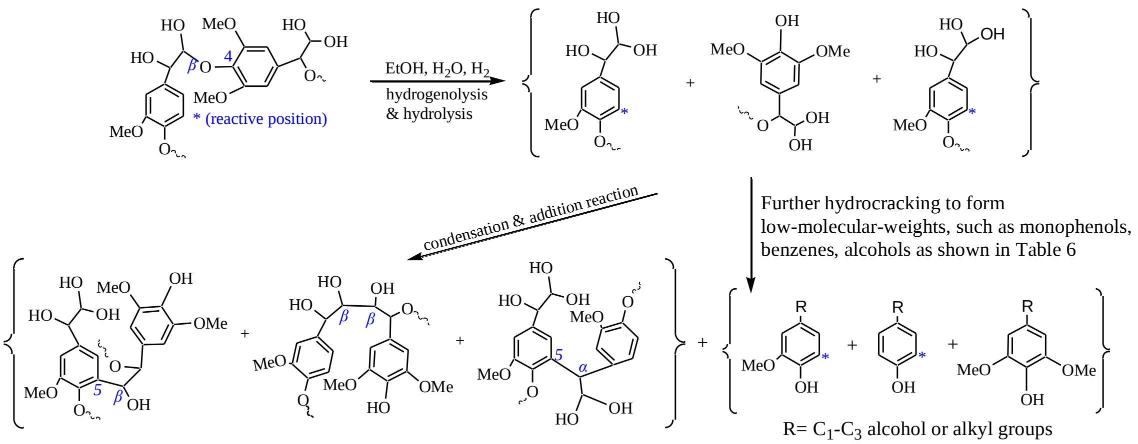


Figure 6-6. Possible lignin hydrothermal degradation mechanism in 50/50 (v/v) water-ethanol co-solvent under hydrogen.

6.5 Conclusions

(1) Hydrothermal degradation of an alkali lignin was achieved in sub-/super-critical ethanol-water or pure ethanol with and without catalyst. The 50/50 (v/v) water-ethanol co-solvent was proven to be the most effective solvent for degradation of the lignin in terms of the yield of degraded lignin (DL). The treatment at 300 ^{o}C for 2 hr led to a yield of DL at 89 %. The molecular weights of the lignin were markedly reduced from its original M_w and M_n of 60,000 g/mol and 10,000 g/mol, respectively to M_n of 415 g/mol and M_w of 1010 g/mol for the DL. Compared with that in 50/50 (v/v) water-ethanol, treatment in pure ethanol led to a much lower yield of DL (< 15 %) with smaller molecular weights (M_n 260 g/mol and M_w 631 g/mol from 300 ^{o}C treatment). Moreover, the DLs from pure ethanol treatment are completely soluble in

THF, compared with only ~30% THF-solubility for the DL from 50/50 (v/v) water-ethanol treatment.

(2) The reaction time had negligible effects on the DL yields and properties, while reaction temperature drastically influenced the product yields and properties: 300 °C to 325 °C and 400 °C appeared to be the optimal temperature for the process with 50/50 (v/v) water-ethanol and pure ethanol, respectively.

(3) Al_2O_3 supported Ni or Ru catalyst slightly reduced the DL yields and increased the solid residue yield in both 50/50 (v/v) water-ethanol and pure ethanol, while active carbon (AC)-supported catalysts could slightly increase the DL yields and lead to a decrease in molecular weights of the DL products.

(4) The DL products obtained at a high temperature in 50/50 (v/v) water-ethanol contain a great amount of monomeric phenolic compounds with short-alkyl substituents ranging from C_1-C_4, while the DLs produced with pure ethanol are rich in esters.

6.6 Acknowledgements

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CHAPTER 7. PRODUCTION OF GREEN PHENOLIC RESINS AND ADHESIVES USING BIO-PHENOLIC COMPOUNDS FROM LIGNIN/FORESTRY RESIDUALS AS A SUBSTITUTE FOR PHENOL AT A HIGH SUBSTITUTION RATIO

7.1 Abstract

The objective of this study is to produce green phenolic resins and adhesives using bio-phenolic compounds from lignin/forestry residuals. To produce bio-phenolic compounds, an organosolv lignin (OL) was catalytically degraded in 50/50 (v/v) water-ethanol and pure ethanol media under sub-/super-critical condition in hydrogen atmosphere. Effects of lignin degradation process conditions (catalyst, temperature, type of reactor, etc.) on the yields and properties (molecular weights) of the degraded lignin (DL) products were examined in this study. The DL products were used to substitute for phenol for the synthesis of bio-phenol formaldehyde resins, denoted as degraded lignin phenol-formaldehyde (DLPF) resins, whose properties (such as viscosity, non-volatile contents, storage time, free formaldehyde contents, curing behavior, and thermal stability.) were compared with pure phenol formaldehyde (PF) resin and organosolv lignin phenol-formaldehyde (OLPF) resins. The plywood samples glued with the OLPF and DLPF adhesives with a phenol replacement ratio up to 75 wt% showed higher dry and wet tensile strengths than that of PF resin. Although the OLPF adhesives have better bond strengths and thermal stability than DLPF adhesives, the DLPFs have lower free formaldehyde content and can be cured at a lower temperature.

7.2 Introduction

Lignin has been successfully used to directly replace petroleum-based phenol in phenol formaldehyde (PF) resin synthesis, while the replacement ratio is generally less than 30-50 % due to its fewer reactive sites and steric hindrance effects resulting from its complex chemical structure (Cetin and Ozmen, 2002; Alonso et al., 2004). Thus, a high level of phenol replacement may be achieved by chemical or biological modification/degradation of lignin to enhance its reactivity. Thermochemical processes were demonstrated to be effective for lignin degradation, e.g., pyrolysis (Jegers and Klein, 1985; Petrocelli and Klein, 1984), hydrocracking/hydrogenolysis (Windt et al., 2009; Kleinert and Barth, 2008), hydrolysis (Benigni and Goldstein, 1971; Fang et al., 2008) and oxidation reactions (Crestini and Caponi, 2006; Hofrichter, 2002). However, pyrolysis oils were found to be less effective in substitution of phenol for the PF resin synthesis. The substitution ratios were normally below 30-50 wt% (Roy et al., 2000; Zhang et al., 2006; Lee, 2003) in order to produce useful resins. Oxidative degradation of lignin in the presence of a catalyst such as a noble metal (Crestini and Caponi, 2006) or peroxide (Hofrichter, 2002) and an oxidant (H_2O_2) usually produce a significant amount of benzaldehydes, ketones, and benzoic acids, which can be perfumes and pharmaceutical intermediates, but these compounds are not suitable for the synthesis of PF resins.

Previous studies (Cheng et al., 2010; 2011; Yuan et al., 2010) in our group have demonstrated that hydrolysis or hydrocracking/hydrogenolysis of woody biomass or alkali lignin in sub-/super-critical water-ethanol is an effective thermo-chemical approach to degrade lignin into aromatic and phenolic chemicals from lignocellulosic biomass and lignin. A recent work yet to be published by our group showed that an alkali lignin (M_n: 10,000 g/mol, M_w: 60,000 g/mol) could be effectively de-polymerized into bio-phenol products (M_n: ~400 g/mol, M_w: ~1000 g/mol) at 300 ^{o}C to 350 °C in 50/50 (v/v) water-ethanol, producing a high yield (85-89 %) of degraded lignin (DL). Some metal catalysts such as Ru, Ni, and Pt supported on γ-Al_2O_3 or active carbon (AC) were effective in altering the process, not for increasing the DL yields but for lowering the molecular weights of the DL.

In this study, organosolv lignin (OL) extracted from pine sawdust via the organosolv de-ligninfication method was used as the precursor for bio-phenolic compounds through the hydrothermal degradation process, and Ru/γ-Al_2O_3 and Ni/AC were selected as catalysts for the process based on our previous work. Effects of catalytic hydrothermal degradation of OL were investigated in sub-/super-critical water-ethanol and pure ethanol media at > 300 ^{o}C in H_2 atmosphere. The degraded lignin (DL) products were used to replace phenol for the synthesis of bio-phenol formaldehyde resins with a high phenol substitution ratio of 50% and 75%. The chemical structures of the DL were characterized by gel permeation chromatography (GPC) and proton nuclear magnetic resonance (^1H NMR). The physical-chemical properties of the degraded lignin phenol-formaldehyde (DLPF) resins were comprehensively analyzed, e.g., non-volatile contents, viscosity, storage time, free formaldehyde level, thermal curing behavior, thermal stability, and plywood bond strength, in comparison with those of a pure PF resin and the organosolv lignin phenol-formaldehyde (OLPF) resins.

7.3 Materials and Methods

7.3.1 Materials and catalyst preparation

The OL was extracted from Eastern White Pine Sawdust using hot-compressed 50/50 (v/v) ethanol-water at 190 °C for 4 hr. The value of the number average molecular weight (M_n) and the weight average molecular weight (M_w) were 307 g/mol and 1157 g/mol, respectively. The OL sample was vacuum-dried overnight at room temperature before use. The proximate and ultimate analyses (on a dry basis) of the OL sample are: 39.3 % fixed carbon, 60.2 % volatile matter, and 0.5 % ash content; 67.6 % C, 6.1 % H and negligible N and S. ACS reagent grade solvents and chemicals were supplied by Fisher Scientific (unless otherwise specified) and were used as received, including ethanol, methanol, acetone and dimethyl sulfoxide-d_6 (DMSO-d_6), nickel nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$) (Sigma-Aldrich), ruthenium nitrosyl nitrate in dilute nitric acid ($HN_4O_{10}Ru$) (Sigma-Aldrich), γ–Al_2O_3 (Inframat Advanced Materials), phenol (99 %, J.T. Baker), sodium hydroxide solution (ca 50%, Ricca Chemical Company), and formaldehyde (ca 37 %, Anachemia). In the GPC analysis for DL products, HPLC grade solvent tetrahydrofuran (THF) containing 0.03 wt% stabilizer of 2, 6-di-*t*-butyl-4-methyl-phenol was used as an eluent.

Ni10/AC and Ru10/γ–Al_2O_3 were prepared by incipient wetness impregnation method using aqueous metal salt solutions of $Ni(NO_3)_2 \cdot 6H_2O$, and $HN_4O_{10}Ru$. γ-Al_2O_3 and a self-prepared AC were used as the catalyst-support materials. The AC was derived from pine wood sawdust (0.85-2mm particle size) activated using H_3PO_4 according to the procedure as detailed elsewhere (Zhang et al., 2011). The metal loading on each supported catalyst was fixed at 10 wt%. The γ-Al_2O_3-supported catalyst was calcined in air at 550 ^oC for 6.5 hr followed by 2 hr reduction in hydrogen at the same temperature. Similar calcinations and reduction procedures were adopted for the AC-supported catalyst, except that the carbon-based catalyst was calcined in N_2 at 550 ^oC for 6.5 h to prevent burn-out of the carbon material. All catalysts were then crushed and sieved to particles less than 300 μm for the experimental use in this study. The surface area, total pore volume and average pore diameter of the selected catalysts were examined by N_2 isothermal (at -196 ^oC) adsorption with a Quantachrome Nova 2200e Surface Area & Pore Size Analyzer (BET). The Ru10/γ–Al_2O_3 has a BET surface area of 66.3 m^2/g and a total pore volume of 0.3 cm^3/g with an average pore diameter of 9.5 nm (mesopores). The Ni10/AC has a BET surface area of 777 m^2/g and a total pore volume of 0.47 cm^3/g with an average pore diameter of 1.2 nm (micropores).

7.3.2 Catalytic hydrothermal treatment of lignin and product separation

The OL degradation was performed under hydrogen for 2 hr with and without catalyst at a temperature of 300 ^oC or 350 ^oC in 50/50 water-ethanol (v/v) or in pure ethanol. In a typical run, the ratio of lignin to solvent was fixed at 1:10 (w:v). In the tests with catalyst, The OL, the solvent and the catalyst (10 wt% of lignin) were charged into a 14 mL micro reactor which was then sonicated in an ultra-sonic bath for 20 min to ensure a uniform mixture. After being securely sealed, the reactor was purged with high-purity nitrogen for three times, and finally pressurized to 5.0 MPa with hydrogen. After a leak check, the reactor top was mounted on a mechanical shaker. Then the reactor was put into a preheated fluidized sand bath at 300 ^oC where the reactor was shaken at 100 rpm for 2 h before quenched in a cold-water bath. The micro-reactor can reach the specific reaction temperature rapidly within 1-2 min, so the reaction time was measured from the time when the reactor was put into the sand bath. During each run, the reaction pressure and temperature were recorded every 20 min. Due to the pressure limit of the 14 mL micro reactor (SS 316L), all tests at temperatures higher than 300 ^{o}C were operated in a 75 mL high-pressure Parr autoclave reactor. The 75 mL reactor is constructed of Hastelloy alloy, with maximum working pressure of 41 MPa at 600 ℃. The reactor was heated through an electric heater without shaking or stirring. The reaction time was measured from the time when the desired temperature was reached. Besides the two reactors mentioned above, an 1 L autoclave high-pressure autoclave reactor equipped with a stirrer and a cooling coil was also employed to investigate the effect of type of reactor (heating rate and stirring) on the OL degradation process operated at the same condition of 340 ^{o}C for 2 hr with Ni10/AC catalyst.

When the reactor was cooled to room temperature, the obtained gaseous product was collected into a pre-vacuumed 2800 mL gas cylinder. The cylinder's pressure was adjusted to 1 atm (abs) using high-purity nitrogen make-up gas. The gas composition (H_2, CO, CO_2, CH_4, and C_2-C_3) was analyzed using a Micro-GC equipped with a thermal conductivity detector (TCD) detector to obtain the yield of gaseous product. The degraded products in the reactor were completed rinsed with acetone and methanol. The obtained mixture was then filtered under reduced pressure through a pre-weighed Ahlstrom Glass microfiber filter (Particle retention in 1.1 um) to remove solid residue (SR). The obtained solid residue (SR) was oven dried at 105 ^{o}C overnight before weighing. Organic solvents (ethanol, acetone and methanol) in the filtrate were removed by a rotary evaporator under reduced pressure at 40 ^{o}C, and water was further removed at 60 ^{o}C. The remaining solid/oily product was vacuum dried at room temperature overnight to remove residue water before weighing and was defined as degraded lignin (DL, acetone-methanol soluble fraction). Yields of DL, SR, and gas were calculated by the weight percentage of the mass of each product to the mass of dry lignin sample added into reactor for each run. For simplicity, the rest by difference (100 wt% - DL - SR - gas) could be approximated as the water yield from the lignin due to the hydrogenolysis/dehydration reactions.

7.3.3 Synthesis of phenolic resole resins

Various OLPF and DLPF resole resins with two different phenol substitution ratios (50 % and 75 %) were synthesized. In a typical run for 50 % phenol substitution ratio, 14.0 g OL (or DL), 11.2 g water, 28 mL pure ethanol, and 5.6 g of 50 % sodium hydroxide solution were charged into a three-neck flask equipped with a pressure equilibrating addition funnel, thermometer, cooling condenser and a water bath with a magnetic stirrer. The mixture was heated to 50 ^{o}C and maintained for 1 hr to ensure a complete solution of OL in the solvent. The flask was then heated to 80 ^{o}C and 14.0 g phenol was added. The combined mixture, subsequently, was kept at 80 ^{o}C for 2 hr to ensure the uniformity of the mixture. The mixture was then cooled to 60 ^{o}C to 70 ^{o}C before adding 31.4 g formaldehyde (37 wt%, the molar ratio of F/(OL + phenol) of 1.3) due to exothermic reactions of formaldehyde and phenol/lignin, The reaction temperature was raised to 80 ^{o}C and maintained at the temperature for 2 hr. The mixture was then cooled to room temperature before collecting the resin product. In terms of the phenol substitute and substitution ratio, the obtained phenolic resole resins were denoted as 50% OLPF, 75% OLPF, 50% DLPF, and 75% DLPF, respectively. A reference sample using pure phenol, denoted as pure PF resin, was also prepared with the same procedure as described for the OLPFs and DLPFs.

7.3.4 Characterizations of the DL and the phenolic resole resins

The molecular weights of the DL products were measured with a Waters Breeze GPC (1525 binary High-performance liquid chromatography (HPLC) pump; UV detector at 270 nm; Waters Styragel HR1 column at 40 ^{o}C) using THF as the eluent at a flow rate of 1 mL/min, and polystyrene standards were used for the calibration. The OL and all DLs samples were completely soluble in THF. The chemical structure of DL products was analyzed on a 500 MHz ^{1}H NMR (Inova NMR instrument) at room temperature in DMSO-d_6.

The non-volatile contents of the phenolic resins were determined at 125 ^oC for 105 min in accordance with ASTM standard D4426-01(2006). Viscosity of all the resins was measured at 50 ^oC by Brookfield CAP 2000+ viscometer according to the standard of ASTM D1084-97. The storage time was simply obtained by observing the status of resins at 4 ^oC. The free formaldehyde levels in the resins were determined using a modified Walker's hydroxylamine hydrochloride method (Walker, 1975) as described briefly as follows. Approximately 2.0 g of resin sample were diluted with 25 mL of water, and pH was adjusted to 4.0 using 0.1 M HCl. Thirty milliliters of hydroxylamine hydrochloride (0.5 M, pH = 4.0) were added to the resin solution, and the mixture was stirred for 10 min. Free formaldehyde was determined by back titration to pH 4.0 using 0.1 M aqueous sodium hydroxide. The thermal curing properties of the resins were evaluated with a differential scanning calorimetry (DSC 1, Mettler-Toledo, Switzerland) under (50-60) mL/min N_2 at 10 ^oC/min between 40 ^oC and 250 ^oC in an aluminum crucible. The thermal stability of the non-volatile resin sample (~10 mg) was determined on a thermalgravimetric analysis (TGA) Instruments (TGA 1000i, Instrument Specialists Inc, USA) from 25 ^oC to 700 ^oC at a heating rate of 10 ^oC/min under 30 mL/min N_2.

All the synthesized phenolic resins were further evaluated as wood adhesives in a-three-layer plywood. The detailed procedure can be seen in the previous study (Cheng et al., 2011). Simply, the resin mixed with wheat flour (15 wt% of the resin) was applied uniformly to the inside surface of the two face veneers at a spread rate of 250 g/m^2 per single glueline. The face and center veneer were bonded in perpendicular directions to each other using a hot press at 140 ^oC under 2500 psi pressure for 4 min. After conditioning (to get 10~12 % MC) in a chamber, the plywood sheet was cut to prepare specimens for shear-stress test in accordance with ASTM D906-98 (2004). Dry tensile strength and wet tensile strength (test after boiling for 3h) of the specimens were measured with a bench-top Universal Testing Machine (Model H10K-T UTM, Tinus Olsen Material Testing Machine Company) at a loading rate of 10 mm/min. The percentage of wood failure in the bonding area for each specimen was assessed visually.

7.4 Results and Discussion

7.4.1 Effects of catalyst and temperature on OL degradation

The effects of catalysts (Ru10/γ-Al_2O_3 and Ni10/AC) on OL degradation at 300 ^{o}C were investigated in 50/50 (v/v) water-ethanol and pure ethanol, respectively. A higher temperature (350 ^{o}C) was also employed to explore the effect of temperature on OL degradation in 50/50 (v/v) water-ethanol. The results were listed in Table 7-1.

As shown in Table 7-1, at 300 ^{o}C, the treatment in pure ethanol without catalyst produced 56 % of DL, which was much lower than 80 % of DL obtained in 50/50 (v/v) water-ethanol at the same conditions. However, the DL from the treatment in pure ethanol has smaller molecular weights (M_n 233 g/mol, M_w 727 g/mol) than that obtained in 50/50 (v/v) water-ethanol at the same conditions (M_n: 395 g/mol, M_w: 1233 g/mol). On the other hand, the treatment in 50/50 (v/v) water-ethanol produced much less solid residue (char) than that in pure ethanol. Thus, the addition of water as a co-solvent into ethanol could improve the solvolytic/hydrolytic degradation of OL (which might account for the higher yield of DL), enhance the solubility of the DL that contains more hydroxyl group, and hence prevent the condensation reaction of de-polymerized products/intermediates to form char. Similar results were obtained in some previous studies (Cheng et al., 2010; Pasquini et al., 2005; Li and Kiran, 1988) for delignification and hydrothermal liquefaction of biomass in the medium of aqueous ethanol.

The effects of temperature on OL degradation are clearly shown in Table 7-1. In 50/50 (v/v) water-ethanol with or without catalyst, the yield of DL rapidly declined with increasing temperature from 300 ^{o}C to 350 ^{o}C, accompanied with an increase in char (Yuan et al., 2010; Tang et al., 2010) and gaseous products (Robert, 2008). At a lower temperature of 300 ^{o}C, the molecular weights of all the DL products were similar to those of the original OL sample. However, the values of M_n and M_w were significantly reduced to 151 g/mol and 271 g/mol at 350 ^{o}C without catalyst and to 270-290 g/mol, and 730-760 g/mol, suggesting that the hydrolysis and hydrogenolysis reactions were promoted at a higher temperature. These results are in a good agreement with the results from recent study on alkali lignin degradation at the similar conditions. Compared with the results without catalyst, the yields of DL were promoted by the catalysts, while the molecular weights of the DL were increased too. The two catalysts tested, Ru10/γ-Al_2O_3 and Ni10/AC, seemed to be similar in activity, producing DL at similar yields and with similar molecular weights. For both temperatures and both reaction media, the application of catalysts effectively inhibited the condensation of the intermediates to form char/coke.

Table 7-1. Yields of DL, SR and s and Gas products from OL with and without catalysts at a temperature of 300 or 350 °C, and GPC results of the DL products.

Catalyst	Temp. /°C	Solvent	Yields/%			GPC results of DL		
			DL	SR	Gas	M_n	M_w	PD[1]
None	300	Pure ethanol	55.6(±2.0)	35.4(±2.1)	1.4(±0.2)	233	727	3.11
Ru10/Al_2O_3			94.2(±1.3)	1.8(±0.4)	3.5(±0.4)	261	953	3.66
Ni10/AC			92.1	5.0	2.9	343	1064	3.1
None	300	50/50 (v/v) water-ethanol	80.1(±3.5)	11.3(±1.4)	2.0(±0.35)	395	1233	3.11
Ru10/Al_2O_3			92.1(±1.1)	0.8(±0.05)	2.0(±0.4)	468	1193	2.55
Ni10/AC			91.4	9.9	2.4	400	1137	2.84
None	350	50/50 (v/v) water-ethanol	33.9	41.9	24.2	151	271	1.81
Ru10/Al_2O_3			67.0	8.1	24.9	270	730	2.70
Ni10/AC			66.0	4.7	29.3	287	764	2.66

[1] PD: Polydispersity = M_w/M_n.

The reaction mechanism of OL degradation with and without catalysts may be discussed here according to the above results. As described previously, the OL was obtained from a thermochemical treatment of pine sawdust at 190 °C for 4 hr in 50/50 (v/v) water-ethanol solution. The molecular weights of the OL were fairly low, i.e., 307 g/mol (M_n) and 1157 g/mol (M_w). All the DLs with and without catalysts at 300 °C, however, have similar values of M_n and M_w compared with the untreated OL. It suggests at 300 °C the aryl-alkyl ether bonds in the lignin did not undergo the cleavage reactions to produce lower molecular weight (Pepper and Lee, 1969; Pepper and Steck, 1963). Upon increasing the reaction temperature, the produced intermediates could be prone to condensation reactions to form more char. Two mechanisms may be involved in lignin degradation. One is hydrolysis of ether bonds. The other is radical cleavage or cracking of C-O or C-C bonds. At a higher temperature, the condensation and C-C bond cracking and reforming reactions would be dominant (Minami et al., 2003; Miller et al., 1999). The presence of a catalyst appeared to inhibit the char forming condensation reactions resulting in a lower yield of SR but higher molecular-weights oligomers. It also suggests that the catalysts could catalyze the capping of intermediates radicals with hydrogen to obtain a better DL yield.

7.4.2 Effects of stirring and heating equipment of reactor on OL degradation

Three different types of reactors were used to explore the influence of stirring and heating on OL degradation as mentioned in the experimental methods. These reactors included a 1L stirred autoclave reactor, the 75 mL non-stirred autoclave reactor and the 14 mL shaken micro reactor. Table 7-2 shows the results of the yield distribution of the degraded products and the molecular weights of the DL. In order to produce approximate 40.0 g DL to prepare phenolic resin, the 1L reactor was charged with 50.0 g OL and 500 mL 50/50 (v/v) water-ethanol and 5.0 g Ni10/AC, and the OL degradation treatment was performed at 340 ^{o}C for 2 hr with 5 MPa hydrogen. The reaction temperature was slightly lower than the standard temperature used in the 75 mL non-stirred autoclave reactor s (i.e., 350 ^{o}C) due to the pressure limit of the reactor (maximum 3800psi). The process of heating lasted almost 3 hr to reach 340 ^{o}C. Surprisingly, the treatment produced approximately 74% yield of DL with low molecular weights (M_n 204 g/mol and M_w 512 g/mol). The results were much better than those obtained at 350 ^{o}C with the 75mL autoclave reactor as shown in Table 7-1. One possible reason could be the stirring during the reaction promoted the solubility of the degraded products/intermediates in the solvent which prevented the re-polymerization of the degraded intermediates to form char. To confirm this assumption, the 75 mL autoclave reactor and the 14 mL micro reactor were employed to conduct the catalytic OL de-polymerization at the same reaction conditions except for a proportionally smaller amount of feedstock in these reactors. As shown in Table 7-2, with the 75 mL non-stirred autoclave reactor, 57% DL yield and 26% SR yield were produced. A very high yield of DL (80.7%) was obtained with the 14 mL shaken micro reactor, which is likely as result of the fast heating (less than 1-2 min) and shaking for the reactor. It implies that faster heating and stirring/shaking promotes the DL yield by reducing the SR formation in the OL degradation treatment. Furthermore, Table 7-2 also showed that all the runs produced similar amount of gas products, and all DLs have similar values of M_n and M_w, suggesting the reaction temperature instead of heat-rate/stirring, is the dominating factor for the molecular-weights distribution of the DL products.

Table 7-2. Effect of type of reactor (heating rate and stirring) on the OL degradation process operated at the same conditions of 340 ^{o}C for 2 hr with Ni10/AC catalyst.

Type of reactors	Substrate /g	Stirring/ shaking	Heating time/min[1]	DL /%	SR /%	Water + Gas /%[2]	GPC results of DL		
							M_n	M_w	PD[3]
1 L	50.0	Yes	~180	74.4	10.2	15.4	204	512	2.51
75 mL	1.0	No	~30	56.5	26.0	17.5	154	523	3.40
14 mL	0.5	Yes	1-2	80.7(±2.9)	5.1(±0.1)	17.7	181	568	3.14

[1]The heating time of reactor is measured from the room temperature to the desired temperature; [2]By difference; [3]PD: Polydispersity = M_w/M_n.

7.4.3 ^{1}H NMR analysis of OL and DL

The ^{1}H NMR spectra of the OL and DL produced at 340 ^{o}C in 50/50 (v/v) water-ethanol with Ni10/AC were displayed in Figure 7-1a and 7-1b, respectively. As shown in the Figure, the two strong peaks at 2.5 ppm and 3.3 ppm are from solvent DMSO-d_6 and water, respectively. The two spectra were adjusted to keep the heights of the aromatic peaks between 6.5-7.7 ppm (which is supposed to be unchanged after degradation) the same. It can be observed that the signals at 2.1 ppm attributed to the protons of secondary alcohols in the DL are much stronger than those in the OL, implying the cleavage of ether bonds. Also the signals of aryl hydroxyl proton at 8.5 ppm are relatively stronger after the catalytic hydrothermal treatment, suggesting the cleavage of aryl-alkyl ether linkages. Moreover, there is a slight increase in the peak area of aliphatic protons signals between 0.6-1.4 ppm, which could be resulted from the cleavage of ether linkages produced hydroxyl groups and alkyl groups by hydrogenolysis and hydrolysis (see Figure 7-2). There is a slight decrease in the signals of the methoxy groups at 3.7 ppm suggesting removal of the methoxy groups in the lignin degradation process.

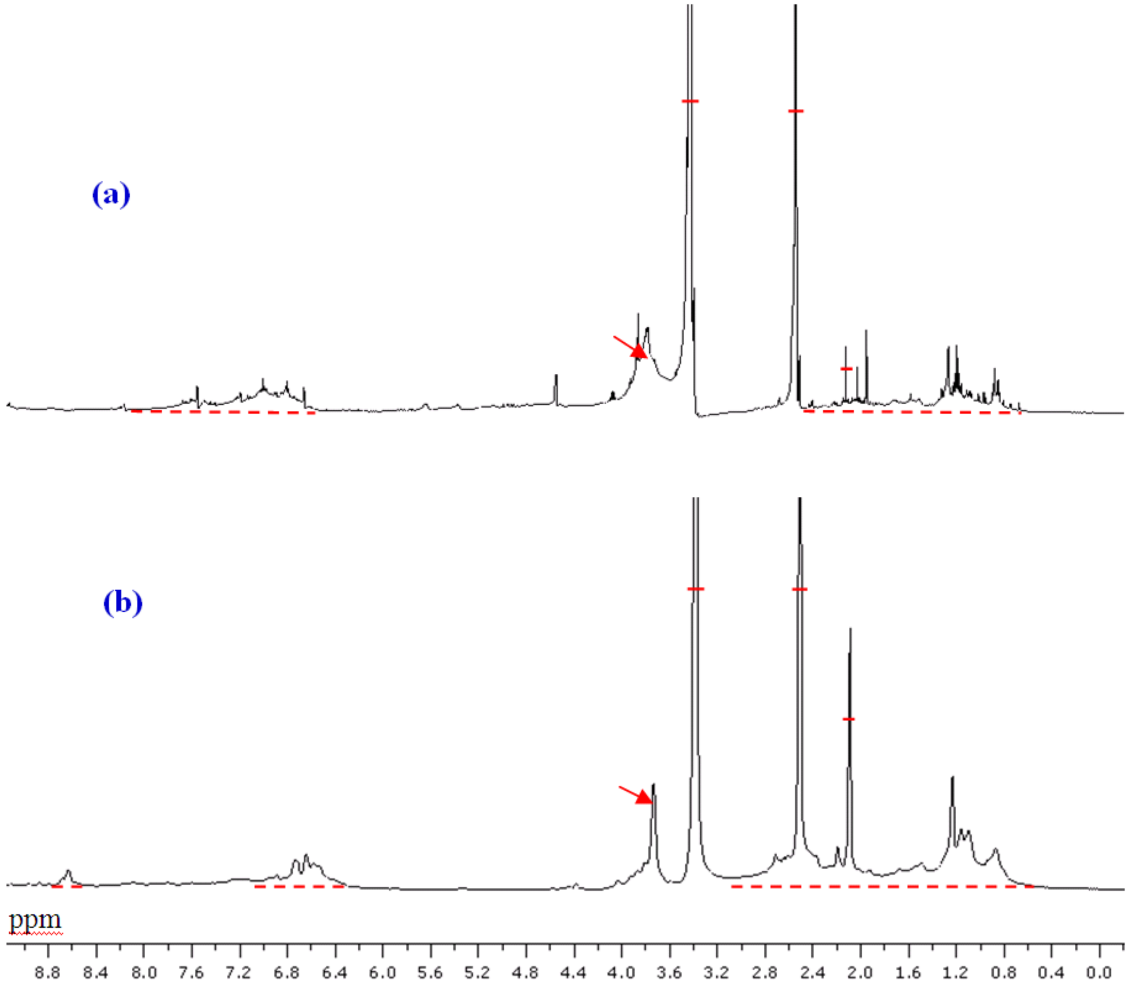

Figure 7-1. ^{1}H NMR spectra of original OL (a) and DL (b) which was obtained at 340 ^{o}C for 2 hr with Ni10/AC in 50/50 (v/v) water-ethanol using the 1 L stirred autoclave reactor.

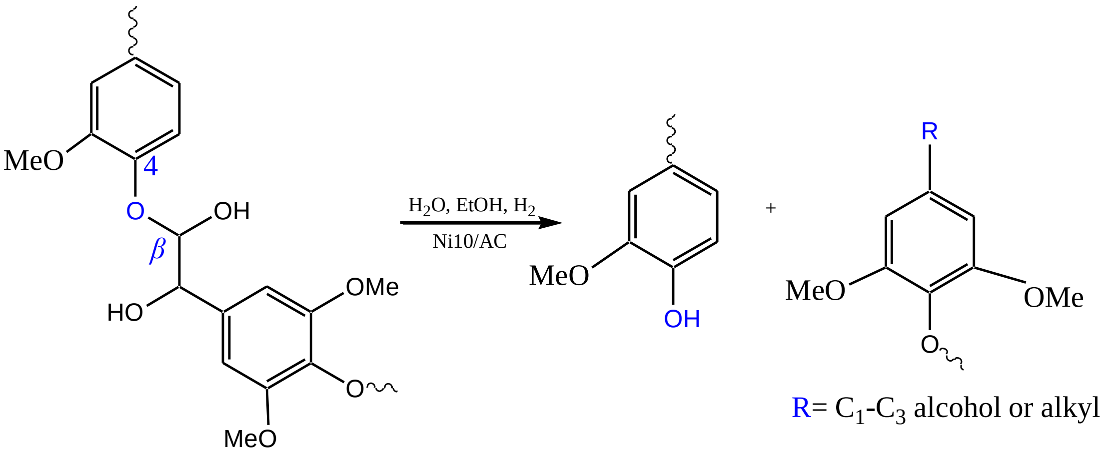

Figure 7-2. A typical hydrogenolysis/hydrolysis cleavage of *β*-O-4 linkage.

7.4.4 Characterizations of OLPF, DLPF and PF resole resins

Physical properties

Some physical properties of synthesized phenolic resole resins derived from OL and DL, such as non-volatile contents, viscosity, storage time at 4 °C and free formaldehyde levels, were measured and shown in Table 7-3. The non-volatile contents of all the OLPF and DLPF resins are slightly higher than that of the pure PF resin. Our previous study (Cheng et al., 2011) proved that the lower non-volatile content in a pure PF resin possibly caused by the evaporation of free phenol (6.2 wt%) upon heating. Phenol may be in excess due to the low molar ratio of F/P ratio of 1.3 used in this study. The viscosity of all the OLPFs and DLPFs increased with increasing the ratio of the OL or DL in the formula, due to the much larger molecular weights of the OL and DL than that of phenol. As expected, the lower molecular weights of DL (M_n 204 g/mol and M_w 512 g/mol) may account for a lower viscosity of DLPF than that of the OLPF at the same phenol substitution ratio with OL (M_n 307 g/mol and M_w 1157 g/mol). All the resins were still liquid after storage at 4 °C for 30 days. The free formaldehyde content was not detected (below the detection limit) for the pure PF resin as formaldehyde was in scarcity as mentioned above, while it was detected in all the OLPF and DLPF resins, and the content increased with increasing the OL or DL ratio. This is due to the fact that OL or DL has fewer reactive sites and hence lower reactivity compared with phenol. There was a markedly less amount of free formaldehyde in DLPFs than that in OLPFs, suggesting that the DL has more reactive sites and higher reactivity than OL because the degraded lignin has more phenol functionality generated by the phenyl ether bond cleavage.

Table 7-3. Physical properties of OLPF, DLPF and PF resins.

Type of resins	**Non-volatile contents[1]/%**	**Viscosity @ 50 °C /cp[1]**	**Storage time @ 4 °C/day**	**Free formaldehyde/%[2]**
50% OLPF	39.3 (±0.4)	22.8 (±0.01)	> 30	1.0 (±0.025)
75% OLPF	38.0 (±0.2)	26.3 (±0.03)	> 30	3.9 (±0.015)
50% DLPF	37.7 (±0.1)	19.6 (±0.03)	> 30	0.5 (±0.05)
75% DLPF	38.6 (±0.1)	23.7 (±0.01)	> 30	0.7 (±0.01)
PF	35.4 (±1.2)	18.4 (±0.03)	> 30	ND[3]

[1]Each value represents an average of 3 samples; [2]Each value represents an average of 2 samples; [3]ND: not detected.

Thermal behavior

The curing behavior of the OLPFs, DLPFs and PF were measured by DSC scans at a heating rate of 10 °C/min from 40 °C to 250 °C with 50 mL/min of N_2. The DSC profile and characteristic curing temperature of all the resins were shown in Figure 7-3 and Table 7-4, respectively. As shown in Figure 7-3, the DSC thermograms of the OLPFs and DLPFs similarly exhibited exothermic peaks as that of pure PF resin, but at different peak positions and intensities. The formation of the exothermic peaks could be attributed to the condensation of phenol or OL/DL with methylol groups ($-CH_2OH$) to form a methylene bridge and the condensation of two methylol groups to form dibenzyl ether bridges and the cross-linking condensation of the methylene bridges (Christiansen and Gollob, 2003; Gabilondo et al., 2007; Wang et al., 2009). Two split peaks were observed for the pure PF resin at 138.8 °C and 149.5 °C, respectively. The first peak could be attributed to the condensation to form methylene and dibenzyl ether bridges. The second peak at the higher temperature might be related to the subsequent reactions, e.g. cross-linking condensation of the methylene bridges (Christiansen and Gollob, 2003; Wang et al., 2009;

Vázquez et al., 2002). Table 7-4 shows that all OLPFs and DLPFs presented lower curing peak temperatures (from 138.5 ^{o}C to 142.9 ^{o}C) than pure PF resin (149.5 ^{o}C). It suggests that the replacement of phenol with the OL or DL can lower the curing temperature of the phenolic resin as has also been observed previously with the bio-oil-phenol-formaldehyde (BPF) resole resins (Cheng et al., 2011). Moreover, the DLPFs, particularly the 75% DLPF, have lower curing peak temperatures than the OLPFs.

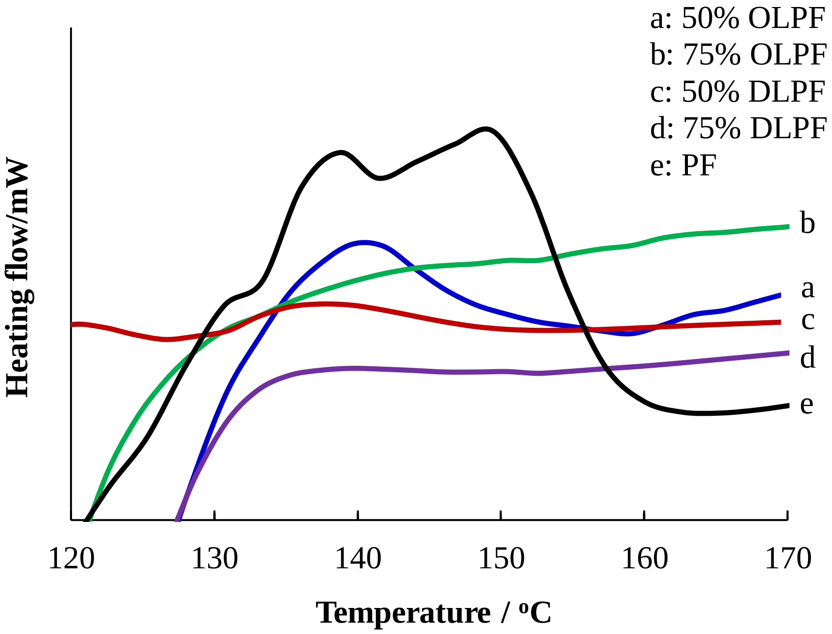

Figure 7-3. DSC curves of OLPFs, DLPFs and PF.

Table 7-4. DSC results of the main exothermic peak of OLPFs, DLPFs and PF.

Type of resins	50% OLPF	75% OLPF	50% DLPF	75% DLPF	PF
Peak temp. / ^{o}C	138.5	142.9	138.6	139.6	149.5

The thermogravimetric analysis was employed to explore the thermal stability of the non-volatile residuals of the OLPF, DLPF and PF resins heated from 25 ^{o}C to 700 ^{o}C with a heating rate of 10 ^{o}C/min under an N_2 of 30 mL/min. Figure 7-4 described the TG and DTG profiles for the resins. Table 5 summarized the characteristic decomposition temperatures, weight loss percentages for the three thermal events (DTG results) and the carbon residue at 700 ^{o}C (TG results) for all the resins. The decomposition of a phenolic resin normally has three steps: post-curing (the removal of terminal groups and further crosslinking or condensation reactions), thermal reforming (break of the bridged methylene linkage) and ring stripping (breakdown of the ring network) (Khan and Ashraf, 2007). As shown in Figure 7-4, all the OLPF and DLPF resins presented similar thermal decomposition patterns as the PF resin, but a lower residual mass ratio at 700 °C, particularly for the DLPF resins as described in Table 7-4. The main decomposition region of PF resin was observed at a higher temperature from 500 °C to 650 °C (the third thermal event). The majority of mass loss for all resins occurred in the second and third thermal event (330 °C to 650 °C). The higher mass loss of the OLPFs and DLPFs could be caused by the breakdown of the methylene linkage, the side chains or methoxy groups presented in the OL/DL molecules. Surprisingly, the OLPFs showed better thermal stability than the DLPFs regarding the mass loss in each thermal event and the final carbon residue at 700 °C. It suggests that the OL or OL-based resins is more stable than the DL and DL-based resins.

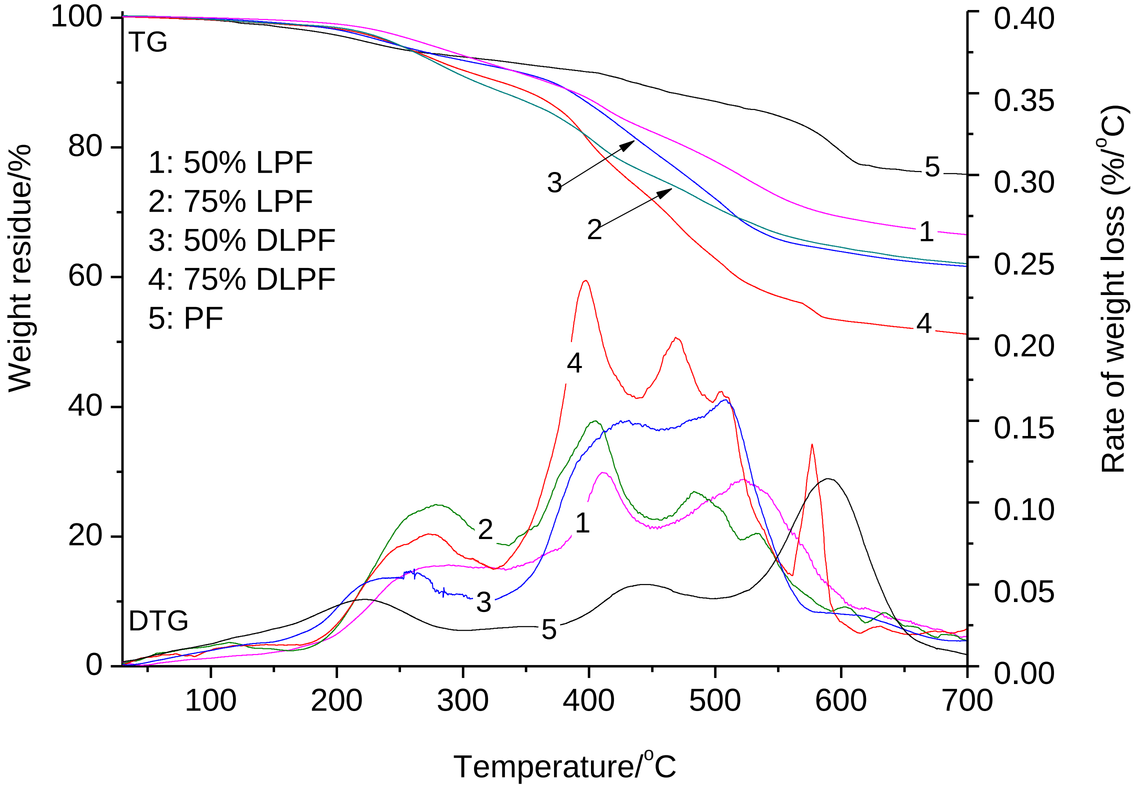

Figure 7-4. TG and DTG profiles of OLPF, DLPF and PF resins.

Table 7-5. TG and DTG results of OLPF, DLPF and PF resins.

Type of resins	Three thermal events (DTG results)			Carbon residue @ 700 ^{o}C (wt%)
	NO.1$T_o/T_p/T_e/^{o}C$	NO.2 $T_o/T_p/T_e/^{o}C$	NO.3 $T_o/T_p/T_e/^{o}C$	
50% OLPF	162/277/340	340/414/459	459/531/617	67.1 (±0.6)
75% OLPF	173/287/339	339/411/454	454/491/625	60.4 (±1.7)
50% DLPF	148/262/323	323/513/587		61.5 (±0.1)
75% DLPF	180/280/334	334/400/564	564/578/618	50.4 (±0.8)
Pure PF	70/223/300	365/445/500	500/589/650	76.0 (±0.1)

7.4.5 Evaluation bond strength of OLPFs, DLPFs and PF

The bond strength for all resins as plywood adhesives was evaluated for their dry and wet tensile strengths as shown in Figure 7-5. The wood failure percentages (WFP) of the dry and wet plywood specimen are presented in Table 7-6. Interestingly, Figure 7-5 clearly shows that both dry and wet strengths of the plywood specimen bonded by an OLPF or DLPF were stronger than those of the pure PF resin adhesive. It should be noted that all the resins have dry and wet strengths which exceed the minimum requirement of the tension shear strength specified by the JIS K-6852 standard (1.2 MPa for dry strength, and 1.0 MPa for wet strength) for resole-type plywood adhesives. These results are superior to the results of previous studies where phenol was substituted with Kraft lignin or cornstarch/tannin at a replacement level of less than 50 wt% (Khan and Ashraf, 2007; Moubarikv et al., 2009). The results were also better than our previous study (Cheng et al., 2011) with the BPF adhesives, likely due to the higher content of phenolic compounds in the OL and DL. For the WFP in Table 7-6, under the dry condition, all OLPF and DLPF resins presented similar value as the pure PF resin, above ~80%. After boiling for 3 h, the WFP of the 50% DLPF and 50% OLPF was still as high as 73% and 85%, respectively. However, the WFP of the wet 75% OLPF and 75% DLPF adhesives drastically dropped to 16 % and 13 %, respectively. It indicates that the OLPF or DLPF adhesives with a high ratio of OL or DL are much sensitive to water. These results demonstrates that OL or DL can successfully substitute phenol at a high substitution level, > 50% and up to 75%, in synthesis of phenolic resins that have improved dry and wet tensile strengths compared to the PF resins. Interestingly, OLPFs perform better than the DLPFs with respect to the dry and wet tensile strengths, in particular the 50% OLPF has the highest dry and wet strengths as well as the dry and wet WFP values among all the adhesives tested. The pinewood-derived OL used in this study has very low molecular weights (M_n 307 g/mol and M_w 1157 g/mol). Further degradation of the OL, increases the reactivity of the DL products, but it breaks the natural cross-linking structures of the lignin molecules, which could deteriorate the performance of the DLPFs as wood adhesives with respect to dry and wet bond strengths.

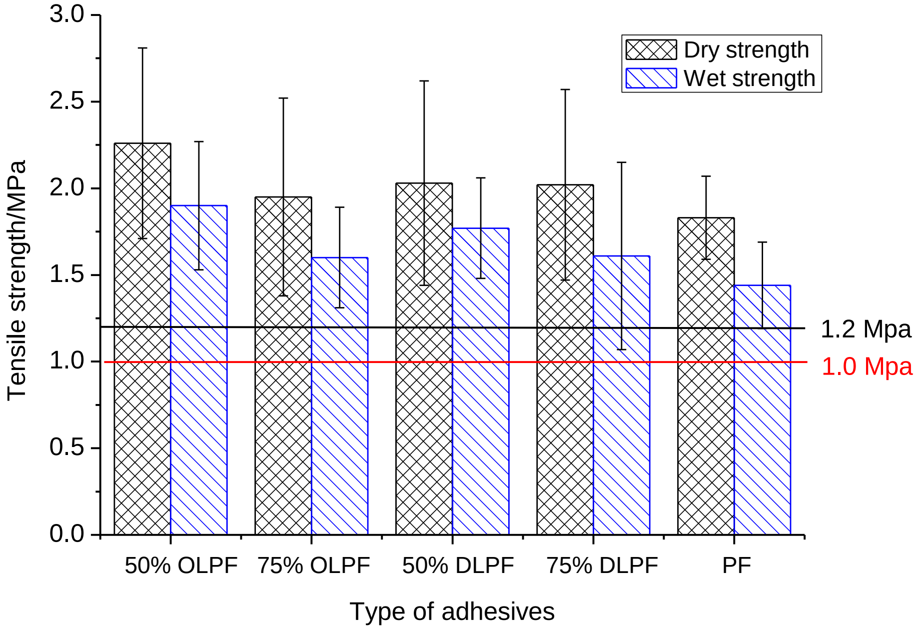

Figure 7-5. Tensile-strength profile of plywood glued by OLPF, DLPF and PF adhesives.

Table 7-6. WFP result of plywood glued by OLPF, DLPF and PF adhesives.

Test conditions	Wood failure [a] (%) (STDEV)				
	50% OLPF	75% OLPF	50% DLPF	75% DLPF	Pure PF
Dry[b]	93 (±19)	82 (±30)	76 (±36)	78(±32)	89 (±19)
Wet[c]	85 (±13)	16 (±31)	73 (±41)	13 (±38)	65 (±43)

[a]An average of 20 specimens; [b]Test after conditioning; [c] Test after boiling in water for 3hr.

7.5 Conclusions

(1) Ni10/AC and Ru10/γ-Al_2O_3 were proved to effectively catalyze the hydrothermal degradation of organosolv lignin (OL) under hydrogen in sub-/super-critical 50/50 (v/v) water-ethanol and pure ethanol, by preventing the formation of char/coke. With Ru/Al_2O_3 catalyst the degradation treatment of OL at 300 °C in sub-/super-critical 50/50 (v/v) water-ethanol and pure ethanol produced a very high yield of DL: 94 % and 92%, respectively.

(2) The treatment temperature was found to be the dominant factor in determining the yield and the molecular-weight distributions of the DL. Among all the tested conditions for OL degradation, the optimal condition was in a shaken micro-reactor at 340 ^oC in 50/50 water-ethanol employing the Ni10/AC catalyst, producing a very high DL yield (~81 %) with very low molecular weights (181 g/mol and M_w 568 g/mol).

(3) Faster heating and stirring had a positive effect on the yield of DL, particularly the stirring.

(4) All the OLPFs and DLPFs have similar physical properties as the pure PF resin in terms of viscosity, non-volatile contents, storage time at 4 ^oC, but have slightly higher free formaldehyde content. The OLPFs and DLPFs can be cured at a lower temperature than the pure PF resin.

(5) In application of OLPF and DLPF resins as plywood adhesives, both dry and wet strengths of the plywood specimen bonded by an OLPF or DLPF were stronger than those of the pure PF resin adhesive. OLPFs perform better than the DLPFS with respect to dry and wet tensile strengths, in particular the 50% OLPF has the highest dry and wet strengths as well as the dry and wet WFP values among all the adhesives tested.

7.6 Acknowledgements

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CHAPTER 8. DE-POLYMERIZATION OF LIGNIN WITH FORMIC ACID IN SUB-/SUPER-CRITICAL SOLVENT OF WATER-ETHANOL

8.1 Abstract

In this study, formic acid that can act as a hydrogen donor at elevated temperatures was employed for degradation of alkali lignin (AL) and organosolv lignin (OL) in the medium of sub-/super-critical 50/50 (v/v) water-ethanol. The obtained degraded lignin (DL) products were further analyzed by gel permeation chromatography (GPC) and proton nuclear magnetic resonance (^{1}H NMR). The degradation of AL and OL led to 77 wt% and 80 wt% yield of DL, and 5 wt% and 0.4 wt% yield of solid residue (SR), respectively. The relative molecular weights of the DL products were significantly decreased compared to those of the original lignin samples. For instance, M_n of the AL reduced from 10,000 to 295 g/mol, while the M_n of the OL decreased from 307 g/mol to 150 g/mol. The ^{1}H NMR analysis of DL demonstrated that the methoxyl groups were significantly decreased after degradation in formic acid compared to the original lignin samples. The use of formic acid was found to be effective for increasing the DL yields while suppressing the formation of solid residues compared with the use of gaseous hydrogen, likely because the in situ formed hydrogen from formic acid can prevent the recombination of reaction intermediates.

8.2 Introduction

Producing renewable bio-phenolic compounds from biomass/lignin suitable for synthesis of phenol formaldehyde resin is increasingly a focus in both research and industry. In the field of lignin degradation, the main challenge is to prevent the recombination of reaction intermediates from forming larger molecules. The application of an appropriate hydrogen donor (e.g., Tetralin, 9,10-dihydroanthracene (AnH_2) and its derivatives and

1,4,5,8,9,10-hexahydroanthracene) that provided reactive hydrogen atoms could be an effective solution (Dorrestijn et al., 1999; Amen-Chen et al., 2001)

However, above mentioned solvents are relative expensive and hard to recover. There is another family of solvent such as formic acid and 2-propanol, which are less thermally stable and will decompose to give hydrogen upon being heated at elevated temperatures. For example, formic acid decomposes completely into hydrogen atom, and carbon dioxide, and 2-propanol can be decomposed into hydrogen atom and acetone by heating. Recently, this type of hydrogen-donating solvents has found special applications in hydro-conversion of biomass and lignin. As reported by Kleinert et al. (Kleinert and Barth, 2008(a); 2008(b); 2008(c); Kleinert et al., 2009; Kleinert and Barth, 2007(a); 2007(b)), formic acid and 2-propanol were used as hydrogen donators for de-polymerization and hydrogenation of lignin. Kleinert and co-workers (2008(a)) obtained a high yield (25-35 wt%) of phenolic fraction, exclusively composed of monoaromatic phenols with alkylation ranging from C_1–C_7 in the side chain(s), by one-step conversion of lignin to oxygen-depleted bio-fuels and phenols using co-solvent of formic acid and ethanol at about 400 °C. The yield was 2 or 3 times that of an earlier work by Dorrestijn et al. (1999) using AnH_2 for de-polymerization of wood lignin at 352 °C.

In this work, formic acid was employed to investigate the degradation of alkali lignin (AL) and organosolv lignin (OL) in sub-/super-critical 50/50 (v/v) ethanol-water and pure ethanol media. The degraded products were characterized using gel permeation chromatography (GPC) and proton nuclear magnetic resonance (^{1}H NMR). The gaseous product was analyzed on a Micro-GC. Meanwhile, the elemental composition of the degraded lignin was also analyzed.

8.3 Materials and Methods

8.3.1 Materials

AL was purchased from Sigma-Aldrich. It was completely soluble in water. OL was extracted from Eastern white pine sawdust, which was collected form a local sawmill in Thunder Bay. Lignin samples were vacuum dried overnight at room temperature before use. ACS reagent grade solvents and chemicals including ethanol, methanol, acetone and DMSO-d_6, and Formic acid (90%, BDH Chemical Ltd Poole England) were all supplied by Fisher Scientific or Sigma-Aldrich and were all used as received. In the GPC analysis for the degraded lignin (DL) products, HPLC grade solvent tetrahydrofuran (THF) containing 0.03 wt% stabilizer of 2, 6-di-*t*-butyl-4-methyl-phenol was used the eluent. All the samples were analyzed for their elemental composition with a Control Equipment Corporation (CEC) 240-XA Elemental Analyzer (Exeter Analytical, Inc.) using helium as the carrier gas. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a 500 MHz ^{1}H NMR (Inova NMR instrument) at room temperature in DMSO-d_6 solvent. And the spectra were calibrated to the signal of DMSO-d_6 of 2.50 ppm. The proximate, elemental compositions and molecular weights of the pine sawdust and lignin samples are listed in Table 8-1.

Table 8-1. Proximate analysis, elemental analysis and molecular weights of AL and OL.

Feedstock	Proximate analysis (wt %, d.b.)^{a,b}			Elemental analysis (d.a,f)^c								Molecular weights
				wt %					Molar ratio			
	FC^{d,e} /%	VM^f / %	Ash / %	C	H	N	S	O^d	H/C	O/C	M_n^{h} g/mol	M_w^{i} g/mol
AL	72.6	17.9	9.5	63.8	4.9	0.1	3.6	27.6	0.92	0.32	10，000	60,000
OL	39.3	60.2	0.5	67.9	6.1	0	0^g	26.0	1.08	0.29	307	1157
Pine sawdust	84.5	15.1	0.4	52.5	6.3	0.1	< 0.05	41.05	1.44	0.59	-	-

^{a} On a dry basis; ^{b} Determined by thermogravimetric analysis (TGA) in N_2 at 10 °C/min to 900 °C, and 900 °C in air for 15 min; ^{c} On a dry and ash-free basis; ^{d} By difference; ^{e} FC: Fixed carbon; ^{f} VM: Volatile matters; ^{g} Sulfur content was ignored in the OL due to its very low content (< 0.05%) identified in the original pine sawdust; ^{h} M_n: number average weight molecular weight; ^{i} M_w: weight average molecular weight.

8.3.2 Degradation of lignin

The lignin-degradation tests were carried out in a 75 mL Parr high-pressure reactor (Parr Instruments, Moline, USA), constructed of Hastelloy alloy, with maximum working pressure of 41.37MPa at 600 °C. The reactor was charged with 1.0g lignin, 10 ml solvent and together with 5ml formic acid as the main hydrogen donor. After the reactor was safely sealed, it was purged using high-purity nitrogen for three times, and subsequently pressurized to 2.0 MPa with N_2. The reactor was heated up to the desired temperature with an electric heater, and soaked at the temperature for 2h before cooling with cold water. After the reactor was completely cooled to room temperature, the gaseous product was collected in a pre-vacuumed 2.8 L gas cylinder and analyzed on a Micro-GC equipped with thermal conductivity detectors (TCDs). The formation (in moles) of gas species (H_2, CO, CO_2, CH_4, and C_2-C_3) was determined. The reactor was completely rinsed with acetone and methanol to recover the degraded products. The acetone-methanol-soluble fraction was separated from the acetone-methanol-insoluble fraction by filtration. The organic solvents (acetone, methanol and ethanol) and water in the filtrate were removed by a rotary evaporator under reduced pressure at 40 ^{o}C and at 65 ^{o}C, respectively. The obtained dark oily product was denoted as degraded lignin (DL), which was vacuum dried at room temperature overnight before weighing. The acetone-methanol-insoluble fraction was vacuum dried overnight at room temperature to obtain the yield of the solid residue (SR).

8.3.3 Analytical methods

The relative molecular weights and their distributions of the DL products were analyzed on a Waters Breeze GPC (1525 binary High-performance liquid chromatography (HPLC) pump; UV detector at 270 nm; Waters Styragel HR1 column at 40 ^{o}C). The mobile phase was THF at a flow rate of 1 mL/min. And polystyrene standards were used for calibration. The chemical structure of the DL products was analyzed with a 500 MHz ^{1}H Inova NMR instrument at room temperature in dimethyl sulfoxide-d_6 (DMSO-d_6) or acetone-d_6 as the solvent.

8.4 Results and Discussion

8.4.1 Effects of formic acid on AL degradation

To determine the effects of formic acid as the main hydrogen donor on the yield and quality of DL, AL was degraded at 300 ^{o}C for 2 hr in N$_2$ atmosphere in 50/50 (v/v) water-ethanol and pure ethanol. The results were listed in Table 8-2.

The degradation carried out with formic acid in 50/50 (v/v) water-ethanol produced 77.1 % yield of DL and 4.7 % SR. The relative molecular weights of DL were drastically reduced from its original value of M$_n$: 10,000 g/mol and M$_w$: 60,000 g/mol to M$_n$: 295 g/mol and M$_w$: 816 g/mol. At the same condition, however, the runs in pure ethanol produced a lower yield of DL with higher values of molecular weights than those in 50/50 (v/v) water-ethanol. It thus suggests that the addition of water might promote the hydrolysis reaction of lignin in the processor enhance the solubility of the DL product which contains more hydroxyl group and thus inhibit the condensation reactions of intermediates to form char/coke. Similar results were also observed in some previous studies (Cheng et al., 2010; Pasquini et al., 2005; Li and Kiran, 1988). As such, 50/50 (v/v) water-ethanol was selected to explore the OL degradation in formic acid, which will be described hereinafter.

Table 8-2. Yields of DL, SR, and Gas products obtained from alkali lignin degradation at 300 ^{o}C with in formic acid.

Solvent	DL /%	SR /%	Gas /%	GPC analysis of DL			Elemental analysis of DLs[b]				
							wt%				Molar ratio
				M$_n$ g/mol	M$_w$ g/mol	PD[a]	C	H	N	(O+S)[c]	H/C
50/50(v/v) water-ethanol	77.1 (±3.3)	4.7 (±2.0)	393.7 (±38.0)	295	816	2.76	62.7	5.9	0	31.4	1.13

Pure ethanol	62.3 (±1.7)	15.45 (±1.25)	388.5 (±11.8)	482	1280	2.66	60.7	5.7	0.07	33.5	1.13

[a] PD: Polydispersity; [b] On dry basis; [c] By difference.

The most marked phenomena shown in Table 8-2 is the large amount of gas produced in all the runs, rich in CO, CO_2 and H_2, as illustrated in Figure 8-1, which can be understood as reflecting the thermal decomposition of excess formic acid (Yu and Phillip, 1998; Kleinert et al., 2011). Yu and Phillip reported the major products from the hydrothermal decomposition of formic acid were CO_2 and H_2 with a small amount of CO. As such, the higher amount of CO produced in this study was likely from the degradation of lignin. The authors also summarized the molecular elimination mechanism for hydrothermal decomposition of formic acid as shown in Figure 8-2. The production of CO_2 and H_2 was the main pathway. In addition, a small amount of ethane, ethylene and methane were also observed. These gaseous products could be derived from Fischer–Tropsch reactions (CO and H_2) or converted from ethanol, also perhaps produced from the exhaustive reduction of the phenolic intermediates.

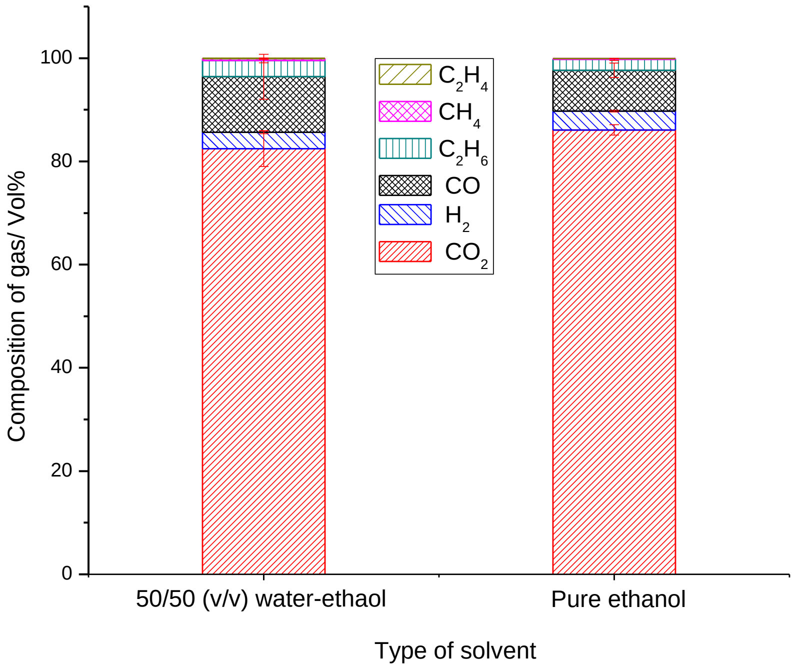

Figure 8-1. Composition of gas products produced from all the runs shown in Table 8-1.

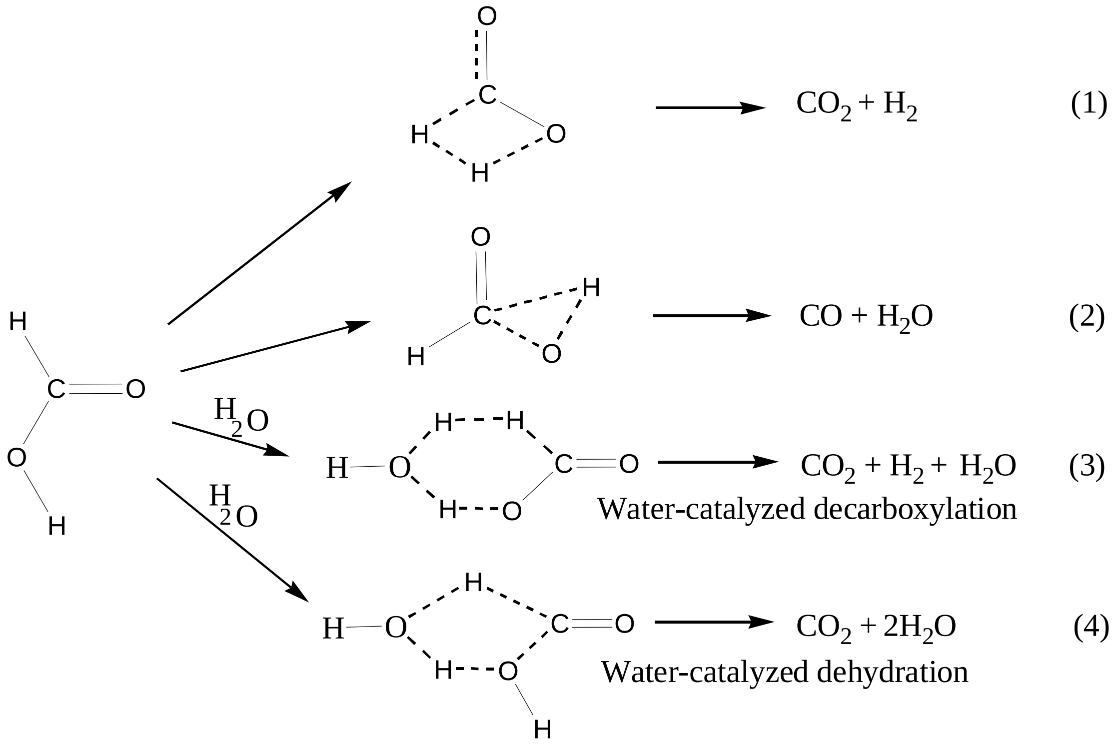

Figure 8-2. Hydrothermal decomposition pathway of formic acid (Yu and Phillip, 1998).

Table 8-2 also shows the elemental composition of the DL samples. The molar ratios of H/C for the DL products were calculated to be 1.13, higher than that of the original AL (0.92) (Table 8-1). The increase of H/C ratio indicated that the hydrodeoxygenation reaction occurred in the presence of formic acid.

Figures 8-3a and 8-3b show the ^1H NMR spectra of AL and DL, respectively. Table 8-3 summarizes the signal positions in ^1H NMR spectra of lignin. The two curves were adjusted to keep the height of the aromatic peaks between 6.0 and 8.0 ppm (which is supposed to be unchanged after degradation) the same. Comparing the ^1H NMR spectrum of AL with that of the DL product, the methoxyl region at 3.5 to 4.0 ppm as shown in Table 8-3 was significantly decreased. Moreover, a higher proportion of hydrogen atoms attached to saturated aliphatic carbon chains was observed in the region at 0.6 to 2.5 ppm, particularly at 0.8, 1.1, 1.8 and 2.1 ppm. The signals at 0.8 and 1.1 ppm are characteristic peak of terminal methyl and methylene group in alkyl chain, respectively (Duan and

Phillip, 2011). The signals between 1.8 and 2.1 ppm are consistent with resonances expected from secondary and primary alcoholic hydroxyl groups, respectively. The peaks at the region between 4.0 and 6.0 ppm that can be ascribed to the aliphatic H_α and H_β of side chains in *α*-O-4 and *β*-O-4 structures (Ibarra et al., 2007) completely disappeared, implying the cleavage of the *α*-O-4 and *β*-O-4 linkage.

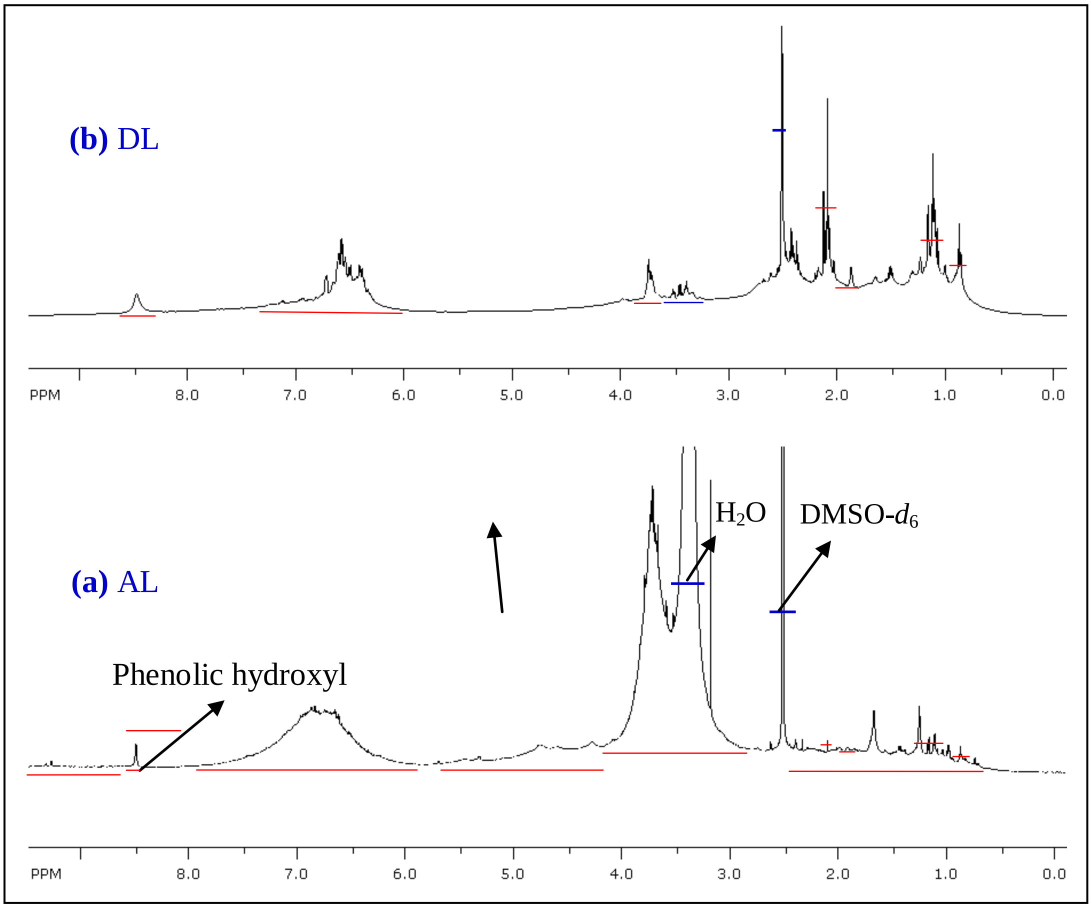

Figure 8-3. ^1H NMR spectra of AL (a) and DL (b) in DMSO-d_6. DL was produced from the case in 50/50 (v/v) water-ethanol together with formic acid. Peak at 2.5 ppm is derived from the solvent. Peak at 3.3 ppm is derived from residual moisture.

Table 8-3. Position of signals in ^1H NMR spectrum of lignin.

δ ^1H NMR (ppm)	Structure
0.6-2.5	Aliphatic C-CH_2-C, C-CH_3, C-HC(OH)-C, C-CH_2-H_2C(OH)
3.5-4.0	Methoxyl
4.0-6.0	Aliphatic CH-O, C-CH_2-O (H_α and H_β)

6.0-8.0	Aromatic, vinylic
8.0-8.5	Substituted phenolic
8.5-9.5	Unsubstituted phenolic

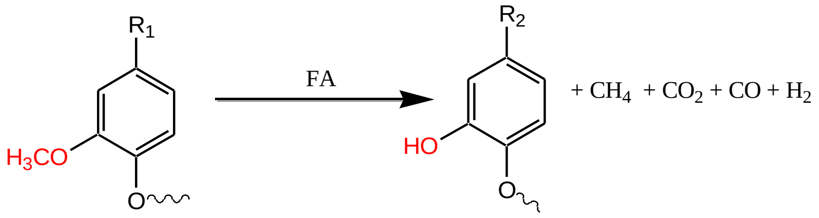

Figure 8-4. A possible cleavage pathway of methxoyl group on lignin polymer (FA: Formic acid).

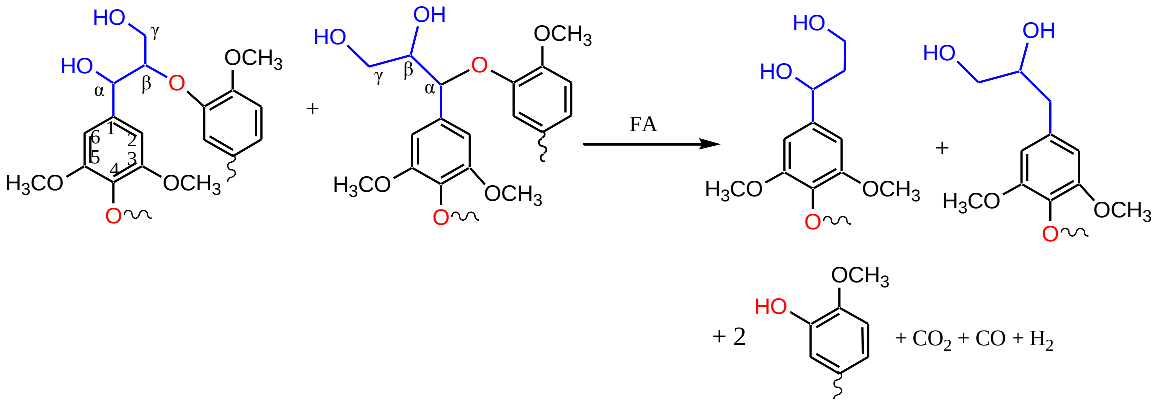

Figure 8-5. A possible cleavage of β-O-4 and α-O-4 structure on lignin polymer (FA: Formic acid).

The degradation mechanism of lignin in formic acid may be discussed accordingly from the above results. A possible cleavage pathway of methoxyl group is described in Figure 8-4. Phenolic hydroxyl (Li and Lundquist, 1993) and CH_4 could be formed from the cleavage of methoxyl groups. Figure 8-5 illuminates cleavage of β-O-4 and α-O-4 structure to form phenolic hydroxyl, some gaseous products (from formic acid), and alcohol/alkyl side chains. With this mechanism, the signals at 8.5 ppm ascribed to the phenolic hydroxyl and the signals at 0.6 and 2.5 ppm (aliphatic hydroxyl groups) would increase (as evidenced by the ^{1}H NMR spectra in Figure 8-3b).

8.4.2 OL degradation

Our recent study on optimizing degradation condition for OL showed that 350 °C and 50/50 (v/v) water-ethanol are the optimal reaction parameters. Herein, the effects of formic acid on OL degradation were carried out at the above optimal reaction conditions. The yield of DL and SR, GPC results of DL, and elemental analysis of DLs are summarized in Table 8-4. The gaseous products from these runs were not analyzed simply because they were of less interest in this study and the yields/composition of the gas products from the AL degradation (Table 8-2) at the similar conditions have been discussed previously. For comparison of the effects of different hydrogen donors on OL degradation, the results with gaseous hydrogen obtained at the same conditions are also listed in Table 8-4. The chemical structures of OL and DL were determined with ^{1}H NMR. All the ^{1}H NMR spectra are illustrated in Figure 8-6. It should be noted, the solvent for OL was DMSO-d_6 while the solvent used in DL analysis was Acetone-d_6, because of running out of DMSO-d_6.

Table 8-4. Yields of DL and SR obtained from OL degradation at 350 °C for 2 hr in 50/50 (v/v) ethanol-water with different hydrogen donor.

Hydrogen donor	DL / %	SR / %	GPC analysis of DL			Elemental analysis of DLs[b,c]					
						wt%				Molar ratio	
			M_n g/mol	M_w g/mol	PD[a]	C	H	N	O[d]	H/C	O/C
H_2	33.9	41.9	151	271	1.81	73.6	7.6	0	18.80	1.24	0.19
formic acid	80.2	0.4	150	464	3.10	72.1	6.5	0.09	21.31	1.08	0.22

[a] PD: Polydispersity; [b] On dry basis; [c] Sulfur content was ignored due to the very low content (< 0.05 %) in the original pine sawdust. [d] By difference of (100-C-H-N).

As shown in Table 8-4, formic acid significantly promoted the yield of DL (80.2 %) compared with gaseous hydrogen (DL: 33.9 %). Furthermore, a much lower yield of SR (0.4 %) was produced with formic acid than that with gaseous hydrogen (41.9 %). As expected, the molecular weights of DL were drastically reduced. For example, the molecular weights of the original OL decreased from M_w 1157 g/mol and M_n 307 g/mol to M_w 464 g/mol and M_n 150 g/mol, respectively, for the DL with formic acid. The DL products have approximately a dimer or trimer structure. The results indicate that the in situ formed hydrogen (Kleinert and Barth, 2008(c)) effectively inhibited the recombination of the reaction intermediates in the hydrothermal treatment process.

The elemental analyses were performed to identify the atomic composition of DLs as shown in Table 8-4. The molar ratios of H/C and O/C for both DLs are in the range of 1.08-1.24, and 0.19-0.22, respectively. The H/C molar ratios are thus similar as or slightly higher than that of the original OL (1.08). However the O/C ratios are lower than that of the original OL (0.29). The values are also similar to those of guaiacol and phenol as shown in Table 8-5. The lignin degradation processes seem to add a small fraction of hydrogen and remove a small fraction of oxygen – the effect of hydrodeoxygenation reactions.

Table 8-5. Elemental ratios of guaiacol, syringol, phenol, and 2-isopropylphenol.

Molar ratio	Guaiacol	Syringol	Phenol	2-isopropylphenol
H/C	1.15	1.25	1.00	1.33
O/C	0.29	0.38	0.17	0.11

^{1}H NMR analysis results of two typical samples, i.e., the original OL and the DL from the run with formic acid are displayed in Figures 8-6a and 8-6b, respectively. As similarly done before with AL and its DL products, the ^{1}H NMR spectra for these two samples were adjusted to keep the height of the aromatic signals between 6.0 and 8.0 ppm the same. The two ^{1}H NMR spectra show similar results as those of AL and DLs (Figure 8-3). Two similar conclusions can be drawn by comparing the spectrum of the OL with that of the DL: (1) The methoxyl group was reduced; (2) The β-O-4 and α-O-4 linkages at 4.0-6.0 ppm were cleaved. The major difference between the AL-derived DL and the OL-derived DL is that there is a very strong signal at 1.3 ppm in the latter. The peak was reported to be methylene groups in alkyl chain (Duan and Phillip, 2011). It suggestes that a higher-degree hydrogenolysis cleavage occurred in the processes of OL degradation compared with that of AL at the same conditions. This conclusion can be supported by the smaller molecular weights of OL-derived DLs (Table 8-4) than the AL-derived DLs (Table 8-3).

The authors believe the degradation mechanism of OL could be similar to that of AL as summarized and illustrated above in Figures 8-4 and 8-5.

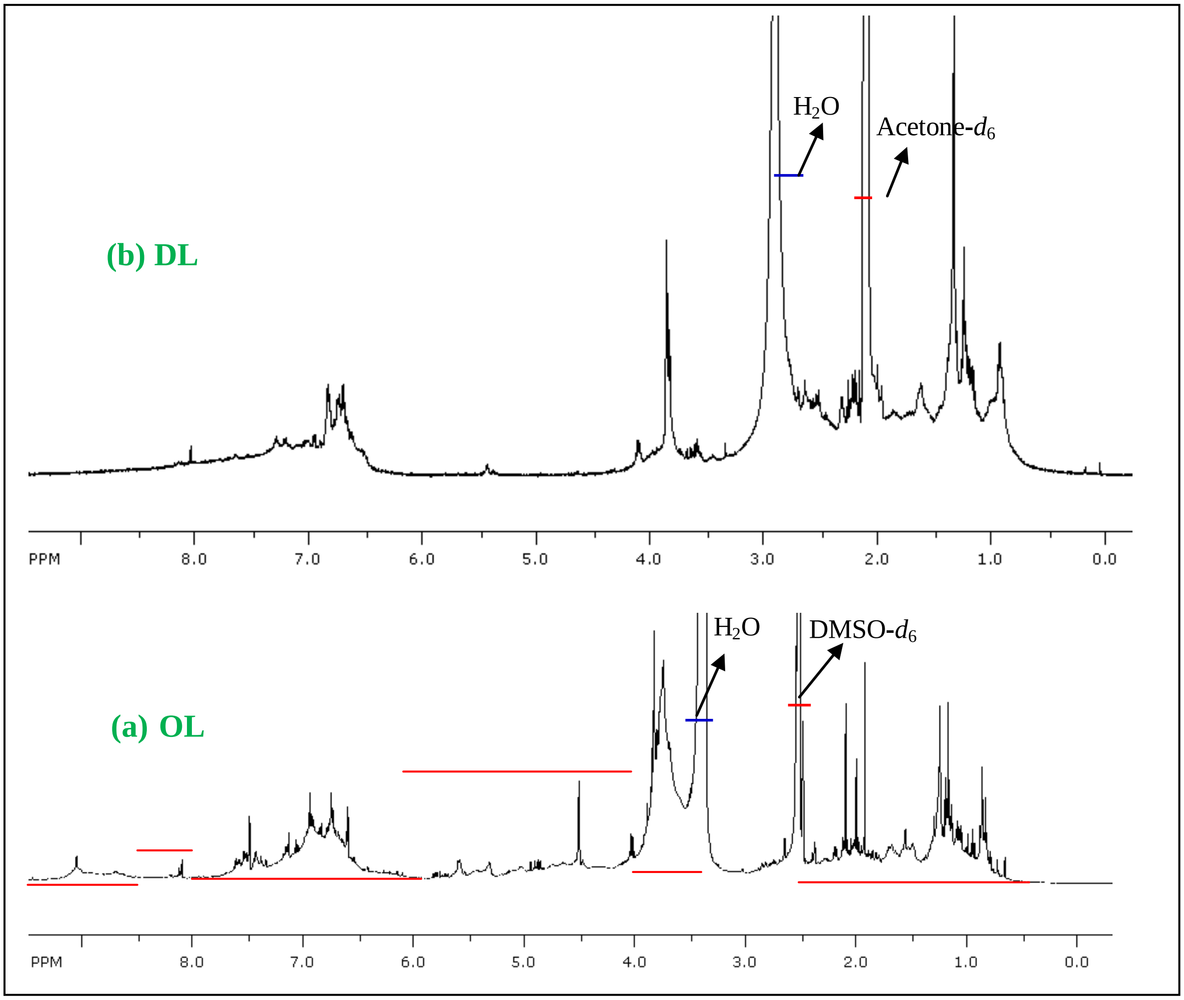

Figure 8-6. ^{1}H NMR spectra of OL (a), and DL (b). OL in DMSO-d_6. DL (350 ^{o}C, formic acid, 2 hr, 50/50 (v/v) water-ethanol) in Acetone-d_6. Peak at 2.08 ppm, 2.5 ppm and 3.3 ppm are derived from Acetone-d_6, DMSO-d_6 and residue moisture in sample, respectively.

8.5 Conclusions

In this study presented here, formic acid as a hydrogen donor has a significant effect on AL and OL hydrothermal degradation in 50/50 (v/v) water-ethanol and pure ethanol.

(1) With formic acid, the treatment for AL at 300 ^oC in 50/50 (v/v) water-ethanol led to a high yield (77 %) of DL. The molecular weights of the lignin were drastically reduced from its original M_w and M_n of 60,000 g/mol and 10,000 g/mol, respectively, to M_n of 295 g/mol and M_w of 816 g/mol for the DL. Compared with that in 50/50 (v/v) water-ethanol, the treatment in pure ethanol led to a lower yield of DL (62 %) with larger molecular weights (M_n 482 g/mol and M_w 1280 g/mol).

(2) With formic acid, a high yield of DL (80 %) of a dimer or trimer structure (M_n 150 g/mol and M_w 464 g/mol) were successfully achieved from the hydrothermal degradation of OL at 350 ^oC in 50/50 (v/v) water-ethanol.

(3) The in situ formed hydrogen from formic acid can prevent the recombination of reaction intermediates, increasing the DL yields while reducing the formation of solid residues.

(4) The degradation mechanism of AL and OL in the presence formic acid was believed through reducing the methoxyl group and cleaving the β-O-4 and α-O-4 linkages in the lignin structure.

8.6 Acknowledgements

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CHAPTER 9. CONCLUSIONS

The thesis work successfully demonstrated the production of bio-phenolic compounds from forestry biomass (residues, wastes and lignin), and substitution of petroleum-based phenol with the bio-phenolic compounds to produce high quality bio-based phenol formaldehyde (PF) resins. Specifically, the conclusions from the research as discussed in the previous chapters are summarized as follows.

(1) White Pine Sawdust was effectively liquefied with hot-compressed mono-solvents of water, methanol and ethanol, and co-solvents of alcohol (methanol- or ethanol) and water at a temperature from 200 ^{o}C to 350 °C. (a) There were synergistic effects of the combination of alcohol (methanol or ethanol) and water on pine sawdust direct liquefaction compared to mono-solvent of alcohol or water. Higher bio-oil yields (65 wt%) and better biomass conversion (95 wt%) at 300°C for 15 min were obtained from liquefaction in co-solvent of 50 wt% aqueous alcohol than that in mono-solvent of alcohol (~25 wt% bio-oil yield, and ~42 wt% biomass conversion) or water (40 wt% bio-oil yield, and 70 wt% biomass conversion); (b) The yields of bio-oil increased continuously from 25 wt% to 66 wt% as the reaction temperature increased from 200 ^{o}C to 300 °C, but the oil yield dropped markedly to below 35 wt% if further increasing the temperature to 350 °C, accompanied by a significant increase in solid residue. These results suggested severe conversion of bio-oil to char by condensation reactions of the liquid bio-oil products at > 300 °C, which was evidenced by the XRD measurements on the solid residues from the liquefaction; (c) The solvent-to-biomass ratio of 10 (wt/wt) was found to be an optimal condition for direct liquefaction of pine sawdust to produce bio-oil using hot-compressed co-solvent of ethanol-water (50%/50%, wt/wt); (d) The FTIR and GC-MS analyses of the obtained bio-oils revealed the presence of high contents of oxygen-containing chemical compounds such as phenolic compounds, aldehydes, long-chain (and cyclic) alcohols and ketones, ethers and esters and carboxylic acids, etc; (e) All the obtained bio-oils exhibited a broad molecular weight distribution, and contained a lot of

oligomers derived from the lignocellulosic feedstock. The bio-oil's molecular weight distribution was strongly dependent on the solvent type. Among all solvents tested, ethanol was the most effective solvent for the degradation of lignin into monomeric phenols; (f) The XRD measurements for solid residues after the liquefaction demonstrated that the cellulosic crystalline structures in the pine sawdust could remain with little change in the co-solvent of ethanol-water at a temperature up to 240 °C, while they would completely decompose to form amorphous carbon at 300 °C.

(2) (a) Phenolic bio-oil with a low molecular weight (M_w = 1072 g/mol and M_n = 342 g/mol) from direct liquefaction of Eastern white pine (*Pinus strobus L.*) sawdust in a hot-compressed ethanol-water (1:1 wt/wt) medium at 300 ^{o}C was successfully used to partially substitute phenol at a high substitution level (up to 75 wt%) in the synthesis of bio-oil phenol formaldehyde resole resins (BPFs); (b) All the BPFs displayed similar physical/chemical properties (non-volatile content, pH value, IR adsorption, etc.) to the reference pure phenol formaldehyde (PF) resole resin, while the viscosities, free formaldehyde levels and molecular weights of BPFs were all greater than those of the pure PF resin, as was expected; (c) All BPFs were curable at a temperature of 130 ^{o}C to 160 ^{o}C. The resins containing bio-oil more than 50 wt% (i.e., the 75 wt% BPF), displayed a higher curing temperature than the pure PF resin. At a low bio-oil ratio ≤ 50 wt%, however, the curing temperatures were lower than the pure PF resin, suggesting that the presence of bio-oil could promote the curing reactions of the BPFs. The curing reaction for all the resole resins proved to be approximately 1st order, and the activation energies of all BPFs are lower than that of the pure PF resin; (d) The residual carbon contents at 700 ℃ for the BPFs (25 ~ 75 wt% bio-oil ratios) are in the range of 72~48 %; (e) The addition of bio-oil to substitute for phenol at a high level (up to 75 wt%) produced useful bio-based resole resins useful as plywood adhesives and had comparable or better dry/wet bond strengths than the reference pure PF resin.

(3) (a) The ^{1}H NMR analysis of the bio-oil before and after methylolation demonstrated that the methylolation treatment could increase the methylol groups. The GPC analysis of bio-oil and MB suggested that condensation reactions occurred to the bio-oil during the methylolation treatment; All MBPF resins showed similar non-volatile contents as the pure PF. Although MBPF resins containing MB of higher than 25% precipitated in about a week at 4 ^{o}C, the resins could become liquid again by re-heating; (b) The experimental MBPF resole resins could be cured in the range from 128 ^{o}C to 155 ^{o}C. All MBPF resole resins exhibited a lower curing temperature, and better or comparable thermal stability than the PF resin. Interestingly, the 75% MBPF showed a higher carbon residue at 700 ^{o}C (59%) than the 75% BPF (48%). This suggests that the methylolation treatment of bio-oil could improve the thermal stability of bio-phenolic resins; When used as plywood adhesives, MBPF resins with 60% substitution for phenol proved to be possible without compromising the bond strength (dry and wet tensile strength) of the plywood specimens. However, the MBPF adhesives were more sensitive to water than the PF and BPF adhesive.

(4) (a) Hydrothermal degradation of an alkali lignin was achieved in sub-/super-critical ethanol-water or pure ethanol with and without catalyst. The 50/50 (v/v) water-ethanol co-solvent was proved to be the most effective solvent for degradation of the lignin in terms of the yield of degraded lignin (DL). The treatment at 300 ^{o}C for 2 hr led to a yield of DL at 89 %. The molecular weights of the lignin were markedly reduced from its original M_w and M_n of 60,000 g/mol and 10,000 g/mol, respectively to M_n of 415 g/mol and M_w of 1010 g/mol for the DL. Compared with that in 50/50 (v/v) water-ethanol, treatment in pure ethanol led to a much lower yield of DL (< 15 %) with smaller molecular weights (M_n 260 g/mol and M_w 631 g/mol from 300 ^{o}C treatment). Moreover, the DLs from pure ethanol treatment are completely soluble in THF, compared with only ~ 30% THF-solubility for the DL from 50/50 (v/v) water-ethanol treatment; (b) The reaction time had negligible effects on the DL yields and properties, while reaction temperature drastically influenced the product yields and properties: 300^{o}C to 325

^{o}C and 400 ^{o}C appeared to be the optimal temperature for the process with 50/50 (v/v) water-ethanol and pure ethanol, respectively; (c) Al_2O_3 supported Ni or Ru catalyst slightly reduced the DL yields and increased the solid residue yield in both 50/50 (v/v) water-ethanol and pure ethanol, while active carbon (AC)-supported catalysts could slightly increase the DL yields and lead to a decrease in molecular weights of the DL products; (d) The DL products obtained at a high temperature in 50/50 (v/v) water-ethanol contain a great amount of monomeric phenolic compounds with short-alkyl substituents ranging from C_1-C_4, while the DLs produced with pure ethanol are rich in esters.

(5) (a) Ni10/AC and Ru10/γ-Al_2O_3 were proved to effectively catalyze the hydrothermal degradation of organosolv lignin (OL) under hydrogen in sub-/super-critical 50/50 (v/v) water-ethanol and pure ethanol, by preventing the formation of char/coke. With Ru/Al_2O_3 catalyst the degradation treatment of OL at 300 °C in sub-/super-critical 50/50 (v/v) water-ethanol and pure ethanol produced a very high yield of DL: 94 % and 92%, respectively; (b) The treatment temperature was found to be the dominant factor in determining the yield and the molecular-weight distributions of the DL. Among all the tested conditions for OL degradation, the optimal condition was in a shaken micro-reactor at 340 ^{o}C in 50/50 water-ethanol employing the Ni10/AC catalyst, producing a very high DL yield (~81 %) with very low molecular weights (181 g/mol and M_w 568 g/mol); (c) Faster heating and stirring had a positive effect on the yield of DL, particularly the stirring; (d) All the OLPFs and DLPFs have similar physical properties as the pure PF resin in terms of viscosity, non-volatile contents, storage time at 4 ^{o}C, but have slightly higher free formaldehyde content. The OLPFs and DLPFs can be cured at a lower temperature than the pure PF resin; (e) In application of OLPF and DLPF resins as plywood adhesives, both dry and wet strengths of the plywood specimen bonded by an OLPF or DLPF were stronger than those of the pure PF resin adhesive. OLPFs perform better than the DLPFS with respect to dry and wet tensile strengths, in particular the 50% OLPF has the highest dry and wet strengths as well as the dry and wet WFP values among all the adhesives tested.

(6) Formic acid as a hydrogen donor has a significant effect on alkali lignin (AL) and organosolv lignin (OL) hydrothermal degradation in 50/50 (v/v) water-ethanol and pure ethanol. (a) With formic acid, the treatment for AL at 300 ^oC in 50/50 (v/v) water-ethanol led to a high yield (77 %) of degraded lignin (DL). The molecular weights of the lignin were drastically reduced from its original M_w and M_n of 60,000 g/mol and 10,000 g/mol, respectively, to M_n of 295 g/mol and M_w of 816 g/mol for the DL. Compared with that in 50/50 (v/v) water-ethanol, the treatment in pure ethanol led to a lower yield of DL (62 %) with larger molecular weights (M_n: 482 g/mol and M_w: 1280 g/mol); (b) With formic acid, a high yield of DL (80 %) of a dimer or trimer structure (M_n: 150 g/mol and M_w: 464 g/mol) were successfully achieved from the hydrothermal degradation of OL at 350 ^oC in 50/50 (v/v) water-ethanol; (c) The in situ formed hydrogen from formic acid can prevent the recombination of reaction intermediates, increasing the DL yields while reducing the formation of solid residues; (d) The degradation mechanism of AL and OL in the presence formic acid was believed through reducing the methoxyl group and cleaving the β-O-4 and α-O-4 linkages in the lignin structure.

In summary, two novelties can be concluded based on the above work: (1) A high yield and high quality of bio-oil can be produced from forestry residues via a hydrothermal liquefaction process without catalyst using green solvents (water, and ethanol) in sub-/super-critical states. The bio-oil phenolic resins with a phenol substitution ratio up to 75% show comparable properties as the pure PF resin. (2) Lignin (alkali lignin and organosolv lignin) can be successfully degraded into bio-phenolic compounds with greatly reduced molecular weights in a sub-/super-critical water-ethanol medium. The obtained bio-phenolic compounds can be used as an excellent phenolic feedstock in the synthesis of high quality phenolic resins at a high substitution ratio up to 75%. The degraded lignin phenol formaldehyde resins when used as plywood adhesives have stronger bond strength than the control resin (PF resin).

CHAPTER 10. FUTURE WORK

The above progress proves that biomass/lignin has a good potential for replacing phenol in the synthesis of phenolic resins. In order to commercialize the bio-phenolic compounds and bio-based phenolic resole resin adhesives, more efforts need to be made in future as follows.

(1) Optimization of the bio-based phenolic resin synthesis process with respect to the molar ratio of formaldehyde to phenols (phenol + bio-phenolic compounds), the pH value or ratio of the basic catalyst to phenols, substitution ratio of bio-phenolic compounds for phenol in PF resin, viscosity or reaction time and the molecular weights of the bio-phenolic compounds.

(2) Optimization of the application process for the bio-based phenol adhesives regarding the hot-pressing temperature, pressure and time, as well as the content of extender such as wheat flour and wood powder.

(3) Evaluation of the production cost of bio-based phenolic resins using biomass and lignin.

(4) Exploration of other applications of the lignin and bio-phenolic compounds, e.g., polyurethane formed materials, thermoplastic plastic molding materials, formaldehyde-free green adhesives for medium density fiberboards (MDF), etc.

PUBLICATIONS

Chapters 2 through 6 included in this thesis have been accepted/submitted for publication in peer-reviewed scientific book or journals. Two patents are under preparation with the work of Chapters 7. Chapter 8 will be submitted. The presented work was carried out by Shuna Cheng, with the assistance of the following co-authors, who provided valuable comments, suggestions and revisions to these manuscripts for publication.

- Chapter 2: Xu, C.*, Cheng, S., Leitch, M. A part of a Book Chapter in *Lignin: properties and applications in biotechnology and bioenergy*, Nova Science Publishers, Inc., New York, 2010 (In press).

- Chapter 3: Cheng, S., Leitch, M., Xu, C.* *Energy & Fuels*, 2010. 24 (9), 4659–4667.

- Chapter 4: Cheng, S., Anderson, M., Leitch, M., Xu, C.* *Journal Applied Polymer Science*, 2011, 121: 2743–2751.

- Chapter 5: Cheng, S., Yuan, Z., Leitch, M., Anderson, M., Xu, C.* *Journal Applied Polymer Science*, 2011 (In press).

- Chapter 6: Cheng, S., Yuan, Z., Leitch, M., Anderson, M., Xu, C.* *Polymer Degradation and Stability*, 2011 (Under review).

- Chapter 7: Cheng, S., Yuan, Z., Leitch, M., Xu, C.* Patents under preparation, 2011

- Chapter 8: Cheng, S., Yuan, Z., Leitch, M., Anderson, M., Xu, C.* *Energy & Fuels*, 2011(To be submitted).