5-2017

Production of Phenol-formaldehyde Adhesives from Catalytic Pyrolysis Oil

Angela M. Akude
Utah State University

Recommended Citation

Akude, Angela M., "Production of Phenol-formaldehyde Adhesives from Catalytic Pyrolysis Oil" (2017). *All Graduate Theses and Dissertations*. 5612.
https://digitalcommons.usu.edu/etd/5612

PRODUCTION OF PHENOL-FORMALDEHYDE ADHESIVES FROM CATALYTIC PYROLYSIS OIL

by

Angela M. Akude

A thesis submitted in partial fulfillment
of the requirements for the degree

of

MASTER OF SCIENCE

in

Biological Engineering

Approved:

Foster Agblevor, Ph.D. Major Professor	Ronald Sims, Ph.D. Committee Member
Yujie Sun, Ph.D. Committee Member	Mark McLellan, Ph.D. Vice President for Research and Dean of the School of Graduate Studies

UTAH STATE UNIVERSITY
Logan, Utah

2017

ABSTRACT

Production of Phenol-formaldehyde Adhesives
from Catalytic Pyrolysis Oil

by

Angela M. Akude, Master of Science

Utah State University, 2017

Major Professor: Dr. Foster Agblevor
Department: Biological Engineering

Phenol-formaldehyde adhesives are important adhesives known to have superior water resistance capacity and high mechanical strength when utilized in wood-based applications. Due to unsustainability and environmental issues associated with the use of fossil fuels, there is an urgent need to look for alternative raw materials, which are renewable in nature. Pinyon-juniper biomass has been found to be a suitable replacement for petroleum-based phenol because it is renewable, abundant, and readily available.

In this thesis, bio-oil produced from the pyrolysis of pinyon-juniper biomass using red mud alumina catalyst was used to produce wood adhesives. The characterization of pinyon-juniper bio-oil showed the presence of phenolics, aromatic hydrocarbons, aliphatic hydrocarbons, carboxylic acids, ethers, ketones, aldehydes, and aliphatic alcohols.

Resol synthesis parameters such as formaldehyde-to-phenol molar ratio (1.8 and 2), catalyst loading (0.25, 0.63, and 1.25 g of NaOH), reaction time (60 minutes), and reaction temperature (95 °C), were investigated in the production of pinyon-juniper adhesives. Based on the results obtained, the extent of phenol substitution with pinyon-juniper bio-oil was dependent on the amount catalyst used during the synthesis process. The maximum phenol substitution of 80% was achieved using a catalyst loading of 1.25 g of NaOH while the minimum phenol substitution of 50% was obtained at a catalyst loading of 0.25 g of NaOH.

Dry shear strength (8.99 to 12.73 MPa) and wet shear strength of (5.16 to 7.36 MPa) for both pure phenol-formaldehyde resols and pinyon-juniper substituted resols were comparable and exceeded the minimum requirement of 0.66 MPa for plywood. Finally, the chemical structure of pure phenol-formaldehyde resols showed the presence of more phenolic OH groups compared to pinyon-juniper substituted resols. This observation was corroborated by the higher concentration of free phenol in pure phenol-formaldehyde adhesives compared to pinyon-juniper substituted resols.

(122 pages)

PUBLIC ABSTRACT

Production of Phenol-formaldehyde Adhesives from Catalytic Pyrolysis Oil

Angela M. Akude

Phenol-formaldehyde adhesives conventionally synthesized from fossil fuel resources pose two major concerns: sustainability issues and environmental concerns. The sustainability issues arise from the inevitable depletion of fossil fuel resources while the environmental concerns, primarily, stem from the emission of volatile organic compounds. Thus, opting for alternative raw materials from renewable resources reduces the dependence on fossil fuels as well as promote the production of environmentally-friendly products.

The successful commercialization of bio-adhesives requires that the substitution of phenol with bio-oil during resin synthesis should be above 40%. In this study, catalytic pyrolysis oil produced from pinyon-juniper biomass and red mud alumina catalyst was used to synthesize phenolic resins. Also, the influence of adhesive synthesis parameters on the degree of phenol substitution with pinyon-juniper bio-oil, the strength of adhesives, and the concentration of free formaldehyde and free phenol contents were examined.

Phenol was successfully substituted with 80% pinyon-juniper bio-oil. The adhesive strengths of pinyon-juniper substituted adhesives were comparable to the adhesive strengths obtained for pure phenol-formaldehyde adhesives. The phenol concentrations of pinyon-juniper substituted adhesives were observed to be lower in

comparison to pure phenol-formaldehyde adhesives.

ACKNOWLEDGMENTS

I would like to thank God Almighty for granting me the grace to complete my master’s education. I am sincerely grateful to my advisor, Dr. Foster Agblevor for supporting my education both financially and intellectually. Also, I would like to thank USTAR and the National Science Foundation for funding this research. My heartfelt gratitude to Dr. Ronald Sims and Dr. Yujie Sun for serving on my committee.

I would like to thank Dr. Nicholas Roberts and Alexander Brown for your support during the mechanical tests. To my previous colleagues: Kyle Christian, Brandon Sargent, Jenna Rydalch, and Michael Castle, I appreciate your diverse roles with regards to my work.

To mum and dad (Elizabeth and Samuel), thank you for all your sacrifices. Dr. Martin Woode, I appreciate your help during my academic journey. Gabriel Anteh, Emmanuel Lartey, and Dr. Patience Akude, I do appreciate your encouragement and support. Finally, I would like to thank my friends – Kwame Ohene Donkor, Dr. James Odei, Sarah Guzman, Rev. Abraham Nyarko, Ohemaa and Joshua Odei, Kathy and Vince Eccles, Jennifer and John Hartman, Yonas Kidane, and Hossein Jahromi, for your love and care during my graduate studies.

Angela M. Akude

CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1 Background

Rapid growth in the construction industry has led to increasing demand for phenolic resins. By 2019, the value of the phenolic resin industry globally is estimated to be $19.31 billion (Marketsandmarkets.com, 2014). Resols dominated the global market share of phenolic resins by more than 75% in 2013, and are expected to maintain their dominance by a steady growth rate of 4.1% until 2019 (Marketsandmarkets.com, 2014).

Resols are phenol-formaldehyde (PF) adhesives produced via addition and condensation reactions of phenol and formaldehyde in alkaline environment (Gardziella et al., 2000; Grenier-Loustalot et al., 1996; Strzemiecka et al., 2016; Wang et al., 2009; Zhao et al., 2013). Wood-based products such as plywood (Zhang et al., 2013), particle boards (Nihat and Nilgül, 2002), oriented strand board (Chan et al., 2002), etc. produced from these adhesives, particularly, have excellent water resistance, high mechanical strength, and low volatile organic compound emissions. These characteristics make phenol-formaldehyde adhesives suitable for diverse construction and building applications (Cai and Ross, 2010).

More than 90% of phenol is produced from petroleum-derived benzene and propylene through the Cumene or Hock process (Ishii and Sakaguchi, 2006; Knop and Pilato, 1985). Formaldehyde is produced via dehydrogenation of methanol over silver catalyst or over iron oxide and molybdenum oxide catalysts (Pilato, 2010). Confronted by depleting fossil fuel reserves and their associated environmental concerns (Maher and

Bressler, 2007; Valliyappan et al., 2008), there is the need to find other sustainable alternatives to petroleum-based phenol.

1.2 Problem statement

Depletion of fossil fuel resources is inevitable, therefore other suitable alternatives to phenol must be investigated. Lignocellulosic biomass is a promising resource for replacing petroleum-derived phenols used in the production of phenol-formaldehyde adhesives (Effendi et al., 2008). The interest in lignocellulosic biomass stems from the fact that it is renewable and readily available (Cheng, 2011). Furthermore, lignocellulosic biomass contains lignin, which is a good source of phenol, phenol derivatives, and other aromatic compounds (Effendi et al., 2008).

Pinyon-juniper wood species, a type of lignocellulosic biomass has been found to be a potential source for phenol (Yathavan, 2013). Over the years, the western part of the United States of America has experienced a widespread expansion of pinyon juniper woodlands (Yathavan and Agblevor, 2013). These woodlands compete with grasslands and other herbaceous vegetation for the same land space. Thousands of acres of pinyon-juniper woodlands have therefore, been cleared in an attempt to restore herbaceous and grassland vegetations (Aro, 1971; Gallo et al., 2016).

Currently, harvested wood species of pinyon juniper are commonly used as firewood. Thus, finding technologies that convert this lignocellulosic biomass from low value firewood to high value products is critical (Yathavan and Agblevor, 2013). Technologies such as pyrolysis have been identified as a useful process for obtaining bio-phenolic compounds from lignocellulosic biomass (Effendi et al., 2008).

1.3 Research objectives

Yathavan and Agblevor (2013), successfully demonstrated that catalytic pyrolysis of pinyon-juniper can be used to produce high quality liquid products, which are not only suitable for fuel use but could also be used in the production of other bio-products. Hence, pinyon-juniper catalytic pyrolysis is a potential source of bio-phenols for resol production. The main objective of this research is to produce good quality adhesives by substitutions (at least 50 wt%) of phenol with pinyon-juniper catalytic pyrolysis oil. The measures for good quality resols are excellent water resistance and high mechanical strength. Secondary properties of resols such as free phenol and free formaldehyde contents will also be evaluated. Other objectives of this research include:

- Resol production from pinyon-juniper catalytic pyrolysis oil, which have similar or even better quality than conventional phenol-formaldehyde adhesives.
- Optimization of reaction parameters for phenol/bio-oil adhesives production.

1.4 References

Aro, R.S., 1971. Evaluation of pinyon-juniper conversion to grassland. J. Range Manag. 24, 188–197.

Cai, Z., Ross, R.J., 2010. Mechanical properties of wood-based composite materials, in: Wood Handbook - Wood as an engineering material.general technical report FPL-GTR-190. U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, WI, pp. 1–12.

Chan, F., Riedl, B., Wang, X.M., Lu, X., Amen-Chen, C., Roy, C., 2002. Performance of pyrolysis oil-based wood adhesives in OSB. For. Prod. J. 52, 31–38.

Cheng, S., 2011. Bio-based phenolic resins and adhesives derived from forestry residues/wastes and lignin. PhD Thesis, Lakehead University.

Effendi, A., Gerhauser, H., Bridgwater, A. V., 2008. Production of renewable phenolic resins by thermochemical conversion of biomass: A review. Renew. Sustain. Energy Rev. 12, 2092-2116.

Gallo, T., Stinson, L.T., Pejchar, L., 2016. Pinyon-juniper removal has long-term effects on mammals. For. Ecol. Manage. 377, 93–100.

Gardziella, A., Pilato, L.A., Knop, A., 2000. Phenolic Resins: Chemistry, application, standardization, safety and ecology. Springer, Berlin.

Grenier-Loustalot, M.F., Larroque, S., Grande, D., Grenier, P., Bedel, D., 1996. Phenolic resins: 2. Influence of catalyst type on reaction mechanisms and kinetics. Polymer 37, 1363–1369.

Ishii, Y., Sakaguchi, S., 2006. Recent progress in aerobic oxidation of hydrocarbons by N-hydroxyimides. Catal. Today 117, 105–113.

Knop, A., Pilato, L.A., 1985. Phenolic resins: Chemistry, applications, and performance: Future directions. Springer-Verlag Berlin.

Maher, K.D., Bressler, D.C., 2007. Pyrolysis of triglyceride materials for the production of renewable fuels and chemicals. Bioresour. Technol. 98, 2351–2368.

Marketsandmarkets.com, 2014. Phenolic Resin Market by Type (Resol and Novolac) and by Application (wood adhesive, molding, laminates, insulation, and others) – Global Trends & Forecast to 2019. http://www.marketsandmarkets.com/Market-Reports/phenolic-resin-market-177821389.html (accessed 7.13.16).

Nihat, S.C., Nilgül, O., 2002. Use of organosolv lignin in phenol formaldehyde resins for particleboard production II. Particleboard production and properties. Int. J. Adhes. Adhes 22, 477–480.

Pilato, L., 2010. Phenolic reisn: A century of progress. Springer-Verlag Berlin Heidelberg.

Strzemiecka, B., Zieba-Palus, J., Voelkel, A., Lachowicz, T., Socha, E., 2016. Examination of the chemical changes in cured phenol-formaldehyde resins during storage. J. Chromatogr. A. 1441, 106–115.

Valliyappan, T., Bakhshi, N.N., Dalai, A.K., 2008. Pyrolysis of glycerol for the production of hydrogen or syn gas. Bioresour. Technol. 99, 4476–4483.

Wang, M., Xu, C., Leitch, M., 2009. Liquefaction of cornstalk in hot-compressed phenol-water medium to phenolic feedstock for the synthesis of phenol-formaldehyde resin. Bioresour. Technol. 100, 2305-2307.

Yathavan, B.K., 2013. Conventional and catalytic pyrolysis of pinyon juniper biomass. Master's Thesis, Utah State University.

Yathavan, B.K., Agblevor, F.A., 2013. Catalytic pyrolysis of pinyon-juniper using red mud and HZSM-5. Energy and Fuels 27, 6858–6865.

Zhang, W., Ma, Y., Wang, C., Li, S., Zhang, M., Chu, F., 2013. Preparation and properties of lignin-phenol-formaldehyde resins based on different biorefinery residues of agricultural biomass. Ind. Crops Prod. 43, 326:333.

Zhao, Y., Yan, N., Feng, M.W., 2013. Thermal degradation characteristics of phenol-formaldehyde resins derived from beetle infested pine barks. Thermochim. Acta. 555, 46-52.

CHAPTER 2

LITERATURE REVIEW

2.1 History of phenol-formaldehyde resins

2.1.1 Background

Studies on resinous products began in 1872, when A. von Baeyer first discovered the formation of a synthetic polymeric resin through the reaction of phenol and formaldehyde (Knop and Pilato, 1985). In that era, however, the reddish-brown polymer had no technical and economic value. Thirty-five years later, another scientist, Leo Hendrik Baekeland, finally developed a series of economically viable applications to phenol-formaldehyde resins (Pilato, 2010). The early applications of Baekeland's resins, which were known to possess excellent insulation properties, were used in the fabrication of a plethora of home appliances (Knop and Pilato, 1985).

Baekeland's invention was remarkable at that time, since phenolic resins reduced dependence on very expensive natural resins such as shellac and gutta percha (Knop and Pilato, 1985). Extensive research since 1907 led to the development of newer applications of phenolic resins in the wood, material molding, and thermal insulation industries (Knop and Pilato, 1985). The focus of this research therefore, was to conduct investigations on the use of resol-type phenolic resins as adhesives for wood-based applications.

2.2 Classification of wood adhesives

Adhesives are normally classified as either being natural or synthetic (Atta-Obeng, 2011). The major difference between natural and synthetic adhesives is simply the source from which they are obtained. Natural adhesives are made using raw materials from natural organic sources such as vegetables, animals, and proteins while synthetic adhesives are produced from man-made raw materials.

2.2.1 Natural adhesives

The use of natural adhesives was very popular prior to the second world war in the early 1900s. The majority of natural adhesives produced at that time was derived from cassava (Eckelman, 1999). The major advantage of using natural adhesives is that they are more environmentally friendly compared to synthetic adhesives. However, some disadvantages of using natural adhesives compared to synthetic adhesives include high viscosity of final resins, poor water resistance of the adhesives, and low adhesive bonding strength. These properties were not desirable. Apart from starch-based glues derived from cassava, other types of natural adhesives were derived from various raw materials (Cheng, 2011; Eckelman, 1999; Siddiqui, 2013).

2.2.1.1 Casein glues

An important constituent in milk, acid-insoluble phosphoprotein commonly referred to as casein, is another source of natural adhesives (Fox and Brodkorb, 2008). Casein can be obtained by acidifying milk at a pH of 4.5. At this pH level, casein becomes insoluble and precipitates out of the milk solution. The production of casein glue competes with human food supply since 8 gallons of skim milk is required to produce a pound of casein glue. The preparation of casein glue involves dissolving the precipitated casein in alkaline solution. Casein glues are usually used for the production of laminated lumber for interior wood work applications (Gu, 2010; Siddiqui, 2013).

2.2.1.2 Animal-based glues

Animal adhesives are made from connective tissues, bones, and hides of animals (Abdallah et al., 2016; Eckelman, 1999). Disadvantages of using animal glues in manufacturing wood-based products include fungi and mold infestation, and low water resistance of wood-based products. Animal glues can be obtained in a powdery, jell-like, or bead-like form. Good quality animal glue is characterized by its ability to retain its gelatinous mass after several soaking cycles in water (Eckelman, 1999; Siddiqui, 2013).

2.2.1.3 Protein-based glues

Protein-based glues are predominantly obtained from soybeans. Proteins are isolated from soybeans and either used singly or together with blood proteins to make glues for wood applications. Wood-based products made from protein-based adhesives have undesirable properties such as low water resistance and low dry strength. Protein-based glues were generally used for the production of douglas-fir plywood. However, these glues have now been replaced by phenol-formaldehyde adhesives (Eckelman, 1999; Siddiqui, 2013).

2.2.1.4 Dextrin or starch-based vegetable glues

Starch-based vegetable glues are obtained from grain and tuber starch sources such as rice, cassava, and potatoes (Eckelman, 1999; Kennedy and Fischer, 1984). Glues of this nature were extensively used in the production of interior-grade hardwood plywood but nowadays, they have been replaced by synthetic adhesives such as urea-formaldehyde (UF) adhesives. Starch adhesives are usually inexpensive, have a long pot life, and have high dry strength (Eckelman, 1999; Singh et al., 2014).

2.2.2 Synthetic adhesives

Synthetic adhesives are produced from man-made raw materials. These adhesives can either be categorized as thermoplastics or thermosets (Jang, 2011). Thermosets are materials, which do not return to their original state after heat exposure (Huang, 2007). Examples of thermosetting synthetic adhesives include phenol-formaldehyde adhesives (resols), melamine-formaldehyde resins, phenol-resorcinol-formaldehyde resins, iso-cyanates, and urea-formaldehyde adhesives (Huang, 2007; Sellers, 2001). Thermoplastics are materials, which are moldable upon heat exposure and regain their rigid nature after cooling. Some examples of thermoplastic adhesives include polyvinyl acetate (PVA) emulsions, polyethylene, polyacrylate, and polyethylene-vinyl acetate (Ashori and Nourbakhsh, 2008; Atta-Obeng, 2011).

2.2.2.1 Urea-formaldehyde resins

Urea-formaldehyde (UF) resins are thermosetting resins produced from the addition and condensation reaction of urea and formaldehyde. The addition reaction involves hydromethylation of urea by formaldehyde leading to the formation of mono-, di-, and tri-hydromethylureas (Gu, 2010). However, the condensation reaction involves the polymerization of the methylolated urea in the presence of an acidic catalyst, usually ammonium chloride. Problems associated with the use of UF resins during wood-based applications include poor water resistance, brittle adhesive layer, and emission of free formaldehyde compounds (Siddiqui, 2013). The advantages of using UF resins include their short pressing time, affordable price, and high reactivity (Dunky, 1998; Gu, 2010). Wood-based products commonly produced from UF resins include particle boards, medium density fiberboard (MDF), and plywood (Gu, 2010).

2.2.2.2 Melamine-formaldehyde resins

Melamine-formaldehyde (MF) adhesives are produced from the addition and condensation reaction of melamine and formaldehyde. MF resins can be classified as an upgrade of urea formaldehyde resins since MF resins have better moisture resistance than UF resins. Furthermore, the free formaldehyde content of MF resins is much lower than that of UF resins. MF resins are used in the production of semi-exterior grade plywood (marine plywood) and particle board. The only downside to using MF resins is their relatively high cost compared to the cost of UF resins. Melamine-urea-formaldehyde (MUF) resins have also been developed in order to incorporate the desirable properties of MF resins into UF resins (Eckelman, 1999; Gu, 2010; Siddiqui, 2013).

2.2.2.3 Isocyanate adhesives

Isocyanate adhesives are adhesives, which are known to form excellent bonds with wood-based materials. Polymeric diphenylmethane diisocyanate (pMDI) is one of the commonest isocyanate adhesive present on the wood adhesives market. Advantages of isocyanates such as pMDI include their fast curing rate, formation of excellent adhesive bonds, and good water resistance. Isocyanate adhesives are used for the production of wood-based products such as oriented strand board (OSB) and particle boards. pMDI is expensive compared to UF and PF resins and also hazardous (Gu, 2010; Siddiqui, 2013).

2.2.2.4 Polyvinyl acetate adhesives

Polyvinyl acetate adhesive (PVA) are thermoplastic resins, which are odorless, non-toxic, and non-flammable. They are commonly referred to as white glue. PVA resins are commonly used to bond plastic laminates and also used during furniture assembly applications. PVA resins have faster curing rates compared to UF resins. Since PVA resins are thermoplastics, they soften rapidly when heated. At temperatures above 70 °C, PVA resins lose their bond strength (Motohashi et al., 1984; Tout, 2000). Disadvantages of using PVA compared to UF include poor moisture and heat resistance. N-(hydroxymethyl) acrylamide is therefore used as a crosslinking monomer to improve the moisture and heat resistance properties of PVA resins (Cho et al., 2000; Gu, 2010; Siddiqui, 2013).

2.2.2.5 Phenol-formaldehyde resins

Phenol-formaldehyde (PF) resins are produced through acidic or base-catalyzed addition and condensation reactions of phenol and formaldehyde (Knop and Pilato, 1985). PF resins are classified as resols or novolacs depending on the type of catalyst involved in the synthesis of the resin. PF resins are typically used for the production of exterior grade wood-based products such as OSB, laminated veneer lumber (LVL), and plywood (Cheng, 2011; Shiraishi et al., 1993). These resins are preferred for the production of exterior-grade wood applications because the wood products manufactured using PF resins have excellent strength and weather resistant characteristics (Pilato, 2010).

2.3 Chemistry of resol synthesis

2.3.1 Methylol phenols formation via addition reaction

The production of resols is derived from the step growth reaction of phenol-formaldehyde systems in basic media (Grenier-Loustalot et al., 1996; Riedlinger,2008). Resols are synthesized using excess formaldehyde-to-phenol (F/P) molar ratio of greater than 1. During the addition reaction, which is the initial reaction stage, unsubstituted tri-functional phenol reacts with di-functional formaldehyde to form methylol phenols or substituted hydroxymethylphenols (Riedlinger, 2008). This reaction occurs at the ortho and para positions of the hydroxyl group of phenol. The ortho and para positions of phenol are shown in Fig. 2.1. The basic catalyst utilized during the production of the PF resol also plays an important role in the formation of hydroxymethylphenols (HMP).

The catalyst during resol synthesis is composed of a hydroxide anion and a metal cation (Grenier-Loustalot et al., 1996). Upon addition of the basic catalyst, the hydroxide anion participates in the formation of reactive phenoxide ions by deprotonating phenol as shown in Fig. 2.1 (Cheng, 2011; Grenier-Loustalot et al., 1996).

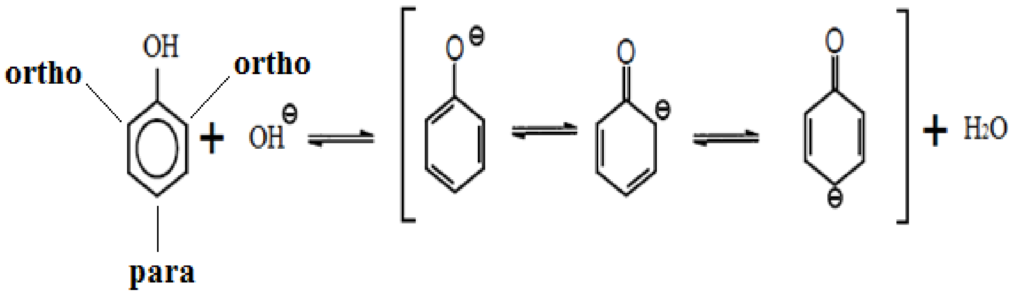

Fig. 2.1. Formation of phenolates in the presence of NaOH during resol production (Grenier-Loustalot et al., 1996).

In Fig. 2.2, formaldehyde, present as methylene glycol leads to the formation of methylol phenols or substituted HMP at the ortho- and para- sites of the phenoxide ions. The para position of the phenoxide anion has a greater affinity for formaldehyde (methylene glycol) than the ortho position (Cheng, 2011; Riedlinger, 2008). The metal cations obtained from the basic catalysts contribute to the reaction by establishing intermediate chelates, which are ortho-directing. The chelating strength is greater when the cation electron delocalization potential is higher. The presence of metal cations influences the ortho or para position substitution ratio. Ortho substitution increases in the following order $K^+<Na^+<Li^+<Ba^{2+}<Sr^{2+}<Ca^{2+}<Mg^{2+}$ (Grenier-Loustalot et al., 1996; Riedlinger, 2008).

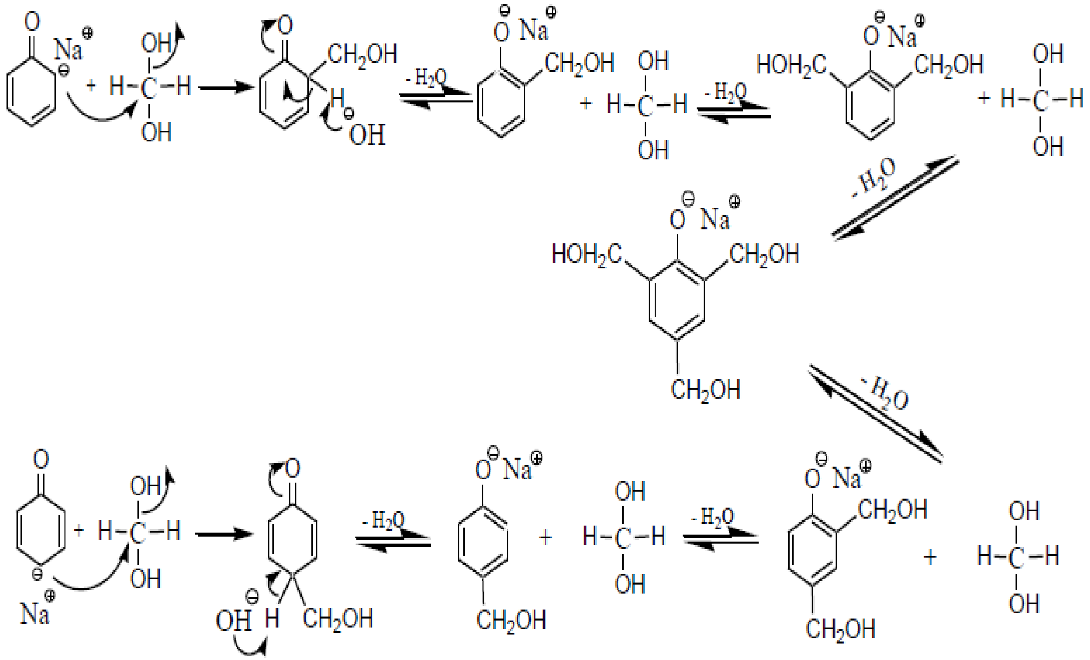

Fig. 2.2. Formation of substituted methylol phenols (Cheng, 2011).

2.3.2 Condensation reactions of methylol phenols

Methylol phenol condensation reactions occur through quinone methide intermediates (Martin et al., 1980; Megson, 1958). Generally, condensation reactions between two HMPs are faster than the reaction between one HMP and one unsubstituted phenol. This phenomenon may account for the reason why unreacted phenols still remain after resol synthesis. Methylene bridges or dimethylene-ether bridges are formed when quinone methides are substituted at the ortho and para positions of phenoxide ions. Dimethylene-ether bridges are usually formed at lower temperatures and neutral pH while methylene bridges are formed at high temperatures (>150 °C) and in very basic conditions (Cheng, 2011).

Condensation reactions at the para position are more dominant than those at the ortho position due to steric hindrance at the ortho position (Cheng, 2011). Hence, the para-para and para-ortho methylene bridges are dominant compared to ortho-ortho methylene bridges (Aierbe et al., 2002; Riedlinger, 2008). In general, there are three major stages during the condensation of methylol phenols: resol, resitol, and resite stages (Cheng, 2011; Riedlinger, 2008; Sellers, 1985). The initial stage, which is the resol stage, contains a mixture of monomers and dimers of hydroxymethylphenols. The resite stage refers to the stage whereby the polymer is completely cured whereas the resitol stage is the stage whereby the resin is made up oligomers of HMP (Cheng, 2011).

2.4 Chemistry of novolac synthesis

Novolacs are produced when the addition and condensation reactions of phenol and formaldehyde are acid-catalyzed. During the production of novolacs, F/P molar ratio of less than 1 is typically used. Phenol and formaldehyde react to form methylol phenols during the addition reaction stage (Cheng, 2011; Strzemiecka et al., 2016). In the condensation reaction stage, phenol reacts with methylol phenols to form methylene bridges. Novolacs usually lack hydromethylene groups compared to resols. Hence, formaldehyde, paraformaldehyde or urotropine are added to the novolac before crosslinking is carried out (Strzemiecka et al., 2016). In wood-based applications hexamethylene tetramine is used to facilitate the curing process of novolacs (Gu, 2010). Apart from wood product manufacturing, novolacs are used for the production of abrasive materials (Gardziella et al., 2000; Pilato, 2010; Strzemiecka et al., 2016).

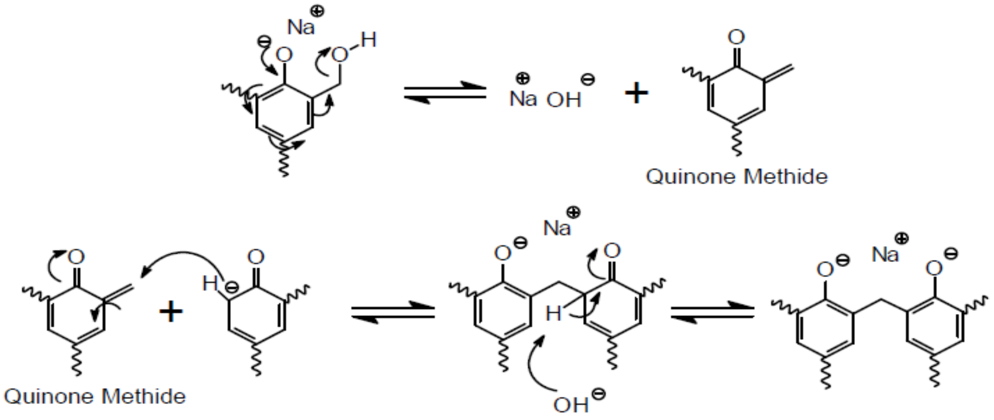

Fig. 2.3. Formation of quinone methide intermediates (Riedlinger, 2008).

Table 2.1
Differences between novolacs and resols in terms of synthesis process conditions (Huang, 2007).

Type of phenolic resin	F/P molar ratio	Reaction time, h	Reaction temperature, °C
Novolac	F/P < 1	3-6	100
Resol	F/P > 1	1-3	79 -100

2.5 Raw materials for resol production

One of the essential raw materials for the production of conventional phenol-formaldehyde (PF) resins is phenol. By definition, phenols are aromatic compounds, which have a hydroxyl group connected to the aromatic ring. Phenols, which may also be referred to as carbolic acids, behave like weak acids: they are insoluble in aqueous sodium carbonate solutions but easily dissolve in aqueous sodium hydroxide solutions. Usually, pure monomeric phenols are used for conventional PF resin synthesis. Apart from monomeric phenol, which is usually described as simply phenol, there are different variations of phenolic compounds available for diverse applications (Knop and Pilato, 1985). The different types of phenolic compounds and their physical properties are shown in Table 2.2.

Table 2.2
Types of phenolic compounds (Knop and Pilato, 1985).

Type of phenolic compound	**Molecular weight**
Phenol	94.1
o-cresol	108.1
m-cresol	108.1
p-cresol	108.1
p-tert. Butyl phenol	150.2
p-tert. Octylphenol	206.3
p-Nonylphenol	220.2

2.5.1 Synthesis of phenol

Phenol is synthesized by a process known as the cumene or the hock process, which was first discovered by H. Hock (Hock and Lang, 1944; Ishii and Sakaguchi, 2006; Jourshabani et al., 2015). The cumene process for phenol production is achieved by series of reactions. The initial reaction step involves alkylation of benzene with propylene using phosphoric acid catalyst to form cumene (isopropylbenzene). The next stage of reactions involves the oxidation of cumene with oxygen to form cumene hydroperoxide (CHP). At the final reaction stage, highly concentrated CHP is catalyzed using sulfuric acid to produce a mixture containing phenol and acetone (Knop and Pilato, 1985). The synthesis of phenol, which is heavily dependent on petroleum based products, accounts for more than 90% of the global phenol production (Knop and Pilato, 1985).

2.5.2 Synthesis of formaldehyde

Another important raw material for the production of conventional phenol-formaldehyde resins is formaldehyde. Formaldehyde is the simplest aldehyde, produced by dehydrogenation of methanol. There are two major stages involved in the dehydrogenation process (Knop and Pilato, 1985). First, formaldehyde could be produced using a metal oxide catalyst or a silver catalyst. When metal oxide catalysts are used in the production of formaldehyde, the process is referred to as the Formox process (Pilato, 2010). In this particular instance, the metal oxide catalyst is made up of a mixture of iron oxide and molybdenum oxide. The reaction occurs between 250 °C and 400 °C (Knop and Pilato, 1985). However, formaldehyde production using silver oxide catalysts occurs at 600 °C to 650 °C (Pilato, 2010). The formation of formaldehyde is achieved by a set of parallel reaction schemes:

$CH_3OH + \frac{1}{2} O_2 \longrightarrow HCHO + H_2O$

$CH_3OH \longrightarrow HCHO + H_2$ (Pilato, 2010).

Methanol, which is the predominant raw material for the production of formaldehyde is most often derived from natural gas, a non-renewable resource (Pilato, 2010).

2.6 The interest in renewable resources for the production of PF resins

The concept of looking for renewable resources for adhesive production is not new. Prior to the 1940s, natural adhesives produced from natural sources were the most dominant in the adhesive industry (Papadopoulou, 2009). However, by the 1970s, the natural adhesive market experienced a decline as petrochemical starting materials for adhesive production gained dominance. Adhesives produced from petrochemical end products were more competitive than natural adhesives in terms of product cost, quality and consistency (Papadopoulou, 2009). Now, in this 21st century, the use of fossil fuel resources for the production of adhesives continues to present serious concerns.

In 2008, a Klass model (Shafiee and Topal, 2009) was used to predict the depletion of crude oil, natural gas, and coal. According to this model, crude oil, natural gas, and coal were expected to be depleted in 35, 37, and 107 years respectively (Shafiee and Topal, 2009). As previously stated, the starting materials for both phenol and formaldehyde are all fossil fuel derived. Thus, the depletion of fossil fuel resources will negatively affect the availability of phenol and formaldehyde for resol production. Aside depleting fossil fuel resources, environmental issues associated with fossil fuel usage such as global warming is also a major concern (Abbasi and Abbasi, 2011; Bridgwater, 2003; Chiari and Zecca, 2011; Zecca and Chiari, 2010). It is therefore important, to opt for both sustainable and environmentally-friendly raw materials for the production of phenol-formaldehyde adhesives.

2.7 Lignocellulosic biomass: a promising alternative to phenol

Biomass is the most promising alternative for phenol replacement because it is a renewable resource, which is readily available and abundant (Amen-Chen et al., 2001). Furthermore, using biomass as a substitute to fossil fuel products reduces the net carbon dioxide concentration in the atmosphere, thereby minimizing the environmental concerns associated with greenhouse gas emissions (Gustavsson et al., 1995; Gustavsson and Svenningsson, 1996; Lucia, 2008).

2.7.1 Composition of biomass

Lignocellulosic biomass is made of three major components: lignin, cellulose, and hemicellulose (Effendi et al., 2008; Sluiter et al., 2010). The cellulose and hemicellulose fraction of lignocellulosic biomass are widely used for the production of bio-ethanol (Chiaramonti et al., 2012; Gupta and Verma, 2015; Yoshikawa et al., 2013). The lignin fraction, which is a rich source of phenols, is of particular interest in the production of phenolic resins (Effendi et al., 2008; Yoshikawa et al., 2013). The different types of feedstocks from which lignocellulosic biomass can be derived from are shown in Table 2.3.

Table 2.3
Classification of lignin-rich feedstocks (Effendi et al., 2008).

Class of feedstock	Examples of feedstocks
Wood	Softwoods and hardwoods (Chum et al., 1993)
Agricultural residues	Corn bran and bagasse (Khan et al., 2004; Lee et al., 2002)
Forest residues	Treetops and limbs (Gallivan and Matschei, 1980)

The weight percentage of lignin, cellulose, and hemicellulose in any type of biomass is determined by several factors. Geographical location (Cuiping et al., 2004), soil type (Jenkins et al., 1998), climatic conditions (Obernberger et al., 1997), plant species (Monti et al., 2008), pH level (Obernberger et al., 2006), soil nutrients (McKendry, 2002), and age of plant species (Werkelin et al., 2005) are some factors that may affect the composition of the three major components of lignocellulosic biomass (Vassilev et al., 2010).

2.7.2 Lignocellulosic biomass feedstocks

The composition of any lignocellulosic feedstock depends on the biomass source. There is a wide array of feedstocks from which lignocellulosic biomass can be obtained. The sources of feedstocks significantly impact the lignin content of the biomass. Depending on the type of biomass involved, woody biomass is made up of 15-30 wt% lignin, 40-45 wt% cellulose, 25-35 wt% hemicellulose, and close to 10 wt% of other compounds (Wahyudiono et al., 2009).

2.8 Previous studies on phenolic resins derived from renewable feedstocks

2.8.1 Substitution of phenol with lignin

Production of PF resins from lignin feedstocks is very attractive primarily because lignin feedstocks such as kraft and organosolv lignins, are usually abundant (Benar et al., 1999; Effendi et al., 2008). The attempt to use lignin directly as a substitute for phenol has proven to be very unfavorable because lignin has very low reactivity. The low reactivity of lignin can be attributed to the fact that lignin has fewer reactive sites compared to phenol (Cheng, 2011). Due to the low reactivity of lignin, lignin-phenol-formaldehyde resins require longer pressing times and very high pressing temperatures (Effendi et al., 2008). In order to improve the reactivity of lignin, lignins are modified through the process of phenolysis before resin synthesis. The phenolysis process usually involves the reaction of lignin with phenol, in the presence of ethanol or methanol (Effendi et al., 2008).

2.8.2 PF resins produced from liquefaction oils

Liquefaction is another method of converting lignocellulosic biomass into bio-phenolic compounds or precursors for the production of PF resins (Effendi et al., 2008). The biomass liquefaction process is conducted at high pressures (2-20 MPa) and moderate temperatures of less than 350 °C (Hognon et al., 2015). The major advantage of using liquefaction over pyrolysis is that wet biomass can be used directly without drying. Bio-oils obtained from liquefaction are more deoxygenated and therefore have a higher energy density compared to pyrolysis oil (Elliott et al., 2015).

The scale-up of the bio-oil production through the liquefaction process is possible. However, the major challenge associated with transporting wet biomass into liquefaction systems must be addressed in order to achieve the successful scale-up of this process (Elliott et al., 2015). Overall, fast pyrolysis is conducted at atmospheric pressure compared to the high pressures required for liquefaction. Thus, fast pyrolysis has the advantage of low capital investment compared to liquefaction.

Also, pyrolysis products such as pyrolysis oil, biochar and non-condensable gases (Dickerson and Soria, 2013) have valuable applications. The non-condensable gases are a source of energy for drying wet biomass as well as for operating the pyrolysis reactor (Balat et al., 2009; Speight, 2008). Biochar is used for soil amendment while pyrolysis oils are used for chemicals, fuels, and electricity (Dickerson and Soria, 2013).

Lee et al. (2002) studied the production of resol resins using liquefied corn bran. The liquefaction process variables were a reaction time of 10-60 minutes, a temperature of 200 °C, and pressure greater than 1 MPa. The liquefied corn bran oil was dissolved in methanol and used in a series of resol synthesis. The characteristics of the corn bran resols were comparable to that of commercial resol in terms of gel time and viscosity (Lee et al., 2002).

Ono et al. (1996) investigated the use of liquefied waste paper for the production of resol resins. In their work, the lignin content of the initial feedstock was approximately 20%. The waste paper was first treated with phenol at 150 °C. Subsequently, the phenolated product obtained was reacted with formaldehyde to produce resols similar to conventional PF resols (Ono et al., 1996).

Alma et al. (1998) evaluated the use of birch wood liquefaction liquid for the production of novolac resins. For the production of birch wood liquefaction oil, the birch wood was first phenolated using sulfuric acid at temperatures of 60-150 °C, catalyst concentration of 1-3%, phenol-to-wood ratios of 2-5, and reaction time of 60-120 minutes. After the liquefaction process, methanol was added to the liquefied product. The methanol soluble fraction was then neutralized using magnesium oxide. Novolac resins were finally obtained by removing unreacted phenol and excess solvent. Information on the actual phenol substitution percentage was not provided (Alma et al., 1998).

2.8.3 Phenolic resins produced from pyrolysis oils

Pyrolysis is defined as the thermochemical decomposition of biomass in the absence of oxygen, at atmospheric pressure and temperatures between 300 and 600 °C (Kidane, 2015; Venderbosch and Wolter, 2011). The by-products of the pyrolysis process include liquid (bio-oil), non-condensable gases, and biochar (Kidane, 2015). The pyrolysis process can be categorized into two major divisions: fast pyrolysis and vacuum pyrolysis (Cheng, 2011). The major difference between fast pyrolysis and vacuum pyrolysis is the operating conditions at which both processes are carried out.

Fast pyrolysis is a thermochemical conversion of biomass at temperatures between 400 and 600 °C (Effendi et al., 2008). This pyrolysis process is characterized by short vapor residence times, rapid heating rates, and higher liquid yields. The maximum liquid yield is 75 wt% on dry basis of woody biomass (Bridgwater and Peacocke, 2000; Cheng, 2011; Effendi et al., 2008). In contrast, vacuum pyrolysis is characterized by longer vapor residence times and lower liquid yields (Effendi et al., 2008).

2.8.3.1 Composition of bio-oils

Pyrolysis oil also referred to as bio-oil is a complex mixture of more than 300 compounds (Mohan et al., 2006). The complex mixture includes organics, water, and lignin fragments. The lignin fragments are present as oligomers having very high molecular weights. Bio-oils have an oxygen content of 45%, and are therefore made up of many oxygenated compounds. The water accounts for 15-30 wt% of the bio-oil (Cheng, 2011). Bio-oils can be classified as containing phenolics, carboxylic acids, sugars, aldehydes, ketones, and alcohols (Effendi et al., 2008).

The interest in pyrolysis oils as a substitute to phenol stems from the fact that bio-oils contain lignin fragments and different kinds of phenolic compounds. Monomeric phenol in bio-oil is very low. Using gas chromatography (GC), the concentration of phenol ranges from 1 to 4 wt% the mass of bio-oil (Effendi et al., 2008). The majority of phenolic compounds within the pyrolysis liquids have very high molecular weights, therefore cannot be analyzed using the GC (Effendi et al., 2008). Previous studies have demonstrated that bio-oils can be separated to obtain the phenolic fraction for resin synthesis. Studies have also shown that using pyrolysis oils directly (without any separation) for the production of PF resins is a more economical approach (Effendi et al., 2008).

2.8.3.2 Phenol-formaldehyde resins produced from vacuum pyrolysis oils

Vacuum pyrolysis oil produced at a temperature less than 550 °C and a pressure less than 50 kPa was directly used in the synthesis of resol resins (Roy et al., 2000). The optimum phenol substitution for the production of resol resins was obtained at 40% the weight of the bio-oil produced. The 40% phenol substituted resols were used for the production of OSB. Based on mechanical tests conducted on the OSB, pyrolysis oils performed better than commercial resols (Chan et al., 2002; Effendi et al., 2008).

Amen-Chen and coworkers investigated vacuum pyrolysis of softwood bark from plants such as white spruce, black spruce, and balsam fir. The pyrolysis reaction was conducted in a vacuum reactor at a temperature of 505 °C and a feed rate of 50 kg/h (Amen-Chen et al., 2002). A scale-up of these vacuum pyrolysis experiments were also conducted industrially, at a temperature of 450 °C and a feed rate of 1000 kg/h. F/P molar ratios of 1.75, 2.25, and 2.20 were also investigated for the production of these resols. Additionally, 25% and 50% substituted resols produced from the bark pyrolysis oils, were used in the production of strand boards. Mechanical tests such as modulus of elasticity, modulus of rupture, and internal bond exceeded the limits for Canadian standard for strand boards (Amen-Chen et al., 2002).

2.8.3.3 Production of PF resins using fast pyrolysis oils

Chaouch et al. (2014) examined the production of resol PF resins using bio-oil from fast pyrolysis of two Canadian whole tree feedstocks (trembling aspen and white spruce). The pyrolysis of the feedstocks was carried out in a laboratory-scale auger reactor. The feedstocks, white spruce and trembling aspen were pyrolyzed at 500 °C and 400 °C respectively, at a nitrogen flowrate of 5 L/min (Chaouch et al., 2014). Using two series of condensers, the pyrolysis vapors were condensed to the final pyrolysis oil products. The first condenser, which was a vertical tube equipped with cooling coils condensed pyrolysis vapors using water at ambient temperature. The second condenser however, condensed pyrolysis vapors at a temperature of -10 °C. The liquid yield for these two feedstocks was estimated at 55 to 65 percent on a dry basis of the initial feed (Chaouch et al., 2014).

Trembling aspen and white spruce pyrolysis oils were used to replace 25%, 50%, and 75% of phenol during the resol synthesis. The bio-oils used in PF resin synthesis were used directly without any phenolic compound separation process. The reaction conditions for the synthesis of the bio-oil PF resols were an F/P ratio of 1.3 (Cheng, 2011), sodium hydroxide-to-phenol molar ratio of 0.7, and reaction time of more than an hour (Chaouch et al., 2014). The reaction temperature for this reaction was not fixed, it varied from 60 °C until the reaction was terminated at a final temperature of 95 °C. Shear strength tests were conducted by applying the bio-oil PF resols and pure PF resols unto maple wood blocks. The researchers in this study concluded that the substitution of phenol up to 50% had similar properties as pure PF resols (Chaouch et al., 2014).

A research group at ACM Wood Chemicals PLC investigated the use of pyrolysis oils for substituting phenol during the production of resol resins. Details of the pyrolysis process and resol synthesis were not provided. However, up to 50% substitution of phenol with pyrolysis oil was achieved (Effendi et al., 2008). Pyrolysis oils were used directly without any separation process. Resols produced by this research group were used in the production of plywood and OSB. Mechanical and water absorption tests conducted by these researchers indicated that resols produced from bio-oils had excellent properties (Nakos et al., 2000).

Chum et al. (1993) carried out fast pyrolysis of softwood, hardwood, and bark residues. The pyrolysis of these feedstocks were carried out in a vortex reactor at temperatures between 480 and 520 °C. The pyrolysis vapors produced at these temperatures were condensed in three condensers with operating temperatures of 20 °C, 2 °C, and -17 °C respectively. The pyrolysis oils produced from the aforementioned process were fractionated, isolating the phenolic fractions for resol and novolac production. The 50% phenol substituted novolacs had a shorter gel time compared to commercial PF novolacs (Chum et al., 1993; Diebold and Scahill, 1995).

The Ensyn's technology was used to produce bio-oils through the fast pyrolysis of forest residues, bark, and wood industry residues. At a temperature of 500 °C, fast pyrolysis process yielding 75% liquid product, 13% biochar, and 12% non-condensable gases was conducted. The reactive part of the pyrolysis oil was then obtained through distillation and evaporation processes. The essence of the evaporation and distillation processes was basically to remove odor and other acid bearing compounds in the pyrolysis oils. These researchers reported a 60% substitution of phenol with bio-oil (Giroux et al., 2001; Giroux et al., 2003).

Himmelblau and coworkers tested the fast pyrolysis of a mixture of feedstocks such as birch, beech and maple at a temperature of 590 °C. Pyrolysis oils produced by this process were used to produce resins for plywood applications. The 50% phenol substituted resin used in the production of southern pine plywood demonstrated excellent water resistant properties comparable to commercial resins (Himmelblau, 1991; Himmelblau and Grozdits, 1999).

2.9 Pinyon-juniper wood species

Pinyon-juniper (PJ) wood species are the third largest vegetative community in the United States of America, occupying more than 40 million hectares of land space (Gallo et al., 2016; Romme et al., 2009). Different species of juniper and pinyon trees exist. Juniper species include Utah juniper, alligator juniper, rocky-mountain juniper, one-seed juniper, and western juniper. Types of pinyon woods include singleleaf and Mexican pinyon (Yathavan and Agblevor, 2013). These wood species provide a source of food for the survival of certain livestock and wildlife species (Schott and Pieper, 1987). Although PJ woodlands are important for the survival of many animals, the expansion of these woodlands into grasslands and shrub lands has posed many challenges to wildlife ecosystems.

Grasslands and shrub lands, which are habitats for animal species such as mule deer and greater sage-grouse are being reduced because of the expansion of PJ woodlands (Terrel and Spillett, 1975). The invasive nature of PJ woodlands had also led to the prevalence of wildfires. Another problem associated with the expansion of PJ woodlands includes erosion (Miller and Wigand, 1994). As PJ woodlands expand, they tend to reduce the population of herbaceous vegetations. Herbaceous vegetations protect the top soil usually from becoming bare and prone to erosion. Statistics show that the tendency of erosion has increased by a magnitude of four due to the presence of these invasive wood species (Carrara and Carroll, 1979).

Due to problems associated with the invasive nature of PJ woodlands, mechanical techniques such as chaining (Ansley et al., 2006) have been put in place as a way of managing the expansion of these woodlands (Aro, 1971; Bergman et al., 2014). Reducing the population of PJ woodlands in order to preserve grasslands, shrub lands, and wildlife species requires a lot of energy and money. Therefore, in order to compensate for the resources required to manage the expansion of PJ woodlands, it is imperative that harvested PJ wood species be converted into high value commodities.

2.9.1 General uses of pinyon-juniper

PJ has been put to a variety of uses both in the past and in current times. People used PJ as a source of food, medicine, and shelter in ancient times. In the basket production industry, juniper has been included in basket-making, in order to make the manufactured baskets watertight (Yathavan, 2013). During alcoholic beverage production, western juniper is used as an ingredient for flavoring gin. Low value utilization of PJ includes its use as firewood. In the wood panel industry, western juniper is used in the production of particle boards. PJ trees are also harvested annually for use as Christmas trees (Yathavan, 2013).

2.9.2 High-value products derived from pinyon-juniper biomass

Apart from the common uses of PJ wood species, there is the need to investigate other value-adding products, which could be derived from PJ biomass. The usage of PJ biomass as a potential energy resource is very important in today’s world since global energy demand is currently on the rise (Vamvuka, 2011). Technologies such as catalytic pyrolysis of PJ presents a promising avenue for increasing the value of PJ biomass. The liquid product obtained from the pyrolysis process can be used for the production of transportation fuels and other important bio-products like adhesives, bio-plastics and biofoams (Vamvuka, 2011).

2.9.3 Catalytic pyrolysis of pinyon-juniper biomass

Yathavan and Agblevor (2013), in their work studied the catalytic pyrolysis of PJ biomass. Pyrolysis studies of PJ biomass was conducted in a fluidized bed reactor (Agblevor et al., 2010) at a temperature of 475 °C and at atmospheric pressure (Yathavan, 2013; Yathavan and Agblevor, 2013). Catalysts such as red mud and HZSM-5 were used in the pyrolysis process in order to determine the effect of these catalysts on the properties of the pyrolysis products. Red mud is an industrial waste product derived from the Bayer process of producing bauxite while HZSM-5 is an industrial catalyst (Yathavan, 2013).

Experiments of this nature were conducted in order to properly observe the effect of catalyst utilization. Nitrogen flow rate of 6.5 L/min was used during the catalytic pyrolysis process while a flow rate of 15 L/min was used for the non-catalytic pyrolysis process (Yathavan and Agblevor, 2013). PJ biomass was fed at a rate of 150 g/h using a K-Tron feeder as shown in Fig. 2.4. The solid products from the pyrolysis reactor were separated from the pyrolysis process via a hot gas filter. Two types of liquid products were obtained from the pyrolysis process. The first liquid product known as the aqueous phase liquid was obtained from a series of two ethylene-glycol cooled condensers. The second type of liquid product known as the organic phase liquid product was obtained from an electrostatic precipitator operating at 20 kV. Non-condensable gases were also analyzed using gas chromatography (Yathavan, 2013).

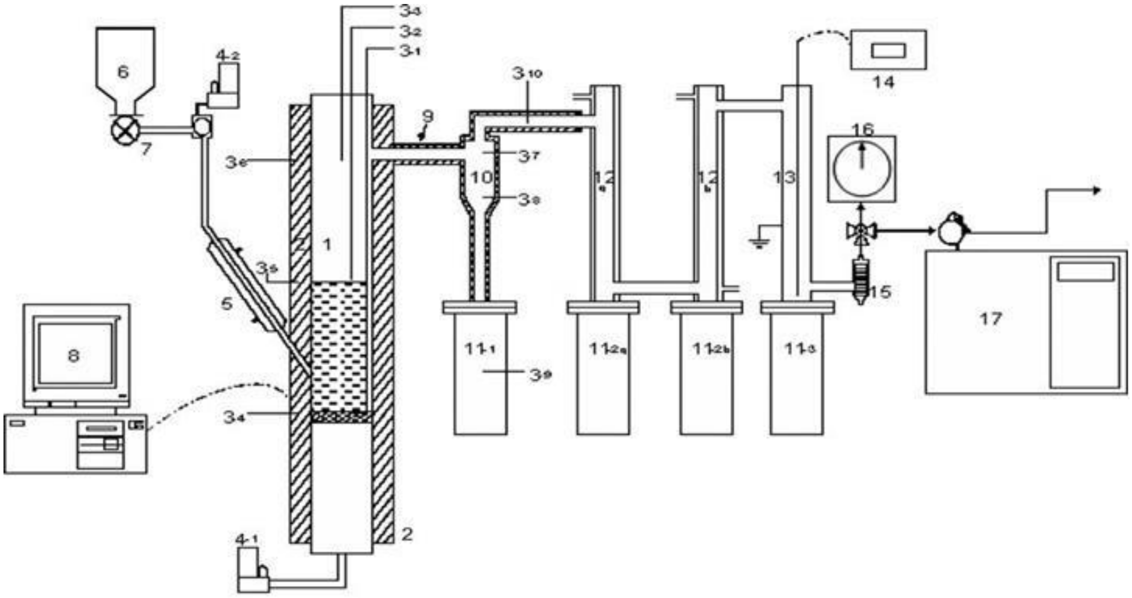

Fig. 2.4. Schematic diagram of a bubbling fluidized bed reactor.
(1. Fluidized bed reactor, 2. furnace, 3. thermocouple, 4. mass flow controller, 5. jacketed air-cooled feeder tube, 6. hopper, 7. screw feeder, 8. computer, 9. insulation, 10. hot gas filter, 11. reservoir, 12. condenser, 13. electrostatic precipitator, 14. AC power supply, 15. filter, 16. mass flow meter, and 17. gas chromatograph) (Yathavan, 2013).

The pyrolysis of biomass without any catalysts tend to produce bio-oils, which are unstable, have low heating values, and are incompatible with standard petroleum fuels (Czernik and Bridgwater, 2004). These undesirable properties are due to the presence of oxygenated organic compounds in the bio-oils. Therefore, the essence of catalytic pyrolysis is to provide a mechanism for eliminating most of the oxygen present in the final pyrolysis oil. Reactions such as decarbonylation, cracking, decarboxylation, and hydrodeoxygenation may occur upon addition of catalysts in the pyrolysis system (Dickerson and Soria, 2013).

The experimental findings from Yathavan and Agblevor's work showed different reaction mechanisms when either red mud or HZSM-5 was used as catalyst. The rejection of oxygen by these catalysts led to the production of water (H_2O), carbon dioxide (CO_2), and carbon monoxide (CO). Even though, the amount of water produced by the two catalysts were similar, HZSM-5 catalyst promoted more CO production over CO_2 production. Conversely, the catalytic pyrolysis of PJ using red mud led to the production of more CO_2 than CO (Yathavan and Agblevor, 2013). The mechanism of rejection of oxygen as CO_2 by red mud is more advantageous than that of HZSM-5. Since red mud leads to the production of more CO_2 than CO, less carbon is required for oxygen rejection. Pyrolysis of PJ biomass with red mud catalyst consequently led to better physico-chemical properties of bio-oils than pyrolysis of PJ with HZSM-5 catalyst (Yathavan and Agblevor, 2013).

The general conclusion of this research was that red mud catalyst, even as a waste product, could be used to produce pyrolysis oils of similar quality as an industrial catalyst. The catalytic pyrolysis of PJ using red mud therefore, is an innovative concept since red mud is a waste product from the Bayer process (Kidane, 2015).

2.10 Influence of process variables on the quality of resols

The physical, chemical and mechanical properties of resols and resol-based products are determined by the synthesis parameters by which those resols were produced. Parameters such as F/P molar ratio, type and quantity of catalyst, formulation procedure, additives, pH level, reaction temperature, and reaction time significantly affect the quality of the finished resol product.

2.10.1 Effect of resol synthesis procedure

The formulation procedure for producing resols is typically specific to the final use of such resols. A common resol formulation procedure is the single caustic cook procedure. During a single caustic cook, all reactants are charged into the reaction vessel simultaneously (Riedlinger, 2008). This approach has since been modified to a newer technique known as double caustic or split cook procedure. The double caustic or split-cook procedure involves charging the basic catalyst into the reaction vessel more than once. This new modification to the single cook procedure enhances the molecular weight of the adhesive and also facilitates the reduction of unreacted phenols in the prepared resol (Riedlinger, 2008).

The incremental addition of formaldehyde to the reaction vessel is another modification to the common resol synthesis procedure. The advantage of this modification is to help control the reaction exotherm usually involved in the production of PF resols. Another benefit of this formulation procedure is that, it helps reduce the toxicity of the resol by minimizing the content of unreacted phenol in the resin (Riedlinger, 2008).

2.10.2 Influence of formaldehyde-to-phenol molar ratio

The initial F/P molar ratio is a very important parameter in resol production. Apart from the fact that the F/P ratio helps to clearly distinguish between resols and novolacs, the value of an F/P ratio is very significant in terms of the final properties of the adhesive. For practical wood applications, F/P molar ratios of 1.8 to 3 are usually used (Riedlinger, 2008). High initial F/P ratios result in low free phenol content while promoting highly substituted branched network of polymers. However, low initial F/P ratios result in the formation of less branched (more linear) polymer networks due to the lesser degree of methylolation (Riedlinger, 2008; Cheng, 2011). At a lesser degree of methylolation, the curing rate of the resin is therefore slower, which is not desirable (Cheng, 2011).

Low F/P ratios lead to the increase in the amount of free phenol monomers. The viscosity of the resol increases with increasing F/P molar ratio. The viscosity increase can be attributed to the fact that at higher F/P ratios, there is a higher degree of polymerization. A decrease in polydispersity has been recorded with increasing F/P molar ratios (Riedlinger, 2008). A higher F/P molar ratio results in a faster curing of resols than a lower F/P molar ratio. This phenomenon can be attributed to higher methylolation at higher F/P molar ratios resulting in more crosslinked resols (Riedlinger, 2008).

2.10.3 Influence of catalyst type and amount

The effect of the type and amount of catalyst used in the production of PF resols is very important. Common basic catalysts used in the synthesis of PF resols include sodium hydroxide, potassium hydroxide, barium hydroxide, and calcium hydroxide. Metallic hydroxide catalysts with high chelating potential influence the formation of ortho-hydromethylation rather than para-hydromethylation during resol preparation (Riedlinger, 2008). Apart from metallic hydroxide catalysts, non-metallic alkali catalysts like ammonia can be used. The amount of catalyst used in resol synthesis can positively influence the flow properties of the resol (Grenier-Loustalot et al., 1996; Riedlinger, 2008).

2.11 Application of adhesives in the production of wood-based products

2.11.1 Wood composite products

The human population heavily depends on forest-based wood resources for diverse applications. As population increases globally, the demand for wood-based products also increases. The development of alternative wood composite products is therefore a means of effectively utilizing our forest resources so as to meet the ever-increasing global demand for wood products. Wood composites are defined as materials such as wood veneers, fibers, particles, chips, and pieces that are bonded together by adhesives (Youngquist, 1999). Currently, wood-based composites are employed in a plethora of structural and non-structural applications (Cai and Ross, 2010).

2.11.2 Importance of wood composite products

There are many advantages of developing wood composites. First, solid wood species originating from the same tree are more likely to vary greatly in terms of wood properties. However, reconstructing solid wood species to their composite forms improves uniformity in the properties of the wood (Youngquist, 1999). This is because properties of solid wood are controlled by the in-built cellular nature of the wood while wood composites are controlled by different elements of the wood such as particles, veneers or flakes to produce composites of uniform properties, stronger than the solid wood (Gu, 2010; Youngquist, 1999).

The development of wood composites also allows for the utilization of small trees. This idea shifts much of the emphasis from felling other larger trees (Stark et al., 2010). Wood composite products can also be produced from waste wood products obtained from other wood manufacturing processes. Furthermore, the presence of common defects (knots, checks, bows, splits, crooks, etc.) in solid wood can be eliminated when these solid woods are reconstructed into composites (Stark et al., 2010). Development of composite solid wood species also improves the mechanical strength of the wood. Also, these wood composites offer more versatility in terms of the shape of the final wood product (Stark et al., 2010).

2.11.3 Classification of wood-based composite products

Wood composites are generally classified as veneer-based materials, composite materials, laminates, and, wood and non-wood composites. The basis of this classification depends on the type of wood material or elements used in the production of the composites.

2.11.3.1 Plywood

Plywood is a specific type of veneer-based wood material produced by bonding an odd number of veneers with an adhesive. The bonding of these adhesives is achieved by subjecting the veneers under the influence of pressure and heat. The theory behind using odd number of plies in the production of plywood is to help overcome differences in the physical strength of wood veneer orientations. In this case, plywood is produced by aligning the grain direction of the veneers perpendicular to the adjacent plies. Two types of plywood are available: structural plywood and decorative plywood.

Structural plywood is usually manufactured from softwood materials. Softwood plywood is used in roofing, flooring, and other sheathing applications. Decorative plywood on the other hand, is manufactured from hardwoods. Applications of hardwood plywood include the manufacture of furniture, cabinets, and other interior fixtures. For structural applications, softwoods are preferred to hardwoods due to their superior strength and stiffness. Adhesives commonly used for plywood production include PF, MF and UF resins (Gu, 2010; Jang, 2011).

2.11.3.2 Laminated veneer lumber

Laminated veneer lumber (LVL) is another class of veneer-based wood material, which is used for different wood-work applications. During the manufacture of LVL, the veneers are bonded in such a way that the grains run in the same direction. LVL is typically used for both structural and non-structural applications. Structural applications of LVL include its use for I-beams, support headers, and rafters while non-structural applications of LVL include its use as furniture, and other interior wood-based products (Gu, 2010; Jang, 2011).

2.11.3.3 Oriented strand board

Oriented strand boards (OSB) are classified as composite materials, which are made by bonding thin and flat rectangular flakes of wood with suitable adhesives. These wood products are produced under controlled heat and pressure. The orientation of the wood grains is perpendicular to the adjacent face and core layers. OSB wood products are typically used in the production of floors, roofs, furniture, etc. PF resins and isocyanates are some of the adhesives used for the production of OSB (Gu, 2010; Jang, 2011).

2.11.3.4 Particle board

Particle board is a composite material produced by bonding wood particles or residues together. The wood particles include sawdust and wood shavings. The process of producing this engineered wood species includes bonding the wood particles with adhesives and sometimes with wax under controlled pressure and temperature. The advantage of producing wood products such as particle boards is that these products utilize wood residues, which are considered as waste for worthwhile applications. UF resins are frequently used for the production of particle boards because of their rapid curing time, low cost, and light color. PF resins, isocyanates, and MUF resins can be also used for the production of particle boards (Gu, 2010; Jang, 2011).

2.11.3.5 Medium density fiberboard

Medium density fiberboards (MDF) are wood composite materials, which are produced by bonding wood fibers with adhesives. MDF are commonly used for interior applications. UF adhesive is normally used for the production of MDF. During the production of MDF, wood pieces are broken down into fibers using a pressurized disc refiner. The wood fibers are then mixed with adhesive and wax. The mixture is then molded into a mat-like form and pressed at a temperature of approximately 170 °C. For external applications, adhesives such as PF and MUF can be used for the production of MDF (Gu, 2010; Jang, 2011). A list of the various types of wood composites available is shown in Table 2.4.

2.12 Conclusion

Pyrolysis oils produced from PJ is a potential bio-phenolic source for the production of PF resins. More than the mere utilization of PJ for firewood, production of resins from PJ catalytic pyrolysis oil is an attractive means of adding value to harvested

PJ biomass. In order to meet the commercial goals of PJ modified resins, the overall pyrolysis process must be less expensive. Thus, utilization of pyrolysis catalysts such as red mud alumina helps to reduce the operational costs involved in producing pyrolysis oils. Ultimately, PJ is a renewable resource, which is an environmentally safer substitute to petroleum-derived phenol.

Table 2.4
Classification of composites (Stark et al., 2010).

Classes of wood-based composites	**Examples of wood-based composites**
Veneer-based materials	Plywood, laminated veneer lumber (LVL) parallel-laminated veneer (PLV).
Composite materials	Waferboard, fiberboard, hardboard, flakeboard, particle board, oriented strand board (OSB), laminated strand lumber (LSL), and Oriented strand lumber (OSL)
Laminates	Glue-laminated timbers, overlayed materials, laminated wood–nonwood composites, and multiwood composites (COM-PLY)
Wood-nonwood composites	Wood fiber–polymer composites and inorganic-bonded composites

2.13 References

Abbasi, T., Abbasi, S.A., 2011. Decarbonization of fossil fuels as a strategy to control global warming. Renew. Sustain. Energy Rev. 15, 1828–1834.

Abdallah, M., Kamar, E.M., Eid, S., El-Etre, A.Y., 2016. Animal glue as green inhibitor for corrosion of aluminum and aluminum-silicon alloys in sodium hydroxide solutions. J. Mol. Liq. 220, 755–761.

Agblevor, F.A., Beis, S., Mante, O., Abdoulmoumine, N., 2010. Fractional catalytic pyrolysis of hybrid poplar wood. Ind. Eng. Chem. Res. 49, 3533–3538.

Aierbe, A.G., Echeverria, J.M., Riccardi, C.C., Mondragon, I., 2002. Influence of the temperature on the formation of a phenolic resol resin catalyzed with amine. Polymer 43, 2239–2243.

Alma, M.H., Yoshioka, M., Yao, Y., Shiraishi, N., 1998. Preparation of sulfuric acid-catalyzed phenolated wood resin. Wood Sci. Technol. 32, 297–308.

Amen-Chen, C., Pakdel, H., Roy, C., 2001. Production of monomeric phenols by thermochemical conversion of biomass: A review. Bioresour. Technol. 79, 277–299.

Amen-Chen, C., Riedl, B., Wang, X.-M., Roy, C., 2002. Softwood bark pyrolysis oil-PF resols. Part 1. Resin synthesis and OSB mechanical properties. Holzforschung 56, 167–175.

Ansley, A.R.J., Wiedemann, H.T., Castellano, M.J., Slosser, J.E., 2006. Herbaceous restoration of juniper dominated grasslands with chaining and fire. Rangel. Ecol. Manag. 59, 171–178.

Aro, R.S., 1971. Evaluation of pinyon-juniper conversion to grassland. J. Range Manag. 24, 188–197.

Ashori, A., Nourbakhsh, A., 2008. Effect of press cycle time and resin content on physical and mechanical properties of particleboard panels made from the underutilized low-quality raw materials. Ind. Crops Prod. 28, 225–230.

Atta-Obeng, E., 2011. Characterization of phenol formaldehyde adhesive and adhesive-wood particle composites reinforced with microcrystalline cellulose. Master's Thesis, Auburn University.

Balat, M., Balat, M., Kirtay, E., Balat, H., 2009. Main routes for the thermo-conversion of biomass into fuels and chemicals. Part 1: Pyrolysis systems. Energy Convers. Manag. 50, 3147–3157.

Benar, P., Gonçalves, A.R., Mandelli, D., Schuchardt, U., 1999. Eucalyptus organosolv lignins: Study of the hydroxymethylation and use in resols. Bioresour. Technol. 68, 11–16.

Bergman, E.J., Bishop, C.J., Freddy, D.J., White, G.C., Doherty, P.F., 2014. Habitat management influences overwinter survival of mule deer fawns in Colorado. J. Wildl. Manage. 78, 448–455.

Bridgwater, A.V., 2003. Renewable fuels and chemicals by thermal processing of biomass. Chem. Eng. J. 91, 87–102.

Bridgwater, A.V., Peacocke, G.V.C., 2000. Fast pyrolysis processes for biomass. Renew. Sustain. Energy Rev. 4, 1–73.

Cai, Z., Ross, R.J., 2010. Mechanical Properties of Wood-based composite materials, in: Wood Handbook - Wood as an engineering material.General Technical Report FPL-GTR-190. U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, WI, pp. 1–12.

Carrara, P.E., Carroll, T.R., 1979. The determination of erosion rates from exposed tree roots in the Piceance Basin, Colorado. Earth Surf. Process. 4, 307–317.

Chan, F., Riedl, B., Wang, X.M., Lu, X., Amen-Chen, C., Roy, C., 2002. Performance of pyrolysis oil-based wood adhesives in OSB. For. Prod. J. 52, 31–38.

Chaouch, M., Diouf, P.N., Laghdir, A., Yin, S., 2014. Bio-oil from whole-tree feedstock in resol-type phenolic resins. J. Appl. Polym. Sci. 131, 40014-40020.

Cheng, S., 2011. Bio-based phenolic resins and adhesives derived from forestry residues/wastes and lignin. PhD Thesis, Lakehead University.

Chiaramonti, D., Prussi, M., Ferrero, S., Oriani, L., Ottonello, P., Torre, P., Cherchi, F., 2012. Review of pretreatment processes for lignocellulosic ethanol production, and development of an innovative method. Biomass and Bioenergy 46, 25–35.

Chiari, L., Zecca, A., 2011. Constraints of fossil fuels depletion on global warming projections. Energy Policy 39, 5026–5034.

Cho, Y.-W., Han, S.-S., Ko, S.-W., 2000. PVA-contianing chito-oligosaccharide side chain. Polymer 41, 2033–2039.

Chum, H.L., Black, S.K., Diebold, J.P., Kreibich, R.E., 1993. Phenolic compounds containing/neutral fractions extract and products derived from fractionated fast-pyrolysis oils. US Patent 5 223 601.

Cuiping, L., Chuangzhi, W., Yanyongjie, Haitao, H., 2004. Chemical elemental characteristics of biomass fuels in China. Biomass and Bioenergy 27, 119–130.

Czernik, S., Bridgwater, A.V., 2004. Overview of applications of biomass fast pyrolysis oil. Energy and Fuels 18, 590-598.

Dickerson, T., Soria, J., 2013. Catalytic fast pyrolysis: A review. Energies 6, 514-538.

Diebold, J.P., Scahill, J., 1995. Improved vortex reactor system. US Patent 5 413 227.

Dunky, M., 1998. Urea–formaldehyde (UF) adhesive resins for wood. Int. J. Adhes. Adhes. 18, 95–107.

Eckelman, C.A., 1999. Brief survey of wood adhesives. Purdue University Cooperative Extension Service.

Effendi, A., Gerhauser, H., Bridgwater, A. V., 2008. Production of renewable phenolic resins by thermochemical conversion of biomass: A review. Renew. Sustain. Energy Rev.12, 2092-2116.

Elliott, D.C., Biller P., Ross A.B., Schmidt A.J, Jones, S.B., 2015. Hydrothermal liquefaction of biomass: Developments from batch to continuous process. Bioresour. Technol. 178, 147-156.

Fox, P.F., Brodkorb, A., 2008. The casein micelle: Historical aspects, current concepts and significance. Int. Dairy J. 18, 677–684.

Gallivan, R.M., Matschei, P.K., 1980. Fractionation of oil obtained by pyrolysis of lignocellulosic materials to recover a phenolic fraction for use in making phenol-formaldehyde resins. US Patent 4 209 647.

Gallo, T., Stinson, L.T., Pejchar, L., 2016. Pinyon-juniper removal has long-term effects on mammals. For. Ecol. Manage. 377, 93–100.

Gardziella, A., Pilato, L.A., Knop, A., 2000. Phenolic resins: Chemistry, application, standardization, safety and ecology. Springer, Berlin.

Giroux, R., Barry, F., Graham, R., 2001. Natural resin formulations. US Patent 6 326 461.

Giroux, R., Freel, B., Graham, R., 2003. Natural resin formulations. US Patent 6 555 649.

Grenier-Loustalot, M.F., Larroque, S., Grande, D., Grenier, P., Bedel, D., 1996. Phenolic resins: 2. Influence of catalyst type on reaction mechanisms and kinetics. Polymer 37, 1363–1369.

Gu, K., 2010. Evaluation of new formaldehyde, soy flour-based wood adhesives for particleboard. Master's Thesis, Oregon State University.

Gupta, A., Verma, J.P., 2015. Sustainable bio-ethanol production from agro-residues: A review. Renew. Sustain. Energy Rev. 41, 550–567.

Gustavsson, L., Börjesson, P., Johansson, B., Svenningsson, P., 1995. Reducing CO_2 emissions by substituting biomass for fossil fuels. Energy 20, 1097–1113.

Gustavsson, L., Svenningsson, P., 1996. Substituiting fossil fuels with biomass. Energy Convers. Manag. 37, 1211–1216.

Himmelblau, D.A., 1991. Method and apparatus for producing water-soluble resin and resin product made by that method. US Patent 5 034 498.

Himmelblau, D.A., Grozdits, G.A., 1999. Bicarbons Co., 1991. Production and performance of wood composite adhesives with air-blown, fluidized-bed pyrolysis oil, in: Overend, R.P., Chornet, E. (Eds.), Proceedings of the 4th Biomass Conference of the Americas. Elsevier Science, Oxford, UK, pp. 541–547.

Hock, H., Lang, S., 1944. Autoxydation von Kohlenwasserstoffen, IX. Mitteil.: Über Peroxyde von Benzol-Derivaten. Berichte der Dtsch. Chem. Gesellschaft 77, 257–264.

Hognon, C., Delrue, F., Texier, J., Grateau, M., Thiery, S., Miller, H., Roubaud, A., 2015. Comparison of pyrolysis and hydrothermal liquefaction of *Chlamydomonas reinhardtii.* Growth studies on the recovered hydrothermal aqueous phase. Biomass and Bioenergy, 73, 23-31.

Huang, J., 2007. Development and characterization of new formaldehyde-free soy flour-based adhesives for making interior plywood. Master's Thesis. Oregon State University.

Ishii, Y., Sakaguchi, S., 2006. Recent progress in aerobic oxidation of hydrocarbons by N-hydroxyimides. Catal. Today 117, 105–113.

Jang, Y., 2011. Development and evaluation of a new formaldehyde-free wood adhesive from renewable materials for making interior plywood. Master's Thesis, Oregon State University.

Jenkins, B.M., Baxter, L.L., Miles, T.R., Miles, T.R., 1998. Combustion properties of biomass. Fuel Process. Technol. 54, 17–46.

Jourshabani, M., Badiei, A., Lashgari, N., Ziarani, G.M., 2015. Highly selective production of phenol from benzene over mesoporous silica-supported chromium catalyst: Role of response surface methodology in optimization of operating variables. Cuihua Xuebao/Chinese J. Catal. 36, 2020–2029.

Kennedy, H.M., Fischer, A.C., 1984. Chapter XX– Starch and dextrins in prepared adhesives, in: Starch: Chemistry and technology. Academic press, pp. 593–610.

Khan, M.A., Ashrafa, S.M., Malhotra, S.M., 2004. Development and characterization of a wood adhesive using bagasse lignin. Int. J. Adhes. Adhes. 24, 485–493.

Kidane, Y.A., 2015. Catalytic Fast pyrolysis of whole field pennycress biomass. Master's Thesis, Utah State University.

Knop, A., Pilato, L.A., 1985. Phenolic resins: Chemistry, applications, and performance: Future directions. Springer-Verlag Berlin.

Lee, S.H., Teramoto, Y., Shiraishi, N., 2002. Acid-catalyzed liquefaction of waste paper in the presence of phenol and its application to novolak-type phenolic resin. J. Appl. Polym. Sci. 83, 1473–1481.

Lucia, L.A., 2008. Lignocellulosic biomass: A potential feedstock to replace petroleum. BioResources 3, 981–982.

Martin, M.L., Delpuech, J.J., Martin, G.J., 1980. Practical NMR spectroscopy. John Wiley & Sons limited, Heyden, London.

McKendry, P., 2002. Energy production from biomass (part 1): Overview of biomass. Bioresour. Technol. 83, 37–46.

Megson, N.J.L., 1958. Phenolic resin chemistry. Academic Press, New York, Butterworths, London.

Miller, R.F., Wigand, P.E., 1994. Holocene changes in semiarid pinyon-juniper woodlands: response to climate, fire, and human activies in the US Great Basin. Bioscience 44, 465–474.

Mohan, D., Pittman, C.U., Steele, P.H., 2006. Pyrolysis of wood/biomass for bio-oil: A critical review. Energy and Fuels 20, 848–889.

Monti, A., Di Virgilio, N., Venturi, G., 2008. Mineral composition and ash content of six major energy crops. Biomass and Bioenergy 32, 216–223.

Motohashi, K., Tomita, B., Mizumachi, H., Sakaguchi, H., 1984. Temperature dependency of bond strength of poly(vinyl acetate) emulsion adhesives for wood. Wood fiber Sci. J. Soc. Wood Sci. Technol. 16, 72–85.

Nakos, P., Tsiantzi, S., Athanassiadou, E., 2000. Wood adhesives made with pyrolysis oils., in: Proceedings of the 3rd European Wood-Based Panel Symposium. Hanover, pp. 1–2.

Obernberger, I., Biedermann, F., Widmann, W., Riedl, R., 1997. Concentrations of inorganic elements in biomass fuels and recovery in the different ash fractions. Biomass and Bioenergy 12, 211–224.

Obernberger, I., Brunner, T., Bärnthaler, G., 2006. Chemical properties of solid biofuels-significance and impact. Biomass and Bioenergy 30, 973–982.

Ono, H., Yamada, T., Hatano, Y., Motohashi, K., 1996. Adhesives from waste paper by means of phenolation. J. Adhes. 59, 135–145.

Papadopoulou, E., 2009. Adhesives from renewable resources for binding wood-based panels. J. Environ. Prot. Ecol. 10, 1128–1136.

Pilato, L., 2010. Phenolic reisn: A century of progress. Springer-Verlag Berlin Heidelberg.

Riedlinger, D.A., 2008. Characterization of PF resol / isocyanate hybrid adhesives. Master's Thesis, Virginia Polytechnic Institute and State University.

Romme, W.H., Allen, C.D., Bailey, J.D., Baker, W.L., Bestelmeyer, B.T., Brown, P.M., Eisenhart, K.S., Floyd, M.L., Huffman, D.W., Jacobs, B.F., Miller, R.F., Muldavin, E.H., Swetnam, T.W., Tausch, R.J., Weisberg, P.J., 2009. Historical and modern disturbance regimes, stand structures, and landscape dynamics in piñon–juniper vegetation of the western united states. Rangel. Ecol. Manag. 62, 203–222.

Roy, C., Liu, X., Pakdel, H., 2000. Process for the production of phenolic-rich pyrolysis oils for use in making phenol–formaldehyde resole resins. US Patent 6 143 856.

Schott, M.R., Pieper, R.D., 1987. Succession of pinyon-juniper communities after mechanical disturbance in southcentral new mexico. J. Range Manag. 40, 88–94.

Sellers, T.J., 2001. Wood adhesive innovations and applications in North America. For. Prod. J. 51, 12–22.

Sellers, T.J., 1985. Plywood adhesive technology. Marcel Dekker, New York.

Shafiee, S., Topal, E., 2009. When will fossil fuel reserves be diminished? Energy Policy 37, 181–189.

Shiraishi, N., Kajita, H., Norimoto, M., 1993. Recent research on wood and wood-based materials. Elsevier Applied Science, London and New York.

Siddiqui, H., 2013. Production of lignin-based phenolic resin using de-polymerized kraft lignin and process optimization. Master's Thesis, The University of Western Ontario. London, Ontario, Canada.

Singh, R., Shukla, A., Tiwari, S., Srivastava, M., 2014. A review on delignification of lignocellulosic biomass for enhancement of ethanol production potential. Renew. Sustain. Energy Rev. 32, 713–728.

Sluiter, J.B., Ruiz, R.O., Scarlata, C.J., Sluiter, A.D., Templeton, D.W., 2010. Compositional analysis of lignocellulosic feedstocks. 1. Review and description of methods. J. Agric. Food Chem. 58, 9043–9053.

Stark, N.M., Cai, Z., Carll, C., 2010. Wood-based composite materials panel products, glued-laminated timber, structural composite lumber, and wood–nonwood composite materials, in: Wood Handbook - Wood as an engineering material.General Technical Report FPL-GTR-190. U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, WI, pp. 1–28.

Speight, J. 2008. Synthetic Fuels Handbook: Properties, process and performance; McGraw-Hill Professional: New York, NY, USA.

Strzemiecka, B., Zieba-Palus, J., Voelkel, A., Lachowicz, T., Socha, E., 2016. Examination of the chemical changes in cured phenol-formaldehyde resins during storage. J. Chromatogr. A. 1441, 106–115.

Terrel, T.L., Spillett, J.J., 1975. Pinyon juniper conversion: its impact on mule deer and other wildlife., in: The pinyon-juniper ecosystem. Logan, Utah, pp. 105–119.

Tout, R., 2000. A review of adheisve for furniture. Int. J. Adhes. Adhes. 20, 269–272.

Vamvuka, D., 2011. Bio-oil, solid and gaseous biofuels from biomass pyrolysis processes—An overview. Int. J. energy Res. 35, 835–862.

Vassilev, S. V., Baxter, D., Andersen, L.K., Vassileva, C.G., 2010. An overview of the chemical composition of biomass. Fuel 89, 913–933.

Venderbosch, R.H., Wolter, P., 2011.Thermochemical processing of biomass, in: Conversion into fuels, chemicals and power. John Wiley & Sons, Chichester.

Wahyudiono, Sasaki, M., Goto, M., 2009. Conversion of biomass model compound under hydrothermal conditions using batch reactor. Fuel 88, 1656–1664.

Werkelin, J., Skrifvars, B.J., Hupa, M., 2005. Ash-forming elements in four Scandinavian wood species. Part 1: Summer harvest. Biomass and Bioenergy 29, 451–466.

Yathavan, B.K., 2013. Conventional and catalytic pyrolysis of pinyon juniper biomass. Master's Thesis, Utah State University.

Yathavan, B.K., Agblevor, F., 2013. Catalytic pyrolysis of pinyon-juniper using red mud and HZSM-5. Energy and Fuels 27, 6858–6865.

Yoshikawa, T., Yagi, T., Shinohara, S., Fukunaga, T., Nakasaka, Y., Tago, T., Masuda, T., 2013. Production of phenols from lignin via depolymerization and catalytic cracking. Fuel Process. Technol. 108, 69–75.

Youngquist, J.A., 1999. Wood-base composites and panel products, in: Wood handbook—Wood as an engineering material. Gen. Tech. Rep. FPL–GTR–113. U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, WI, pp. 1–31.

Zecca, A., Chiari, L., 2010. Fossil-fuel constraints on global warming. Energy Policy 38, 1–3.

CHAPTER 3

EFFECT OF SYNTHESIS CONDITIONS ON THE PHENOL SUBSTITUTION LEVEL OF PINYON-JUNIPER RESOLS

3.1 Abstract

Catalytic pyrolysis oils can be potentially used to replace petroleum-derived phenols in the production of phenol-formaldehyde adhesives. In order to efficiently commercialize bio-oil based adhesives, there is a need to achieve very high substitutions of phenol with bio-oil. In this study, pinyon juniper wood, catalytically pyrolyzed at 450 °C using red mud alumina, was used as a bio-phenolic substitute for petroleum-based phenol.

Resol synthesis parameters such as formaldehyde-to-phenol molar ratios, temperature, reaction time, and catalyst loading determine the quality of resols. The amount of catalyst loading affected the extent to which phenol could be replaced with pinyon-juniper catalytic pyrolysis oil. The reference catalyst in this case was sodium hydroxide. Catalyst loadings 0.25, 0.63, and 1.25 g of sodium hydroxide were investigated for the synthesis of pinyon-juniper substituted resols.

A maximum of 80% substitution of phenol with pinyon-juniper catalytic pyrolysis oil was achieved at a catalyst loading of 1.25 g while the least phenol substitution of 50% was achieved at 0.25 g of sodium hydroxide.

3.2 Introduction

Biomass is a valuable resource for the production of hydrocarbon liquid transportation fuels and other bio-products (Effendi et al., 2008). The focus on the development and use of biomass-based products as opposed to fossil fuel end products is critical in these modern times. Fossil fuels are non-renewable resources and are expected to deplete in the near future (Maher and Bressler, 2007; Valliyappan et al., 2008). This conventional energy resource is not sustainable and raises a lot of carbon dioxide (CO_2) emission-related concerns (Jin et al., 2010). Biomass is environmentally friendly, and renewable, thereby, presents an alternative to using fossil fuel resources (Zhang et al., 2013) .

Since 1907 (Knop and Pilato, 1985), phenolic resins have been utilized in the construction, automotive, aerospace, and computing industries because of their robust physical and mechanical properties (Chaouch et al., 2014; Guo et al., 2013). Common phenolic resins used in the wood composite industry include phenol-formaldehyde (PF), urea formaldehyde (UF), and melamine-urea-formaldehyde (MUF) adhesives (Danielson and Simonson, 1998; Zhang et al., 2013). Particularly, PF adhesives used in wood composite production are known to have high water resistance and excellent mechanical strength. These properties make PF resols a good choice for exterior wood applications (Nihat and Nilgül, 2002; Zhang et al., 2013).

Phenol is a petroleum-derived product whereas formaldehyde is a natural gas-derived product (Knop and Pilato, 1985). It is therefore desirable to look for potential biomass resources in order to reduce the dependence on fossil fuel derived products, which are unsustainable. The focus of this research was the use of lignocellulosic biomass as an alternative to phenol.

Many attempts have been made to replace phenol with bio-resources such as tannins (Hoong et al., 2011), cardanols (Chaouch et al., 2014), lignin (Khan et al., 2004), and bio-oils (Effendi et al., 2008). Lignocellulosic biomass is made up of lignin, cellulose, and hemicellulose (Effendi et al., 2008). Lignin, which is a polyphenolic compound obtained from phenylpropanoid monomers including sinapyl alcohol, coniferyl alcohol, and p-coumaryl alcohol, is important in PF adhesive production (Zhang et al., 2013). Depending on the biomass species, softwoods contain about 25 to 35% of lignin while hardwoods contain about 16 to 25% of lignin (Rover, 2013). In order to obtain the phenolic component of lignocellulosic biomass, thermochemical technologies such as pyrolysis and liquefaction have been employed to convert the lignin into monomeric phenols (Chaouch et al., 2014; Cheng et al., 2011; Effendi et al., 2008; Wang et al., 2009).

Fast pyrolysis of woody biomass has been identified as an efficient method for producing high yield liquid pyrolysis products (Bridgwater and Peacocke, 2000). During the fast pyrolysis process, which is normally carried out between 400 and 600 °C (Effendi et al., 2008), the different components of the lignocellulosic biomass are decomposed into smaller molecular compounds. This thermochemical process yields approximately 60 to 75 wt%, 15 to 25 wt%, and 10 to 20 wt% of bio-oil, biochar, and non-condensable gases respectively (Mohan et al., 2006).

The biochar produced from the pyrolysis process contains essential nutrients for soil amendment purposes (Chaouch et al., 2014). Also, the non-condensable gases could be used as an additional heating source for the pyrolysis process (Chaouch et al., 2014). Pyrolysis oil, also known as bio-oil can be used as a source of liquid transportation fuels, resins, binders, and coatings (Rover, 2013). The bio-oil contains hundreds of compounds, making it very complex. Organic compounds normally found in bio-oils include aldehydes, sugars, phenolics, ketones, alcohols, and organic acids (Rover and Brown, 2013).

The phenolic compounds in bio-oils are mixtures of monomers and oligomers (Rover and Brown, 2013). Depending on the parameters used during the pyrolysis process, the phenolic oligomers may range from hundreds to about 5000 g/mol (Effendi et al., 2008). Using methods such as Folin–Ciocalteu colorimetry and liquid–liquid extraction, the total phenolic content of bio-oils could be quantified. The total phenolic content in bio-oil is between 24 to 30 wt% on dry basis (Rover and Brown, 2013). This concentration of phenolic compounds may vary depending on the biomass species and the conditions applied during the fast pyrolysis process. However, the concentration of phenol in bio-oil is very low, generally ranging from 0.1 to 3.8 wt% (Diebold, 2000; Fraps, 1901; Stamm and Harris, 1953).

Over the years, the rapid expansion of pinyon-juniper (PJ) woodlands has led to problems such as erosions, wildfires, and reduction in the population of herbaceous vegetations (Carrara and Carroll, 1979; Yathavan and Agblevor, 2013). In order to control the invasive nature of PJ wood species, the United States Bureau of Land Management has been harvesting PJ wood species so as to control their expansion rate (Yathavan, 2013). Thus far, the commercial prospects of harvested PJ species has been limited to firewood, carvings, and fence posts (Yathavan, 2013). The pyrolysis of PJ biomass presents a means of boosting the economic value of PJ wood through the development of value-added fuels and chemicals. Yathavan and Agblevor, in their work, demonstrated that catalytic pyrolysis of PJ biomass using red mud and HZSM-5 catalysts yielded excellent bio-oils (Yathavan and Agblevor, 2013).

In this chapter, catalytic pyrolysis oil produced from PJ biomass and red mud catalyst was tested in order to investigate the phenol substitution potential of these bio-oils for the production of PF resols. In order to make bio-oil resol production economical, the phenol substitution level should be above 40% (Nakos et al., 2000). The cost of catalysts directly impacts the operating costs of any process. Hence, using red mud, a waste product from the Bayer process, is a strategic way of reducing the production costs of PJ bio-oils (Yathavan, 2013). The objective of this study was to increase the substitution potential of phenol with bio-oil. The least substitution of phenol with PJ bio-oil, which was investigated was 50%. Achieving even higher substitutions (greater than 50%) of phenol with bio-oil would help improve the economic value of PJ substituted resols.

The extent of phenol substitution is dependent on the conditions chosen for resol synthesis. Factors such as formaldehyde-to-phenol (F/P) molar ratio, catalyst loading, reaction time, reaction temperature, and type of resol formulation procedure affect the quality of the final adhesive produced (Riedlinger, 2008). Good quality PF resols were determined by their ability to be water resistant. The water resistance property of wood composites prepared using PF adhesives was the measure of the phenol substitution potential of PJ bio-oils. Different resol synthesis parameters were evaluated in order to determine the optimum conditions necessary to achieve a high substitution of phenol with

PJ bio-oil. Finally, this chapter would focus on PJ bio-oil characterization, resol synthesis, wood curing, and water tests.

3.3 Materials and methods

3.3.1 Characterization of pinyon-juniper catalytic pyrolysis oil

3.3.1.1 Bio-oil feedstock

PJ biomass supplied by the USA Bureau of Land Management (BLM), was used for the production of the PJ bio-oil. Fast pyrolysis of the PJ biomass was conducted in a pilot-scale fluidized bed reactor in the thermochemical laboratory located in the USTAR BioInnovations Center, 620 at Utah State University, Logan, UT. The fast pyrolysis process was carried out using red mud alumina at a reaction temperature of 450 °C.

3.3.1.2 pH determination

The pH of PJ pyrolysis oil was measured using a pH meter (Mettler Seven Easy S20 pH meter, Mettler-Toledo AG, Switzerland). Before determining the pH of the bio-oil, the pH meter was calibrated using pH calibration buffers in a pH order of 7, 4, and 10.

3.3.1.3 Dynamic viscosity and density analysis of bio-oil

The density and dynamic viscosity of the bio-oil was determined at 40 °C using an Anton Paar Stabinger Viscometer, SVM 3000 (Anton Paar USA Inc., Ashland, VA). The instrument was first calibrated using an N415 viscosity standard (Cannon instrument company) before analyzing the viscosities and densities of the catalytic pyrolysis oil samples. Measurements were carried out in triplicates.

3.3.1.4 Fourier transform infrared analysis of pyrolysis oil

The Fourier transform infrared spectrum of the bio-oil was obtained using a Nicolet Avatar IR spectrometer model 370 DTGS (Nicolet Instrument. Inc, Madison, WI, USA) equipped with a DTGS-KBR detector. The analysis was conducted over a range of 4000 to 600 cm^{-1} at resolution of 4 cm^{-1}.

3.3.1.5 Initial free formaldehyde and free phenol content of bio-oil

A high performance liquid chromatography (HPLC) (SCL-10 A, Shimadzu Scientific, Columbia, MD, USA) was used to determine the initial free formaldehyde and free phenol content of the PJ bio-oil. The initial formaldehyde and phenol content were analyzed on a Kromasil C18 column (5 µm, 100 Ǻ, 4.6 × 250 mm). The mobile phase used was 43/57 (v/v) methanol/water mixture and the oven temperature was kept at 30 °C. Using an ultraviolet (uv) detector, formaldehyde was detected at a wavelength of 360 nm while phenol was detected at wavelength of 270 nm. The mobile phase flow rate used for this analysis was 0.8 ml/min. A sample injection volume of 20 µl was used (Liu et al., 2007).

In order to quantify the concentration of phenol and formaldehyde, calibration curves were developed using phenol and derivatized formaldehyde (formaldehyde hydrazone) standard solutions. The phenol standard solution was prepared by dissolving 0.05 g of phenol in methanol in a 50 ml volumetric flask. The standard calibration curve for phenol was produced using concentrations of 50, 200, 500, and 1000 mg/L. The derivatized formaldehyde standard calibration curve was obtained at concentrations of 5, 20, 60, 150, and 300 mg/L (Liu et al., 2007).

Prior to conducting the HPLC analysis, the bio-oil was derivatized using 2,4-diphenylhydrazine (DNPH) derivatization reagent. The 2,4- DNPH derivatization reagent was prepared by mixing 5 g of 2,4- DNPH with 2.5 g of glacial acetic acid in a 500 ml volumetric flask. Acetonitrile was used to fill up the volume of the flask to its 500 ml mark. The solution was swirled and stored in dark environment. Formaldehyde hydrazone standard was prepared by mixing 0.015 g of formaldehyde and 30 ml of 2,4-DNPH derivatization reagent in a 50 ml volumetric flask. Methanol was then added to fill the volumetric flask to its mark. The resulting solution was then kept at 40 °C for 4 hours in the dark. Dilutions of the initial formaldehyde derivative concentration were performed to obtain the other concentrations needed to plot the standard calibration curve (Liu et al., 2007).

For the derivatization procedure of bio-oil, 0.1 g of the bio-oil was mixed with 10 ml 2,4- DNPH derivatization reagent in a 50 ml volumetric flask. Methanol was then added to top up the volume of the 50 ml volumetric flask. The derivatization procedure was completed in water bath set at a temperature of 40 °C, for 4 hours in a dark room (Liu et al., 2007).

3.3.2 Resol synthesis

3.3.2.1 Materials

A 37 wt% formaldehyde solution (10-15% methanol as stabilizer), and crystalline phenol were obtained from Sigma-Aldrich. Reagent ACS grade methanol was obtained from Pharmaco-AAPER. Sodium hydroxide (NaOH) was purchased from Fisher Chemical. Finally, PJ bio-oil was produced in-house from USTAR BioInnovations

Center, 620 at Utah State University, Logan, UT.

3.3.2.2 Preparation of phenol-formaldehyde resins

The PF resins were prepared in a 50 ml three neck flask following a single caustic cook formulation procedure. The quantities of phenol, formaldehyde solution, bio-oil, and catalyst were dependent on the reaction conditions under consideration. In producing pure PF resols, no bio-oil was incorporated during the synthesis process. Pure PF resols were considered as having a 0 wt% phenol substitution. Table 3.1 shows the process conditions investigated.

Table 3.1
Summary of process variables for resol production.

F/P molar ratio	1.8, 2.0
Reaction time	60 minutes
Reaction temperature	95 °C
Catalyst loading [a]	0.25, 0.63, and 1.25 g
Phenol substitution	At least 50 wt%

[a] Catalyst loading = Mass of NaOH.

For instance, in order to produce a 50% PJ substituted resol at F/P molar ratio of 2.0 and catalyst loading of 1.25 g of NaOH, the following procedure was used. 2.50 g of PJ, 2.50 g of phenol, 8.62 g of formaldehyde solution, and 1.25 g of NaOH were charged into the three-neck flask. The NaOH catalyst was introduced into the flask in aqueous form: 50 wt% NaOH aqueous solution. The content of the flask was then stirred to achieve homogeneity of the mixture. The reaction vessel was mounted in a water bath operating at a temperature of 95 °C. In addition, the three-neck flask was equipped with a water-cooled condenser, for refluxing volatiles back into the reaction medium. A nitrogen source was connected to the reaction flask to keep the reaction under an inert environment throughout the experiment. Overall, the experiment was conducted for 60 minutes.

At end of the reaction, the reaction mixture was allowed to cool to room temperature and 70 ml of methanol was added to the three-neck flask. The mixture was stirred under nitrogen environment for 24 hours. This methanol-dissolved resol was vacuum filtered and concentrated to the final product, using a rotary evaporator operating at 43 °C. The experimental set-up is illustrated in Fig. 3.1.

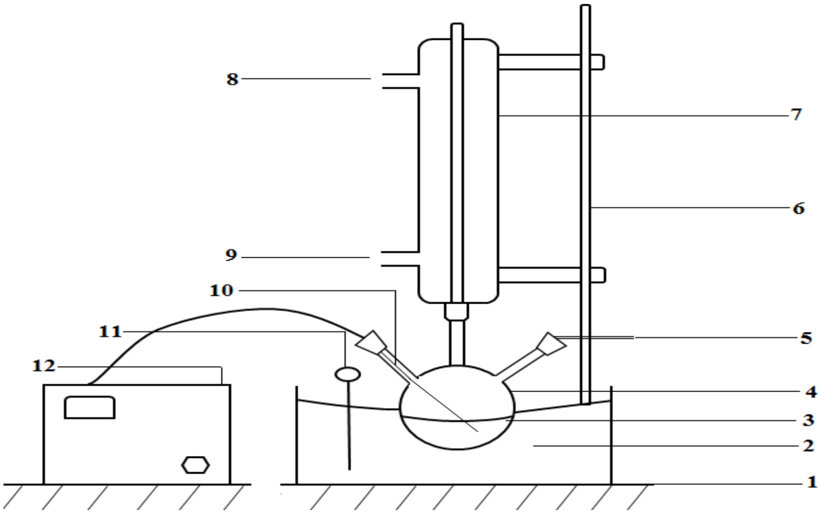

Fig. 3.1. Schematic diagram for resol production.
1) Hot plate and stirrer, 2) water bath, 3) resol, 4) three neck flask, 5) nitrogen gas inlet, 6) retort stand, 7) water-cooled condenser, 8) water outlet, 9) water inlet, 10) thermocouple, 11) thermometer, 12) temperature controller.

3.3.3 Wood composite preparation and curing

3.3.3.1 Materials and methods

Red oak *(Quercus rubra)* wood was purchased from Lowe's and cut into 2 in x 2 in x ¼ in pieces. Approximately 1 g of resol was evenly spread on the two red oak veneers and adhered together. The composite wood block was clamped using a hand-screw clamping system. Pressure was exerted on the specimen by tightening the wing nuts connected to the clamping system. Afterwards, the clamped wood composite system was cured in a vacuum oven at a selected temperature and time.

The curing temperature, time and pressure of composite blocks are important parameters that affect the strength and water resistance capacity of wood composites. Curing parameters were chosen so as to achieve acceptable water resistance characteristics of the resols being evaluated. Heat curing of resols are normally conducted between 130 and 200 °C. A curing temperature of 180 °C was therefore selected to accommodate the wide range of resols being tested. The pressure exerted on the wood specimens was not determined because of the nature of the clamping system. However, the bolts and wing nuts were evenly distributed on the clamping system to ensure even pressure distribution on the wood interface.

Generally, hot presses are used in the curing process of wood composites. A press pressure of 200 psi and short press times of approximately 6 minutes are used in the preparation of plywood (Siddiqui, 2013). Using an oven instead of a hot press typically requires longer curing times, sometimes as long as 2 hours (Khan et al., 2004). In order to determine the optimum curing time for wood composite preparation in the vacuum oven system, different curing times were evaluated. Curing times of 30, 45, 60, and 90 minutes were investigated to determine their impact on the delamination resistance of wood composites during and after water tests. Among the different curing times screened, the best delamination resistance of the oak wood specimen before and after the water tests was achieved at 45 minutes. Hence, 45 minutes was used as the curing time for all the different resol formulations.

3.3.4 Water tests

The cured wood composites were immersed in 500 ml of tap water for a period of 48 hours in order to observe the water resistance capacity of the resol. All water resistance tests were conducted at ambient temperature.

3.4 Results and discussion

3.4.1 Chemical functionality of PJ bio-oil

FTIR spectra of PJ bio-oil revealed the presence of phenolics, aromatic hydrocarbons, aliphatic hydrocarbons, carboxylic acids, ethers, ketones, aldehydes and primary aliphatic alcohols. Table 3.2 shows the functional groups and wavenumbers observed for PJ bio-oil. The functional groups observed in PJ bio-oil is in agreement with the chemical functionalities of most bio-oils in literature (Poljanšek and Krajnc, 2005). Based on the FTIR analysis, the presence of phenolic compounds in PJ bio-oil proved the substitution potential of phenol with bio-oils.

Table 3.2
Functional groups and wavenumbers observed for PJ bio-oil.

Observed wavenumber, cm^{-1}	Functional group
3360	O-H stretch
2961	In-phase stretching vibration of $-CH_2-$ alkane stretch
1698	C=O aldehyde or carboxylic acid stretch
1598	C=C aromatic ring
1514	C=C aromatic ring
1452	C=C benzene ring obscured by a $-CH_2-$ methylene bridge
1361	OH in plane
1265	Asymmetric stretch of phenolic C-C-OH
1202	Asymmetric stretch of phenolic C-C-OH
1153	C-O stretch
1120	C-O stretch
1079	Single bond C-O stretching vibrations of $-CH_2-OH$ group
1033	=C-O-C ether system with asymmetric stretch
966	1,2,4-trisubstituted benzene ring
855	1,3-disubstituted benzene ring
812	Asymmetric stretch of phenolic C-C-OH
752	CH aromatic, out-of-plane
692	C-H bend

3.4.2 Physico-chemical analysis of PJ pyrolysis oil

To gain a better understanding of the starting material being used for the resol synthesis, PJ bio-oil was analyzed for its physical and chemical properties. The measurements were carried out following the procedures in the materials and methods section of this chapter. Table 3.3 is a summary of the measured physico-chemical properties of PJ bio-oil.

Table 3.3
Measured physical and chemical properties of PJ bio-oil.

pH at 23.2 °C	3.25 ± 0.13
Dynamic viscosity, cP at 40 °C	290.91 ± 2.35
Density, g/cm^3 at 40 °C	1.15 ± 0.01
Free phenol content, wt%	0.72 ± 0.07
Free formaldehyde content, wt%	0.51 ± 0.04

Based on the results in Table 3.3, PJ bio-oil produced using red mud catalyst was acidic and viscous in nature. Generally, the pyrolysis oils derived from woody lignocellulosic biomass have an acidic pH of 2.8 to 3.8 and viscosities ranging from 25 cP to 1000 cP (Bridgwater and Peacocke, 2000; Mohan et al., 2006; Venderbosch and Prins, 2010). The acidic nature of the bio-oil could be attributed to carboxylic acids such acetic acid and formic acid, present in the pyrolysis oil (Kidane, 2015). The average viscosity of PJ bio-oil at the time of production was 97.11 cP. By the time of its usage in the production of resols, the viscosity had increased dramatically to 290.91 cP. This increase in bio-oil viscosity at the point of use was an indicator that pyrolysis oils aged with time (Venderbosch and Wolter, 2011).

The aging phenomenon of pyrolysis oils could be attributed to the presence of oxygenated compounds, which undergo chemical reactions over time (Agblevor et al., 2010; Bridgwater, 2003; Bridgwater et al., 1999; Yildiz et al., 2014). Possible reactions, which may be responsible for the increased viscosity of PJ bio-oil, include the reaction of:

- Organic acids with olefins to produce esters.
- Phenolics and aldehydes to form resins and water.
- Aldehydes to form oligomers and resins.
- Alcohols and aldehydes to yield acetals and water.
- Unsaturated compounds to form polyolefins.
- Alcohols and organic acids to produce esters and water (Diebold, 2000).

Literature available on free formaldehyde content in bio-oils is within the range of 0.1 to 3.3 wt% (Diebold, 2000; Hawley, 1923) while the phenol in bio-oil is usually within the range of 0.1 to 3.8 wt% (Diebold, 2000; Fraps, 1901; Stamm and Harris, 1953). The analysis of free phenol and free formaldehyde content of PJ bio-oil was slightly below 1 wt%, which was within the range published in literature. Although, the percentage of free phenol in bio-oils are generally low, phenolic compounds other than phenol may be present in the bio-oils (Effendi et al., 2008). Possible phenolic compounds in bio-oils may include 2-methyl phenol, guaiacol, syringol, vanillin, cresol, 2,3-dimethyl phenol, 2-ethyl phenol, and 4-methoxy catechol (Diebold, 2000).

3.4.3. Effect of catalyst addition on the temperature of reaction species

The quantity of NaOH employed at the beginning of each reaction had an influence on the initial temperature of the reaction species. As the catalyst loading increased from 0.25 g to 1.25 g, the temperature of the reaction species was observed to increase linearly from 27 °C to 50.33 °C as shown in Fig. 3.2. The addition reaction of phenol and formaldehyde in the presence of NaOH catalyst leads to the formation of mono-, di-, tri-substituted methylolated phenols (Cheng, 2011; Freeman and Lewis, 1954). The formation of substituted methylolated phenol is important since formaldehyde must react with phenoxide ions in the second stage of the addition reaction. Hence, these methylol phenols are formed because the ortho and para positions in phenoxide anions are susceptible to electrophilic aromatic substitution (Cheng, 2011).

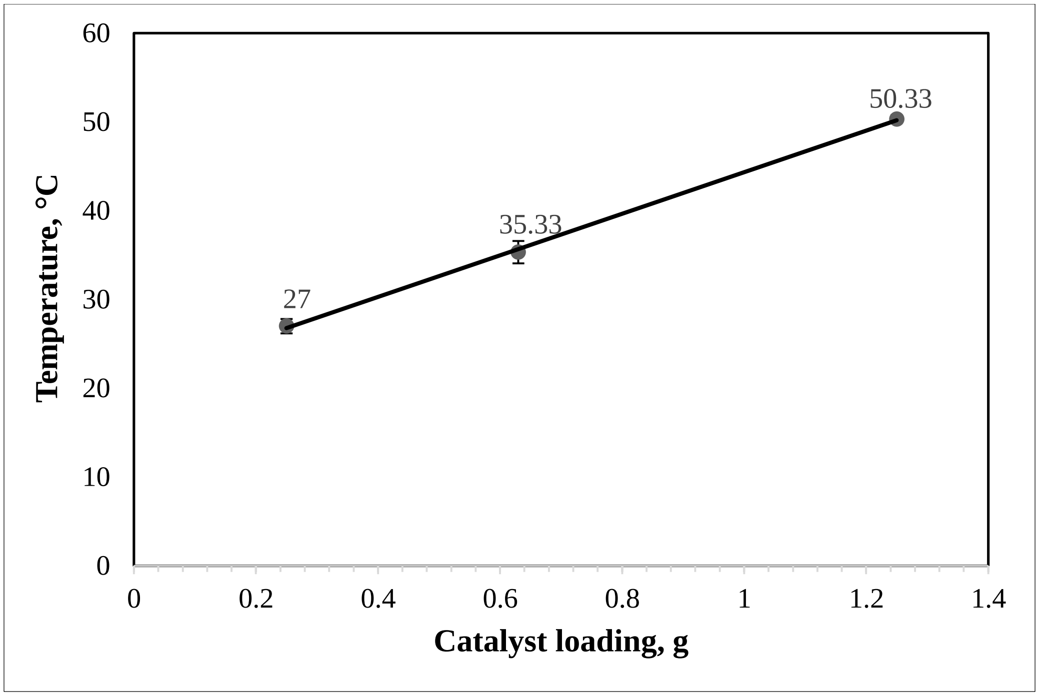

Fig. 3.2. Influence of catalyst loading on the temperature of reaction species.

The aforementioned addition reactions are exothermic in nature (Pilato, 2010), thus, explains why the initial temperature of reaction species increased as the amount of catalyst increased. It is important to control the reaction conditions in order to avoid potential explosions during resol production. The temperature trend observed as NaOH amount increased could help explain in detail the trend of free phenol and free formaldehyde concentrations, which would be discussed in Chapter 4. Additionally, the initial reaction temperatures (27 °C, 35.33°C, and 50.33 °C) recorded for the different catalyst loadings were within the addition reaction temperature range, which is less than 60 °C (Pilato, 2010).

3.4.4 Chemical structure of PJ resols and pure PF resols

The same method for FTIR analysis of PJ bio-oils was employed to investigate the structural changes that occurred within pure PF and PJ substituted resols as demonstrated in Fig. 3.3. There were a number of observable differences between the PJ substituted resols and the pure PF resol. The band observed at 1259 cm^{-1} could suggest the presence of C-O stretching vibration of phenolic C-OH, and phenolic C–O (Ar) units while the band at 1015 cm^{-1} could be attributed to the presence of -C-OH groups in phenol.

Furthermore, the peak at 989 cm^{-1} could suggest the presence of -C-H- stretching compounds whereas the band at 1120 cm $^{-1}$ could be assigned to C-O stretch compounds. Collectively, the functional groups at 1259 cm^{-1}, 1015 cm^{-1}, 989 cm^{-1}, and 1120 cm $^{-1}$, indicate the likelihood of PF resols containing more unreacted phenols than resols produced from PJ catalytic pyrolysis oil. Based on this observation, it is important to perform confirmatory tests for free phenol. A detailed free phenol and free formaldehyde analysis of both PF resols and PJ substituted resols has been discussed in Chapter 4.

The peak at 1259 cm^{-1} for the pure PF resol was more intense than that of the PJ substituted resols. Thus, this result suggests the presence of more phenolic OH groups in the PF resol compared to the PJ substituted resols. In Fig. 3.3, the peak at 989 cm^{-1} observed for the PF resol began to decrease and eventually disappeared when the phenol substitution increased. This implies that there was more -C-H- stretching compounds in the PF resol compared to the PJ substituted resols. Another structural difference between the PF resol and the PJ substituted resols occurred at 1120 cm^{-1} in the FTIR spectrum. No peaks of this nature were observed in the PJ substituted resols.

Furthermore, at the wavenumber of 1015 cm^{-1}, the intensity of the peak for the PF resol was greater than that of the PJ substituted resols. This may be due to the presence of more -C-OH groups from phenolic compounds in the PF resol than in the PJ substituted resols. Based on these findings, the PF resol could contain a higher phenolic compound concentration than the PJ substituted resols. Similar results were observed for F/P molar ratio of 1.8. FTIR spectra at 50, 60, 70, and 80 wt% were fairly similar in terms of their chemical structures.

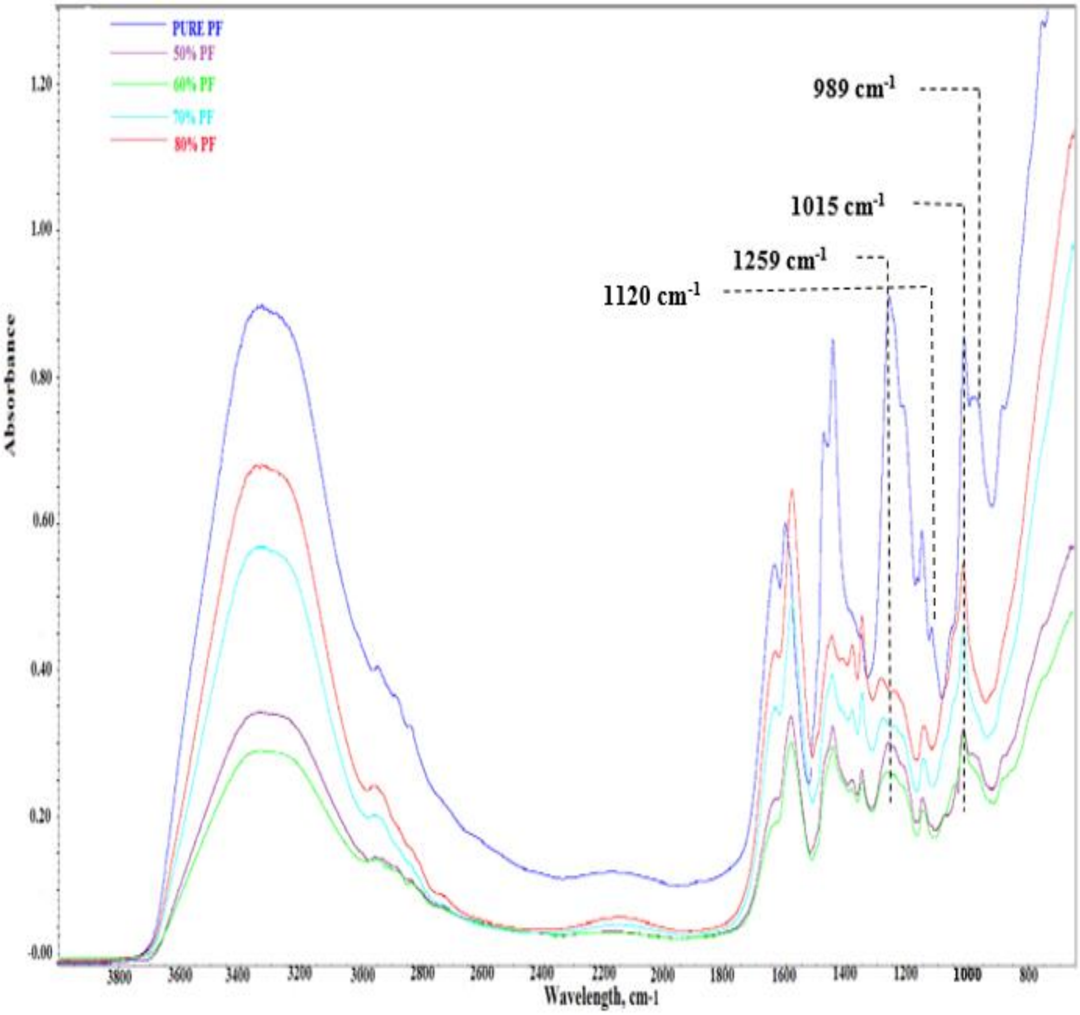

Fig. 3.3. FTIR spectra of PJ resols at F/P = 2.0 and 1.25 g of NaOH.

3.4.5 Influence of catalyst loading on the chemical structure of PJ catalytic pyrolysis oil resols

The band at 1019 cm^{-1} in Fig. 3.4, could be attributed to the presence of -C-OH groups of phenolic compounds in the resol. The spectra for PJ resol prepared at catalyst loading of 0.63 g and 1.25 g are very similar in intensity compared to that at catalyst loading of 0.25 g. At 1019 cm^{-1}, the spectrum for 0.25 g catalyst loading was more intense than those at catalyst loadings of 0.63 g and 1.25 g.

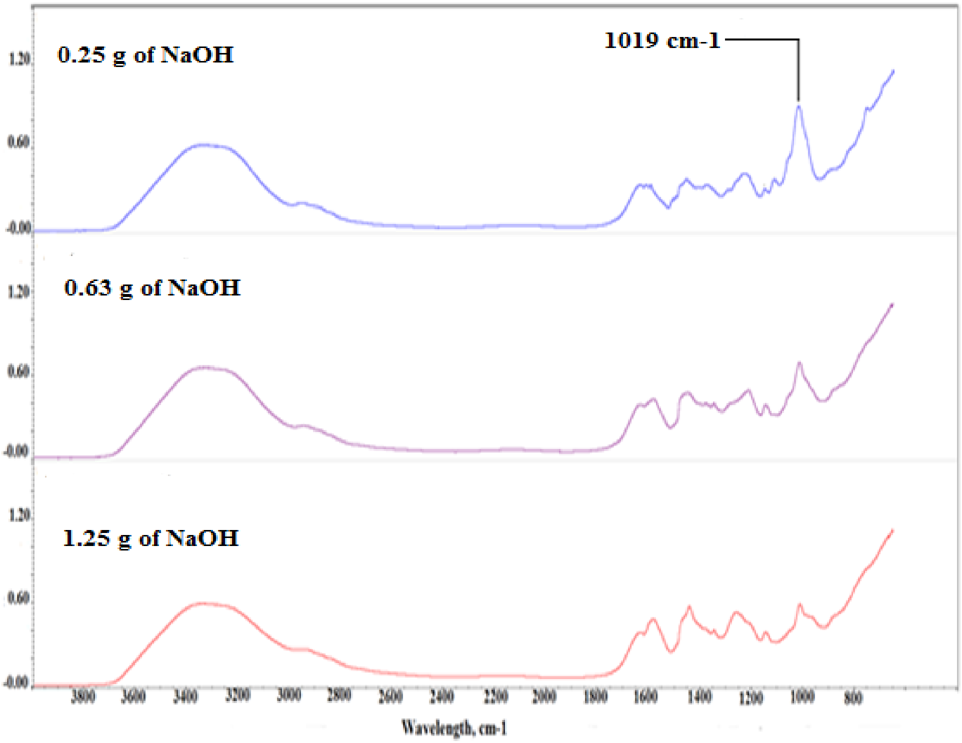

Fig. 3.4. FTIR spectra of PJ catalytic pyrolysis oil resols produced at F/P=2.0, 50% phenol substitution, and 2.5 g of phenol.

At the least catalyst loading, the chances of obtaining a higher concentration of unreacted phenols is typically common since addition and condensation reaction are the slowest (Pizzi and Mittal, 2003). Thus, the spectrum could suggest the presence of higher concentration of phenolic groups at 0.25 g catalyst loading than at 0.63 g and 1.25 g catalyst loadings. Based on this result, it could be inferred that PF resols produced at 0.25 g catalyst loading may have the highest concentration of residual phenolic compounds compared to the other catalyst loadings. Confirmatory analysis such as free phenol content determination can help establish this fact. The confirmatory tests were conducted and have been explained in Chapter 4 of this study.

3.4.6 PJ modified resols

The average yield obtained at the final stage of the resol production was 87%. pH measurements of a random PJ resol sample yielded a pH of 9.61 with a viscosity of 177.36 cP. The analysis of pH and viscosity was the same as the method used in the analysis of PJ bio-oil.

3.4.7 Influence of synthesis conditions on the water resistance of composites

In order to determine the water resistance capacity of PJ modified resols, wood composites prepared using a curing temperature of 180 °C and curing time of 45 minutes were soaked in water for 48 hours. The water test was carried out according to Test Condition Designation C of ASTM D1183-03 (Li et al., 2011). The cured wood specimens were immersed in tap water for 48 hours at 23 °C (Li et al., 2011). The wood specimens that did not delaminate during and after the water resistance tests were considered to have passed the water test. This test was conducted in triplicates.

The F/P molar ratio notwithstanding, the catalyst loading had an effect on the extent to which phenol was substituted with PJ bio-oil. From Table 3.4, at a catalyst loading of 0.25 g for both F/P = 1.8 and 2, the maximum percentage substitution of PJ bio-oil with phenol was 50%. A maximum substitution of 70% was achieved when the catalyst loading increased to 0.63 g. In conclusion, the highest percentage of phenol substitution of 80% was achieved at 1.25 g of NaOH. Thus, the extent of phenol substitution increased with the increase in the amount of sodium hydroxide catalyst employed in the resol synthesis.

Fig. 3.5. A 48-hour soaking test.

Based on similar findings reported in literature (Grenier-Loustalot et al., 1996), increasing the amount of sodium hydroxide has an impact on the activation and polymerization rates of resols. Thus, increasing the amount of catalyst leads to higher degree of polymerization degrees, which in turn enables the resin to cure faster (Pizzi and Mittal, 2003). In light of these inferences, increasing the amount of sodium hydroxide led to faster reactant consumption and product formation rates. Hence, the optimum catalyst loading was achieved at 1.25 g of NaOH.

As phenol substitution with bio-oil increased above 50%, the chances of finding more lignin fragments and other phenolic compounds other than phenol abound. For instance, during pyrolysis, lignin, which is a complex molecule, may be broken down into guaiacol, cresol, and methyl guaiacol (Kim et al., 2016). Phenol has three reactive sites: one at the para-position and two at the ortho-positions of the molecule, while other lignin fractions have fewer reactive sites compared to phenol.

Table 3.4
Water resistance test of oak wood composites produced from PJ resol.

SN [a]	Substitution (wt%)	F/P molar ratio	Catalyst loading [b] (g)	Delamination during water test (N [c]/Y [d])	Water test (P [e]/F [f])
1	0	1.8	1.25	N	P
2	50	1.8	1.25	N	P
3	60	1.8	1.25	N	P
4	70	1.8	1.25	N	P
5	80	1.8	1.25	N	P
6	90	1.8	1.25	Y	F
7	50	1.8	0.63	N	P
8	60	1.8	0.63	N	P
9	70	1.8	0.63	N	P
10	80	1.8	0.63	Y	F
11	50	1.8	0.25	N	P
12	60	1.8	0.25	Y	F
13	70	1.8	0.25	Y	F
14	80	1.8	0.25	Y	F
15	0	2	1.25	N	P
16	50	2	1.25	N	P
17	60	2	1.25	N	P
18	70	2	1.25	N	P
19	80	2	1.25	N	P
20	50	2	0.63	N	P
21	60	2	0.63	N	P
22	70	2	0.63	N	P
23	80	2	0.63	Y	F
24	50	2	0.25	N	P
25	60	2	0.25	Y	F
26	70	2	0.25	Y	F
27	80	2	0.25	Y	F

[a] SN-Serial number
[b] Catalyst loading- Amount of NaOH
[c] N – No, [d] Y-Yes, [e] P – Pass, and [f] Fail

Therefore, at very high phenol substitution of about 90% and above, other phenolic compounds other than phenol are less reactive and may be prone to steric effects (Cheng, 2011; Nihat and Nilgül, 2002). In contrast, since pure phenol has more reactive sites compared to other bio-phenolics in bio-oils, pure PF resols synthesized without bio-oil passed the water tests at both F/P molar ratios of 1.8 and 2.

Another reason why less than 90% phenol substitution was achieved could be due to the various chemical reactions associated with aging bio-oils. One of these reactions being the reaction of phenolics and aldehydes to form resins (Diebold, 2000). These reasons may account for why less than 90% phenol substitution was achieved at even a high catalyst loading of 1.25 g of NaOH.

3.5 Conclusion

The characterization of PJ bio-oil as a suitable source for phenol replacement was successfully achieved using a number of analytical techniques. PJ bio-oil was made up of phenolics, aromatic hydrocarbons, aliphatic hydrocarbons, carboxylic acids, ethers, ketones, aldehydes, and primary aliphatic alcohols. The free phenol and free formaldehyde content of PJ bio-oil of 0.72 wt% and 0.51 wt% respectively, were within the range for free phenol (0.1 to 3.8 wt%) and free formaldehyde (0.1 to 3.3 wt%) contents, reported in literature.

The extent of phenol substitution with PJ bio-oil was dependent on the amount of catalyst used during resol synthesis. The maximum replacement of phenol with PJ bio-oil that was achieved was at 80% substitution using a catalyst loading of 1.25 g of NaOH. The highest phenol substitution achieved at catalyst loading of 1.25 g was attributed to faster reaction rates and higher polymerization of monomers compared to the other catalyst loadings. Thus, the lower the catalyst loading, the lower the extent of phenol substitution with PJ bio-oil.

The chemical structure of PF resols revealed the possibility of obtaining higher concentration of phenolic OH compounds in PF resols than in PJ substituted resols. According to the FTIR analysis, resols produced using the least catalyst loading of 0.25 g, may contain a higher degree of phenolic compounds compared to catalyst loadings of 0.63 and 1.25 g since addition and condensation reactions are slower at the least catalyst loading. It can be concluded that resol synthesis parameters such as catalyst loading has an impact on the degree of phenol replacement with PJ bio-oil.

3.6 References

Agblevor, F.A., Beis, S., Mante, O., Abdoulmoumine, N., 2010. Fractional catalytic pyrolysis of hybrid poplar wood. Ind. Eng. Chem. Res. 49, 3533–3538.

Bridgwater, A.V., 2003. Renewable fuels and chemicals by thermal processing of biomass. Chem. Eng. J. 91, 87–102.

Bridgwater, A.V., Peacocke, G.V.C., 2000. Fast pyrolysis processes for biomass. Renew. Sustain. Energy Rev. 4, 1–73.

Bridgwater, A. V., Meier, D., Radlein, D., 1999. An overview of fast pyrolysis of biomass. Org. Geochem. 30, 1479–1493.

Carrara, P.E., Carroll, T.R., 1979. The determination of erosion rates from exposed tree roots in the Piceance Basin, Colorado. Earth Surf. Process. 4, 307–317.

Chaouch, M., Diouf, P.N., Laghdir, A., Yin, S., 2014. Bio-oil from whole-tree feedstock in resol-type phenolic resins. J. Appl. Polym. Sci. 131, 40014-40020.

Cheng, S., 2011. Bio-based phenolic resins and adhesives derived from forestry residues/wastes and lignin. PhD Thesis, Lakehead University.

Cheng, S., D'Cruz, I., Yuan, Z., Wang, M., Anderson, M., Leitch, M., Xu, C., 2011. Use of biocrude derived from woody biomass to substitute phenol at a high-substitution level for the production of biobased phenolic resol resins. J. Appl. Polym. Sci. 121, 2743–2751.

Danielson, B., Simonson, R., 1998. Kraft lignin in phenol formaldehyde resin. Part 1. Partial replacement of phenol by kraft lignin in phenol formaldehyde adhesives for plywood. J. Adhes. Sci. Technol. 12, 923–939.

Diebold, J.P., 2000. A review of the chemical and physical mechanisms of the storage stability of fast pyrolysis bio-oils, Nrel/Sr-570-27613.

Effendi, A., Gerhauser, H., Bridgwater, A. V., 2008. Production of renewable phenolic resins by thermochemical conversion of biomass: A review. Renew. Sustain. Energy Rev. 12, 2092–2116.

Fraps, G.S., 1901. The composition of wood oil. Am. Chem. J. 25, 26–53.

Freeman, J.H., Lewis, C.W., 1954. Alkaline-catalyzed reaction of formaldehyde and the methylols of phenol; A kinetic study1. J. Am. Chem. Soc. 76, 2080–2087.

Grenier-Loustalot, M.F., Larroque, S., Grenier, P., 1996. Phenolic resins: 5. Solid-state physicochemical study of resoles with variable F/P ratios. Polymer 37, 639–650.

Guo, C., Zhou, L., Lv, J., 2013. Effects of expandable graphite and modified ammonium polyphosphate on the flame-retardant and mechanical properties of wood flour-polypropylene composites. Polym. Polym. Compos. 21, 449–456.

Hawley, L.F., 1923. Wood distillation. The chemical catalog company, Inc, New York.

Hoong, Y.B., Paridah, M.T., Loh, Y.F., Jalaluddin, H., Chuah, L.A., 2011. A new source of natural adhesive: Acacia mangium bark extracts co-polymerized with phenol-formaldehyde (PF) for bonding Mempisang (Annonaceae spp.) veneers. Int. J. Adhes. Adhes. 31, 164–167.

Jin, Y., Cheng, X., Zheng, Z., 2010. Preparation and characterization of phenol-formaldehyde adhesives modified with enzymatic hydrolysis lignin. Bioresour. Technol. 101, 2046–2048.

Khan, M.A., Ashraf, S.M., Malhotra, V.P., 2004. Development and characterization of a wood adhesive using bagasse lignin. Int. J. Adhes. Adhes. 24, 485–493.

Kidane, Y.A., 2015. Catalytic Fast pyrolysis of whole field pennycress biomass. Master's Thesis, Utah State University.

Kim, Y.-M., Jae, J., Myung, S., Sung, B.H., Dong, J.-I., Park, Y.-K., 2016. Investigation into the lignin decomposition mechanism by analysis of the pyrolysis product of *Pinus radiata*. Bioresour. Technol. 219, 371-377.

Knop, A., Pilato, L.A., 1985. Phenolic resins: Chemistry, applications, and performance: Future directions. Springer-Verlag Berlin.

Li, N., Wang, Y., Tilley, M., Bean, S.R., Wu, X., Sun, X.S., Wang, D., 2011. Adhesive performance of sorghum protein extracted from sorghum DDGS and flour. J. Polym. Environ. 19, 755–765.

Liu, X., Zhang, W., Sui, G., Ning, Q., 2007. Determination of phenol and formaldehyde in resol resins by high performance chromatography. Chinese J. Chromatogr. 25, 562–564.

Maher, K.D., Bressler, D.C., 2007. Pyrolysis of triglyceride materials for the production of renewable fuels and chemicals. Bioresour. Technol. 98, 2351–2368.

Mohan, D., Pittman, C.U., Steele, P.H., 2006. Pyrolysis of wood/biomass for bio-oil: A critical review. Energy and Fuels 20, 848–889.

Nakos, P., Tsiantzi, S., Athanassiadou, E., 2000. Wood adhesives made with pyrolysis oils., in: Proceedings of the 3rd European Wood-Based Panel Symposium. Hanover, pp. 1–2.

Nihat, S.C., Nilgül, O., 2002. Use of organosolv lignin in phenol formaldehyde resins for particleboard production II. Particleboard production and properties. Int. J. Adhes. Adhes. 22, 477–480.

Pilato, L., 2010. Phenolic reisn: A century of progress. Springer-Verlag Berlin Heidelberg.

Pizzi, A., Mittal, K.L. Handbook of adhesives technology, second ed., Marcel Dekker. New York.

Poljanšek, I., Krajnc, M., 2005. Characterization of phenol-formaldehyde prepolymer resins by in line FT-IR spectroscopy. Acta Chim. Slov. 52, 238–244.

Riedlinger, D.A., 2008. Characterization of PF resol / isocyanate hybrid adhesives. Master's Thesis, Virginia Polytechnic Institute and State University.

Rover, M.R., 2013. Analysis of sugars and phenolic compounds in bio-oil. Master's Thesis, Iowa State University.

Rover, M.R., Brown, R.C., 2013. Quantification of total phenols in bio-oil using the Folin-Ciocalteu method. J. Anal. Appl. Pyrolysis 104, 366–371.

Siddiqui, H., 2013. Production of lignin-based phenolic resin using de-polymerized kraft lignin and process optimization. Master's Thesis, The University of Western Ontario. London, Ontario, Canada.

Stamm, A.J., Harris, E.E., 1953. Chemical processing of wood. Chemical publishing company, New York.

Valliyappan, T., Bakhshi, N.N., Dalai, A.K., 2008. Pyrolysis of glycerol for the production of hydrogen or syn gas. Bioresour. Technol. 99, 4476–4483.

Venderbosch, R.H., Prins, W., 2010. Fast pyrolysis technology development. Biofuels, Bioproducts, and Biorefining 4, 178–208.

Venderbosch, R.H., Wolter, P., 2011. Thermochemical Processing of Biomass, in: Conversion into Fuels, Chemicals and Power. John Wiley & Sons, Chichester.

Wang, M., Xu, C., Leitch, M., 2009. Liquefaction of cornstalk in hot-compressed phenol-water medium to phenolic feedstock for the synthesis of phenol-formaldehyde resin. Bioresour. Technol. 100, 2305-2307.

Yathavan, B.K., 2013. Conventional and catalytic pyrolysis of pinyon juniper biomass. Master's Thesis, Utah State University.

Yathavan, B.K., Agblevor, F.A., 2013. Catalytic pyrolysis of pinyon-juniper using red mud and HZSM-5. Energy and Fuels 27, 6858–6865.

Yildiz, G., Lathouwers, T., Toraman, H.E., Van Geem, K.M., Marin, G.B., Ronsse, F., Van Duren, R., Kersten, S.R.A., Prins, W., 2014. Catalytic fast pyrolysis of pine wood: Effect of successive catalyst regeneration. Energy and Fuels 28, 4560–4572.

Zhang, W., Ma, Y., Xu, Y., Wang, C., Chu, F., 2013. Lignocellulosic ethanol residue-based lignin-phenol-formaldehyde resin adhesive. Int. J. Adhes. Adhes. 40, 11–18.

CHAPTER 4

EVALUATION OF MECHANICAL STRENGTH PROPERTIES, FREE FORMALDEHYDE AND FREE PHENOL CONTENTS OF PINYON-JUNIPER PHENOL-FORMALDEHYDE RESOLS

4.1 Abstract

Phenol-formaldehyde adhesives used in the production of wood-based materials are known to have excellent mechanical properties. As phenol is substituted with pinyon-juniper catalytic pyrolysis oil, it is imperative that the phenol substitution process does not compromise the strength of the adhesives. Furthermore, the substitution of phenol with pinyon-juniper bio-oil should lead to the production of resols with less concentration of toxic substances.

The performance of pinyon-juniper substituted resols in terms of shear strength was comparable to pure phenol-formaldehyde adhesives. Both the dry shear strength (8.99 to 12.73 MPa) and wet shear strength (5.16 to 7.36 MPa) exceeded the minimum requirement of 0.66 MPa for plywood. Resol synthesis conditions such as formaldehyde-to-phenol molar ratio, catalyst loading, and phenol substitution percentage affected the residual formaldehyde and phenol in the resols. Pinyon-juniper substituted resols exhibited a lower free phenol content compared to pure phenol-formaldehyde resols. At the optimum catalyst loading of 1.25 g of NaOH, free formaldehyde content drastically reduced, the formaldehyde-to-phenol ratio notwithstanding. An hour was enough to achieve the optimum results. Pure phenol-formaldehyde adhesives had a higher concentration of free phenol compared to pinyon-juniper substituted resols.

4.2 Introduction

Thermosetting resins such as phenol-formaldehyde (PF) resols exhibit excellent properties when incorporated in wood-based materials (Roslan et al., 2014; Vázquez et al., 2012). PF resins are produced via the addition and condensation reactions of phenol and formaldehyde in either acidic or basic environments. Thus, these resins are categorized as resols or novolacs depending on the type of catalyst and formaldehyde-to-phenol (F/P) molar ratios employed in the resin synthesis process (Cheng, 2011; Riedlinger, 2008).

Novolacs, which are thermoplastic phenolic resins, are acid-catalyzed and produced at F/P molar ratios of less than 1. Conversely, resols (thermosetting phenolic resins) are synthesized under basic conditions and at F/P molar ratios greater than 1 (Siddiqui, 2013). Resols, which are of particular interest in this research have superior water resistance, high strength, good thermal and dimensional stability, and excellent wettability properties in wood composite applications (Atta-Obeng, 2011; Dunky, 2003).

The aforementioned properties of resol-based engineered wood products make them very suitable for exterior applications. Since wood-based products are widely used in the construction and building sectors, it is important that engineered wood products have excellent strength so that wooden structures are built with a great degree of confidence. Wood-based products designed for exterior applications are exposed to harsh outdoor conditions such as rainfall, heat, snow, or even floods (Unsal et al., 2009), and therefore must be strong enough to withstand these conditions. For PF resols, which are a preferred choice for producing exterior grade wood products (Nakos et al., 2000), it is important to understand the impact of water on the strength of the wood composites.

A number of mechanical testing procedures are employed to determine the strength properties of adhesives. Common strength properties include tensile (Moubarik et al., 2009), shear (Roslan et al., 2014), and bending strength properties (Atta-Obeng, 2011). The determination of these strength properties is usually governed by the adherence to standard mechanical test methods. In this study, the short beam shear test (SBS) according to ASTM D 2344/ D 2344 M-00, was used to determine the interlaminar shear strength of oak wood composites (Short, 1995). This test is typically employed for the comparative testing of composites for quality control purposes.

Although no limits of shear strength are stipulated for the SBS standard test method, shear strengths obtained from SBS test were compared to the shear strength limit specified by the Engineered Wood Association (APA), which follows ASTM D 2718 (Method B). According to APA, the minimum shear strength requirement for plywood at a performance category of ½ is 0.66 MPA, considering a planar shear strength of 570 lbf/ft. (APA, 2010) and an area of 6 in^2/ft. (APA, 2012). The performance category is a means of labelling plywood in terms of the range of its panel's thickness (APA, 2010). The wood composite for this study was made from two pieces of ¼ inch veneers, hence the performance category of ½.

Researchers have reported that wet conditions decrease the strength of wood composites (Cheng et al., 2011; Tan et al., 2011). Utilizing the short beam shear test, the impact of wet conditions on the shear strength of oak wood composites was examined. Additionally, the shear strengths of oak composites prepared using resol synthesis parameters such as F/P molar ratios, catalysts loadings, and percentage phenol substitutions were evaluated. Using statistical tools, shear strengths obtained from these experimental conditions were analyzed, to determine their influence on the strength properties.

The final resol product is made up of polymeric chains, monomeric methylol-phenols, unreacted phenols, and free formaldehyde compounds (Dunky, 2003). Therefore, the knowledge of the toxicological behavior of phenol and formaldehyde is important in order to know the potential risks associated with handling PF adhesives.

Phenol is a toxic substance, which has many debilitating effects (Gardziella et al., 2000; Knop and Pilato, 1985). The toxicity of phenol is dependent on the amount of phenol an individual is exposed to. Exposure to phenol may lead to skin irritations, headaches, dizziness, kidney and liver damage, and in extreme cases, paralysis or death in humans (Knop and Pilato, 1985). Table 4.1 shows the exposure limits and health effects of phenol. TWA represents the time-weighted average of phenol exposure within 8 hours.

Table 4.1
Exposure limits of phenol (OSHA, 2012).

Organization	**Exposure values, ppm**	**Health effects**
Occupational Safety and Health Administration	5 (TWA)	Eye, nose, and throat irritations
National Institute for Occupational Safety and Health	5 (TWA)	Kidney and Liver damage
American Conference of Governmental Industrial Hygienists	5 (TWA)	Cardiovascular, hepatic, and renal toxicity

Formaldehyde is a mutagenic and cancer-causing compound (Salthammer et al., 2010). From previous studies, people exposed to formaldehyde had symptoms of nasal or respiratory tract cancer. The mutagenic effect of formaldehyde is also observed in bacteria, fungi, and insects (Knop and Pilato, 1985). Due to the carcinogenic effects of formaldehyde, different countries around the world have set exposure limits for formaldehyde in working facilities as shown in Table 4.2. TWA is used to denote the time-weighted average of formaldehyde exposure within 8 hours while TLV is used to represent the threshold limit of formaldehyde exposure.

Table 4.2
Formaldehyde exposure limits (Knop and Pilato, 1985).

Countries	**Exposure limits, ppm**
United States of America	3 (TWA)
United Kingdom	2 (TLV)
Germany	1 (TLV)
Switzerland	1 (TLV)

To engender the safe application of adhesives, wood adhesives must contain low concentrations of volatile organic compounds. Although, the curing stage of PF resols removes most of the free phenol and formaldehyde in the resol (Chaouch et al., 2014), it is equally important to determine the free formaldehyde and free phenol content of resols after synthesis. Generally, common analysis of free phenol and free formaldehyde could be carried out using titration and other instrumental methods.

High concentrations of unreacted free formaldehyde and phenol pose health and environmental concerns. Thus, it is important that PF resins contain low concentrations of free formaldehyde and free phenol. For a low free formaldehyde content according to US Patent 9 102 040, a phenolic resin should contain preferably less than 0.5 wt% of formaldehyde (Tumler, 2015). In addition, a low free phenol resin should contain less than 10 wt% of free phenol (Tumler, 2015).

4.3 Materials and methods

4.3.1 Short beam strength

The shear strength of the oak wood composite produced from 2 in x 2 in x ¼ oak veneers was determined in accordance with the ASTM D 2344/ D 2344 M-00 standard for composite materials and their laminates. The shear strength test was carried out at a support span length-to-specimen thickness ratio (s/t) of approximately 4:1 and a support span of 49 mm. The short beam shear test fixture was purchased from Wyoming Test Fixtures Inc. (Salt Lake City, Utah) and the test was conducted on a Tinius Olsen Testing equipment having a maximum of 50 kN load capacity. Triplicate wood composite samples were tested for their shear strength. The short beam strength was calculated using Equation 4.0, considering a three-point bending test configuration as shown in Fig. 4.1. The short beam strength experiments were carried out for oak wood composites at dry and wet conditions.

$$F^{sbs} = 0.75 \times \frac{P_m}{b \times h} \quad \text{………………………………………………...…Equation 4.0}$$

Where:

F^{sbs} = short beam strength, MPa (psi);

P_m = maximum load observed during the test, N (lbf);

b = measured specimen width, m (in.), and

h = measured specimen thickness, mm (in.) (Short, 1995).

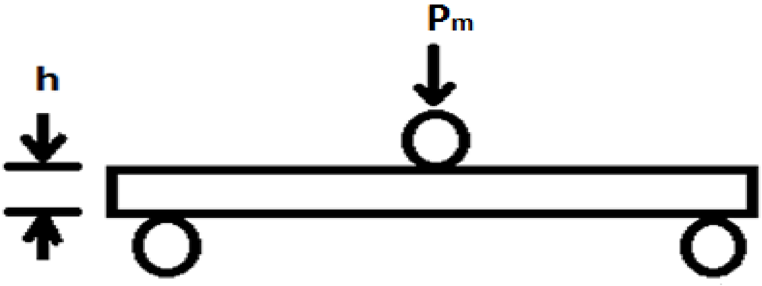

Fig. 4.1. Three-point bending test.

4.3.2 Determination of free formaldehyde and free phenol content of resols

A high performance liquid chromatography (HPLC) (SCL-10 A, Shimadzu Scientific, Columbia, MD, USA) was used to determine the free formaldehyde and free phenol content of the resols. The free formaldehyde and free phenol content were analyzed on a Kromasil C18 column (5 µm, 100 Ǻ, 4.6 × 250 mm). The mobile phase was prepared from a 43/57 (v/v) methanol/water mixture and the oven temperature was kept at 30 °C (Liu et al., 2007). Formaldehyde was detected at a wavelength of 360 nm while phenol was detected at a wavelength of 270 nm on an ultraviolet (uv) detector. The mobile phase flow rate used for this analysis was 0.8 ml/min at a sample injection volume of 20 µl (Liu et al., 2007).

In order to quantify the concentration of phenol and formaldehyde, calibration curves were developed using phenol and derivatized formaldehyde (formaldehyde hydrazone) standard solutions. The phenol standard solutions were prepared at concentrations of 1000, 500, 200, and 50 mg/L. The derivatized formaldehyde solution was prepared at concentrations of 300, 150, 60, 20 and 5 mg/L (Liu et al., 2007).

Prior to the HPLC analysis, the resol was first derivatized using 2,4-diphenylhydrazine (DNPH) derivatization reagent (Liu et al., 2007). The 2,4-DNPH derivatization reagent was prepared by mixing 5 g of 2,4-DNPH with 2.5 g of glacial acetic acid in a 500 ml volumetric flask. Acetonitrile was used to fill up the volume of the flask to its 500 ml mark. The solution was swirled and stored in a dark environment. Formaldehyde hydrazone was prepared by mixing 0.015 g of formaldehyde and 30 ml of 2,4-DNPH derivatization reagent in a 50 ml volumetric flask. Methanol was then added to fill the volumetric flask to its mark. The resulting solution was then kept at 40 °C for 4 hours in the dark. Also, 0.1 g of the resol was mixed with 10 ml 2,4-DNPH derivatization reagent in a 50 ml volumetric flask. Methanol was then added to top up the volume of the flask to 50 ml. The derivatization procedure was completed in a water bath, set at a temperature of 40 °C, for 4 hours in a dark room (Liu et al., 2007).

4.3.3 Statistical analysis

All response variables such as shear strength, residual formaldehyde, and phenol were analyzed using the SAS software. The principal objective of using this statistical platform was to help compare the influence of synthesis factors such as F/P molar ratio, catalyst loading, and percent phenol substitution on the response variables.

4.4 Results and discussion

4.4.1 Evaluation of shear strength of pinyon-juniper modified resols

4.4.1.1 Effects of water tests on the shear strength of oak wood composites

A number of researchers have stated that soaking wood composites in water certainly has a negative impact on their mechanical behavior (Cheng, 2011). Laminated wood exposed to water tends to decrease the strength of such wood composites. For all the different formulations of resols examined, a general trend for dry shear strength and wet shear strength was observed. Fig. 4.2 shows the dry and wet shear strength of oak composites at F/P molar ratio of 2.0, catalyst loading of 1.25 g of NaOH, and phenol substitutions from 0 wt% to 80 wt%. The dry shear strengths of oak laminated composites were generally higher than their wet shear strengths. The dry shear strength of oak composites ranged from 8.99 MPa to 12.73 MPa while the wet shear strength ranged from 5.16 MPa to 7.36 MPa.

Considering this range of shear strength values, the dry shear strengths of oak composites were at least 1.5 times greater than the wet shear strengths. Furthermore, the shear strength values obtained at both dry and wet conditions exceeded the minimum requirement of 0.66 MPa for shear strength set by the Engineered Wood Association (APA).

The soaking test of wood composites was not only carried out to evaluate the water resistance of wood laminates but also to investigate the impact of water on the strength of the wood. The presence of water in wood composites tends to soften and expand the wood cell walls and the hydrogen bonds within the polymeric wood components begin to break (University of Cambridge, 2004). Subsequently, stronger hydrogen bonds are formed between water and cellulose molecules than between cellulose and other cellulose molecules. Thus, as the cell wall expands the amount of cellulose microfibrils within the composites reduces per unit area, leading to the reduction in the strength of the composites (University of Cambridge, 2004).

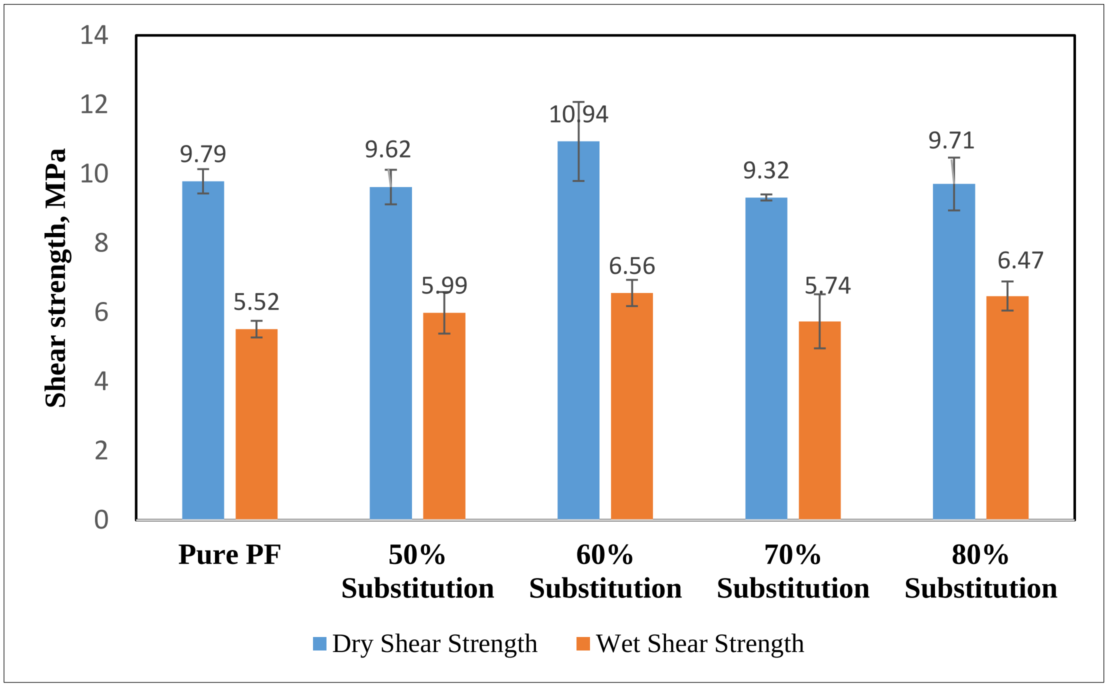

Fig. 4.2. Shear strength of oak composites at F/P molar ratio of 2 and 1.25 g of NaOH.

T-tests are carried out to determine whether there are differences between the means of two independent populations (Peng and Tong, 2011). The test is based on the assumption of whether the variances are equal are not. For the equal variance assumption, the Pooled method is used while the Satterthwaite method is employed for unequal variance assumption (Schechtman and Sherman, 2007). ANOVA is used for pairwise comparison of the means of more than two independent populations (Popescu et al., 2016). It is based on the assumption that the populations of interest have the same distributions and same variances but differ in their centers (e.g. mean, median) (Popescu et al., 2016).

A t-test was conducted using the SAS software to determine whether the average shear strength values obtained for dry and wet conditions were significantly different from each other. The analysis was performed using data obtained at both F/P molar ratios of 1.8 and 2.0, and phenol substitutions of 0 to 80 wt%. The results from the equality of variances test in Table 4.3 indicate a significant difference in the variability of the dry and wet shear strengths (F = 3.46, p-value = 0.0144 < 0.05). In other words, there was evidence for the violation of the equal variance assumption in this case. Hence, the Satterthwaite (unequal variance) method was used to perform the t-test for the shear strength means.

Table 4.3
Equality of variance test.

Equality of variances					
Variable	**Method**	**Numerator DF**	**Denominator DF**	**F-value**	**Pr > F**
Shear Strength	Folded F	17	17	3.46	0.0144

In Table 4.4, using the Satterthwaite method, we observed that there was extremely strong evidence that the average dry and wet shear strengths were significantly different (t = 14.45, p-value < 0.0001). Here, we also noticed that the equal (pooled) variance method produced a similar result. According to these results, we can conclude that soaking wood composites in water reduces the mechanical strength of the wood composites.

Table 4.4
T-test results according to equal and unequal variance methods.

Variable	Method	Variances	DF	t-value	Pr > |t|
Shear Strength	Pooled	Equal	34.00	14.45	< 0.0001
	Satterthwaite	Unequal	26.07	14.45	< 0.0001

4.4.1.2 Influence of synthesis conditions on the shear strengths of oak composites

The statistical analysis of dry and wet shear strength was performed using analysis of variance (ANOVA) at a 5% significance level for a completely randomized 2x3x5 factorial design based on three main factors: F/P molar ratio, catalyst loading, and phenol substitution. The levels of catalyst loading considered for the analysis were 0.25, 0.63, and 1.25 g of NaOH, and F/P molar ratios of 1.8 and 2.0. In addition, 0, 50, 60, 70, and 80 wt% of phenol substitution were investigated. The model derived from the statistical analysis is expressed in Equation 4.1.

$Y_{ijkl} = \mu + A_i + B_j + C_k + AB_{ij} + BC_{jk} + AC_{ik} + \varepsilon_{ijkl}$……………………..Equation 4.1

i = 1 and 2   j = 1, 2, and 3   k = 1, 2, 3, 4, and 5

Where:

Y_{ijkl} = The dry or wet shear strength of oak composites for kth experimental unit.

μ = Overall mean.

A_i = The mean effect of F/P molar ratio of level ‘i’.

B_j = The mean effect of catalyst loading of level 'j'.

C_k = The mean effect of phenol substitution of level 'k'.

AB_{ij} = Interaction effect of F/P molar ratio and catalyst loading.

BC_{jk} = Interaction effect of catalyst loading and phenol substitution.

AC_{ik} = Interaction effect of F/P molar ratio and phenol substitution.

ε_{ijkl} = Random error.

Table 4.5
ANOVA results for wet shear strength of oak composites.

Source	**DF**	**Sum of Squares**	**Mean Square**	**F-value**	**Pr > F**
Model	15	5.25	0.35	1.27	0.5267
F/P	1	0.12	0.12	0.43	0.5789
NaOH [a]	2	0.62	0.31	1.1	0.4769
F/P*NaOH	2	2.56	1.28	4.61	0.1781
Substitution [b]	4	1.76	0.44	1.57	0.4241
F/P*Substitution	4	0.20	0.05	0.19	0.9217
NaOH*Substitution	2	0.04	0.02	0.07	0.9317

[a] NaOH – catalyst loading and [b] substitution – phenol substitution.

From the ANOVA results in Table 4.5, it was observed that the main effect: F/P molar ratio (p-value = 0.5789 > 0.05), catalyst loading (p-value = 0.4769 > 0.05), and phenol substitution (p-value = 0.4241 > 0.05), had no significant effect on the wet shear strength of the oak composites. Similarly, the interaction effect of F/P molar ratio and catalyst loading (p-value = 0.1781 > 0.05), catalyst loading and phenol substitution (p-value = 0.9317 > 0.05), and F/P molar ratio and phenol substitution (p-value = 0.9217 > 0.05), had no significant effect on the wet shear strength of the oak composites. Also, the overall model (Equation 4.1) containing variables for the main and interaction effects was found to be insignificant (p-value = 0.5267 > 0.05).

Table 4.6
ANOVA results for dry shear strength of oak composites.

Source	DF	Sum of Squares	Mean Square	F-value	Pr > F
Model	15	17.85	1.19	1.01	0.6043
F/P	1	1.79	1.79	1.51	0.3435
NaOH [a]	2	3.16	1.58	1.34	0.4269
F/P*NaOH	2	1.82	0.91	0.77	0.5651
Substitution [b]	4	4.80	1.20	1.02	0.5508
F/P*Substitution	4	2.52	0.63	0.53	0.7328
NaOH*Substitution	2	3.84	1.92	1.63	0.3803

[a] NaOH – catalyst loading and [b] substitution – phenol substitution

Based on the ANOVA results in Table 4.6, it was observed that the main effect: F/P molar ratio (p-value = 0.3435 > 0.05), catalyst loading (p-value = 0.4269 > 0.05), and phenol substitution (p-value = 0.5508 > 0.05), had no significant effect on the dry shear strength of the oak composites. In a similar manner, it was observed that the interaction effect of F/P molar ratio and catalyst loading (p-value = 0.5651 > 0.05), catalyst loading and phenol substitution (p-value = 0.3803 > 0.05), and F/P molar ratio and phenol substitution (p-value = 0.7328 > 0.05), had no significant effect on the dry shear strength of the oak composites. Also, the overall model containing variables for the main and interaction effects was found to be insignificant (p-value = 0.6043 > 0.05).

Table 4.7
Shear strength data of oak composites.

SN [a]	**F/P molar ratio**	**Phenol substitution, wt%**	**Catalyst loading, g**	**Dry shear strength, MPa**	**Wet shear strength, MPa**
1	1.8	0	1.25	9.42 ± 0.33	5.47 ± 0.30
2	1.8	50	1.25	10.35 ± 0.96	5.93 ± 0.42
3	1.8	60	1.25	9.95 ± 0.71	5.92 ± 1.25
4	1.8	70	1.25	10.15 ± 0.54	5.32 ± 0.54
5	1.8	80	1.25	11.95 ± 1.89	5.78 ± 1.10
6	1.8	50	0.63	9.28 ± 0.27	6.44 ± 0.42
7	1.8	60	0.63	12.25 ± 0.79	7.36 ± 1.52
8	1.8	70	0.63	12.73 ± 0.86	6.10 ± 0.83
9	1.8	50	0.25	8.99 ± 0.22	5.16 ± 0.35
10	2.0	0	1.25	9.79 ± 0.35	5.52 ± 0.24
11	2.0	50	1.25	9.62 ± 0.50	5.99 ± 0.60
12	2.0	60	1.25	10.94 ± 1.14	6.56 ± 0.38
13	2.0	70	1.25	9.32 ± 0.09	5.74 ± 0.78
14	2.0	80	1.25	9.71 ± 0.76	6.47 ± 0.42
15	2.0	50	0.63	9.43 ± 0.85	6.48 ± 0.62
16	2.0	60	0.63	9.80 ± 0.16	5.87 ± 0.75
17	2.0	70	0.63	11.01 ± 0.28	5.39 ± 0.69
18	2.0	50	0.25	9.78 ± 0.39	6.93 ± 0.49

[a] SN-Serial number.

From the statistical analysis, it can be inferred that none of the resol synthesis parameters had a major effect on the wet and dry strength properties of oak composites. A summary of the dry and wet shear strength of the oak composites is shown in Table 4.7.

4.4.2 Free formaldehyde and free phenol content of PJ substituted resols

4.4.2.1 Influence of catalyst loading on the content of free formaldehyde and phenol

The amount of catalyst plays an important role in the residual formaldehyde and phenol remaining in the final resol. During the synthesis of resols, addition of higher quantities of catalyst can affect the kinetics of PF reactions by increasing the reactant consumption and product formation rates of these reactions. A 50 wt% sodium hydroxide aqueous solution was used in this investigation. The actual amounts of sodium hydroxide used as catalyst loadings were 0.25, 0.63, and 1.25 g.

At both F/P molar ratios of 1.8 and 2, and 50 wt% phenol substitution, a similar trend for free phenol and free formaldehyde contents was observed. At F/P molar ratio of 1.8, the free formaldehyde content decreased from 11.99 to 2.70 wt% as catalyst loading increased from 0.25 to 0.63 g. Also, as catalyst loading further increased from 0.63 to 1.25 g, free formaldehyde content decreased from 2.70 to 0.20 wt%. In a similar manner, at F/P molar ratio of 2, free formaldehyde content decreased in the order: 12.84 wt%, 4.83 wt% and finally 0.34 wt% as catalyst loading increased in the order: 0.25, 0.63, and 1.25 g respectively.

At F/P molar ratio of 1.8, free phenol content initially decreased from 3.21 to 0.38 wt% and increased from 0.38 to 1.27 wt% as catalyst loading increased from 0.25 to 0.63

g, and from 0.63 to 1.25 g respectively. Similarly, at F/P ratio of 2.0, free phenol content decreased from 2.93 to 0.08 wt% when catalyst loading increased from 0.25 to 0.63 g. Finally, as catalyst loading further increased from 0.63 to 1.25 g, free phenol content increased from 0.08 to 0.74 wt%. The influence of free formaldehyde and free phenol as a function of catalyst amount is shown in Fig. 4.3.

Phenol-formaldehyde resol synthesis is controlled by two major reactions: addition and condensation. During addition reactions, the presence of the basic catalyst initiates the addition of formaldehyde to phenolic compounds by formation of phenolate ions (Grenier-Loustalot et al., 1996). The formation of phenolates and subsequent reaction of phenolates and formaldehyde to form hydroxymethylphenols (HMP) occur below 60 °C (Pilato, 2010). The second reaction, which is the condensation reaction occurs above 60 °C.

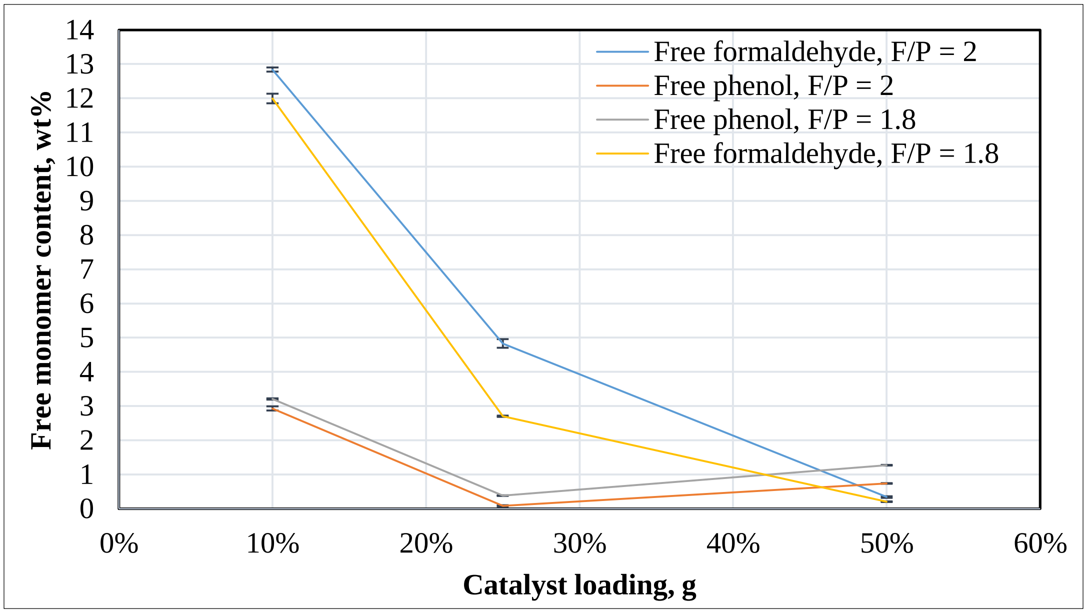

Fig. 4.3. Free monomer content at 50 wt % phenol substitution.

At catalyst loading of 0.25 g of NaOH, the rate of both the addition and condensation reactions were the slowest compared to catalyst loading of 0.63 and 1.25 g. This observation could be corroborated by the temperature of reaction species: 27 °C as reported in Chapter 3. In effect, the slower the rate of addition and condensation reactions, the higher the amount of unconsumed reactants. Thus, the higher the amount of free monomers such as free phenol and free formaldehyde in the resol.

For both F/P ratios of 1.8 and 2.0, it was observed that the free phenol content at catalyst loading of 0.63 g of NaOH was lesser than that at catalyst loading of 1.25 g. This trend could be attributed to the mechanism by which addition reactions occur at catalyst loadings of 0.63 and 1.25 g. During the addition reaction process, phenoxide anions are most likely to form aromatic substitutions with formaldehyde to produce mono-, di-, and tri- substituted methylolated phenols (Cheng, 2011).

The formation of these substituted methylolated phenols are exothermic in nature. Furthermore, the rate of reaction of dimethylol-substituted phenols with formaldehyde is at least 2 to 4 times faster than the rate of reaction of phenol and formaldehyde (Cheng, 2011). This phenomenon leaves a higher concentration of unreacted phenols in the resol. Thus, the reaction between dimethylol-substituted phenol with formaldehyde may be favored at a higher catalyst loading of 1.25 g of NaOH than at 0.63 g of NaOH. The initial reaction temperature of 50.33 °C observed at 1.25 g of NaOH also supports the evidence of exothermic reaction during the formation of substituted methylolated phenols.

4.4.2.2 Effect of F/P ratios and phenol substitutions on phenol and formaldehyde in resols

Fig. 4.4 and 4.5 show the influence of the initial F/P molar ratio and phenol substitution on the free phenol and free formaldehyde content of resols. Comparing Fig. 4.4 and 4.5, it was observed that with an increase of F/P ratio from 1.8 to 2.0, the free formaldehyde content increased while the free phenol content decreased for all the phenol substitutions investigated. An inverse relationship was observed as the F/P molar ratio decreased from 2.0 to 1.8.

The higher concentration of free formaldehyde at F/P molar ratio of 2.0 was due to the presence of a greater quantity of formaldehyde at the beginning of resol synthesis. Furthermore, the free phenol content was greater at F/P molar ratio of 1.8 because of the higher portion of phenol at the beginning of the reaction compared to the quantity of phenol at F/P molar ratio of 2. Based on these results, the F/P molar ratios had an impact on the free formaldehyde and free phenol contents of the resol.

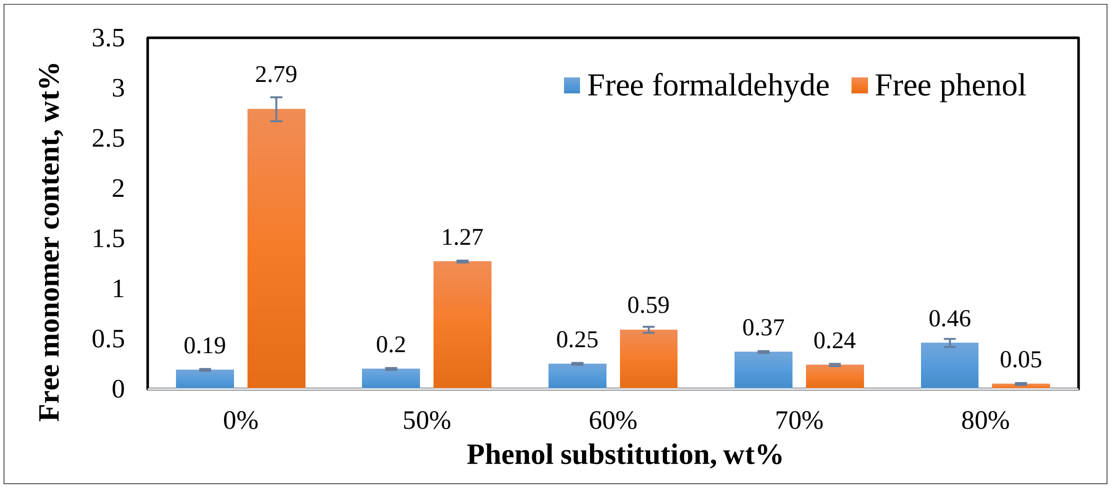

Fig. 4.4. Residual formaldehyde and phenol at F/P = 1.8 and 1.25 g of NaOH.

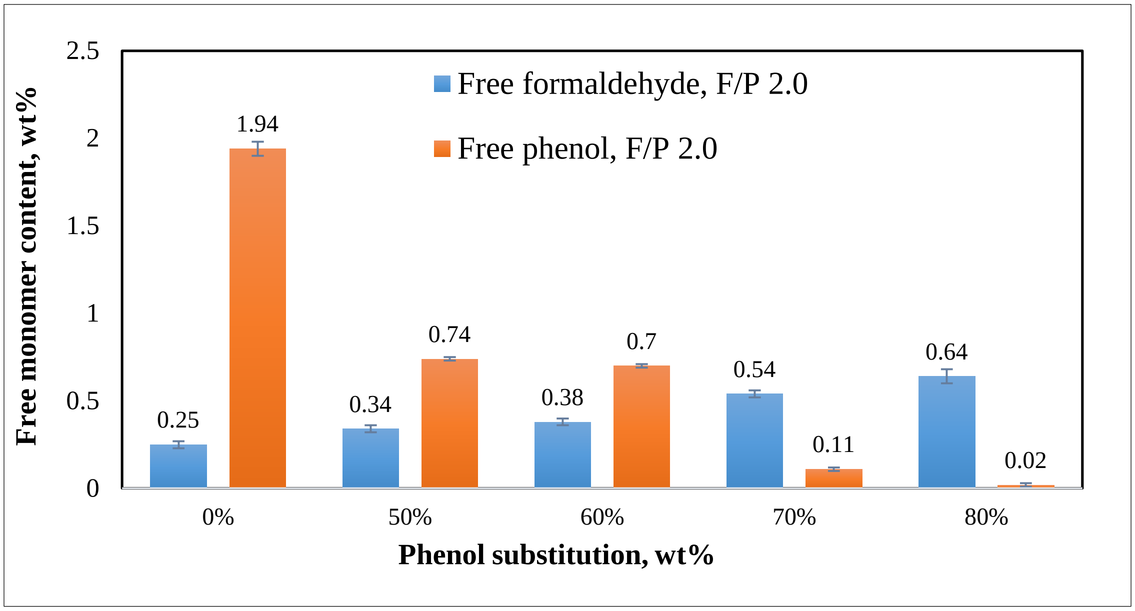

Fig. 4.5. Free formaldehyde and free phenol content at F/P = 2.0 and 1.25 g of NaOH.

Furthermore, as phenol substitution percentage increased, it was observed that free formaldehyde content also increased whereas free phenol content decreased. The reduction in free phenol content as phenol substitution with bio-oil increased could be attributed to the decreasing phenol amounts at the beginning of the reaction. PJ contains about 0.51 wt% of formaldehyde. As more bio-oil is utilized in resol synthesis, it is expected that the starting amount of formaldehyde would also increase.

4.4.2.3 Statistical evaluation of free-formaldehyde and free phenol results

4.4.2.3.1 Effect of resol synthesis conditions on free formaldehyde content

With the aid of the SAS software, the influence of resol synthesis conditions on the free formaldehyde content of resols was determined. The results are summarized in

Table 4.8. Based on the ANOVA results in Table 4.8, an effects model was generated, as expressed in Equation 4.2.

$Y_{ijkl} = \mu + Q_i + R_j + S_k + QR_{ij} + RS_{jk} + QS_{ik} + \varepsilon_{ijkl}$...................................Equation 4.2

i = 1 and 2 j = 1, 2, and 3 k = 1, 2, 3, 4, and 5

Where:

Y_{ijkl} = Free formaldehyde content of resols for kth experimental unit.

μ = Overall mean.

Q_i = The mean effect of F/P molar ratio of level ‘i’.

R_j = The mean effect of catalyst loading of level ‘j’.

S_k = The mean effect of phenol substitution of level ‘k’.

QR_{ij} = Interaction effect of F/P molar ratio and catalyst loading.

RS_{jk} = Interaction effect of catalyst loading and phenol substitution.

QS_{ik} = Interaction effect of F/P molar ratio and phenol substitution.

ε_{ijkl} = Random error.

From the ANOVA results in Table 4.8, it was observed that the main effect variables: F/P molar ratio (p-value = 0.0644 > 0.05) and phenol substitution (p-value = 0.1972 > 0.05) had no significant effect on the expected free formaldehyde content of the resols. However, the main effect of catalyst loading on the expected free formaldehyde content of the resols was highly significant (p-value = 0.0034 < 0.05). Thus, there is a strong evidence of the free formaldehyde content being different for the catalyst loadings.

The interaction effect of F/P molar ratio and catalyst loading (p-value = 0.0994 > 0.05), catalyst loading and phenol substitution (p-value = 0.1242 > 0.05), and F/P ratio and phenol substitution (p-value = 0.7568 > 0.05), had no significant effect on the expected free formaldehyde content of the resols. Also, the overall model (Equation 4.2) was found to be significant (p-value = 0.0226 < 0.05), an indication that at least one of the resol synthesis factors had a significant effect on the average free formaldehyde content.

Table 4.8
ANOVA results for free formaldehyde content.

Source	**DF**	**Sum of Squares**	**Mean Square**	**F-value**	**Pr > F**
Model	15	320.55	21.37	43.59	0.0226
F/P	1	6.88	6.88	14.04	0.0644
NaOH [a]	2	288.44	144.22	294.16	0.0034
F/P*NaOH	2	8.88	4.44	9.06	0.0994
Substitution [b]	4	8.44	2.11	4.31	0.1972
F/P*Substitution	4	0.96	0.24	0.49	0.7568
NaOH*Substitution	2	6.92	3.46	7.05	0.1242

[a] NaOH – catalyst loading and [b] substitution – phenol substitution.

In order to identify the specific conditions that caused a significant effect on the free formaldehyde content, a pair-wise comparison method known as Ryan-Einot-Gabriel-Welsch (REGWQ) multiple range test for comparing means was employed. For this post hoc analysis, means with the same REGWQ grouping letter were considered not to be significantly different from each other. In Table 4.9, we noticed a significant difference between the mean effect of 50 wt% and either 0 wt% or 80 wt% phenol substitution. The remaining pairwise comparisons for the mean effect of phenol substitutions were not significantly different.

Table 4.9
REGWQ analysis for the influence of phenol substitution.

REGWQ grouping		Mean	N	Phenol substitution, wt%
	A	5.4833	6	50
	A			
B	A	4.0575	4	70
B	A			
B	A	3.105	4	60
B				
B		0.55	2	80
B				
B		0.22	2	0

In Table 4.10, we observed that the means for the F/P molar ratio of 1.8 and 2 shared the same REGWQ grouping letter ‘A’. Thus, the means obtained for these two F/P molar ratio levels were not significantly different from each other.

Table 4.10
REGWQ analysis for the effect of F/P molar ratio.

REGWQ grouping	Mean	N	F/P molar ratio
A	4.1233	9	2
A			
A	2.8867	9	1.8

Table 4.11 showed that the mean effects of the 0.25, 0.63, and 1.25 g catalyst loading were all significantly different from the each other. Thus, each level of catalyst loading had a significant effect on the expected free formaldehyde content.

Table 4.11
REGWQ analysis for the effect of catalyst loading.

REGWQ grouping	Mean	N	Catalyst loading, g
A	12.415	2	0.25
B	5.7733	6	0.63
C	0.362	10	1.25

4.4.2.3.2 Influence of resol synthesis conditions on free phenol content

An effects model derived for free phenol content is expressed in Equation 4.3.

$Y_{ijkl} = \mu + X_i + Y_j + Z_k + XY_{ij} + YZ_{jk} + XZ_{ik} + \varepsilon_{ijkl}$....................................Equation 4.3

i = 1 and 2   j = 1, 2, and 3   k = 1, 2, 3, 4, and 5

Where:

Y_{ijkl} = Free phenol content of resols for kth experimental unit.

Where:

μ = Overall mean.

X_i = The mean effect of F/P molar ratio of level ‘i’.

Y_j = The mean effect of catalyst loading of level ‘j’.

Z_k = The mean effect of phenol substitution of level ‘k’.

XY_{ij} = Interaction effect of F/P molar ratio and catalyst loading.

YZ_{jk} = Interaction effect of catalyst loading and phenol substitution.

XZ_{ik} = Interaction effect of F/P molar ratio and phenol substitution.

ε_{ijkl} = Random error

In Table 4.12, ANOVA is again employed to investigate the differences of the free phenol content based on the different experimental conditions explored.

Table 4.12
ANOVA results for free phenol content.

Source	**DF**	**Sum of Squares**	**Mean Square**	**F-value**	**Pr > F**
Model	15	20.40	1.36	98.13	0.0101
F/P	1	0.28	0.28	20.52	0.0454
NaOH [a]	2	12.78	6.39	462.24	0.0022
F/P*NaOH	2	0.02	0.01	0.37	0.7276
Substitution [b]	4	6.72	1.68	121.7	0.0082
F/P*Substitution	4	0.28	0.07	5.33	0.1642
NaOH*Substitution	2	0.26	0.13	9.08	0.0992

[a] NaOH – catalyst loading and [b] substitution – phenol substitution.

From the ANOVA results in Table 4.12, it can be observed that all the main effect variables: F/P molar ratio (p-value = 0.0454 < 0.05), catalyst loading (p-value = 0.0022 < 0.05), and phenol substitution (p-value = 0.0082 < 0.05) had significant effect on the expected free phenol content of the resols. However, the interaction effect of F/P molar ratio and catalyst loading (p-value = 0.7276 > 0.05), catalyst loading and phenol substitution (p-value = 0.0992 > 0.05), and F/P ratio and phenol substitution (p-value =

0.1642 > 0.05), had no significant effect on the expected free phenol content of the resols. Also, the overall model (Equation 4.3) was found to be significant (p-value = 0.0101 < 0.05), an indication that at least one of the resol synthesis factors had a significant effect on the average free phenol content.

A post hoc analysis was performed in order to give a detailed description about where the specific differences in free phenol contents occurred. In Tables 4.13, 4.14, and 4.15, different **REGWQ grouping** letters denoted the difference between the means.

In Table 4.13, it can be noticed that the mean effects of all the different levels of catalyst loading were significantly different from each other. Thus, the mean effect at 0.25 g NaOH was significantly different from the mean effects at 0.63 g and 1.25 g.

Table 4.13
REGWQ analysis of the effect of catalyst loading on the free phenol content.

REGWQ grouping	Mean	N	NaOH, g
A	3.07	2	0.25
B	0.845	10	1.25
C	0.15167	6	0.63

The mean effect of 0 wt% phenol substitution was significantly different from all the other phenol substitutions as shown in Table 4.14. Also, the mean effect at 50 wt% phenol substitution was significantly different from the effect at phenol substitution of 0, 60, 70, and 80 wt%. Furthermore, the mean effect of treatments at phenol substitutions of 60, 70, and 80 wt% were not significantly different from each other.

Table 4.14
REGWQ analysis of the effect of phenol substitution on free phenol content.

REGWQ grouping	Mean	N	Phenol substitution, wt%
A	2.365	2	0
B	1.435	6	50
C	0.385	4	60
C			
C	0.1375	4	70
C			
C	0.035	2	80

In Table 4.15, the mean effect of the treatment at F/P molar ratio of 1.8 and 2 were significantly different from each other. Table 4.16 is a summary of the free formaldehyde and free phenol contents.

Table 4.15
REGWQ grouping for the influence of F/P molar ratio on free phenol content.

REGWQ grouping	Mean	N	F/P molar ratio
A	0.98667	9	1.8
B	0.73556	9	2

Table 4.16

A summary of the free phenol and free formaldehyde content.

SN	F/P molar ratio	Phenol substitution, wt%	Catalyst loading, g	Free formaldehyde content, wt %	Free phenol content, wt %
1	1.8	0	1.25	0.19 ± 0.01	2.79 ± 0.12
2	1.8	50	1.25	0.20 ± 0.01	1.27±0.01
3	1.8	60	1.25	0.25 ± 0.01	0.59 ± 0.03
4	1.8	70	1.25	0.37 ± 0.01	0.24 ± 0.01
5	1.8	80	1.25	0.46 ± 0.04	0.05 ± 0.01
6	1.8	50	0.63	2.70 ± 0.02	0.38 ± 0.01
7	1.8	60	0.63	3.51 ± 0.08	0.19 ± 0.04
8	1.8	70	0.63	6.31 ± 0.42	0.16 ± 0.01
9	1.8	50	0.25	11.99 ± 0.14	3.21 ± 0.02
10	2	0	1.25	0.25 ± 0.02	1.94 ± 0.04
11	2	50	1.25	0.34 ± 0.02	0.74 ± 0.01
12	2	60	1.25	0.38 ± 0.02	0.70 ± 0.01
13	2	70	1.25	0.54 ± 0.02	0.11 ± 0.01
14	2	80	1.25	0.64 ± 0.04	0.02 ± 0.01
15	2	50	0.63	4.83 ± 0.13	0.08 ± 0.02
16	2	60	0.63	8.28 ± 0.74	0.06 ± 0.01
17	2	70	0.63	9.01 ± 0.94	0.04 ± 0.01
18	2	50	0.25	12.84 ± 0.06	2.93 ± 0.06

4.5 Conclusion

The evaluation of shear strengths of oak wood composites demonstrated the effect of water on the strength of the wood composites. Dry oak wood composites were at least 1.5 times stronger than wet oak wood composites. The shear strength data obtained for dry oak wood composites (8.99 to 12.73 MPa) and wet oak wood composites (5.16 to 7.36 MPa) exceeded the minimum shear strength of 0.66 MPa as stipulated by APA. This means that the PJ substituted adhesives had high mechanical strength even at wet conditions. Based on the statistical evaluation of shear strengths for different phenol substitution rates, it can be concluded that PJ resols had comparable strength to pure PF resols.

In Chapter 3, the observation of a higher concentration of phenolic OH groups in pure PF resols compared to PJ substituted resols was confirmed from the free phenol data. At catalyst loading of 1.25 g, the free phenol contents at F/P molar ratios of 1.8 and 2, for pure PF adhesives were greater than that of PJ substituted resols in that category. This result implies that substitution of phenol with PJ bio-oil reduces the potential risks associated with toxic phenol compounds.

The F/P ratio generally had an impact on the free phenol and the free formaldehyde contents for both PF and PJ substituted resols. The free phenol contents of 2.93 wt% and 3.21 wt% observed at F/P ratios of 2 and 1.8, corroborated the observed high concentration of phenolic compounds at the least catalyst loading of 0.25 g. PJ substituted resols produced at F/P 1.8, phenol substitutions of 50, 60, 70 and 80 wt%, and catalyst loading of 1.25 g, and PJ substituted resols produced at F/P molar ratio of 2, phenol substitutions of 50 and 60 wt% at catalyst loading of 1.25 g, completely conformed to the provisions of US Patent 9 102 040, for free phenol and free formaldehyde content (Tumler, 2015).

Since the shear strength properties were generally similar, the optimum conditions for producing good quality PJ substituted resols were at F/P molar ratio of 1.8, catalyst loading of 1.25 g of NaOH, phenol substitutions of 50, 60, 70, and 80 wt%, and at F/P molar ratio of 2, phenol substitutions of 50 and 60 wt%, and catalyst loading of 1.25 g of NaOH.

4.6 References

APA, 2010. Voluntary product standard: PS 1-09 structural plywood (with typical APA trademarks). Form No. L870A. The Engineered Wood Association, Tacoma, Washington.

APA, 2010. Product design specification. Form No. D510C. The Engineered Wood Association, Tacoma, Washington.

Atta-Obeng, E., 2011. Characterization of phenol formaldehyde adhesive and adhesive-wood particle composites reinforced with microcrystalline cellulose. Master's Thesis, Auburn University.

Chaouch, M., Diouf, P.N., Laghdir, A., Yin, S., 2014. Bio-oil from whole-tree feedstock in resol-type phenolic resins. J. Appl. Polym. Sci. 131, 40014-40020.

Cheng, S., 2011. Bio-based phenolic resins and adhesives derived from forestry residues/wastes and lignin. PhD Thesis, Lakehead University.

Cheng, S., D’Cruz, I., Yuan, Z., Wang, M., Anderson, M., Leitch, M., Xu, C., 2011. Use of biocrude derived from woody biomass to substitute phenol at a high-substitution level for the production of biobased phenolic resol resins. J. Appl. Polym. Sci. 121, 2743–2751.

Dunky, M., 2003. Adhesives in the wood industry., in: Handbook of adhesive technology. Marcel Dekker, New York, pp. 887–956.

Gardziella, A., Pilato, L.A., Knop, A., 2000. Phenolic Resins: Chemistry, application, standardization, safety and ecology. Springer, Berlin.

Grenier-Loustalot, M.F., Larroque, S., Grande, D., Grenier, P., Bedel, D., 1996. Phenolic resins: 2. Influence of catalyst type on reaction mechanisms and kinetics. Polymer 37, 1363–1369.

Knop, A., Pilato, L.A., 1985. Phenolic resins: Chemistry, applications, and performance: Future directions. Springer-Verlag Berlin.

Liu, X., Zhang, W., Sui, G., Ning, Q., 2007. Determination of phenol and formaldehyde in resol resins by high performance chromatography. Chinese J. Chromatogr. 25, 562–564.

Moubarik, A., Pizzi, A., Allal, A., Charrier, F., Charrier, B., 2009. Cornstarch and tannin in phenol formaldehyde resins for plywood production. Ind. Crops Prod. 30, 188–193.

Nakos, P., Tsiantzi, S., Athanassiadou, E., 2000. Wood adhesives made with pyrolysis oils., in: Proceedings of the 3rd European Wood-Based Panel Symposium. Hanover, pp. 1–2.

OSHA, 2012. Phenol. http://www.osha.gov./dts/chemicalsampling/data/CH_261100. html (10.31.16).

Peng, L., Tong, T., 2011. A note on a two-sample T test with one variance unknown. Stat. Methodol. 8, 528-534.

Pilato, L., 2010. Phenolic reisn: A century of progress. Springer-Verlag Berlin, Heidelberg.

Popescu, V., Muresan, A., Popescu, G., Balan, M., Dobromir, M., 2016. Ethyl chitosan synthesis and quantification of the effects acquired after grafting it on a cotton fabric, using ANOVA statistical analysis. Carbohyd. Polym.138, 94-105.

Riedlinger, D.A., 2008. Characterization of PF resol / isocyanate hybrid adhesives. Master's Thesis, Virginia Polytechnic Institute and State University.

Roslan, R., Zakaria, S., Chia, C.H., Boehm, R., Laborie, M.P., 2014. Physico-mechanical properties of resol phenolic adhesives derived from liquefaction of oil palm empty fruit bunch fibres. Ind. Crops Prod. 62, 119-124.

Salthammer, T., Mentese, S., Marutzky, R., 2010. Formaldehyde in the indoor environment. Chem. Rev. 110, 2536-2572.

Schechtman, E., Sherman, M., 2007. The two-sample t-test with a known ratio of variances. Stat. Methodol. 4, 508-514.

Short, S.R., 1995. Characterization of interlaminar shear failures of graphite epoxy composite materials. Composites 26, 431-449.

Siddiqui, H., 2013. Production of lignin-based phenolic resin using de-polymerized kraft lignin and process optimization. Master's Thesis, The University of Western Ontario. London, Ontario, Canada.

Tan, H., Zhang, Y., Weng, X., 2011. Preparation of the plywood using starch-based adhesives modified with blocked isocyanates. Procedia Eng. 15, 1171-1175.

Tumler, A., 2015. Low free formaldehyde phenolic resins for abrasive products. US Patent 9 102 040.

Unsal, O., Buyuksari, U., Ayrilmis, N., Korkut, S., 2009. Properties of wood and wood based materials subjected to thermal treatments under, in: International Confereance Wood Science And Engineering In The Third Millenium (ICWSE). pp. 81-94.

University of Cambridge, 2004. Water's effect on the mechanical behavior of wood. Dissemination of IT for the promotion of material science, University of Cambridge. http://www.doitpoms.ac.uk/tlplib/wood/water_effect.php (accessed 10.31.16).

Vázquez, G., Santos, J., Freire, M.S., Antorrena, G., González-Álvarez, J., 2012. DSC and DMA study of chestnut shell tannins for their application as wood adhesives without formaldehyde emission. J. Therm. Anal. Calorim. 108, 605–611.

CHAPTER 5

SUMMARY

To achieve commercial success of bio-phenolic based resols, it is imperative that the substitution rate of phenol with the bio-phenolic compound be very high. Pinyon-juniper catalytic pyrolysis oil was used to investigate the extent of phenol replacement during resol production. Apart from the fact that pinyon-juniper biomass is a renewable resource, the catalytic pyrolysis of pinyon-juniper with red mud alumina makes this biomass even more attractive. Red mud is a waste product from the Bayer process, which makes this catalyst very affordable compared to many commercial catalysts. Hence, the utilization of red mud as a pyrolysis catalyst helps reduce the operational costs associated with pinyon-juniper bio-oil production.

The main objective of this research was to produce good quality adhesives by substitutions (at least 50 weight percent) of phenol with pinyon-juniper bio-oil. The other objectives of this research were:

- To produce resols from pinyon-juniper catalytic pyrolysis oil, which had similar or even better quality than conventional phenol-formaldehyde adhesives.
- To determine the conditions that best optimized the properties of adhesives produced from the substitution of phenol with bio-oils.

After examining different resol synthesis conditions, a maximum of 80% substitution of phenol with pinyon-juniper bio-oil was achieved at a catalyst loading of 1.25 g of NaOH. Pinyon-juniper substituted resols were comparable to pure phenol-formaldehyde adhesives in terms of shear strength. Even under wet conditions, pinyon-juniper substituted resols’ wet shear strengths (5.16 to 7.36 MPa) exceeded the minimum requirement of 0.66 MPa for plywood. Resols produced with pinyon-juniper bio-oils had lower phenol concentrations compared to pure phenol-formaldehyde adhesives. The optimum conditions for excellent pinyon-juniper resols were at formaldehyde-to-phenol (F/P) molar ratio of 1.8, catalyst loading of 1.25 g of NaOH, phenol substitutions of 50, 60, 70, and 80 wt%, and at F/P molar ratio of 2, phenol substitutions of 50 and 60 wt%, and catalyst loading of 1.25 g of NaOH.