TOWARD LIGNIN-BASED POLYMERIC MATERIALS USING GREENER

MODIFICATION METHODS

by

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Abstract

The urgent necessity for replacing fossil resources has driven researchers to develop more sustainable materials from technical lignin. However, the heterogeneous nature of this complex material must be improved, as industrial feedstocks require a large degree of uniformity. Therefore, the hydroxyethyl modification of lignin was first developed as a platform derivatization method to convert the phenolics and carboxylic acids of industrial lignins into aliphatic hydroxyls. Ethylene carbonate was used as both the reagent and solvent resulting in a variety of hydroxyethyl lignins (HELignins) derived from technical lignin resources. The HELignin derivative was further utilized as a polyol and reacted with diisocyanates to make polyurethane foams. While effective at various substitution levels of polyol, HELignins only had partial solubility in the polyol. As a result, the reaction conditions that led to increased lignin molecular weight and low solubility required optimization to avoid crosslinking. Addressing this issue, an in situ real-time monitoring technique was created to control the quality of the resulting HELignin. An empirical model was built to ensure the reaction could reach near completion without significant by-product formation. The optimized reaction conditions created a HELignin that could be further modified; a catalyst free esterification was developed using organic acid as solvent and reagent. Due to the high selectivity toward aliphatic hydroxyl groups, HElignin which had over 85% aliphatic hydroxyls, showed an advance as a starting material useful for lignin esters with tailored thermal properties based on the organic acid of choice. In one application for an aqueous hydrophobic coating, inspired by the natural suberin compounds, oleic acid was used as a solvent and reagent to esterify the HELignin and subsequently transformed into an aqueous dispersion. These coating materials significantly improved the hydrophobic properties of wood-based products. Critically, the above hydroxyethylation and esterification of lignin satisfied many green chemistry requirements including the adoption of solvent-free reactions, low environment factor (E-factor) reactions, high atom economy, high pot economy, the adoption of low-toxic reagents, and real-time monitoring. Overall, the reaction of lignin with ethylene carbonate led to a greener modification route to convert technical lignin into more sustainable feedstock for society.

Lay Summary

Lignin is the second most abundant biopolymer biosynthesized by plants, which offers a promising avenue to solve problems of sustainable development in this century. One of the most seemingly straightforward applications of lignin is to utilize it in bioplastics taking advantage of its natural characteristics such as UV absorbance, biodegradability, and stiffness. However, the chemical modification of lignin resources plays a crucial role to conquer the complexity of raw lignin. Here, we developed a greener and highly efficient route to obtain a platform lignin compound with controllable properties useful for bioplastics. Moreover, these platform lignin products satisfied many fundamental requirements of green chemistry. By adopting these modified lignin materials, we successfully developed two types of materials: polyurethane foams and hydrophobic coatings. The former one is important to improve the energy efficiency of buildings when used as insulation materials. The latter may extend the storage of wood products by improving their durability.

Preface

With the guidance of my supervisor (Scott Renneckar), I made a major contribution to this thesis, including but not limited to the design of the research program based on the hydroxyethylation of lignin, performed the experiments, analyzed the data, and wrote this thesis. A version of chapter 4, 7 and 8 have been published as indicated below. I conducted all the testing, data analysis, and wrote the main draft of the manuscripts listed. Sudip Chowdhury helped to establish a parallel plate rheological analysis of the lignin samples, Mijung Cho, assisted with protocol development for the TGA. Further, Noppadon Sathitsuksanoh guided the development of the NMR analysis protocols, interpretation of NMR data, and further editing. The HSQC NMR in chapter 7 was performed by Mark Okan in Biochemistry who ran samples I prepared and provided data files that I analyzed. Muzaffar Karaaslan helped with the SEM and AFM in chapter 8. Under my instruction, Hua Qi helped to prepare the polyurethane foam and aqueous hydrophobic lignin solution for the work Chapter 5 and Chapter 8. With my supervision, Kim Besselar and Siwei Chen contributed to some of the experiments on the hydroxyethyl modification using real-time monitoring technique in Chapter 6.

[Liu, L.Y.], Cho, M.J., Sathitsuksanoh, N., Chowdhury, S., and Renneckar, S., (2018). Uniform chemical functionality of technical lignin using ethylene carbonate for hydroxyethylation and subsequent greener esterification. ACS Sustain. Chem. Eng. 6 (9): 12251-12260.

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List of Abbreviations

1-MIM: 1-Methylimidazole

AE: Atom economy

AHKL: Acetone soluble hardwood Kraft lignin

AlOH: Aliphatic hydroxyl groups

AlOH primary: Primary aliphatic hydroxyl groups

AlOH secondary: Secondary aliphatic hydroxyl groups

ArOH: Aromatic hydroxyl groups

$ArOH_{5-sub}$: Ortho-substituted aromatic hydroxyl groups

$ArOH_{5-free}$: Ortho-free aromatic hydroxyl groups

ArH: Aromatic hydrogen

ASKL: Acetone soluble softwood Kraft lignin

COOH: Carboxylic acid

cEF: Complete environmental factors

DC: Degree of condensation

DMF: Dimethylformamide

DS: Degree of substitution

DSC: Differential scanning calorimetry

G: Guaiacyl units

GPC: Gel permission chromatography

H: p-hydroxyphenol units

HELignin: Hydroxyethyl lignin

HKL: Hardwood Kraft lignin

HESKL: Hydroxyethyl softwood Kraft lignin

HPSKL: Hydroxypropyl softwood Kraft lignin

KL: Kraft lignin

MeO: Methoxy groups

M_w: Weight average molecular weight

M_n: Number average molecular weight

N-AS: No additional solvent

NMR: Nuclear magnetic resonance

OB: Oak bark

OBL: Organosolv oak bark crude lignin

OSL: Organosolv lignin

OSHL: Organosolv hardwood lignin

PB: Pine bark

PBL: Organosolv pine bark crude lignin

PDI: Polydispersity index

r.t. : Room temperature

SL: Soda lignin

SKL: Softwood Kraft lignin

S: Syringyl units

s-EF: Simple environmental factors

THF: Tetrahydrofuran

Total OH: Total hydroxyl groups

TGA: Thermal gravimetric analysis

T_g: Glass transition temperature

$T_{D5\%}$: 5% mass loss decomposition

WWI: Wastewater index

Acknowledgments

I would like to express my sincere gratitude to my supervisor Prof. Scott Renneckar for his persistent support for my Ph.D. study and research. To be his student is the luckiest thing I ever have in my life. I learned so much from him about how to be a good teacher, scholar, scientist, and friend. In the last four and a half years, I really enjoyed all the meetings with him. Prof. Scott Renneckar was patient to answer my endless questions and enlarge my vision of science. His appreciation, encouragement, and affirmation make me feel more confident about myself and my choices to continue my work in this area. I could not have imagined having a better supervisor for my Ph.D. study and research.

I also offered my enduring gratitude to my committee members, Prof. Noppadon Sathitsuksanoh, Prof. Feng Jiang, and Prof. Jack Saddler, who has inspired me to continue my work in this field. I own particular thanks to Prof. Noppadon Sathitsuksanoh for providing coherent answers to my endless questions and showing me how to use NMR, prepare presentations, and think about my project in a different view.

I am also grateful to my colleagues in the Advanced Renewable Materials Lab: Amanda Johnson, Dr. Mijung Cho, Dr. Saurabh Patankar, Dr. Muzaffer Karaaslan, and Dr. Li-Ting Lin. Your kindly help and enthusiasm in this area mean a lot to me. Thanks also to Qi Hua, Kim Besselar, Siwei Chen, and Monica Xia for helping my research projects. Instructing or training you also has driven me to think about my projects more deeply. I thank Lun Ji for his help not only on my work but also on my life. Thank Mark Okon in the Faculty of Chemistry for his kind help on NMR analysis.

Special thanks are owed to my parents XiFa Liu and BaoLing Zhang, who gave me unconditional support throughout my years of education. Last but not least, I am very much thankful to my wife Xinxin Shen for her continued love, support, and sacrifices to complete this research work.

Dedication

This thesis is dedicated to my supervisor, parents, wife, and friends

Thank you for all your support along the way!

Chapter 1: Literature review

1.1 Introduction

Materials and energy based on fossil resources currently are the foundation of modern society and support the daily consumption habits for billions of people.[1, 2] However, the excessive exploitation of fossil fuels is unsustainable.[3, 4] Synthetic plastic materials derived from fossil fuel have poor environmental compatibility.[5] So far, humans have made 8300 Mt plastics. Besides recycled and in-use plastic materials, Geyer and his collaborator estimated that 4900 Mt of these plastics were discarded and another 800 Mt were incinerated.[6] This pollution is global with nearly no pollution-free zones left on the planet, as seen in plastic reaching the Arctic region due to atmospheric transportation.[7] Moreover, burning fossil-derived materials releases CO_2, once stored underneath the earth's surface; there is increasing evidence showing a high correlation between the growing concentration of CO_2 in the atmosphere and climate change. The latter has led to extreme weather conditions.[8] The overall loss from severe weather exceeds 150 billion dollars per year making climate change both an environmental and economic problem.[9] Therefore, one of the most significant challenges for modern researchers is to develop greener technologies to convert renewable resources, avoiding fossil-based carbon, into valuable products for our daily demands. This effort will lead us to achieve the lofty goal of sustainable development across the globe.[10, 11]

Lignin is the second most abundant biopolymer found in the cell wall of terrestrial plants. The annual production of terrestrial plant biomass is around 80-164 billion tons of dry matter.[12] With a significant portion of this amount, we estimate that 30-50 billion tons are produced annually. Lignin synthesis is carbon negative, as it is derived from the photosynthesis of plants, which sequesters carbon dioxide and water from the atmosphere. This polymer currently is readily separated during chemical pulping of lignocellulose biomass such as wood.[13] In this process, lignin is partially degraded, separated from the cell wall, and transferred into the pulping liquor. To recover the chemical reagents used in delignification during the Kraft process, lignin is burned as fuel source in the lime kiln. This action accounts for more than 90% of the industrial lignin utilization.[14, 15] Lignin has high heat of combustion (HHV=26 MJ/kg),[16] which is not only higher than wood (HHV=21.20 MJ/kg) but 81% (32.80 MJ/kg) of coal and 60% of diesel (44.80 MJ/kg).[17] However, the economic benefit of lignin as a fuel resource is low. Also, in this application, lignin is not used for its original purpose as a structural polymer. Further, it is difficult to achieve

long-term carbon storage if lignin is simply burned for energy, releasing CO_2 back into the atmosphere. The effective use of plant resources should include conversion into longer lasting chemicals and materials to help maximize carbon storage, and potentially meet the rapid consumption needs of society. Not only can smart utilization effectively reduce greenhouse gas emissions and the ecological footprint of materials, but it can also achieve longer-lasting carbon storage for sustainable development (i.e. materials for our built environment derived from plant-based carbon).[14]

Lignin has great potential to produce high-performance composite materials due to its chemical structure and physical properties. Outside of select amino acids, it is noteworthy that lignin is the only biopolymer in nature which has an aromatic ring structure used for demanding structural applications. For this purpose, scientists developed various methods to modify technical lignin from the pulp industry to make it useful for polymeric engineering applications. These methods change lignin from the polymer perspective that enables the formation of lignin derivatives into a series of valuable materials such as adhesives, foams, or as blend components for thermoplastics.[18, 19] However, despite the high value-added utilization potential, currently, only 2% of lignin resources from the pulp industry were recovered to make lignin-based materials and most of them are lignosulfonates.[15, 20] There are several reasons for these limited applications of lignin resources from materials perspective: 1) there is a great variation in lignin structure by isolation method and origin of species;[21, 22] 2) the complicated chemical structure, as highlighted below, with mixed functionality leading to differences in reactivity;[23] 3) a wide distribution of molecular weight;[24] 4) thermal instability when lignin is processed on extrusion equipment and high-temperature reactors, undergoing depolymerization and repolymerization reactions;[25, 26] and 5) making value-added materials from lignin has relied on unsustainable chemistries that are difficult to scale commercially.[27]

As a result of these issues, lignin utilization requires methods to make its structure more uniform with greener transformation methods. More specifically, fractionation[28-30] and chemical modification[23] have been adopted to obtain controlled molecular weight with specific functional groups for corresponding applications. Though there are not many functional groups available for the modification process of lignin, the hydroxyl groups of lignin allow esterification[31, 32],

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etherification[33, 34], and urethane formation[35, 36]. By these methods, researchers can create lignin with new functional groups, enhance their reactivity, and modify its solubility. Traditional chemical modification methods can generate waste and cause serious environmental problems by the use of additional solvent, toxicity or instability of some of the reagents and catalysts, and harsh reaction conditions. Therefore, utilizing greener modification methods is vital as benign processes should be used to scale-up to industrial levels for the preparation of commodities and advanced materials.

In recent decades, the twelve principles of green chemistry had been applied in various areas of synthesis and engineering.[37, 38] These principles offer a guide for the evaluation of traditional chemical modification methods for lignin that are helpful for both research laboratories and commercial technologies in order to develop and utilize greener modification methods. Based on principles of green chemistry, procedures such as one-pot reaction,[39] techniques such as real-time control,[40] the use of greener solvents and catalysts,[41, 42] more stable and safe reagents, and reducing waste as measured with the environmental factor (E-factor)[43] should be considered for the modification of lignin. Lignin-based materials should be designed or developed, encompassing green chemistry principles at the beginning stages in the design phase. In this thesis, our goal is to create a greener and robust modification method for a uniform lignin material; this outcome will allow for processing lignin into new materials such as polyurethane and polyester materials that address both environmental and economic requirements.

1.2 Lignification process

The name of lignin was derived from the Latin word "lignum" which was named by F. Schulze in 1857[44] and discovered by the French chemist Anselme Payen in 1838.[45, 46] After nearly two centuries, the basic chemical structure of native lignin is widely understood as a biopolymer synthesized by the dehydrogenative polymerization of phenylpropane units,[47] yet it is still especially challenging to characterize and understand the chemical structure of its isolated counterpart, technical lignin, thoroughly.

Biosynthesis reactions of monolignols are carried out in the cytoplasm of a plant via the phenylpropanoid pathway. Precisely, the related enzymes can convert glucose into aromatic amino

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acids (L-phenylalanine and tyrosine). These amino acids are then converted into cinnamic acid and p-coumaric acid by catalytic deamination reaction, following with a series of modifications including aromatic ring hydroxylations, O-methylation, and side-chain modification.[48] Lignin units, that are methylated, can form sinapyl alcohol and coniferyl alcohol along with some acids such as ferulic acid. These types of phenolic alcohols combine with p-coumaric alcohol to constitute the predominante monomers of lignin.

These monomers are transferred into the plant cell wall to form lignin macromolecules by a combinatorial radical polymerization. A series of enzymes, including peroxidases, laccases, polyphenol oxidases, conifer alcohol oxidase, and chemicals such as H_2O_2 and O_2 are involved in completing the lignification process. In detail, lignin monomers are first transported to the cell wall, following by the formation of quinone-methide intermediates via the peroxidases / H_2O_2 or lacasse/O_2; these enzymes were preliminarily immobilized within the carbohydrate matrix. The half-life of this radical is about 45s based on the analysis of electron spin resonance.[49, 50] Therefore, the radical will couple with other units resulting in the dimerization of lignin. A variety of bonds can form as the radicals are stabilized through resonance, and the coupling occurs with both the aryl and alkyl carbons to form different types of linkages such as β-O-4, β-β, and β-5. (**Figure 1**)[51] The ratio of these chemical bonds is different due to differences in carbon electron density of the conjugated lignin radicals, wherein β-O-4 covalent bond occupied more than 50% of all formed chemical bonds. The resulting dimers still contain free phenols and will further polymerize with lignin radicals by the so-called "end-wise" process. In this polymerization process, the reaction is random as monomers are diffused into the wall and activated, this process is not as strict as the traditional biochemical synthesis process as found within the cytoplasm, which is manipulated by genes in the nucleus.[52]

 Further reactions with these structural units, mainly the quinone methide, occur during polymerization: the α carbon (benzylic carbon) in the alkyl chain of the lignin monomer will also react with H_2O or other highly electronegative compounds such as hydroxyls and carboxylic acids on carbohydrates forming ether or ester bonds during this process. [53-55] The exact nature is not known as once lignin is broken down, new chemical linkages will form new functional groups such as secondary aliphatic hydroxyls, ketones, and carboxylic acid functional groups in resulting isolated lignin as described below.
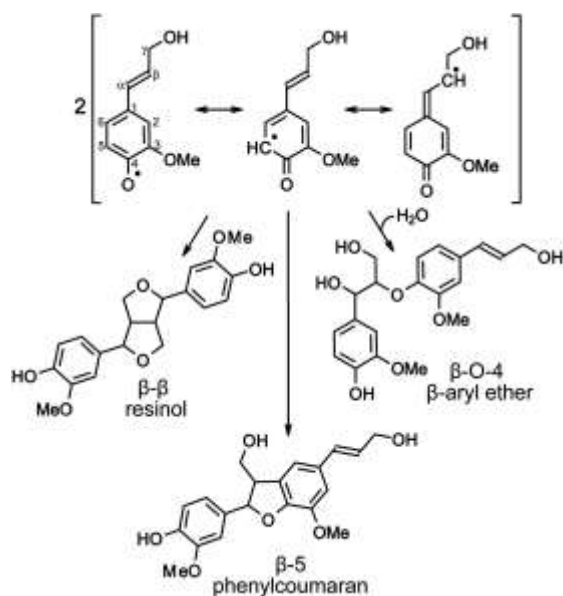
Figure 1 The dimerization of two dehydrogenated coniferyl alcohol monomers to produce β-O-4, β-β, and β-5 linkages Reprinted with the permission from ref [51] Copyright 2003 American Society of Plant Biologists

1.3 Lignin isolation or delignification process

Lignin components can be combined with the carbohydrate components, especially hemicellulose, via chemical bonds. This heterogeneous copolymer was named as lignin carbohydrate compound (LCC), which makes up a recalcitrant structure of the cell wall to protect the plant in a harsh terrestrial environment.[55, 56] From the perspective of biorefinery, the separation or fractionation of lignocellulose is always the first step to realize the valorization of lignin components; the delignification plays a central role in the conversion of biomass. Many ways have been developed in the last decades to delignify woody biomass. Some of the methods to isolate lignin from both a laboratory and industrial-scale will be discussed comprehensively.

1.3.1 Laboratory scale isolation of lignin

Lab-scale lignin isolations are divided into two techniques that produce a highly modified lignin (Klason lignin) and a partially modified milled wood lignin (MWL).[57] These two techniques were developed to analyze the composition and chemical structure of lignin. Actually, these two standard techniques are the most widely used methods for the lab to obtain lignin due to their high repeatability and accuracy.

Klason lignin was first extracted in the 1890s by Swedish chemist Peter Klason, who adopted a two-step acid hydrolysis method to degrade lignocellulose. Due to the strong acid condition, the carbohydrate compounds and a small amount of acid-soluble lignin were degraded and dissolved in the supernatant. Most of the lignin was kept in the solid residue, named as acid-insoluble lignin. This method was widely used to analyze the main components of lignocellulose quantitatively when both the acid-soluble and insoluble lignin is accounted for during analysis. As described above, lignin components have a variety of ether bonds and are integrated with carbohydrates through the ether or ester bonds. Utilizing strong acid at high temperature will destroy and change the chemical linkages of lignin, such as the aryl-alkyl ether bonds in lignin.[58]

Therefore, it was essential to develop a method that can isolate lignin while maintaining its native structure. This so-called native lignin allows researchers to characterize a less modified structure of lignin and provide instructive information for the lignification and/or delignification process. This process goes back to the 1950s, where the milder physical-chemical way was developed by Björkman.[57] He adopted ball milling to grind the lignocellulose to hundred micro-meter particle size. The dioxane/water (pH=2) was then used to extract the lignin under the temperature near the boiling point of the azeotrope. The hypothesis was that milder conditions during the process led to only a slight change of the main chemical bonds or functional groups of lignin, so the isolated lignin resources were closer to its native structure than other methods. The yield of lignin is in a range from 20% to 50% (usually less than 30%) based on the Klason compositional analysis, which represents the most accessible lignin. To improve the yield, Wu and collaborators used the enzymatic hydrolysis, followed by a mild acid hydrolysis to improve the extraction of lignin in aqueous dioxane to approximately 50%.[59, 60] Though conditions to extract MWL are mild, it is difficult to represent all native lignin in the lignocellulose of MWL with relative low-yield and minimum of structural change. Moreover, the utilization of toxic organic solvents makes this process difficult to satisfy requirements for greener and more sustainable chemistry processes. It is thus only applicable at the laboratory scale and used as model lignin for the structural characterization rather than to be used for high-value applications such as materials or chemicals. Hence, MWL lignin has specific chemical structures that are not typically found in high abundance within technical lignin.[61]

Otsuka et al. developed a more efficient method to extract lignin from milled wood than previous methods. They used an ultrafine bead milling machine to grind wood powder (pretreated by knife milling) with an aqueous buffer solution at 50 °C for 2hrs. An enzyme cocktail was added to degrade the polysaccharides during bead milling as the cell wall was fractured. This procedure led to the improvement of the grinding process to obtain smaller wood particles, as small as 38 nm. Since most of the carbohydrate compounds were degraded by the added enzyme cocktail, the small particle residue contained a high amount of lignin, close to the theoretical yield based on Klason compositional analysis. Moreover, the greener process described above provided the opportunity for researchers to develop advanced lignin materials with "native" lignin, since this method minimized toxic chemicals and obtained both a high quantity and quality of lignin.[62]

1.3.2   Industrial-scale delignification

Though plenty of delignification methods have been developed toward high-value chemicals, materials, and fuels, few of these techniques were able to recover a large amount of high-purity lignin resources on the industrial scale. Commercially available lignin is mainly from the chemical pulp industry with a potential yield of 140 million tons annually.[15] The purpose of the chemical pulping process is to attain high-purity cellulose fibers. This process requires the removal of as much lignin ("waste") as possible while retaining most of the cellulose component. An acid or alkali solution at a high temperature is used to degrade and/or isolate lignin from the lignocellulose substrate. A suitable solvent would dissolve the degraded lignin fragments and stabilize them from further reactions. Due to harsh conditions in the extraction process, the obtained technical lignin is different from native lignin regarding the chemical structure, molecular weight, and related properties.[63]

As mentioned above, the polymerization of lignin monomers occurs typically through the phenolic oxygen and β or α carbon in the alkyl side-chain with other monomers' propyl side chains, aromatic rings, or carbohydrates. The mechanisms of traditional pulping processes usually attack these ether linkages, as shown in **Figure 2** [64-67] Three reactions were involved: 1) the dissociation of the lignin component from the matrix of lignocellulose, 2) the depolymerization of the lignin including the cleavage of side-chains of lignin monomers under severe conditions, and 3) the

subsequently re-polymerization such as condensation reactions, a term used to define C-C linkage in lignin subunits.
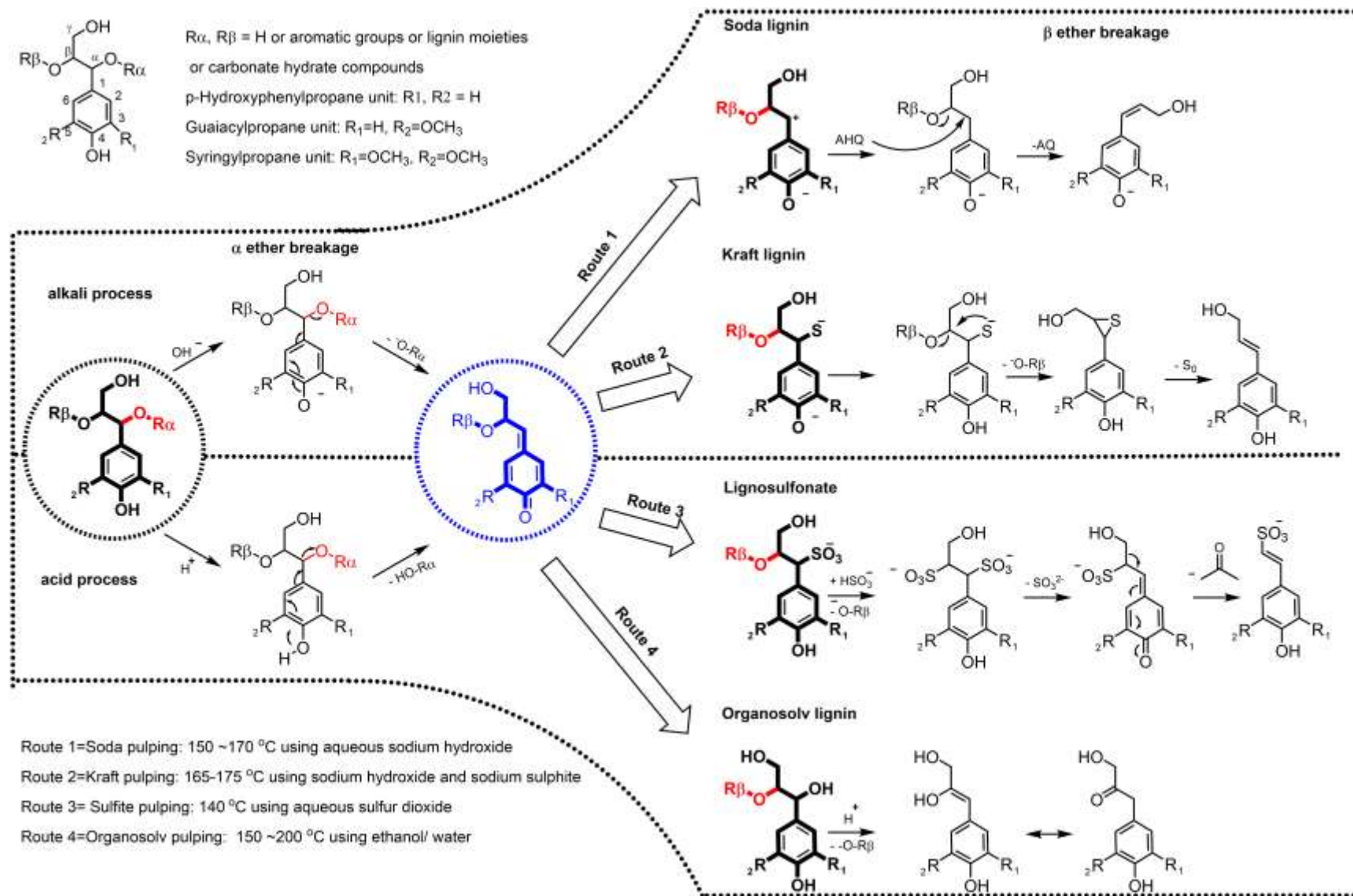
Figure 2 The reaction mechanism of delignification and depolymerization of lignin under different pulping conditions [66, 68-70]

Under high-temperature conditions, an aqueous system or organic solvent with the addition of acidic (H_3O^+) or base (OH^-) reagent as catalysts can destroy ether or ester bonds between lignin and hemicellulose to form a benzyl-carbonium ion that then generates a conjugated quinone-methide. Such intermediate molecules can readily combine with other nucleophilic compounds such as sulfite, bisulfide or hydroxyls from sugar components, along with the rearrangement of the conjugated quinone-methides.[65, 71] Depending on adopted chemical reagents, the chemical pulping process is divided into soda pulping, Kraft pulping, sulfite pulping, and organosolv pulping.

1.3.2.1   Soda pulping

For the soda pulping process, wood chips or typically agriculture waste such as wheat straw, are treated at 150-170 °C using an aqueous NaOH solution. Specifically, OH^- at a high temperature can break down the ether bonds in the lignin polymers with a reduction of lignin's molecular weight. (**Figure 2 Route 1**) The NaOH will react with the fragmented phenolic OH groups to form a lignin salt (sodium phenolate), further increasing its solubility in the aqueous alkali, allowing it to leach into the pulping liquor. The soda pulping process also has side reactions such as retro-aldol condensation. This reaction causes the $\gamma-$carbon with hydroxyl functional groups to leave in the form of formaldehyde, reducing the hydrophilic properties of lignin. (**Figure 3 a**) In addition, the quinone methide intermediate formed during the degradation of lignin under alkaline conditions will also polymerize with the newly formed vinyl phenolic, thereby increasing the molecular weight of lignin(**Figure 3 b**).[72]
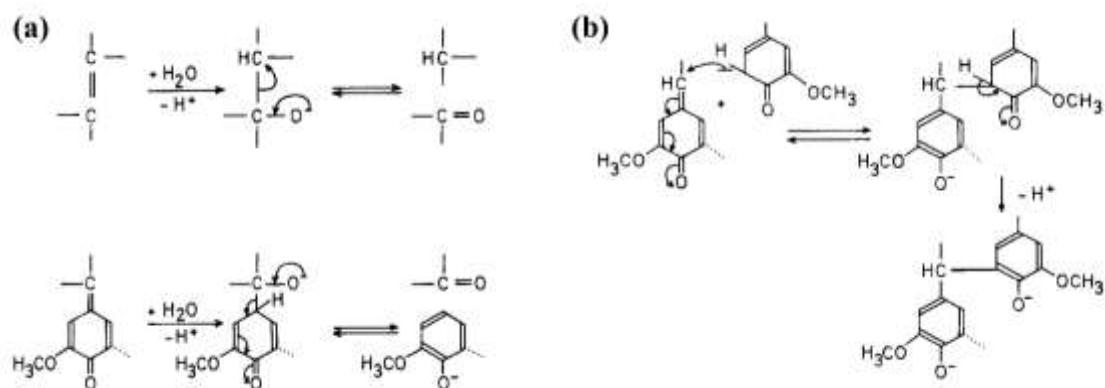
Figure 3 Retrograde aldo reactions including the cleavage of the Cα-Cβ and Cα-aryl bonds (a), and the primary condensation of depolymerized lignin during alkaline pulping (b). Reprinted with permission from ref. [73] Copyright 1980 Springer-Verlag

1.3.2.2 Kraft pulping process

Kraft pulping is the offspring of soda pulping that adds sodium sulfide during the soda pulping process. The sulfide ion acts as a nucleophilic reagent to react preferentially with the intermediates of quinone-methide structures (**Figure 2 Route 2**) and further promote the cleavage of β ether bonds. Moreover, the HS⁻ can help prevent the condensation of the isolated lignin, maintain a lower molecular weight of the lignin, thereby increasing its solubility in the solvent. However, excessive addition of sodium sulfide reduces the alkalinity of the solution system, which may limit the dissolution of separated lignin. Lignin solubility in the alkali system changes due to the extracted wood resources.[74] Therefore, the added amount of sodium sulfide varies with the type of wood to ensure the effective removal of lignin. Kraft pulping is viewed as highly economical, as the reagents can be recycled in the lignin recovery furnaces.

1.3.2.3 Sulfite pulping process

The sulfite pulping process uses H_2SO_3 and SO_3^{2-} to treat lignocellulose at 140 °C for several hours. The use of sulfite as a nucleophilic compound can suppress the reaction of the degraded lignin with other lignin monomers or carbohydrate contents and thus lead to a low molecular weight of lignin. Also, the introduction of sulfonic acid groups will improve the hydrophilic properties of lignin and also increase the solubility of lignin in the supernatants. (**Figure 2 Route 3**). The aromatic structures of lignin as weak nucleophiles react with the carbonium ion to form

carbon-carbon linkage. This intermolecular condensation reaction leads to an increased molecular weight of lignosulfonates. (**Figure 4**)
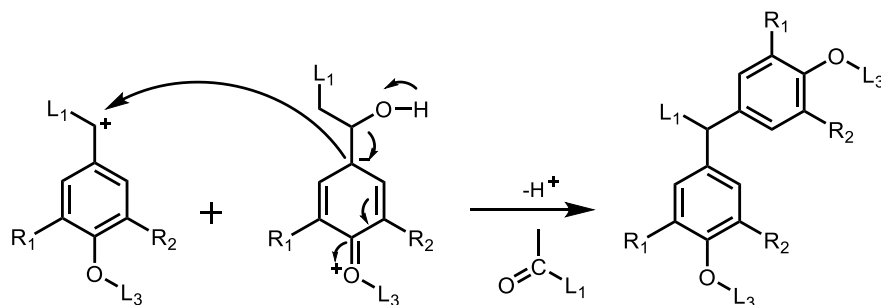
Figure 4 The condensed reaction of lignin during the sulfite pulping process Reprinted with the permission from ref [66]. Copyright 2000 American Chemical Society

1.3.2.4   Organosolv pulping process

Organosolv pulping is used to treat wood or agriculture residue with neutral or acidic conditions at 160-180 °C using an aqueous organic solvent solution. The diluted acid at a high temperature can promote the degradation of ether bonds in the alkyl side chains of lignin. Moreover, different types of organic solvents such as formic acid,[75] ethanol,[76] methanol,[77] and glycerol[78] generally have better solubility for lignin fragments to aid in the separation of lignin and carbohydrate components. Recently, a series of emerging greener organic solvents such as γ-valerolactone,[79] ionic liquids,[80] and deep eutectic solvents[81] were used as solvents for the fractionation of biomass and obtain high-purity lignin for the preparation of materials and chemicals.

Organsolv pulping is similar to more traditional pulping processes with the breakage of ether bonds in lignin, a dominant role for the delignification process. As shown in **Figure 2**, the α-ether was readily degraded under neutral or acid organosolv pulping conditions to form quinone methides or benzyl carbocations; following this structure formation β -ether cleavage occurred to form ω-guaiacyl acetone and Hibbert ketones.[82] A counterproductive process is the intermolecular condensation reaction since the carbocation can readily react with an electron-rich aromatic ring of another lignin units to form carbon-carbon linkages.[83] (**Figure 4**)

1.4 Chemical structure of technical lignin

Depending on above pulping process, technical lignin can be classified as soda lignin, Kraft lignin, lignosulfonate, and organosolv lignin. Their chemical structure and elements are quite different when compared with native lignin due to the chemical reactions such as the loss of functional groups, breakages of repeating units, the substitution of nucleophilic compounds, and the formation of a new C-C bond. As a type of macromolecular, understanding technical lignin structure and repeating units, major chemical linkages, and functional groups are crucial to study the structure-property relationship of lignin-based materials.

1.4.1 Monomer impact on the structure

Lignin is a co-polymer of mixed aromatics, with the majority of the basic units for this polymer derived from p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol based upon the species. (**Figure 2**) However, these three types of lignin monomers do not represent all the fundamental building blocks of lignin. Additional lignin monomers (11 different classes) were discovered as more species, tissues, cell types, and cell wall layers were examined recently.[54] Genes for the different families of plants control the production of monomers for lignification. *Angiosperms* known as hardwoods generally produce all three monomers for lignification, and while it is a mixed co-polymer, sinapyl alcohol is polymerized into syringyl (S) lignin, coniferyl alcohol is polymerized into guaiacyl (G) lignin, and p-coumaryl alcohol is polymerized into p-hydroxy phenol (H) lignin.[84] The difference is that softwood does not contain any S content and contains about 90% of the G component. Grasses plants such as straw and corn stover contain more H content than wood species, and it also contains S content. The ratio of G lignin to other components in the lignin of the root tissue is higher than in other parts.[85] Further, in other tissues, the enzyme for the methylation reaction in the bark cell has lower activity. Therefore, bark lignin contains more H content and a high amount of polyphenols.[86, 87] The relative amounts of these monomers in lignin can substantially impact the isolation and conversion of lignin. For example, the organosolv process extracts more lignin from hardwood than from softwoods, because it has a high S/G ratio. Under the same processing conditions, the methoxy groups in the ortho aromatic position prevent the self-condensation of the lignin during the separation process.[82]

1.4.2   Chemical linkages

As described earlier, after deprotonation, lignin monomers readily form radicals- quinone methides, which had active positions including α, β carbons on the alkyl chain and the para and ortho carbons on the ring. These are readily reacted to form different types of chemical bonds by random copolymerization. The sum of β-O-4, β-β, and β-5 bonds are about 79 per 100 Ar (hardwood) and 58 per 100 Ar (softwood) in native lignin (MWL) respectively (**Table 1**). During the delignification process, these chemical bonds break down with the formation of new aromatic hydroxyl groups and then polymerize to form C-C and C=C which are more difficult to be degraded. **Table 1** showed that technical lignin has a higher degree of condensation (such as C-C bonds) than native lignin (milled wood lignin). Due to these complex chemical linkages, the configuration of lignin (especially technical lignin) is more closely thought to be a cross-linked network; the isolated structures are affected by pulping conditions including the catalyst, solvent, and temperature. Further, the complex structure of the resulting lignin makes it difficult for further processing into new materials, such as copolymerization or blending with other compounds. Therefore, it is necessary to adopt appropriate chemical means to modify the lignin to create biobased materials that are easier to process with known industrial methods.

Table 1 Chemical linkages and functional groups of milled wood lignin and technical lignin (100 Ar)[88-91]

	Milled wood lignin			Softwood Kraft lignin			Hardwood Kraft lignin		Soda Lignin	Organosolv Lignin	
	Spruce	Birch	Eucalyptus	Indulin AT	BioChoice	Amallin	Eucalyptus	Birch		Alcell	Eucalyptus
β-O-4	45	66	51	6~8	2	5	12	2	3.4	8	7
β-β	4	11	13	4~5	6	4	2	3	0.7	3	6
β-5	9	2	4	0.3~4	2	1	1	2	0	3	3
DC	38	16	n.a.	65	71	n.a.	37	65	n.a.	33	n.a.
OCH_3	95	177	182	68~80	63	99	141	141	140	117	179
AlOH	107	129	(5.79)	49~51 (2.29)	44 (1.55)	(1.87)	51	26	(1.31)	32	(1.56)
ArOH	31	20	(1.01)	63~67 (3.75)	66 (3.41)	(3.86)	77	80	(3.13)	72	(3.68)

1.4.3   Functional groups of lignin

Since the basic structural monomer of lignin is phenylpropane with a gamma hydroxyl on the side chain and phenolic hydroxyl on the ring, there are a large number of aliphatic hydroxyl groups in the polymerized lignin with some free phenolic hydroxyls remaining. (**Figure 2**) Moreover, "technical lignin" is extracted by breaking down the aryl-alkyl ether bonds (β-O-4) in the original lignocellulose during pulping. Therefore, in comparison with native lignin (MWL) in plants, technical lignin contains a higher amount of aromatic OH groups and carboxylic acids (degradation products), and less aliphatic OH groups. There is typically some reduction of methoxyl groups, dependent upon the severity of the pulping method.[89] (**Table 1**) These functional groups are important since they impact the solubility of lignin in solvents, thermal stabilities, and thermal mobility, especially the glass transition temperature (T_g).[92] Further, the abundant hydroxyl groups provide lignin to be viewed as a kind of potential polyol precursor; these hydroxyl groups thus can be used as "handles" for further modification to make lignin-based plastics including polyesters, polyethers, and polyurethanes.[23] Moreover, the reactivity of the different types of hydroxyl groups including primary aliphatic OH, secondary aliphatic OH, syringyl OH, and guaiacyl OH groups, changes due to their different pKa values and steric hindrance.[93]

1.5   Molecular weight of technical lignin

The molecular weight and its distribution substantially impact the strength and thermal processing properties of lignin-based materials. Random depolymerization or condensation reactions will lead to extracted lignin with wider molar mass distribution than native lignin. Overall, the absolute molar mass of the technical lignin was around 10- 40 KDa (PDI=3 - 19.7) based on light scattering data. (**Table 2**). As found with the chemical structure of lignin, the molecular weight and distribution of the lignin are affected by the pulping process and species of the resource.[24] For a broad comparison, lignin with high sulfur content generally has a larger molecular weight and a wider distribution. For example, lignosulfonates have larger molecular weights and are more widely distributed than the organosolv lignin and Kraft lignin.

Table 2 Resources, composition, producers, and application of technical lignin[15, 19, 94, 95]

	Lignosulfonate	Kraft lignin			Soda Lignin	Organosolv Lignin
		Indulin AT	BioChoice	Amallin		
Sulfur content	6~7	3.3	1.6	1.3~2.6	1	0
Carbohydrate	10.1	1~2	1.98	0.3~2.4	2~3	0.2
Ash	29.4	2~3	1.36	0.04~0.8	2~3	<0.1
Producer	Borregard	MeadwestVaco	Domtar	WestFraser	GreenValue	Fibria Innovation
Major application	Water reducer, vanillin	Carbon fibres, Plastics, coatings, fuel	Plastics, coating, resin, fuel	Resins		Carbon fibres, Polyurethane foam, Coatings. Surface active materials
M_w/kDa	33	14	16	28.3	19	10
M_n/kDa	1.7	6.0	3.4	7.7	3.6	3.3
PDI	19.7	2.4	3.8	3.7	5.3	3.1
T_g(°C)	140-150	140~150	140~150	162~185	140	117
Production (kt/year)	14000	60	27	10	0.5	n.a.

1.6 Thermal properties of technical lignin

The thermal properties of lignin are impacted by chemical structure and molecular weight of lignin, which is controlled by the types of raw materials and separation conditions.[96] (**Table 2**) Therefore, different kinds of lignin would have different thermal properties; Kraft lignin has a higher T_g than organosolv lignin.[92] Common analysis of the thermal stability of lignin is based on the thermogravimetric analysis. More advanced techniques couple thermogravimetric analysis to chromatography and spectroscopy methods. Lignin decomposes in the temperature range from 200 °C to 700 °C.[97] However, lignin reactions below 200 °C can impact its structure without the loss of gaseous degradation products. The methoxy and hydroxyl groups significantly alter the degradation curve and the final char yield. More methoxy groups cause lignin to generate more volatile compounds, thereby reducing the 5% mass loss decomposition ($T_{D5\%}$) temperature. Under high temperature, the hydroxyl groups in lignin become ionization to generate mobile protons and electrons, which in turn promote the depolymerization of lignin.[97]

Differential scanning calorimetry(DSC) curves of lignin always show a significant enthalpy relaxation at fairly low temperatures.[26] Previous studies show that there had slight changes on the molecular weight distribution of lignin even below 100 °C because of the complicated hydrogen bonding network of lignin was highly prone to radical polymerization with increasing temperature. This phenomenon will make the final T_g results become unclear and unrepeatable. Cui et al. adopted a three-cycle thermal treatment to analyze the glass transition temperature of lignin to obtain a more reliable T_g. In detail, the first cycle was an annealing procedure, which heated the lignin below 120 °C to weaken the enthalpy relaxation within the lignin samples. Then samples were cooled down to 0 ˚C, followed with a second-cycle treatment: the sample was heated to the temperature at $TD_{5\%}$ resulting in a clearer T_g.[26] The amorphous technical lignin had a T_g in a range from 90 - 160 °C. This high T_g provides justification to use lignin resources in heat-tolerant applications.[92]

1.7 Sulfur, carbohydrate, and ash analysis of technical lignin

The sulfur content in lignin generally will cause odor issues when heated to high temperatures. Further, it is a well-known poison for different types of catalysts in the reductive depolymerization and hydrogenolysis/hydrodeoxygenation reactions of lignin.[98] The lignosulfonate contains the

highest amount of elemental sulfur; every 2 monomeric units contain 1 sulfonate group. Kraft lignin, of course, contains sulfur content as the utilization of Na_2S. Kraft lignin from an innovative recovering process in recent decades, such as Lignoboost and Lignoforce, contains a lower amount of sulfur than Indulin AT.[99] Soda lignin also contains less than 1% of sulfur content, which may originate from the washing process. Organosolv lignin from the Alcell process includes a small amount of sulfur content arising from the H_2SO_4 used as a catalyst during pulping operations.

The carbohydrate content will negatively impact the solubility of lignin. The carbohydrate content is unavoidable during most of the pulping processes such as Kraft pulping, sulfite pulping, and soda pulping. The organosolv process contains the lowest amount of carbohydrate content, while lignosulfonates and enzymatic hydrolysis lignin from biorefinary[100] contain the highest amount. The highest amount of ash content was found in the lignosulfonates, as it was recovered as salt compounds. Higher purity lignin is typically sought for enhanced performance in making advanced materials.[101-104]

1.8 Toxicity and compostability of lignin

Most industrial technical lignin is a fine particle powdered substance with volatiles. When handling high surface area materials as air-born particles and caution should be used as these small particles can be a lung irritant and explosion hazard. On the other hand, the biodegradability of native lignin has been studied by using microorganisms from the natural environment.[105] Generally, with proper conditions, the ambient environment with moisture will degrade terrestrial plants, while the lignin is the last compound to be decomposed when compared with the carbohydrate fraction. One of the most effective microorganisms to degrade lignin is a white-rot fungus *Basidiomycotina* that degrades lignin at upper temperatures such as 36 - 49 °C. Noteworthy, technical lignin such as Kraft lignin can also be degraded by the white-rot fungus, though it has relatively lower biodegradability than native lignin. [106] Overall, potentially lignins can serve as an environmentally friendly feedstock because of its low toxicity and biodegradable properties and bioplastics based on lignin thus would not cause serious problems with pollution. Glasser et al. developed the first commercial lignin-based polyester film, which had degradable properties in the compost environment. [107]

1.9 Availability and application of technical lignin

Since the pulp and paper industry faces challenges of a "paperless society", it is imperative to create more products from wood and agricultural waste for high-value applications besides paper products to continue to use renewable carbon for our needs.[108] Lignin is a significant by-product of the pulp and paper industry and can be used to produce high-value products to provide the entire pulping process with economic advantages and promote sustainable consumption. As a result, more and more enterprises are considering the development of new methods to realize the recycling of lignin for the conversion into new products.

Lignosulfonates from the sulfite pulping process has been widely used to produce high-value products. Most of these products have been commercially successful for nearly three quarters of a century.[15] One of the most critical applications is the use of lignosulfonate as an anionic surfactant for the production of cement water reducer to promote the dispersion of cement particles in concrete; lignosulfonates also improve the performance of cement, while reducing the amount of unit cement consumption for the construction.[109] Besides, lignosulfonate can be used to produce vanillin, a flavoring agent for pharmaceutical, beverage, and food products.[110] The Borregard plant in Norway uses oxidative degradation methods to produce a large amount of vanillin, accounting 15% production of vanillin around the world annually.[111] Due to high-value products, the lignosulfonates have a higher demand than other lignin in the market. Its annual production can account for 90% of the total commercial production of lignin resources, reaching 1.4 million tons per year. (Table 2) Borregaard Ltd in Norway is one of the most important producers; its production accounts for more than 40% of the total lignosulfonate production in the world.[111]

As an alkaline treatment method, Kraft pulping emerged in 1890s. Although the lignosulfonate is the largest amount of lignin resources each year, the Kraft pulping process is increasingly replacing the sulfite pulping process. The Kraft pulping process generally produces pulping fibers with higher strength and shorter reaction time than sulfite pulping. On the other hand, obtained waste liquors are easier to recover pulping chemicals for reuse.[74] For these reasons, the potential amount of recoverable Kraft lignin was much higher than other types of lignin as it is more economical to produce Kraft fiber. The potential amount is about 78 million tons annually.[15]

For a long time, less than 60,000 tons of Kraft lignin resources were recovered from the Mead Westvaco Company (WestRock) annually. (Table 2) In the last century, this company was one of the largest producers for Kraft lignin. However, this lignin generally contains higher ash content. In recent decades, some innovative extraction technologies for Kraft lignin such as "Lignoboost" and "Lignoforce" were developed that have different purification processes. Compared with traditional WestRock recovery with the tradename of Indulin AT, the Lignoboost process can improve the purity of Kraft lignin by reducing the sulfur and salt contents while consuming less water. (Table 2) These characters enhance the solubility of Kraft lignin, which makes it easier to process. This technology was developed by the Chalmers University of Technology in Sweden and later adopted by Domtar Corp., which was able to recycle more than 75 tons of Kraft lignin per day. It is interesting that these two types of lignin have a similar structure, though they were obtained from different pulping conditions.[95, 112] LignoForce is a method developed by FPInnovations and scaling the process was done by Noram Engineering in Canada. West Fraser Corp. later adopted the process of being able to recover more than 35 tons of Kraft lignin (Amallin) per day. Compared with Lignoboost techniques, this lignoforce process utilized O_2 to oxidize lignin, before inputting CO_2 to reduce the pH of black liquor. This procedure improves the filterability of lignin and oxidizes the hydrogen sulfide to minimize the cost of lignin recovery and enhances the purity of lignin.[113, 114] Since Kraft lignin contains more carbon than lignosulfonate and soda lignin, it has higher calorific value. Different from burning as fuels directly, Kraft lignin can also be blended with fossil fuels such as coal or petroleum to reduce the consumption of fossil fuels when burned for energy production. On the other hand, Kraft lignin, with lower salt content and sulfur content, can more easily be transformed into high-value materials or fine chemicals.

Also, the emergence of the bioeconomy offers significant potential for the pulp and paper industry to integrate their plants into the biorefinery system. Based on this point, the organosolv pulping process has attracted attention. The benefits of using organosolv pulping are apparent compared with Kraft lignin and lignosulfonates, which use chemicals from renewable resources such as ethanol, methanol, acetic acid, and glycerol.[115] Some have a lower boiling point, which aids solvent recovery. More importantly, obtained lignin resources in this process have good solubility and high-purity. Although there were some challenges regarding solvent recovery and lower efficiency of delignification, industry, with support of the government, still has a keen interest to invest in

this area in realizing commercial success. Some pilot-scale plants were built in the last decades, including LignolTM (Alcell, ethanol-water with acid) from Canada's Fibria innovation, GlycerllTM (glycerol-water) from Australia, and CIMV from France and ECN from the Netherlands. In the future, this organosolv process will draw more attention to the increasing shortage of energy (cellulosic liquid biofuels) and requirements for renewable resources.[115]

1.10 Pros and cons of lignin-based polymeric materials

1.10.1 Pros and cons

A simple fact is that 40% of forestry traded wood was converted to paper products. This number went up to 50% in British Columbia (Canada).[108, 116] The world's forest is still one of the largest carbon sink we have now. Burning ~15% of those forests (separated lignin residue) will definitely lead to the production of greenhouse gas and is a waste of stored carbon. The application of these forest-based resources as chemicals or materials will play more crucial roles from the carbon storage perspective.

Lignin is synthesized by three fundamental phenylpropane units, so it is one of the largest amounts of aromatic resources from natural plants.[117] The three most important aromatic chemicals benzene, toluene, xylene served as fundamental building blocks for a lot of chemicals or materials.[18] Theoretically, it is capable to produce these chemicals by depolymerizing natural lignin, which can reduce the consumption or reliance on fossil-based chemicals. Although this topic has attracted emerging interests in recent decades, few of these studies have yet applied on a commercial scale due to the cost and efficiency.[118] As we talked above, the pulping process always adopted a hush chemical conditions to cleave the less-stable aryl-ethyl ether bond, which leads to the production of more stable carbon-carbon linkages (5-5, β-1) in harsh conditions. Hence, it is very difficult for researchers to convert technical lignin such as kraft lignin and organosolv lignin (enriched with carbon-carbon linkages) to valuable monomers. [118, 119]

Instead of breaking down this macromolecule to functionalized aromatic monomers,[119] many studies have focused on the materials' application taking the native positive aspects of lignin such as UV absorption, high stiffness, and biodegradability to make polymeric materials.[120] Lignin has the potential to help realize the valorization of biomass into exciting materials such as carbon-

based materials,[101] bioplastics,[107] and coatings. Though these studies proposed valuable products for society, there exist some problems for the sustainable conversion of lignin resources. The limited commercial value of lignin resources has been discussed since probably the first pulp company was built. We concisely summarized the positive attributes and negative drawbacks of lignin-based materials below.

Advantages of lignin as a feedstock：

1) Lignin is made from renewable resources, meaning it is stored carbon, found in plant cell walls, which is widely distributed around the world; the annual output can reach 30 - 50 billion tons and nearly 141 million tons of lignin are recoverable;

2) Infrastructure is in place for the isolation of lignin from both a harvest and conversion standpoint, as such pulping and biorefinery companies have increasing interest to recover lignin and supply the market;

3) There is a large diversity of chemical structures in lignin compared to other compounds; lignin is partially hydrophobic with rigid aromatic units in the polymer backbone. Further, during isolation there is a substantial amount of hydroxyl groups that provide an opportunity for further derivatizing into new materials;

4) Lignin has interesting aspects of being both thermoplastic and thermosetting dependent upon the material structure and heating regime;

5) Lignin has low toxicity and compostable characteristics that could be used for the creation of compostable materials.

Negative aspects of utilizing lignin：

1) Due to the isolation process, there is a wide distribution of the molecular weight of lignin with different structural attributes; this heterogeneity leads to varying solubility of lignin fractions in solvents or blends with other polymers resulting in negative impacts for complete derivatization and lower mechanical properties of lignin-based materials;

2) During derivatization or processing, lignin is thermally sensitive and can undergo depolymerization and self-crosslinking reactions under high temperature causing the inevitable change of chemical structure of lignin. This aspect, in turn, increases the difficulties of defining structure-property relationships;

3) The conformational structures of lignin make it difficult for lignin to blend or copolymerize with other polymers when there are new condensation bonds.

1.10.2 Chemical modification is the cornerstone for lignin utilization

Due to the structure-property relationship of materials, modification of lignin is an important topic for biologists, botanists, chemists, and engineers. Currently, developed methods contain transgenic modification,[121, 122] structure-control during isolation,[123] and chemical modification of isolated technical lignin.[124] However, the first way still faces challenges due to public concerns about potential environmental impacts.[125] Controlling its structure during the isolation step would be the simplest way with a lignin-first strategy.[123] However, we need to change pulping conditions (such as the H-factor),[29] which were set to obtain high-quality pulp rather than lignin. In the absence of high-value lignin-based products, it is difficult for pulping companies to make a balance between the quality of lignin structure and the performance quality and purity of cellulose pulp.

Therefore, the most direct and practicable way is the fractionation and chemical modification of recovered technical lignin on the market now. Researchers have developed a series of methods to fractionate lignin or modify those technical lignins targeting on the hydroxyl groups by etherification, esterification, or urethane formation. The feasibility of these methods has been proved to some extent.[18, 19] However, we must evaluate those modification methods based on the green chemistry principles to satisfy sustainable requirements in this century.

1.11 Lignin-based polyether: derivatives and copolymers
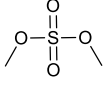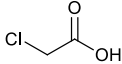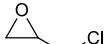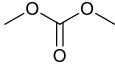
The chemical modification of lignin by etherification, including derivatization reactions and copolymerization reactions, is an important route to obtain useful lignin-based materials. Also, consumable products contain a large number of polyether polymers like polyethylene glycol (PEG) and polypropylene glycol (PPG) for medical, chemical, and biological applications making this a broad class of polymers.[126]
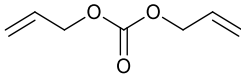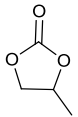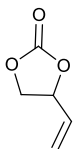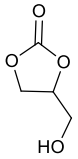
1.11.1 Derivatization and copolymerization

1.11.1.1 Halogenated compounds

Using halogenated compounds as a nucleophilic reagent allows the selective modification of the aromatic hydroxyl groups in lignin. Halogenated reagents, such as epichlorohydrin, allyl chloride, methylene iodide, and chloric acetic acid, had been studied to convert the aromatic OH groups into epoxy,[127] allyls,[128] methyls,[129] and carboxylic acid groups.[130] (Table 3) The addition of these new functional groups is capable to improve the solubility of lignin, adding functional groups for more advanced application, and change their thermal properties or enhance .[120]

Table 3 The etherified lignin preparation using halogenated, alkyl oxide, and organic carbonate compounds and corresponding metrics

Chemicals	NFPA 704	Lignin	Temp./Time	Solvents	Catalysts	DS /%	AE /%	cEF-WWI /(g/g)	Ref.
Propylene oxide	4/3/2	SKL	40 °C/18 h	0.5M NaOH	KOH	99	100	10.75	129
Methyl iodide	1/3/1	SKL	R.T./18 h	DMF	K$_2$CO$_3$	60	44	16.31	129
Dimethyl sulfate	2/4/1	SKL	80 °C/2 h	0.7 M NaOH	NaOH	99	63	16.48	129
Chloroacetic acid	1/3/0	SKL	55 °C/3.5 h	70% aqueous ethanol	NaOH	30	80	27.46	131
allyl chloride	3/3/1	SKL	55 °C/30 h	40% aqueous ethanol	NaOH	95	78	50.28	132, 133
Epichlorohydrin	3/3/2	SKL	55 °C/5 h	50% aqueous acetone	NaOH	61	80	347.60	127, 134
Dimethyl carbonate	3/1/0	SKL	120 °C / 3h	DMSO	NaOH Cs$_2$CO$_3$	99	70	18.04 20.12	135, 136

Chemicals	NFPA 704	Lignin	Temp./Time	Solvents	Catalysts	DS /%	AE /%	cEF-WWI /(g/g)	Ref.
Diallyl carbonate		OSL	120 °C / 3~15h	N-AS[e]	TAB[e]	80	66	3.84	128
Ethylene carbonate		SL KL OSL	150 °C 0.25 h 120 °C 3 h	N-AS	K$_2$CO$_3$ Na$_2$CO$_3$	99 99	88 88	4.94 2.23	33
Propylene carbonate		SL, KL OSL	150°C 1~3 h	N-AS	K$_2$CO$_3$	99	88	6.48	137
Vinyl ethylene carbonate		SL, KL OSL	150 °C /1~15 h	N-AS	K$_2$CO$_3$	NA	89	6.02	138
Glycerol carbonate		SL, KL OSL	150 °C 1~3 hrs,	N-AS	K$_2$CO$_3$	99	89	6.02	33

The epichlorohydrin modification can add an epoxy group into the aromatic backbone of lignin. The epoxy group can be cured with diamine or triamine to form thermosetting resins.[127] Van de Pas and his collaborators studied the deconstructed native softwood lignin using a hydrogenolysis reaction.[139] The resulting products were further fractionated by diethyl ether solvents to obtain separated lignin fractions for epoxidation. The epoxidized lignin was mixed with glycerol diglycidyl ether or phenyl glycidyl ether in the desired ratio and further reacted with different types of amine reagents for the curing reaction. The obtained lignin-based resin showed promising flexural properties in comparison with industry-standard resins. Gioia later adopted fractionated lignin using a series of organic solvent to do the same reaction to obtain epoxidized lignin. Lignin

fractions were chemically cross-linked with a flexible polyether diamine. Based on the tensile test results, the lignin fraction with a higher molecular weight produced stronger materials.[127]

Reactions of lignin with allyl chloride[132] or allyl bromide[140] converted the aromatic OH group into an allyl functional group by etherification. The allylated lignin could further react with the trimethylolpropane thiol group to obtain thermosetting plastics. By this typical thiol-ene cross-linking reaction, the resulting thermoset materials showed a glass transition temperature above room temperature.[133]

Carboxymethylation is one method to convert the aromatic OH groups into carboxylic acids, which could increase the solubility of lignin in aqueous solutions and enable there use as a surfactant. Li and his collaborators used the amphiphilic properties of carboxymethylated lignin to formulate oil-in-water (O/W) emulsified fuel.[131] Further, this carboxymethylated lignin was used as a surfactant in the stabilization of ceramic materials as well as aqueous dispersions of graphene.[141, 142]

Other reactions have included methyl iodide, and dimethyl sulfate, which are mainly used to mask the aromatic hydroxyl groups in lignin, blocking the side radical crosslinking reactions, and improving the thermal stability of lignin for subsequent processing.[129]

The mechanism for the above modifications is quite similar. Technical lignin or fractionated technical lignin were first dissolved in aqueous solutions or organic solvents. Halogenated reagents were added with base catalysts at less than 100 °C for several hours to convert the phenolic hydroxyl groups in lignin. The reaction mechanism (**Figure 5**) revealed that the aromatic hydroxyl group becomes deprotonated with a Lewis base to form a lignin phenolate that reacts with halogenated compounds by an SN_2 nucleophilic substitution reaction - called the Williamson ether synthesis.[143] Since the halogenated salt is formed during the reaction, the atom economy is generally less than 100%.
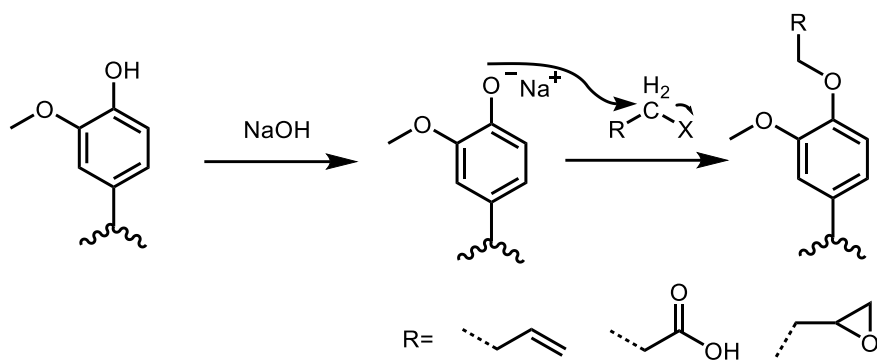
Figure 5 The chemical modification of lignin using Williamson ether synthesis

These methods have been widely adopted by researchers, attributed to the mild reactive conditions. However, these methods also have challenges, listed below, for attaining green chemistry and the industrial-scale production:

1) Halogenated compounds typically have problems with their stability, flammability, and health hazards, and most of them are carcinogenic reagents. The large-scale production based on these compounds will potentially cause severe environmental pollution and impose a significant burden on waste disposal. Further, some of the halogenated compounds have been banned in industrial production and need virtual elimination.[144] (**Table 3**)

2) Typically, the degree of substitution is not high enough (DS=30% - 62%, **Table 3**) and has high selectivity towards ArOH groups; most of AlOH groups are retained without modification.

3) Besides the low atom efficiency, using volatile organic solvents such as ethanol as the solvent increases the environmental (E)-factor and the cost for recovery.

4) Kraft lignin has low solubility in most of the organic solvent, except DMSO and DMF. Solvent fractionation is necessary to inhibit the side reactions of undissolved lignin. However, the insoluble lignin in this process has not been reported to be converted into new materials, which would be treated as waste. This would further increase the E-factor of this process.

1.11.1.2 Alkylene oxide compounds

Using alkyl oxide compounds is another method to modify hydroxyl groups in lignin. At relatively low temperatures, Sadeghifar et al. [129] and Glasser et al.[145] adopted propylene oxide to selectively modify the ArOH groups of lignin to AlOH groups to obtain hydroxypropyl lignin derivatives. The resulting oxypropylated lignin showed similar molecular weight distribution. Under the high temperature, the epoxide compounds are widely used in the production of polyethers like polyethylene oxide. As a result, these compounds can also copolymerize with lignin under specific conditions. In the 1980s, Glasser and co-workers used alkyl oxide reagents, including ethylene oxide, propylene oxide, and butylene oxide, to modify the phenolic hydroxyl groups in the lignin.[146, 147] Among them, the oxyalkylation of technical lignin by propylene oxide was noted to be a promising route to modify lignin. In part, this was because of the limited homopolymerization of the reagent. The resulting lignin only contained AlOH, which showed good solubility in a series of solvents or polymers for subsequent further modification and processing. This modified lignin had been widely applied to make polyurethane foam, resins, and polyesters. Later, they further adopted this hydroxypropyl lignin as precursor to mix with eco-flex (BASF Corp.); by blending 30% of lignin, the resulting film showed obvious protection from photo-degradation and improvement on modulus. This product demonstrated successful commercialization for melt-blown film thermoplastic materials.[107]

Schmidt and his collaborators performed the copolymerization between lignin and ethylene oxide.[148] The reaction involved reductive catalytic hydrogenation in degrading technical lignin into smaller lignin fragments. In the tetrahydrofuran solvent, these lignin fragments were used as an initiator to react with ethylene oxide. This lignin-based polyether was used as a stabilizer or surfactant for a styrene emulsion polymerization process. Its performance was comparable with commercial stabilizer reagents.

Both the derivatization and copolymerization showed a similar mechanism. The deprotonated aromatic OH group would attack the carbon in the epoxy group by the SN_2 nucleophilic substitution with the opening of the ether ring. Depending on the position of attacked carbon, the resulting lignin would contain either primary aliphatic OH groups or secondary aliphatic OH groups. At room temperature, the epoxidize compounds showed high selectivity toward the

aromatic OH group.[129] Since, no by-products were formed during this reaction, the atom economy could reach 100% for this derivatization reaction if homopolymerization is avoided. (**Figure 6**)
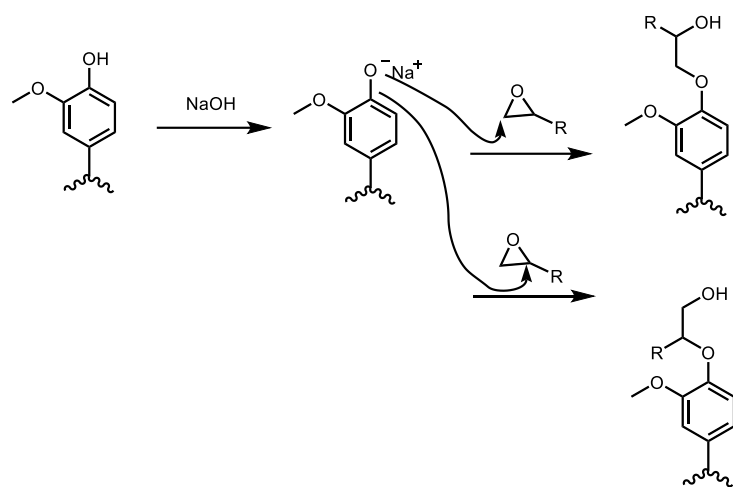
Figure 6 Alkylation of lignin using alkylene oxide compounds; R=H, - CH₃, or -CH₂-CH₃

However, this reaction process still has challenges because of requirements for green chemistry:

1) The alkylene oxide compounds are generally toxic, noted carcinogens, which would be harmful to the human body after short-term exposure. These compounds also have high flammability and poor stability at room temperature, which makes storage difficult and very dangerous for explosions. (**Table 3**)

2) The alkali solution, used to dissolve lignin, produced a high salt content in the resulting reaction mixture. Washing the modified lignin with more water would further increase the E-factor of the whole reaction.

1.11.1.3   Alkylene carbonate compounds

Another way to perform the modification of ArOH groups in lignin is to use alkylene carbonate compounds. These compounds can be classified into cyclic carbonates and linear carbonates. The former one includes ethylene carbonate, propylene carbonate, glycerol carbonate, and butylene carbonate, while the latter one includes diallyl carbonate and dimethyl carbonate. The organic carbonates can also convert the hydroxyl group or even add additional functionality like allyl groups in the lignin. The alkylene carbonate compounds are greener and safer than above alkyl

oxide and halogenated compounds (**Table 3**). Previous researchers showed that the organic carbonate groups had high reactivity towards COOH, aliphatic OH, aromatic OH, and NH_2 groups.[149] By using this process, all the functional group lignin can be successfully modified.

Under the alkaline conditions, these functional groups were deprotonated, following nucleophilic substitution reaction with carbon atoms from the carbonate group and the cleavage of this carbonate group. (**Figure 7**). The terminal ester group in the new alkyl chain was easily cleaved resulting in the release of CO_2 and creating a terminal hydroxyl group. With further acid washing, the resulting lignin only contained AlOH groups.[150] The reactivity of organic carbonate towards the ArOH group in the lignin would change dependent upon on the side group of the carbonate: -H > -CH_2OH> -$CH=CH_2$ > -CH_3.[33, 137] Also, specifically for lignin, the aromatic conjugated compounds after deprotonation were subjected to condensation, based on quinone methide intermediates at high temperature to generate carbon bonds and lead to a higher molecular weight lignin compound. [151]
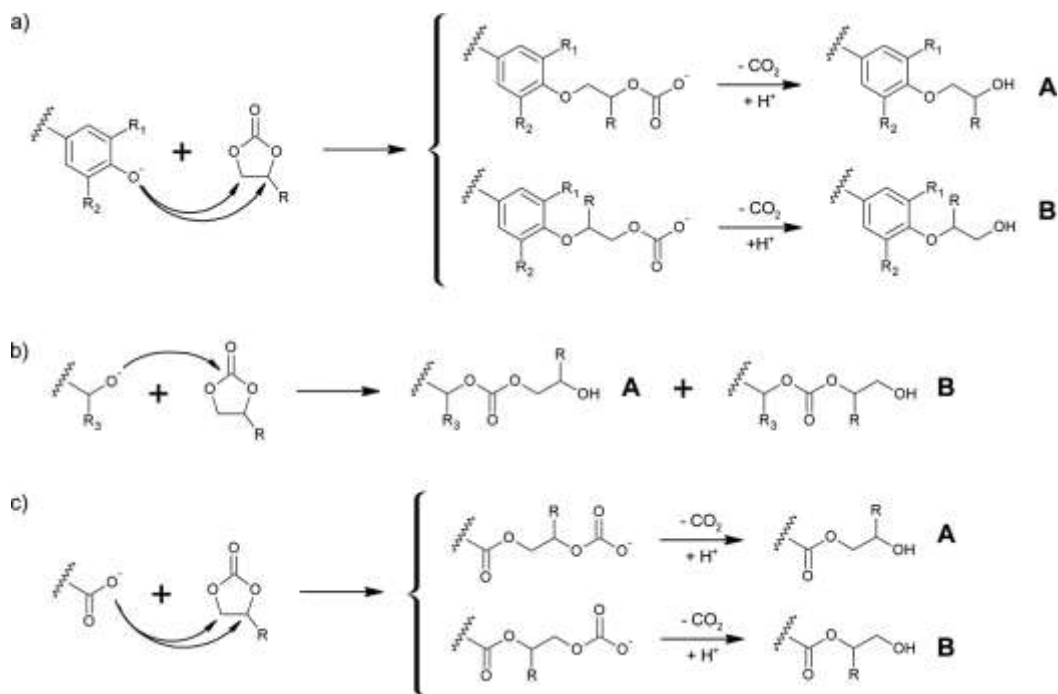
Figure 7 Alkylation of lignin using cycle organic carbonate; R= -H, -CH₃, -CH₂OH, -CH₂CH₃, -CH=CH₂. Reprinted with the permission from ref [33] Copyright 2017 American Chemical Society

In comparing with traditional alkyl oxides and halogenated compounds, advantageous aspects for this reaction are the following:

1) As an alternative to epoxide chemicals, the greener organic carbonate compounds are more stable and safer with low flammability.

2) During the reaction, it is not necessary to add additional reagent as a solvent, thereby reducing the difficulty of solvent recovery in the later stages and avoiding a higher E factor of the reaction.

3) The conversion rate of the reaction process can reach nearly 90%, resulting in a uniform chemical structure to the lignin.

However, this modification method with carbonates also has drawbacks which need further improvement;

1) Side reactions will change the skeletal structure of the lignin by forming new condensed carbon-carbon bonds and carbonate linkages, accompanied with increased molecular weight; therefore, these side-reactions will lead to a negative impact on the solubility of modified lignin.[138]

2) Researchers need to develop new procedures to make organic carbonate compounds from renewable resources by greener procedures rather than from fossil fuel, as epoxides, such as ethylene oxide are often the starting materials for these reagents.

1.11.1.4 Blending lignin with polyether

Without any modification, lignin typically has good compatibility with a polyether, more than with a polyolefin or polyesters.[152] For example, lignin and polyethylene oxide (PEO) can be miscible due to the strong hydrogen bond formed with the ether oxygen of PEO acting as a hydrogen bond acceptor. In PEO, a small amount of organosolv lignin (<25%) plays the role of internal plasticizers to increase the thermal mobility of mixture.[103] This lignin-PEO blends also showed a promising route to produce sub-micron fibers by electrospinning, with less than 1% PEO. This lignin-based

microfiber can further heat to 1000 °C under N$_2$ atmosphere to produce high-performance carbon fibers.[153]

1.12 Lignin-based polyester: derivatives and copolymers
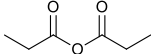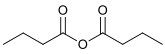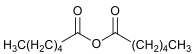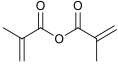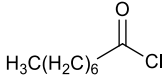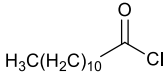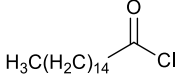
Polyesters are an essential polymer class that can be made synthetically (polyethylene teraphthalate) or biologically (polyhydroxybutyrate).[154] Also, there is growing attention to biodegradable polymers being synthesized, such as polylactic acid[155] and polybutylene succinate,[156] which are used in fields such as packaging. However, the bulk of these materials use non-compostable repeat units, leading to severe environmental pollution. Renewable lignin resources, which contain abundant hydroxyl groups, have been demonstrated to be an excellent precursor to form lignin-based polyester for compostable plastics.[107]
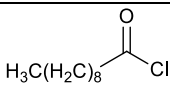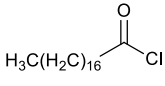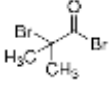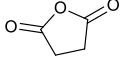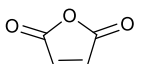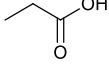
1.12.1 Derivatization

1.12.1.1 Anhydride compounds

It is a standard method to use anhydride compounds to modify the hydroxyl groups in biopolymers such as cellulose and lignin to prepare ester derivatives. (**Table 4**) Ghosh et al.[157] and Thielemans et al.[32] used C$_2$ - C6 anhydride compounds, including acetic anhydride, propionic anhydride, butyric anhydride, hexanoic anhydride to obtain derivatized lignin esters with various carbon lengths. As the number of carbon atoms in the anhydride compounds increased, the molecular weight and hydrophobic properties of the derivatized lignin increased correspondingly. Also, the thermal mobility of lignin increased, because the esterified chain will weak the interection of intermolecular. The modified lignin had a decreased glass transition temperature with increased carbon atoms in the ester chain. Further, Thielmans and Wool used the Hoy-Huggins theory to study the thermodynamic properties and solubility of lignin ester derivatives in styrene.[32] Higher carbon numbers decreased the density and hydrogen bonding of lignin chains, resulting in increased solubility in styrene. Another approach was to use cyclic anhydride compounds, such as succinic anhydride, to modify the lignin, but it showed high selectivity toward AlOH groups in the lignin due to the steric hindrance of ArOH group structure [30] or the change of pKa value of different types of hydroxyl group.[93]

Table 4 Lignin ester derivative preparation using halogenated compounds and acetic anhydride compounds and corresponding metrics

Chemical structure	Safety	Lignin	Temp./Time	Solvents	Catalysts	DS /%	AE /%	cEF-WWIg/g	Ref.
Acetic anhydride	2 / 3 / 0	SKL	65 °C /24 h	N-AS	1-MIM	73~100	69	26.92	[158]
Propionic anhydride	2 / 3 / 0	SKL / HKL	95 °C /24 h / 50 °C/24h	N-AS	1-MIM	67	66	22.45 / 2.05	[32,] [158]
Butyric anhydride	2 / 3 / 1	SKL / HKL	120 °C /24 h / 50 °C /24 h	N-AS	1-MIM	83	64	11.52 / 2.05	[32,] [158]
Hexanoic anhydride	1 / 3 / 0	SKL	140 °C /24 h / 50 °C /24 h	N-AS	1-MIM	43	62	11.91	[32,] [158]
Methyacrylic anhydride	2 / 2 / 0	SKL	50 °C /24 h	1,4-dioxane	1-MIM	nd	65	10.31	[32]
Acetyl chloride	3 / 3 / 2	SKL	65 °C /24 h	DMF, THF	Pyridine	100	78	14.33	[31]
Octanoyl chloride	2 / 2 / 0	SKL	65 °C /24 h	DMF, THF	Pyridine	100	86	15.40	[31]
Lauryl chloride	0 / 3 / 0	SKL / HKL	r.t. /20 h / 65 °C /24 hrs	NS DMF THF	Pyridine Triethyl--amine	90	88	7.79	[159,] [160]
Palmitoyl chloride	1 / 3 / 0	SKL / HKL	r.t. /20 h / 65 °C /24 hrs	NS DMF THF	Pyridine	90	90	7.73	[160]

34

Chemical structure	Safety	Lignin	Temp./Time	Solvents	Catalysts	DS /%	AE /%	cEF-WWIg/g	Ref.
H₃C(H₂C)₈—C(O)Cl Dodecanoyl chloride		OSL	20 °C /2 h	DMF	Pyridine	97	88	44.48	[102]
H₃C(H₂C)₁₆—C(O)Cl Stearic chloride		SKL	80 °C /18 h	Dioxane	Pyridine	97	91	32.08	[161]
2-bromoisobutyryl bromide		SKL	Rt/24h	DMA	Triethyl--amine	n.a.	n.a.	n.a.	[162]
Succinic Anhydride		SKL*	60 °C/3h	THF	1-MIM	28	100	nd	[163]
Maleic anhydride		SKL HKL	50 °C /24 h	1,4 dioxane	1-MIM	<41	100	30.6	[164]
Propionic acid		SKL	120 °C /24 h	Propionic acid	Propionic acid	95	89	3~10	[165]

The reaction mechanism of an imidazole catalyzed esterification is shown in **Figure 8**. The anhydride group was first reacted with 1-methylimidazole (1-MIM) or pyridine to form N-alkyl-N'-methylimidazolium ion or pyridinium. These ions can then react with hydroxyl groups in lignin in a reversible reaction to achieve an ester derivative. In the latter process, 1-MIM or pyridine also plays the role of proton scavenger to promote this modification.[32] Interestingly, lipase B has an active pocket with a histidine amino acid residue that has an imidazole side chain that can facilitate the esterification linking the biological catalyst approach to a known mechanism (**Figure 20**). The reaction process using anhydride reagents was further evaluated based on principles of green chemistry:
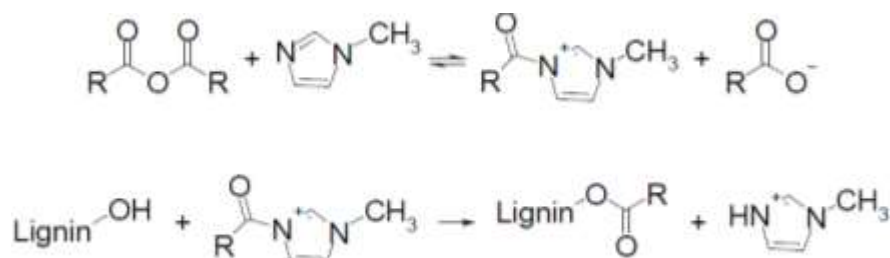
Figure 8 The esterification of lignin using anhydride compounds Reprinted with permission from ref. [32] Copyright 2005 American Chemical Society

Advantageous aspects:

1) The reaction conditions are mild with a marginal impact on the molecular weight and skeletal structure of lignin. As anhydrides with higher carbon numbers are used, the reaction requires higher temperatures to achieve full conversion. (**Table 4**)

2) The conversion of this esterification can reach 100%, and the conversion rate of aromatic OH groups in lignin is generally higher than the rate of conversion for aliphatic OH groups. In contrast, cyclic anhydride compounds are different for the modification of different hydroxyls, as they generally have a higher conversion rate for the aliphatic OH group than for the aromatic OH. Further, the cyclic anhydrides allow this reaction to reach a 100% atom economy (AE).[163]

Disadvantageous aspects:

1) In this reaction, the byproducts of linear anhydrides are acid compounds that reduce the atom economy substantially.

2) It is a necessity to develop alternative chemical reagents or reactions processes to replace unstable and hazardous chemical compounds, including pyridine or 1-MIM, and organic anhydride compounds.

3) New reaction schemes need to be developed, as there are two methods to recover the modified lignin with a high potential for waste, which results in higher E-factors.
   a) washing with 0.01 M HCl solution causes an increase in the wastewater index

b) ethanol rinsing combined with roto-evaporation recovery reduces the waste but still has issues with separating the acid by-products from the solvent. It is imperative to minimize the E factor, by developing an efficient way to recover lignin and reagents simultaneously.

1.12.1.2 Halogenated compounds

Typically, when modifying lignin or cellulose with fatty acids containing over 6 carbon atoms, researchers need to convert the fatty acid into halogenated acids.[166] The reaction mechanism for the modification of lignin hydroxyl groups with acid chlorides is shown in **Figure 9**. With the increased carbon chain length, the result is similar to the modification by anhydride compounds; the T_g of derivatized lignin ester decreased as the number of carbon atoms increased.[31] Moreover, the increase of degree of substitution also corresponded with a decreased T_g. Finally, by increasing the length of the fatty acid chain on the modified lignin, the intrinsic viscosity of the derivatized lignin increased correspondingly when measured in THF solutions, indicating the impact of the modification on the molecular weight of derivative.
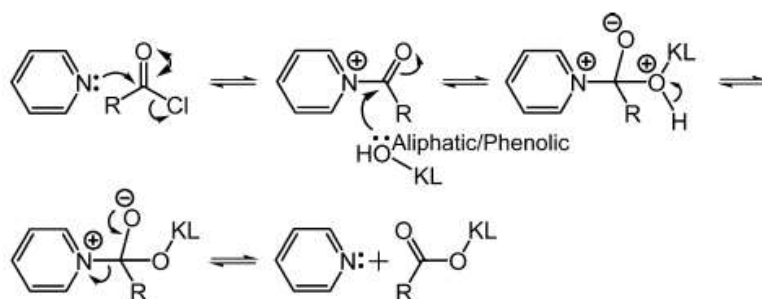
Figure 9 the esterification of Kraft lignin using fatty acid chloride. Reprinted with the permission from ref. [31] Copyright 2016 America Chemical Society

The reaction with acid chlorides showed a slight selectivity towards the aliphatic OH group, in comparison with the aromatic OH group.[31, 160] This reaction was further evaluated based on the principles of green chemistry:

1) Except for the renewable lignin resource, chemical reagents or solvents involved in this reaction are typically toxic or highly flammable such as DMF or THF, pyridine, and the halogenated fatty acid;

2) Moreover, the mixture of reagents with different types of solvents would lead to a higher cost for solvent recovery and potentially increase the E factor of the whole process;

3) The conversion rate is not especially high, and this is evident for longer carbon chain fatty acid chloride reagents.

4) Once the reaction finished, it is very difficult to thoroughly remove the unreacted long-chain fatty acids from lignin, which may negatively impact the properties of subsequent materials.

1.12.1.3   The application of esterified lignin derivatives

Esterified lignin has been an excellent resource for further lignin characterization because of its enhanced solubility allowing an analysis of its molecular weight (GPC)[167, 168] and chemical structure (NMR),[169] and provides enhanced miscibility when blended with other plastics.[170] Lignin ester derivatives can be used to produce water vapor and oxygen barriers for fiber coating materials. Hult and co-workers modified Kraft lignin with palmitic chloride acid; this modified lignin derivative was used as a coating for the paper board, which showed hydrophobic properties with contact angle around 110°.[160]

Lignin can also be used as thermoplastic materials, blended with other polymeric materials including both biodegradable polymers or non-degradable polymers. Without modification, lignin can be blended with non-degradable materials such as polypropylene,[158] polystyrene,[171] and polyethylene.[172] In some applications, the ArOH group in lignin can scavenge free radicals, and thus can be used as stabilizers against UV radiation.[152] However, the addition of unmodified lignin will cause an important issue on the homogeneity of lignin/polymer blends. Therefore, the esterification was widely used to improve its miscibility with a variety of hydrophobic polymers.[152] Though the addition of lignin will make negative impacts on the tensile strength of polylactic acid, the extent of decrease for acetylated lignin is much smaller than unmodified lignin.[173] (**Figure 10**)
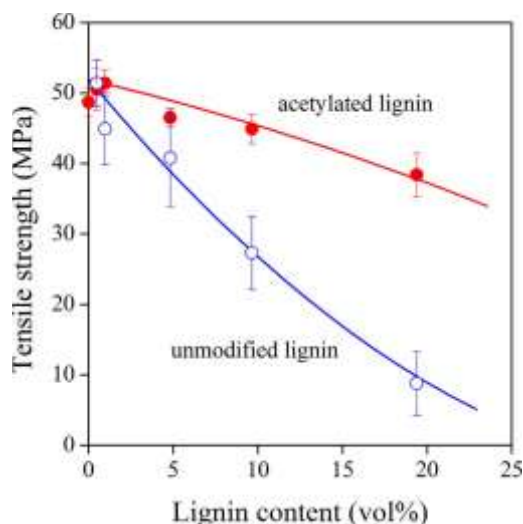
Figure 10 Tensile strength of lignin/PLA blends as a function of lignin and acetylated lignin content Reprinted with permission from ref [152] Copyright 2017 Elsevier

Glasser et al. adopted derivatized lignin to blend with biodegradable polymers such as cellulose acetate butyrate, polyhydroxybutyrate (PHB), starch-caprolactone copolymer (SCC) by solvent casting or melt processing.[157] They found that the addition of lignin ester derivatives and unmodified lignin had different effects on properties of those materials dependent upon the ratio between lignin and polymer. Noteworthy, adding 10% lignin or 20% lignin ester derivatives had enhanced the tensile strength of SCC co-polymers. Further, the addition of unmodified lignin and lignin ester derivatives had substantial impacts on crystallization temperature (T_c) and melting temperature (T_m) of the final material. Conversely, adding lignin will make negative impacs on the tensile strength and modulus of the cellulose acetate butyrate materials.[157] McDonald and his collaborators blended lignin ester derivatives (stearyl chloride) with poly(3-hydroxybutyrate-co-3-hydroxyvalerate (PHBV) by melt processing.[158] The two materials showed good compatibility with an improvement in the tensile strength and elongation at break. Esterified lignin may play the role of a plasticizer, but larger amounts than 20% negatively impacted the performance of the material. Additional lignin amounts typically would make the material full of defects and cause issues for further processing. Gordobil et al. blended esterified lignin (dodecanoyl chloride) with polylactic acid (PLA).[102] They found that the added lignin ester derivatives served as a plasticizer and improved the elongation at break and ductility, while reducing the rigidity of PLA.

1.12.2 Copolymerization

1.12.2.1 Ring-opening copolymerization

Ring-opening copolymerization is used for the preparation of heterochain polymers by using monomers such as cyclic ethers, cyclic esters, and cyclosiloxanes. One green characteristic of this reaction is that there are no by-products formed during this process. Some polymers formed with these monomers include polylactic acid[174] and polycaprolactone[175]. Using lignin that was copolymerized with similar monomers improved the properties of the lignin-based blends with materials such as polylactic acid or poly(ε-caprolactone). Sattely and co-workers reacted lignin with lactic acid using organocatalysts without additional solvents at 130-140 °C for 2–4 hrs.[176] It was found that a small amount of the co-polymer of lignin-g-PLA improved the stability of PLA under UV conditions. Without sacrificing the tensile modulus of the original PLA, adding a slight amount of modified lignin (0.4%) also surprisingly improved the tensile strength and strain at the break of the PLA substantially. However, this small addition of modified lignin is not enough, considering the urgent requirements for cheaper and renewable bioplastics. Chile et al. adopted graft copolymerization to synthesize lignin-graft-poly(lactide).[174] Three routes included two types of "grafting from" strategy (using racemic lactide as reagent, route 1: indium as catalysts, route 2: 1,5,7-triazabicyclo[4.4.0]dec-5-ene(TBD) as organocatalyst) and one type of "graft to" strategy, and route 3 using halogenated polylactic acid as reagent and K_2CO_3 as catalyst. Results showed that all these methods could produce star-like graft copolymers and cyclic polymers. However, at a higher lignin loading (>10%), they found that the star-graft copolymers are preferentially generated, while the low lignin loading will preferably produce cyclic PLA. They also blended this lignin-graft-PLAs with pure PLA polymer. Less than 10% addition of lignin could improve the elastic response since some modified lignin was used as a plasticizer to the matrix.

1.12.2.2 Atom transfer radical polymerization (ATRP)

The ATRP process is a very effective radical polymerization process that requires milder reaction conditions (room temperature for 24 hrs) in comparison with cationic or anionic polymerization.[162] In this process, 2-bromoisobutyryl bromide (BiBB) reagent was used to obtain BiBB modified lignin. (**Table 4**) This modified lignin was an excellent precursor for ATRP polymerization, especially for the reaction with acrylate monomers. Meanwhile, BiBB modified lignin had a higher solubility in some solvents than unmodified lignin, especially low boiling-point solvents such as

THF, acetone, dichloromethane.[177] (**Figure 11**) However, this reaction needed improvement to satisfy the requirements for green chemistry. Like similar reactions using halogenated compounds, toxic reagents, and solvents (DMF) involved in the process makes the separation and recovery at the end of reaction extremely important and may subsequently increase the E-factor. As a result, materials based on this process are costly and have limited applications except for fields with value-added products such as biomedical and personal care materials.[175] For example, Shah et al. and Dan et al. and adopted ATRP to obtain lignin copolymers.[178] They firstly obtained BiBB-modified lignin, which was then used as a macroinitiator. (**Figure 11**) Dan et al. adopted this to react with poly(ethylene glycol) methyl ether methacrylate (PEMG) in acetone at room temperature by two types of catalysts: both metal and organic compounds. The resulting lignin-PEGMA copolymer showed higher thermal stability. Using phosphate-buffered saline as a solvent, this lignin-copolymer could be used as self-healing materials by adding cyclodextrin as a "guest" based on reversible host−guest inclusion complexation, pushing the boundaries of lignin-based materials.[178]
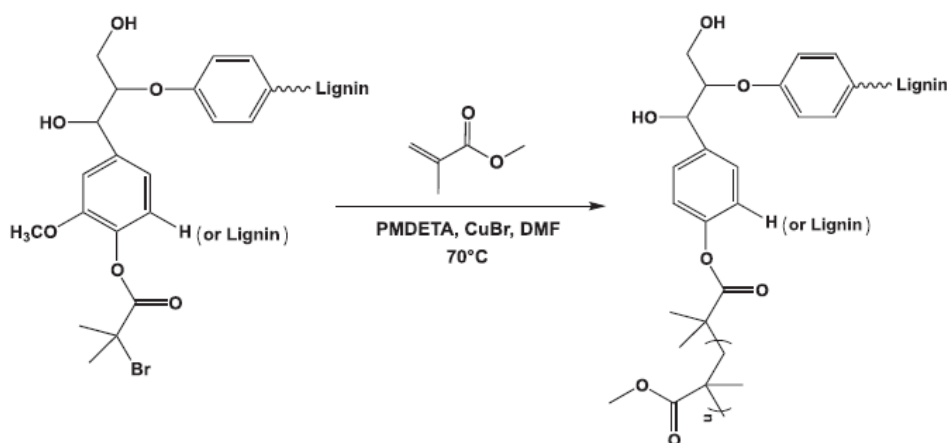
Figure 11 Methyl methacrylate polymerization from a lignin-based ATRP initiator. Reprinted with the permission from ref [179] Copyright 2015 Elsevier

1.12.2.3   Other methods

Different from those processes, lignin was also copolymerized with diacids to produce lignin-ester thermoplastic materials, with strong acid or alkali used as catalysts.[180, 181] Along these lines, Naskar and co-workers at Oak Ridge National Laboratory developed a promising lignin-based thermoplastic material by the copolymerization between lignin and dicarboxylic-terminated

polybutadiene.[181] In detail, they used methanol fractionated lignin to react with (PBD-(COOH)$_2$) using KOH as a catalyst in dioxane at 100 °C for 24 h. The newly formed lignin-polybutadiene copolymer contained not only ester bonds but also ionic bonds from carboxylic acid groups on the lignin fragments. In this copolymer, the lignin fragments served as hard segments to provide robust mechanical properties, while polybutadiene had a lower T$_g$ and provided rubbery flow characteristics. (**Figure 12**)
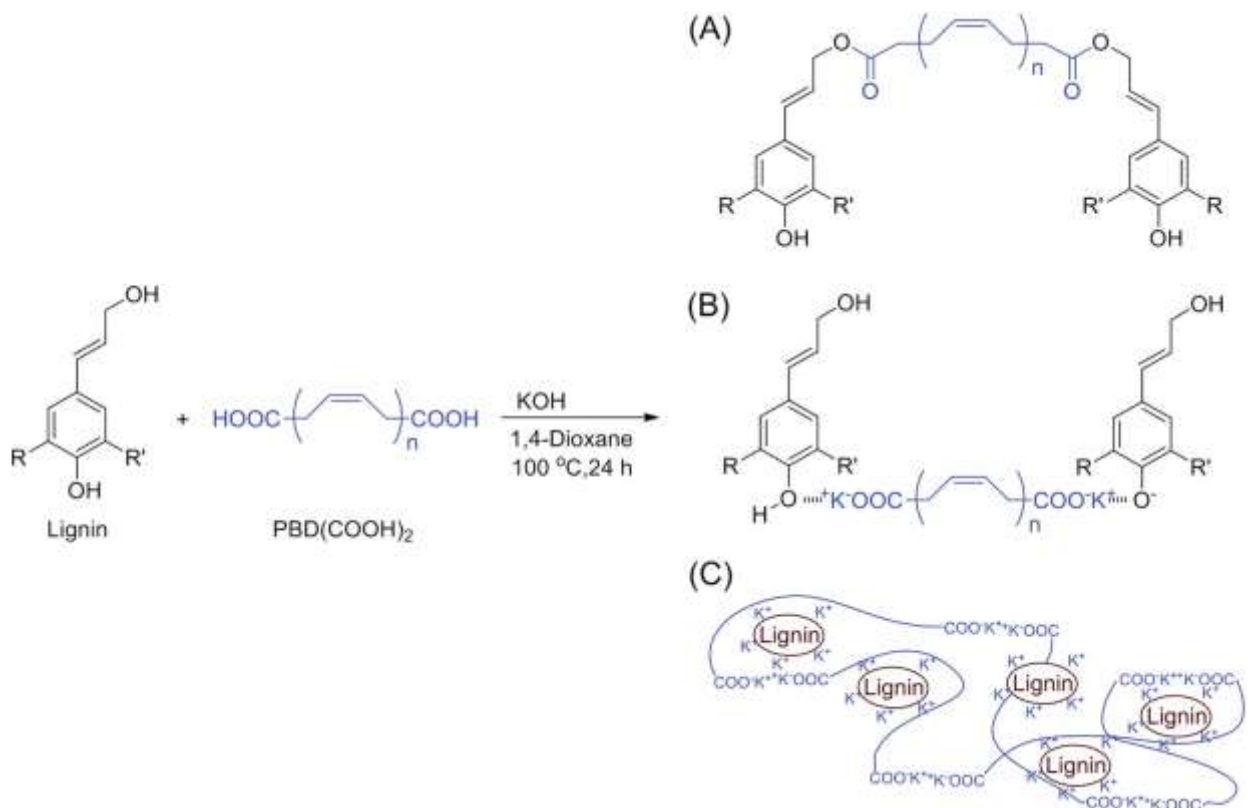
Figure 12 Lignin-polybutadiene linkage: ester linkage (A), ionic linkage (B), and interpenetrating network (C). Reprinted with permission from Ref. [182] Copyright 2016 Royal Society of Chemistry

Lee and co-workers used the hydroxypropyl process to modify methanol insoluble Kraft lignin and further reacted the hydroxyalkyl derivative with (PBD-(COOH)$_2$) at a high temperature of 100 °C in dioxane using H$_2$SO$_4$ as catalysts. This lignin-based polyester had more stable thermal properties than non-hydroxypropylated material. [178] Griffini et al. fractionated lignin by THF to obtain THF soluble lignin fraction. By using succinic anhydride, they selectively modified the aliphatic OH group into carboxylic acid functional groups. [161] The newly formed lignin derivatives

could be a precursor for polymeric materials. By adding hexamethoxy methylmelamine as a crosslinking reagent, the resulting coating with the lignin acid derivative showed good mechanical hardness and hydrophobic properties. As this lignin contained both ArOH and COOH groups, it allowed this derivatized lignin to further polymerize using NaHP as catalysts.

Evaluating these copolymerization reactions from the perspective of green chemistry, reagents such as diacids involved in this reaction are safer and more stable than conventional halogenated compounds. The atom economy is also higher due to the formation of water as a byproduct. These newly created materials, whether for coating or thermoplastic materials, extend the application field of lignin. However, there is a need to further improve the reaction conditions including greener catalysts and solvents for this system. In addition, fractionation is always the first step to convert those lignin resources, which would further increase the E-factor for this process if the other lignin is not utilized.

1.13 Lignin-based polyurethane

Polyurethane materials were first discovered in 1937 by Germany chemist Otto Bayer.[183] In the beginning, this material was developed as an elastomer; a type of material has a low Young's modulus and an extremely high failure strain. Later, this material showed additional applications in the field of construction materials such as polyurethane foams, coatings, and adhesives, and account for more than 5% annual consumption of polymeric materials.[184]

Two types of compounds, including polyisocyanates and polyols, are reacted by addition reactions to make polyurethanes. (**Figure 13**) Properties of the resulting materials are controlled by selecting different types of compounds with specific chemical structures from rigid aromatics to flexible aliphatics. However, the preparation process can cause serious health and environmental problems due to the use of toxic chemical reagents and nonrenewable compounds. Moreover, the toxic polyisocyanates are mainly made by the reaction between toxic phosgene and diamine.[185] As the increasing global demand for polyurethane, it is urgent to develop a greener synthesis route for this material.
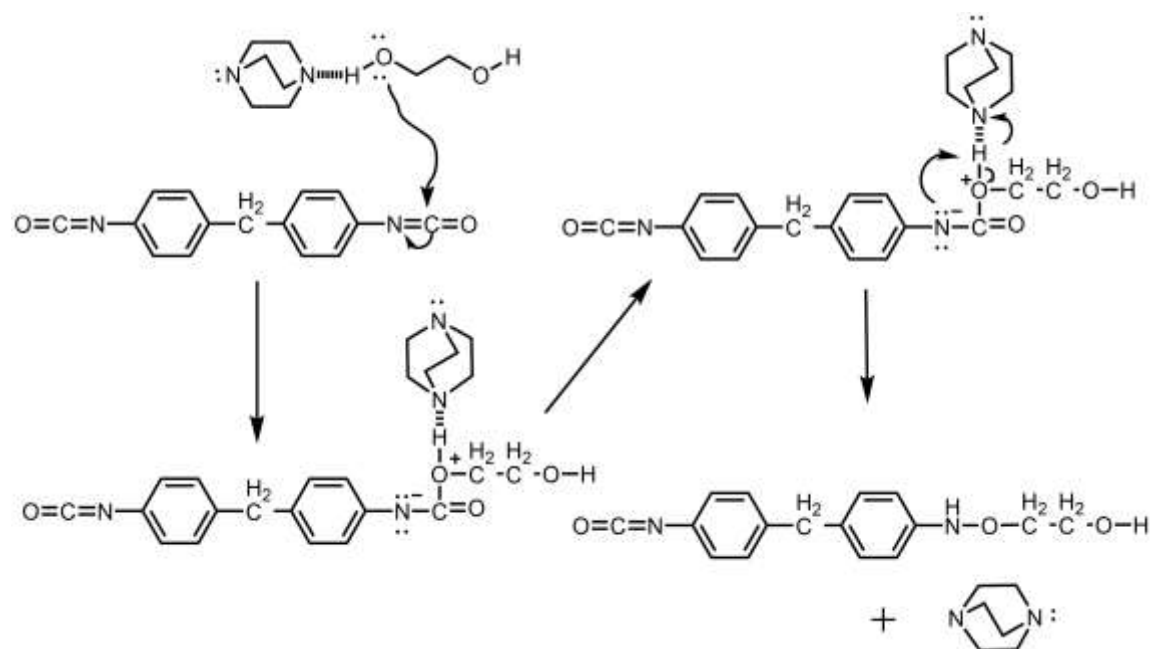
Figure 13 Reaction mechanism to synthesize polyurethane

Typically, the polyol includes a possibility of two chain types: polyester polyols or polyether polyols. Compared with polyester polyols, polyether polyols account for 69% of the whole production of polyol[186] for polyurethane foam due to the low viscosity, more extensive polydispersity index, and stronger polyurethane foams.[187] Some representatives of polyether polyols are polypropylene glycols (PPG) or polyethylene oxide (PEG). These polyol compounds are polymerized by monomers derived from fossil fuel. Due to the environmental costs associated with petroleum use, researchers are now paying more attention to the adoption of renewable resources derived from plants.[188] As lignin contains a large amount of OH group, it has been used as one of the alternative polyol precursors to produce polyurethane materials.[189]

1.13.1 Lignin-based polyol

Since technical lignin generally has a T_g over 90 °C, lignin polyol is a solid form at room temperature. Lignin is difficult to directly react with polyisocyanate to produce a foam with the appropriate blowing agent. Therefore, when preparing lignin-based polyurethane foams, researchers blend lignin or modified lignin with traditional petroleum-derived polyols.[190] Without any modification for lignin, a limited amount of technical lignin (10%) can be adequately mixed with the polyol for subsequent PU foam formation.[188] To address this issue, researchers have

developed procedures to modify lignin to improve their solubilities in polyols or copolymerize with other monomers to obtain liquid-based lignin polyol.[187] Depending on the modification method, lignin-based polyols can also be classified into polyether or polyester polyols.

1.13.1.1 Polyether polyol

To make a liquid lignin-based polyether polyol, the oxypropylation reaction has been carried out to extend the aromatic hydroxyl groups at high temperature (180 °C) by using propylene oxide that derivatizes the lignin and forms a co-polymer (**Figure 14**).[180, 187, 191] The reaction mechanism is similar to previous etherification methods by epoxide compounds. Nadji et al. explored the oxypropylation for different types of lignin resources.[36] In general, soda lignin and organosolv lignin were more reactive than Kraft lignin as the reaction was completed in shorter time periods. For this reaction, the total OH group number of the produced lignin polyol was between 100 and 200 mg KOH/g. Cateto et al. explored the reaction conditions for the oxypropylation when the lignin/PO ratio was 20/80 near the 20% limit of modified lignin mixed in the polyol. The obtained lignin polyol had the lowest viscosity (5 Pa/s), which satisfied requirements for PU foam formation.[192] The obtained foam showed a closed-cell structure with good thermal conductivity. Xu and co-workers studied this polyol reaction by using depolymerized Kraft lignin (DKL) as a raw material.[191] This polyol was made by the copolymerization of DKL/propylene oxide/glycerol mixed in acetone with KOH as a catalyst. The formed liquid polyol contained about 50% of the biobased components and resulting PU foam showed similar thermal conductivity and mechanical properties to PU foam made from pure PPG.
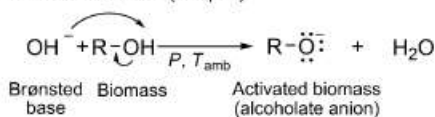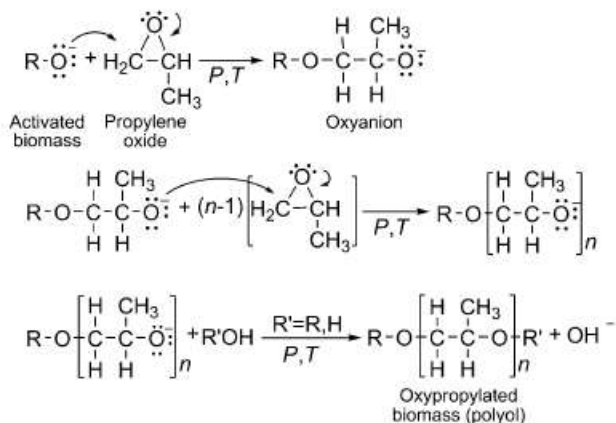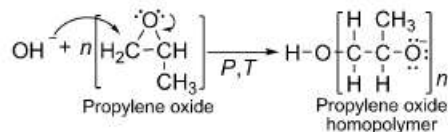
Figure 14 Representative scheme of the oxypxypropylation of biomass. Reprinted with the permission from ref [187] Copyright 2012 Wiley-VCH Verlag GmbH& Co. KGaA, Weinheim

1.13.1.2 Polyester polyol

Avérous et al. used oleic acid and organosolv lignin as raw materials to obtain lignin-based polyester polyol as a building block using a multi-step modification method.[166] The oleic acid was first converted to oleoyl chloride using a chlorination step, followed by esterification with organosolv lignin in an alkaline solution. The double bond in the unsaturated oleic acid was further modified using peracetic acid at room temperature, following epoxidation. The obtained epoxidized lignin oleate was further reacted with methanol to produce lignin-oleic acid polyol (LOAP) utilizing the catalyst, para-toluene sulfonic acid (PTSA). (**Figure 15**) The LOAP dissolved in THF, and the prepolymer and isocyanate were polymerized in a certain ratio by solution polymerization, and the mechanical properties of the obtained PU foam were measured as a function of the molecular weight of the soft PPG segment.

Lignin-Oleic Acid based Polyol- **LOAP**
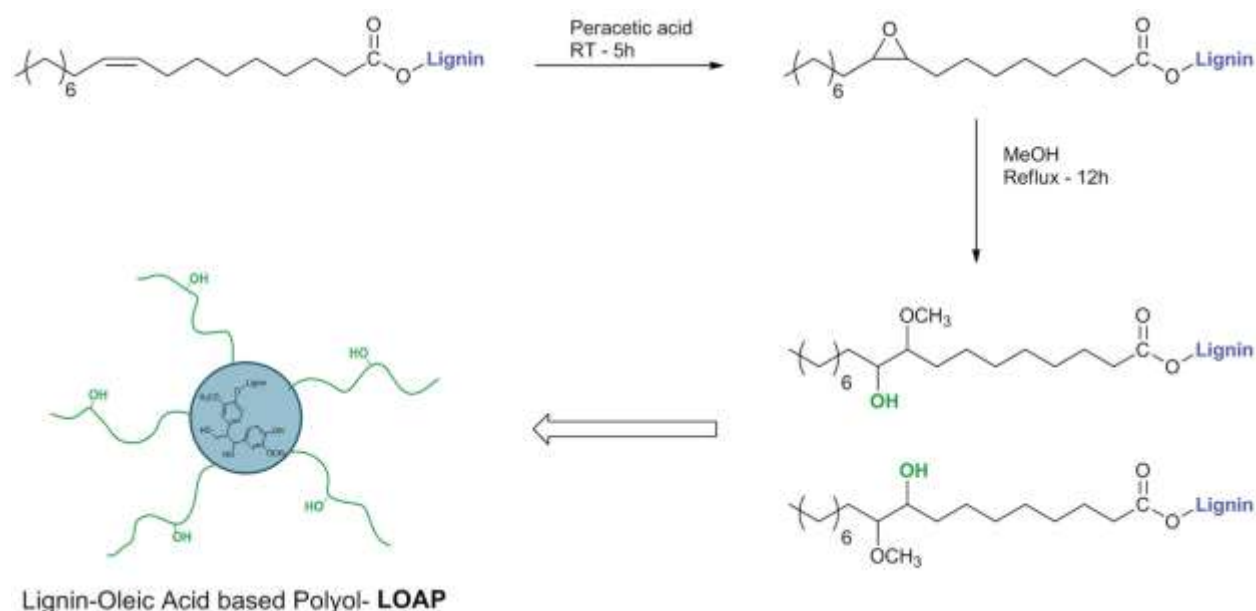
Figure 15 The synthetic polyester polyol from lignin and oleic acid. Reprinted with permission from ref [166] Copyright 2014 Royal Society of Chemistry

1.13.2   Non-isocyanate approaches

In addition to finding renewable polyol resources, a more urgent problem is finding safer and more stable reagents and greener reaction pathways to replace traditional toxic isocyanate compounds to produce polyurethane materials. One promising method is to use cyclic carbonate compound to react with diamine reagents producing polyurethane linkages, which now has been adopted by industry.[193] (**Figure 16**) As discussed above, cyclic carbonate compounds are generally seen to fit into a green chemistry pathway. This reaction route was awarded the 2015 Presidential Green Chemistry Challenge.[194]

poly(hydroxy-urethane)
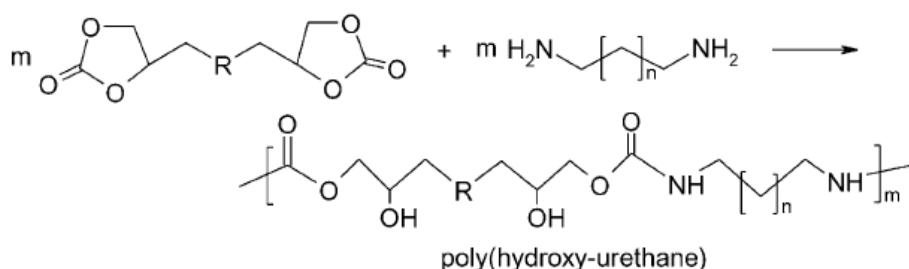
Figure 16 The polycondensation reaction of diamine and diethylene carbonate. Reprinted with permission from ref. [195] Copyright belongs to

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This non-isocyanate route was developed in the 1960s, attributed to Groszos et al.[196] Later, Garipov, etc. studied the reaction mechanism and kinetics; two stages were involved for this reaction.[197] In the first stage, a nucleophilic attack of the amine at the carbonyl group resulted in the formation of a tetrahedral intermediate. In the second stage, a sequenced attack by another amine at the tetrahedral intermediate resulted in the removal of hydrogen ions. Finally, favored by the strong electron-withdrawing effect of nitrogen atoms, the carbon-oxygen bond was cleaved, and the newly generated alkyl-oxygen ion combined with hydrogen ions, resulting in a rapid formation of the product. As a type of addition reaction, the atomic economy can reach 100%. The cyclic carbonate not only shows a high reactivity toward the diamine but also was used as a solvent. Further, properties of the resulting polyurethane changed dependent upon the chemical structure of monomers.[198] The polyurethane made with this method showed excellent performance in its chemical resistance and limiting water absorption. Therefore, this polyurethane was used in coating and adhesion applications, as well as a matrix for fiber-reinforced materials.

This non-isocyanate route was also applied to prepare lignin-based polyurethane materials. Lee and co-workers adopted lignin and soybean oil as raw materials to make green polyurethane films. The unsaturated bonds in soybean oil were converted into epoxidized compounds and further reacted with CO_2 for the preparation of carbonated soybean oil. The carbonate group was then reacted with (3-aminopropyl)triethoxy silane. By adding lignin for curing, the ethoxy silane group would not only undergo self-condensation but also have condensation with the aromatic OH group to form the non-isocyanate polyurethane lignin.[199] The resulting thermoplastic utilized the soybean oil chain as the soft segments, while the aromatic structure in lignin functioned as the rigid segment.
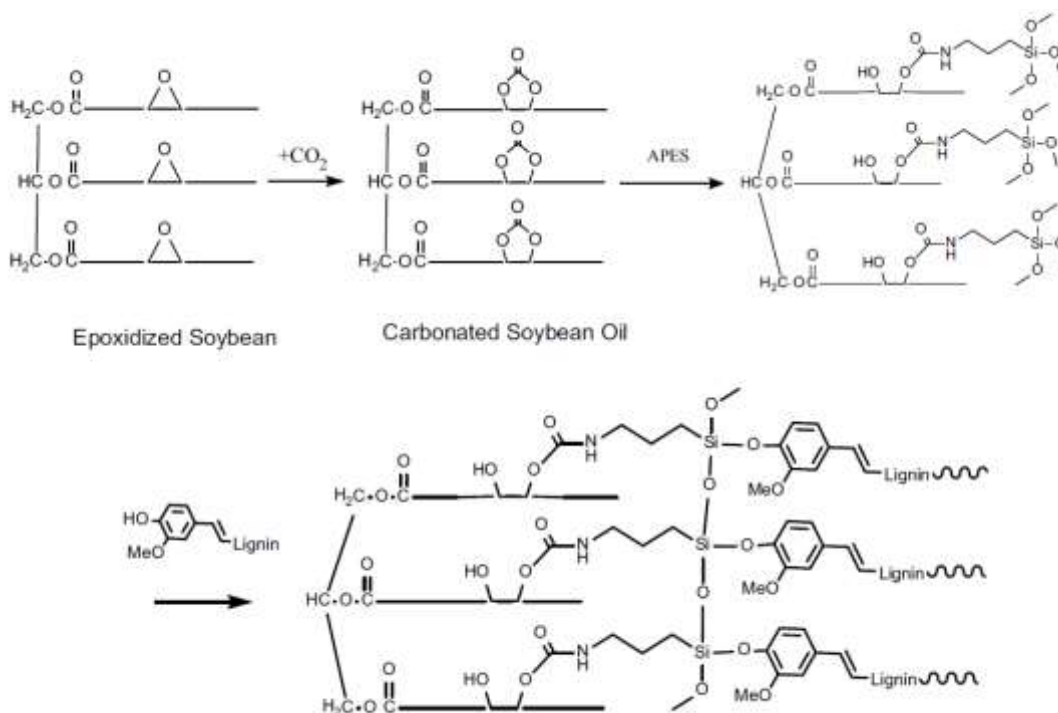
Figure 17 Schematic illustration of lignin-based polyurethane. Reprinted with permission from ref. [199]. Copyright 2015 Elsevier

Different from this method, researchers developed a promising route to modify the OH groups in lignin to obtain carbonated functionalized lignin. One way was to use epichlorohydrin to react with lignin to obtain epoxidized lignin.[200] The epoxidized group in this compound was further reacted with CO_2 to obtain carbonated lignin in the ionic liquid. In this process, the imidazolium-based ionic liquid was used both as a solvent and as a catalytic group, so that the epoxidized group was fully converted into a carbonate group. Zoia et al. used Kraft lignin and soda lignin as raw materials. The content of the carbonate compounds in the obtained lignin was about 2 mmol/g.[201]

These methods, in which lignin was reacted with epichlorohydrin for the epoxidized group functionalization, rely on a highly toxic reagent (Epichlorohydrin). In contrast, Kühnel et al. used a two-step procedure to convert the OH groups in lignin to carbonate groups.[202] Specifically, using glycerol carbonate as a solvent and a reagent, the organosolv lignin was converted to an oxyalkylated lignin at 170 ° C for 3 hrs. Then the transesterification reaction was carried out using dimethyl carbonate or ethylene carbonate in an alkaline DMSO solvent. (**Figure 18**) The conversion rate of this reaction process reached 95%, and the carbonate groups contained in lignin

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reached 1.54 mmol/g. Overall, this simple reaction process with high efficiency avoided the use of toxic and unstable epichlorohydrin reagent. As a result, the reaction process was improved with the by-products of mainly CO_2, and so the E-factor was lower and the reaction considered greener.
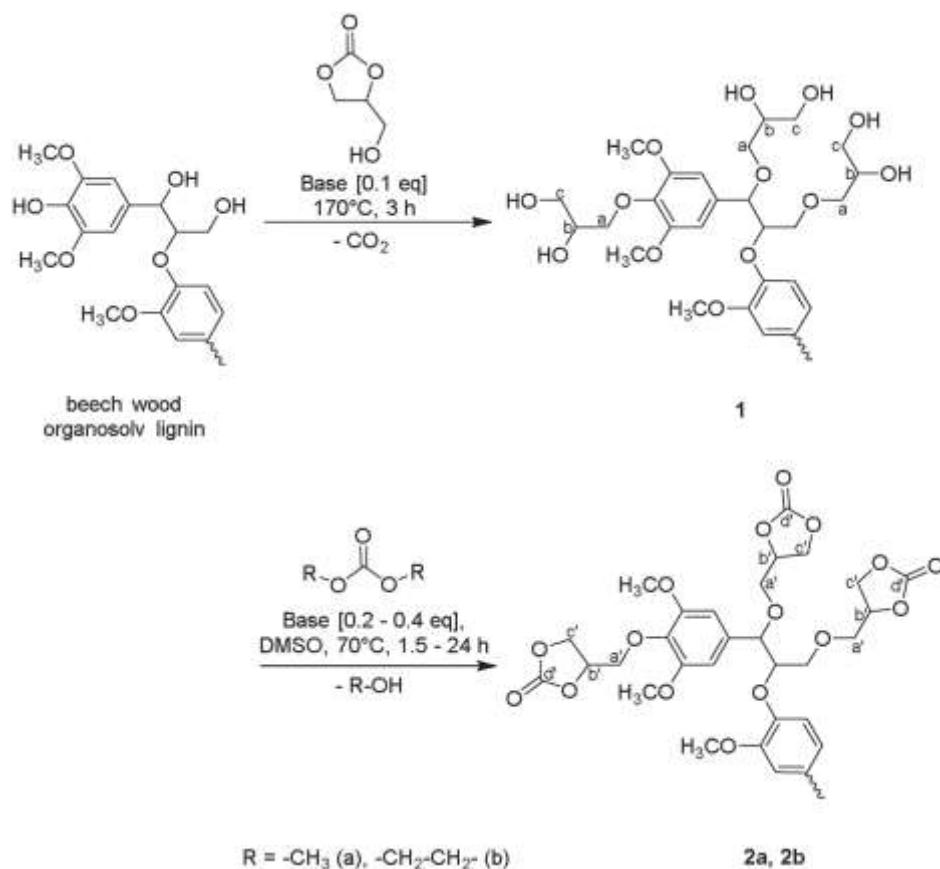
Figure 18 Two-step synthesis involving oxyalkylation with GC generating lignin terminated with a 1,2-diol function (1) and transesterification with DMC or EC to cyclic carbonate functionalized lignin. Reprinted with permission from ref. [202] Copyright 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

1.14 Why are green modification methods important for future lignin utilization?

1.14.1 Introduction of green chemistry

In the middle of the last century, the traditional production process for chemicals and polymer materials based on fossil fuel began, which has led to a severe environmental crisis. A landmark event is the publication of Silent Spring (in 1962), which expounded the environmental problems brought by the application of pesticides.[203, 204] Without considering negative effects of those pesticides, the adoption of toxic dichlorodiphenyltrichloroethane (DDT) as pesticide caused a

catastrophic impact on the environment: animals and plants, especially birds and insects, suffered from the potential of extinction. Fundamentally, this was a problem with sustainable chemical reactions and compounds; in other words, it was necessary to look for products and chemical reaction processes and reagents that were more specific and environmentally friendly.[205] As a result, the contradiction between environmental protection and the development of human society has aroused public attention and discussion. A series of environmental protection movements were launched, which indirectly led to the establishment of the US Environmental Protection Agency (EPA) in 1970. Moreover, the increasing shortage of traditional fossil fuels further promoted the government and industry to concentrate on renewable resources, which is a tenant of green chemistry.[206]

In 1998, American chemists Paul Anastas and John Warner proposed the twelve green chemistry principles based on a large number of previous works, such as atom economy and E-factor. These principles aim at designing products and processes that effectively reduce or even eliminate the utilization and production of toxic materials.[38] At the same time, the EPA established the US Presidential Green Chemistry Challenge Award, which is designed to award companies and scientists who have successfully used the concept of green chemistry in their research or production processes.[207] Since then, the concept of 12 principles of Green Chemistry (**Figure 18**) it has been accepted by researchers, industry people, and government and applied in various fields such as Chemistry,[208-210] Materials,[210] and Engineering[211].

Figure 19 Twelve fundamental principles of green chemistry Reprinted and modified with permission from ref.
[37] Copyright 2010 Royal Society of Chemistry

1.14.2 Atom Economy and Environmental Impact Factor

The most widely used evaluation metrics of green chemistry are atom economy (AE) and environmental impact factor (E-factor), with the latter as a backbone for other metrics. These metrics can help researchers quickly evaluate the economic and environmental benefits of the reaction process. The atom economy was firstly proposed by Barry Trost in 1990.[212] It was calculated based on equation 1. The ideal chemical reaction process has an atomic economic indicator of 100%, which means all original reagents have been converted into final products. Therefore, the addition or cycloaddition and rearrangements (atom economy= 100%) are more ideal reactions than substitution and elimination reactions.[212, 213]

$$Atom\ Economy\ (AE) = \frac{Molecular\ weight\ of\ product}{Molecular\ weight\ of\ reagents} \qquad (1)$$

The E-factor was proposed by Roger Sheldon in 1992, which was used to measure the waste produced during the reaction process, which will significantly impact the environment as well as profitability.[214] Equation 2 is the simple E-factor, while equation 3 is to calculate the complete E-factor; the lower E-factor means a lower output of waste products, which would lead to a more environmentally friendly process. In comparing with the theoretical value determined by the atom efficiency, E-factor is more practical to assess the environmental impact of one reaction. As indicated in the equation (3), the E-factor will consider the yield of products, the solvent recovery, and catalysts, in addition to the original reagents. Given the acceptance of the E-factor and the limitations, researchers also developed other factors such as solvent intensity, waste-water index, and process mass intensity to evaluate the impacts of solvent, wastewater, and mass inputs.[43] These factors provided researchers or industry with quantifiable tools to measure and assess the efficiency of chemical reaction processes. Overall, to realize the reduction of the waste during the reaction, researchers should focus on greener processes, such as developing recyclable and reusable catalysts, reducing the amount of organic solvent or adopt a solvent-free reaction, and avoid using highly toxic or dangerous reagents.

$$sEF = (\sum m(raw\ materials) + \sum m(reagents) - m(products))/m(products) \qquad (2)$$
$$cEF = (\sum m(raw\ materials) + \sum m(reagents) + \sum m(solvents) + m(water) - m(product))/m(product) \qquad (3)$$

1.14.3 Greener catalysts
The use of catalysts to achieve results with significantly decreased inputs such as energy is an important aspect of green chemistry (**Figure 19**). In addition to catalysts being non-stoichiometric in the reaction, they reduce the activation energy required for the reaction to proceed and accelerate the reaction rate. On the premise of ensuring efficient reaction processes, the adoption of rational catalysts would be helpful for the optimization of reaction conditions such as lowering the temperature and/or pressure and reducing amounts of chemical reagents.[215] For natural biopolymers, the isolation and modification process usually requires low-intensity reaction

conditions to minimize changes to the native structure. Therefore, using catalysts is one of the crucial steps.

A good example is that catalysts can play an important role in the preparation of cellulose nanofibers. This nanomaterial, which has a diameter of less than 100 nm with high mechanical stiffness (143 GPa), was studied as a reinforcing reagent,[153] aerogel component,[216] and even transparent displays for electronic screens.[217] Isogai and co-workers[218] developed an innovative oxidizing process to obtained cellulose nanofibres in replace of traditional methods using strong acid as catalysts.[219] In detail, they dispersed cellulose pulp into alkali and then added 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) as a catalyst. The primary aliphatic hydroxyl groups in the cellulose chains were oxidized by adding oxidizing reagents such as NaClO with controlled pH=10 at room temperature. After the reaction, the primary OH group of cellulose was converted into carboxylic acids, when deprotonated in its ionized form helped to isolate individualized fibrils. This process satisfied the requirements of green chemistry due to these merits: 1) the room temperature reaction conditions; 2) the high conversion rate; and 3) the real-time control for the reaction process by measuring the pH.[42] Further avoiding waste and reusing the catalysts, Patankar and Renneckar developed reusable and recoverable TEMPO catalysts, by reacting this reagent onto the magnetic nanoparticles. This new type of catalyst could be recycled for repeated utilization.[220] Further, this catalyst was also used to oxidize Kraft lignin to achieve the depolymerization of lignin in preparing different types of aromatic monomers.[221]

Another good example is the adoption of lipase enzyme as catalysts for the degradation of polyesters and the esterification and transesterification of dicarboxylic acids,[222] diols, and lipids in making polyester materials or biodiesels. For the latter esterification, the organic solvent with logP value(2 - 4)[223, 224] is necessary to create a hydrophobic environment to open the pocket structure of lipase.[222] The catalytic serine residue is located at the bottom of a deep and narrow pocket. **Figure 20** shows the macromolecular biological catalysts, with high selectivity toward various OH groups achieving milder reaction conditions. Depending on the organisms, the most commonly used lipase in organic synthesis included *Canadian antarctica* lipase B,[225] *Rhizomucor meihei* lipase,[226] *Canadian rugosa* lipase,[227] and *Pseudomonas cepacia* lipase[228]. The commercial *Canadian antarctica* lipase B (CALB) is the most widely used and has been an efficient enzyme for industrial

adoption. Moreover, this enzyme was immobilized on a porous acrylic resin, which had a particle size of 0.3 to 0.9 mm, for enzyme recycling.[229]

An important application of this lipase was to make polyesters for the polymer industry. Gross and his collaborators developed a new process to make polyesters by using lipase as a catalyst. The esterification reaction was completed under mild conditions (lower temperatures) with high selectivity (primary hydroxyl selection vs. secondary hydroxyls). For example, they produced polyester polyol by the reaction between glycerol, diol, and adipic acid which had selectivity towards primary hydroxyl groups in glycerol with the lipase catalyst at mild conditions. This lipase catalyst satisfied requirements for green chemistry by replacing the heavy metal catalysts and the use of strong acid for traditional polyester synthesis. As a result, Richard A. Gross won the 2001 Presidential Green Chemistry Challenge Award for this process.[207, 230, 231]
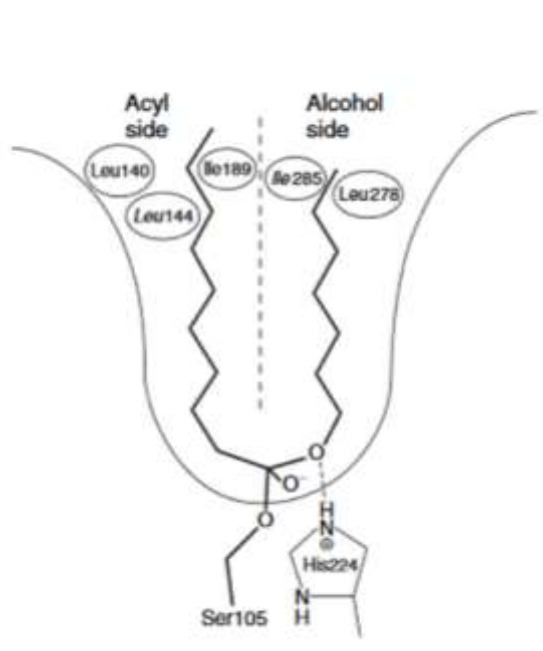
Figure 20 Micro-structure of lipase enzyme. Reprinted with permission from ref [222]. Copyright 1995 American Chemical Society

1.14.4 Greener solvent and reagent

Using a solvent to dissolve lignin is always the first step to modify or convert lignin resources in homogeneous reactions for high-value applications. However, there are some drawbacks of using

additional solvents; it will impact the E-factor of the entire reaction process. There is also a problem for those residual solvents since the best solvent for the first step is potentially bad for the subsequent processing and separation steps.[232] Moreover, utilizing solvents may produce a large amount of volatile organic compounds (VOC) causing serious health and environmental problems.[233] For the conversion of lignin, a widely adopted toxic solvent is dimethylformamide (DMF), which is an excellent solvent for lignin dissolution in preparation of plastics,[160] and carbon fibers.[153] Due to its toxicity, this solvent was recently restricted in European countries for consumer products, and most likely, will be banned in other countries. So, it is necessary to find new greener solvents for biopolymers.[234]

Fortunately, greener solvents such as ionic liquids, deep eutectic solvent, and organic carbonates were developed in recent decades and applied in biopolymer conversion and transformation. Because of their high solubility towards lignin, these organic solvents have been applied for the isolation of lignin.[81] The ionic liquid is a compound composed of a cation (usually organic) and an anion with a relatively low melting temperature. It is stable and has very low vapor pressure, which makes it an excellent alternative organic solvent for eliminating VOCs during processing. The invention of ionic liquid dates back to 1920s, but it has attracted researchers' attention in recent years. Rogers and his collaborators found that IL could effectively dissolve cellulose components without additional pretreatment.[235] Since then, researchers began to use different types of ionic liquids to pretreat biomass to realize the fractionation of biomass with mild conditions for further high value-added fuels, chemicals, and materials.[236] Sathitsuksanoh et al. adopted recyclable and non-toxic ionic liquid, [C_2mim][OAc] to extract lignin from biomass. The isolated lignin showed a particular structure depending on the IL pretreatment conditions.[237]

Organic carbonate is an emerging organic solvent and is widely used in organic synthesis and catalytic processes since the 1960s. As a kind of aprotic highly dipolar solvents (AHD), it can be used as an alternative candidate for NMP or DMF, and other polar solvents. It is greener solvent and reagent due to its low toxicity and degradability. Since their high boiling point, it is a suitable alternative to replace VOC. Further, by ring-opening polymerization, it is also able to produce some polycarbonate polymers with appropriate reactive conditions.[238, 239] The organic carbonate compound is a suitable solvent for the organosolv pretreatment. Zhang et al. showed that wood

powders could be treated by the mixture of ethylene carbonate and ethylene glycol to dissolve the lignin and obtain cellulose materials for subsequent enzymatic hydrolysis.[240]

A cyclic carbonate generally has a higher boiling point, density, and viscosity than a linear carbonate. For ethylene carbonate and propylene carbonate, the main synthetic route for production is to use ethylene oxide or propylene oxide compounds to react with CO_2 to form carbonate analogs. Besides these routes, a greener approach is to use renewable diols to react with CO_2.[241] In contrast, the linear carbonates are mainly synthesized by the reaction of alcohol and phosgene compounds in industry. This process, of course, has drawbacks, which require an alternative route for the synthesis of dimethyl carbonate or diethyl carbonate. The most straightforward approach is the dehydrative condensation with CO_2. This reaction would allow organic carbonate to be treated as carbon storage chemicals. This may further improve the sustainability of reaction process based on these chemicals.[238]

1.14.5   Why green chemistry is important for lignin-based materials

In recent decades, lignins were studied not only by wood scientists but also by scientists with a background in other disciplines. It is an important topic for the green chemistry process, considering that lignin is one of the most important renewable resources. However, it is hard to imagine that lignin-based materials are sustainable materials if there is no consideration for greener processing during the modification. Lignin-based materials always include isolation, modification, and material preparation and design. All these procedures should be evaluated based on green chemistry principles.

Lignin can also cause serious environmental problems without a greener process. For example, it is difficult for some small-scale soda or Kraft pulping companies to recover lignin and salt from the waste black liquor due to the high cost.[242-244] Companies that adopted this pulping method are typically small and located in Asia and Latin American. These companies cannot undertake the intensive capital investment required for the recovery of lignin. Due to the incomplete legal system in some developing countries, illegal factories still dump black liquors without any treatment into rivers and lakes, causing serious environmental pollution. Though these drawbacks could be offset

by scaling up or adopting other isolation methods or developing new-advanced materials from lignin, the public would avoid the high-cost for environmental remediation.

Therefore, the 12 green chemistry principles should also be used to instruct the design of lignin-based materials, especially chemical modification or copolymerization of lignin. Actually, most chemical modification methods of lignin were developed before the 1990s,[244] when the green chemistry principles had not been proposed. Though those chemical methods developed a series of new advanced materials, the processes do not satisfy requirements for the greener process nowadays. So far, there are few published reviews focused on those derivatization methods with evaluation based on green chemistry principles. The goal of **chapter 1** is to measure the AE and E-factor of traditional lignin chemical modification and polymerization methods, along with the view of the degree of utilization and toxicity of reagents, solvents, and catalysts. These principles also illustrate the whole thrust of this thesis to develop greener and efficient modification techniques.

1.15   Conclusion

The biosynthesis of the three types of lignin monomers could date back to 400 million years ago.[245] This biopolymer has made significant contributions to help plants change the face of our earth and support various life. Lignin, ubiquitous in the cell wall of vascular plants, enhanced the mechanical strength of plants and the ability to transport water, thus helping plants effectively overcome Earth's harsh environment on land, which included fluctuating temperatures, intense ultraviolet rays, and wind. Further, it has been nearly two hundred years that researchers realized the existence of this remarkable biopolymer. Since then, lignin has been used as a resource for a diverse set of prototype polymeric materials that included epoxy-based circuit boards and polyurethane foams. These materials provided proof-of-concept ideas for substitution of fossil-based polymeric materials found within the built environment[18, 244]. These trailblazing studies were important to highlight the array of complex polymeric materials from lignin; however, they do not necessarily highlight how these materials can be synthesized utilizing green chemistry principles. Unfortunately, technical lignin from the pulping industry requires derivatization through chemical modification for widespread applications for reasons as shown below;

1) lignin has poor solubility in typical organic solvents stemming from its heterogeneity;

2) lignin has a variety of reactivities based on its functional groups (includes primary and secondary hydroxyls, phenolics, aldehydes, and carboxylic acids);[88, 246]

3) lignin is sensitive to elevated temperatures where uncontrolled reactions cause changes in molecular weight and its distribution;[101]

4) lignin is difficult to be thoroughly characterized to understand its chemical structure, molar mass, and resulting structural conformation.

The derivatization of lignin can be partly achieved with etherification or esterification. Traditional modifications provide a set of methods to produce methylated lignin[129, 136], "clickable" lignin[247], and hydroxyalkyl lignin[145, 200]. The methylation does not provide a clear route for additional modification steps. The introduction of "clickable" groups will significantly increase the cost of lignin-based materials. The low atom economy and high E-factor of modified lignin, further weaken the greener feature of using a renewable feedstock. Hydroxyalkyl lignin derivatives offered the opportunity to create reactive segments for step-growth polymers where the aliphatic hydroxyl groups served as a handle for further preparation of polyesters[248] and polyurethanes[249]. Based on the co-reactants that create segments, properties of these polymeric materials were tuned to form materials that range in properties from high modulus strong fibers[153] to extremely flexible plastics[107], and even coatings[250]. Therefore, hydroxyalkylated lignin was seen as a platform to prepare lignin for a set of advanced polymeric materials.

Overall, it is worth investigating more efforts to use lignin building blocks, utilizing more sustainable modification methods, to produce high-performance polymeric materials for society.
As discussed in the literature review, alkyl oxide or organohalide compounds were generally adopted to prepare hydroxyalkyl lignin derivatives; but these methods have chemical and environmental problems, such as low efficiency, low atom economy, high E-factors, explosiveness, and the utilization of carcinogenic compounds. Traditional hydroxyalklylation of lignin thus cannot satisfy the requirement of greener chemistry, which further limits the application of lignin-based materials.

Chapter 2: Hypothesis and objectives

In this thesis, we hypothesize that if we can replace traditional unsustainable etherified or esterified modification methods with the utilization of fundamental principles of green chemistry, we can create a greener platform lignin with engineered properties and well-characterized structure in order to make advanced lignin-based polymeric materials.
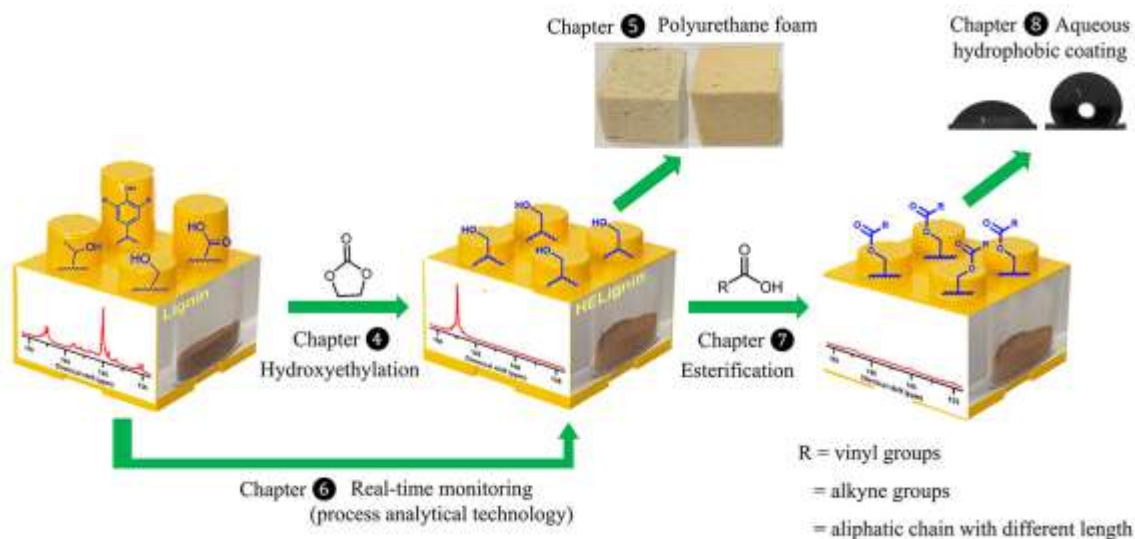
Figure 21 Major objective of each chapter. Reprinted with permission from ref [150]. Copyright 2018 American Chemical Society

Chapter 4 provides the framework of the thesis for a greener route to prepare hydroxyethyl lignin derivatives utilizing ethylene carbonate. In so doing, we can produce lignin derivatives with more uniform chemical functionality (90% of aliphatic hydroxyl groups) that would be a platform for further chemical derivatization and enhance the thermal stability of the lignin (**Figure 21**).

In chapter 5, the modified hydroxyethyl lignin derivatives and other derivatives of lignin were utilized as a partial polyol substitute to make lignin-based polyurethane foams. With the higher reactivity of aliphatic hydroxyl groups in the lignin, this modified lignin theoretically should have advances in making polyurethane and polyester materials. (**Figure 21**)

In chapter 6 a real-time monitoring technique was developed, which is also a green chemistry principle. Our hypothesis was that the amount of CO_2 produced during the hydroxyethyl reaction

as a byproduct from ethylene carbonate will have a direct relationship with the degree of modification. By developing a simple lab-designed process, the amount of CO_2 was quantitatively measured and used as a detector to control the modification. This work showed how the side reactions and cross-linking of lignin was manipulated via monitoring of CO_2. However, excess time and heat would cause the crosslinking of lignin with ethylene carbonate. An optimized condition was thus required for each lignin type making the reaction challenging to realize high-quality control of resulting hydroxyethyl lignin derivatives. (**Figure 21**),

In chapter 7 (**Figure 21**), a simple esterification reaction was developed to obtain esterified lignin derivatives, replacing traditional routes using toxic and unstable pyridine, anhydride, or organohalide compounds. The organic acid was used as catalyst, solvent, and reagent to modify the lignin. The pre-experiments showed that this esterification had high selectivity toward the aliphatic hydroxyl groups. Our hypothesis was that the hydroxyethyl lignin would be an excellent precursor for this esterification reaction. A series of organic acids were explored to engineer thermal properties of resulting lignin or add additional functional groups such as vinyl and alkyne groups, dependent upon the acid type. Further, multiple reactions in one pot recently emerged as one of the principles of green chemistry.[39] We also combined this two-step reaction of hydroxyethyl derivatization and catalyst-free esterification into one-pot.

If the lignin could be modified with hydrophobic aliphatic side chains and fully remove the hydrophilic hydroxyl groups, this would mimic natural wax and suberin like compounds. In chapter 8, our hypothesis was that if we can thoroughly esterify hydroxyl groups in lignin using oleic acid, we can prepare a kind of environmentally friendly hydrophobic coating material. In the work mineral acid was added as a catalyst to make a comparison with the catalyst-free esterification; the acid-catalyzed reactions led to a series of side-reactions for the lignin derivative.

Chapter 3: Materials and methods

3.1 Lignin resources

Softwood Kraft lignin: three types of industrial softwood Kraft lignin (SKL) were used in this research. Indulin-AT (SKL-IA), BioChoice (SKL-BC), and Amallin A™ (SKL-A) were kindly donated by MeadWestvaco Company (Now it was Westrock company, US), Domtar Company (CA, US), and West Fraser Company (BC, Canada), respectively. The Amallin A™ Kraft lignin (pH=4.2 at 15% solid contents) was first washed with distilled water until the pH reached 5 - 6 before drying in the freeze dryer.

Hardwood lignin: The hardwood Kraft lignin (HKL) and organosolv hardwood lignin (OSHL) were obtained from FPInnovations (BC, Canada) and Fibria Innovations (BC, Canada), respectively.

Organosolv bark lignin: Organosolv bark lignins were extracted from pine bark (softwood) and oak bark (hardwood). In detail, the ground bark particles (<2 mm) were submerged in aqueous ethanol (60% wt.) with the solid content 0.025-0.1 g/ml. Then concentrated sulfuric acid (98%) was added in a weight ratio of 1% (wt.) to solid bark content, used as a catalyst. After soaking overnight, bark samples were treated in a custom rotary digester (2 L, Aurora Products Ltd. Savona, BC, Canada) at 160 – 180°C for 1 hour. After cooling the reactor down, mixtures were filtered utilizing a Buchner funnel across Whatman No. 1 filter paper. The solid residues were washed with another 3×300 ml hot ethanol-water solution (60 °C). The lignin in the liquor section was subsequently concentrated utilizing a roto-evaporator. The concentrated solution was poured into 500 ml 0.01 mol/L hydrochloric acid to precipitate the crude lignin and residual extractives. The resulting organosolv bark lignin was further washed with another 2×500 mL 0.01 mol/L hydrochloric acid and dried in the vacuum oven (50 °C). The crude lignin yield was calculated based on the dry weight of bark. More detail explanation was shown in Appendix B.[76]

Prior to use, all the above lignin samples were dried at 50 °C in a vacuum oven until no weight change was recorded.

Black liquor: Lignin black liquors were obtained from Domtar Pulp Corporation with lignin concentration 41% wt.

3.2   Compositional analysis of bark resources

Bark samples were ground (particle size>40 mesh) and dried in the vacuum oven before the extractive and composition analysis.[251]

Extractives analysis: Extractives in the bark were removed by the treatment of three types of solvents: toluene/ethanol, ethanol, and hot water based on the ASTM Standard D1105.[252] Specifically, 3 g bark samples were added into cellulose thimbles and placed in the Soxhlet apparatus for 8 hrs. 300 ml toluene/ethanol (2:1) mixture was used to extract the aromatics in the bark. After the extraction, the solid residues were further extracted with 300 ml 95% ethanol until the alcohol in the siphons appeared colorless. Solid residues in the thimble were poured into 500 ml distilled water and boiled for 1 h, followed with filtration with a Buchner funnel and washed with another 500 ml boiled water. The fiber was air-dried and stored in an airtight container for further compositional analysis.[253]

Structural carbohydrate and lignin analysis: 200 mg of dried extractive-free bark was mixed with 3 ml 72% sulfuric acid in septa bottles at room temperatures for 2 hrs, stirring every 10 min. Another 112-ml distilled water was added to dilute the solution down to a 4% sulfuric acid concentration, following with treatment in sterilizer at 121 °C for 1 hr. The solution was then filtered using pre-weighted sintered disc filter funnels. The funnels with the solid components were dried in the oven (105 °C) for the analysis of acid insoluble lignin (AIL) and ash. The liquor was used to analyze acid-soluble lignin (ASL) and sugar content. ASL was determined from the absorption at UV 205 nm against a 4% H_2SO_4 blank. For the sugar analysis, samples were filtered through a 0.45 μm HV filter (Millipore, Bedford, MA, USA). Samples were then analyzed using a Dionex DX-2500 HPLC equipped with an ion-exchange PA1 column (mobile phase: nano-pure water, flow rate: 1.0 ml/min), following analysis with a pulsed aromatic detector. [254]

3.3 Acetone fractionation of lignin

100 g of lignin powders were gradually added (25 g per 30 min) into 1000 ml acetone and vigorously stirred for 24 hrs with magnetic stirring. Solutions were filtered in a Buchner funnel (Whatman No. 1 filter paper), followed by washing with 200 ml acetone. Acetone soluble solution was then air-dried in the fume hood and then dried in the vacuum oven at 50 °C for 48 hrs to obtain acetone soluble softwood Kraft lignin (ASKL) and acetone soluble hardwood Kraft lignin (AHKL).

3.4 Carbamylation of lignin

600 mg lignin powders were loaded into a 25-ml round bottom flask. Then 3 ml phenyl isocyanate (warning highly toxic) and 3 ml pyridine were added to dissolve the lignin. The reactive bottle was loaded into an oil bath at 80 °C for 18 hrs. After cooling down, 3 ml methanol was added to quench the reaction, and the mixture was added dropwise into 300 ml methanol and filtered by 0.45 μm PTFE membrane and washed by another 300-ml methanol and 600 ml distilled water. The obtained lignin samples were then freeze-dried.

3.5 Synthesis of hydroxypropyl lignin

10 g lignin was dissolved into 100 ml 0.1 mol/L sodium hydroxide (NaOH) solution. Then 5 ml propylene oxide was added to modify the lignin at room temperature for 24 h. After the modification, the liquid mixture was poured into 500 mL 0.1 mol/L HCl to precipitate the modified lignin.[255]

3.6 Synthesis of hydroxyethyl lignin

Dried lignin powders were mixed with ethylene carbonate (EC) in a molar ratio: EC/aromatic hydroxyl groups equaled 1 to 20 in a 100 mL round-bottom flask. Three types of alkaline catalysts, including Na_2CO_3, NaOH, and K_2CO_3, were added to the flask in a molar ratio of alkali/aromatic hydroxyl groups equaled 0 to 2, respectively. The container was then closed with a rubber septum bound with steel wire. For the system with solvent, dimethylformamide (DMF) was added via syringe (0−6 mL/g, v/m). The flask was then purged with nitrogen for 5 min, placed in an oil bath (preheated to 60−170 °C), and stirred for 1 to 20 h. At completion, the hot solution was added dropwise into 400 mL of 0.01 mol/L hydrochloric acid (HCl) to precipitate the modified lignin.

The supernatants were filtrated by vacuum filtration with 0.45 μm PTFE membrane, and the residue was thoroughly washed by another 400 mL 0.1 mol/L HCl. Solid lignin powders were dried via lyophilization for 24 h and then vacuum-dried at 50 °C for another 48 h.[256]

3.7   Real-time monitoring of hydroxyethylation

2.5 g dried lignin powders were mixed with 8 g ethylene carbonate in 50 ml round-bottom flask and sealed with a rubber-septa, Teflon film, and parafilm to ensure no leakage. After purging N_2 gas for 5 min, the flask was then loaded into an oil bath and reacted at 80 °C – 120 °C for 0 – 6h. The CO_2 gas was collected using our self-designed analytical equipment and recorded as a function of time (**Figure 22**). **Appendix A.1** showed a more detail explanation about the equipment. In the end, the resulting mixture of modified lignin was mixed with 300 ml aqueous sulfuric acid (pH=2) with continuous stirring. The modified lignin particles were filtrated using Whatman No. 1 filter paper, washed by another 2×300 ml distilled water, and dried by lyophilization before the analysis.[150]
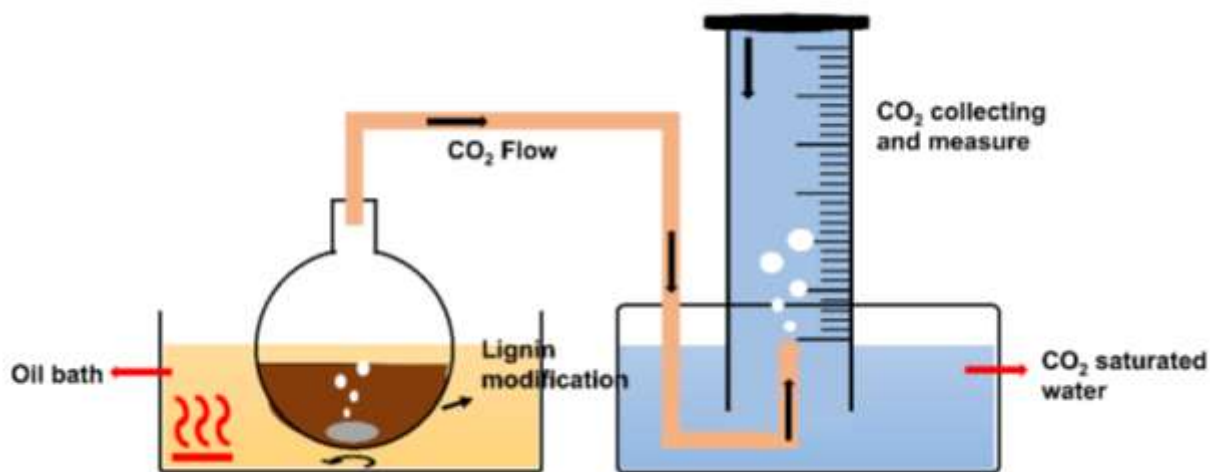
Figure 22 the design of CO₂ measuring equipment and the amount of CO₂ changing with the reactive time

3.8   Acetylation of lignin

300 mg of dried lignin powder was dissolved in a solvent, composed of 6 mL of anhydrous pyridine followed by the addition of an equal volume of anhydrous acetic anhydride. Mixtures were reacted at room temperature for 48 h in a nitrogen atmosphere with continuous stirring. To recover the

product, the solution was added dropwise into 600 mL of pH=2 aqueous acid solution. Precipitated acetylated lignin was collected by filtration using the 0.45 μm nylon membrane and washed by another 3x-200 mL of the aqueous acid solution and 3x-200 mL of distilled water. Acetylated lignin powders were dried in a vacuum oven at 50 °C.[78]

3.9   Catalyst-free esterification

5 g of dried lignin powder was mixed with 50 ml propionic acid and treated at 90-120 °C for 24-96 h in an oil bath and magnetically stirred. At the end of the reaction, the propionic acid was recovered using a roto-evaporator. 90% of propionic acid was recovered in this step. Subsequently, the mixtures were poured into water and then thoroughly washed twice with 500 ml distilled water and further lyophilized. Due to the different solubility of lignin in propionic acid, the yield (weight change) of esterified lignin was 75-80% (SKL and OSHL) and 95-110 % (HESKL and HEOSHL).

For the longer chain acid, including valeric acid (C_5), octanoic acid (C_8), and oleic acid (C_{18}), 5 g HELignin samples were mixed with 50 ml organic acid at 160 °C for 24 h. After the reaction, the respective hot solution was mixed with filter aid (Celite 545, Sigma Aldrich). Then 500 ml of aqueous ethanol was added to remove the excess acid following vigorous stirring; the valeric acid (C_5), octanoic acid (C_8), and oleic acid (C_{18}) would require a different ethanol concentration (50%, 75%, and 100%) for washing. The modified lignin had lower solubility in aqueous ethanol and would precipitate and mix with the filter aids as a solid residue. After filtration with 0.45 μm PVTF filter membrane and washing with another 500 ml of ethanol-water or pure ethanol, 200 ml of THF were mixed with the solid residue to extract the derivatized lignin (to ensure only covalently-bond acid remained for analytical analysis). The filter aids were removed by filtration using Whatman No.1 filter paper. This step was repeated until the THF was colorless. The THF was further removed by rotation evaporator, and esterified lignin was then washed with 200 ml water using a centrifuge and lyophilized. The derivatized lignin yield for different acids varied. Based on the weight of the original lignin, the yield of valerate and octanoate HElignin was 90%-100%, while the oleate HELignin was around 60-70%. The supernatants after removing solid lignin were then separated using a roto-evaporator to obtain aqueous ethanol and unreacted organic acid. 90% of organic acid could be recovered and separated in this step.[165]

3.10 Synthesis of esterified lignin in one-pot

Hydroxyethyl reaction: 3.0 g lignin was mixed with ethylene carbonate (9.3 g) as solvent and reagent in a 50 ml round-bottom flask. Na_2CO_3 (0.4 g) was then added as a catalyst. The mixture was loaded in an oil bath at 120°C with continuous stirring. During the reaction, the produced CO_2 was collected and measured by the above-mentioned measuring device.

Esterification: once the CO_2 reached 90 ml per 1 g lignin, 54 ml propionic acid was added directly into the above mixture to quench the hydroxyethyl reaction at 120 °C and to continue the reaction for esterification for another 48 hrs until all lignin was thoroughly dissolved in the reagents.

3.11 Preparation of polyurethane foam

Lignin powder was mixed with aromatic polyester polyol (STEPANPOL PS-2352) in a range from 0.1 to 0.25 by weight ratio, followed by thorough stirring. The viscosity of the lignin-polyol mixtures was analyzed with an AR-2000 (TA Instrument, USA) with a shear rate from 0.1-10 s^{-1} at 25 °C.

The mixture was combined with a blowing agent (water), surfactant (Silstab 2755), and catalysts (JEFFCAT®ZF 20) using a specific ratio. After thorough stirring, the mixtures were then reacted with polymethylene diphenyl diisocyanate (pMDI, Lupranat® M 20S) in the specific ratio (1:1.1). In the process vigorously stirred was used with a mixer until the rising of the foam and the foams were left to fully cure at room temperature for four days.

3.12 Characterization of untreated and modified lignin
3.12.1 Nuclear Magnetic Resonance (NMR) analysis
3.12.1.1 Sample preparation

^1H NMR: 50 mg dried lignin powders were weighed in a 1.5 ml vial and another 500 μL deuterium chloroform or deuterium dimethyl sulfoxide were added to dissolve lignin thoroughly.

^{31}P NMR: A solution mixture was prepared by mixing pyridine and $CDCl_3$ in a ratio 1.6/1 v/v. The pyridine was protected from the moisture with molecular sieves. The relaxation reagent and internal standard were prepared by dissolving the chromium(III) acetylacetonate and N-hydroxy-

5-norbornene-2,3-dicarboximide into the solution with a concentration of 5.6 mg/ml and 10.0 mg/ml, respectively. An exact amount of 20 mg dried lignin powder was then dissolved in 400 μL above solution, followed with the addition of 100 μL internal standard solution, 40 μL relaxation reagent solution, and 50 μl 2-Chloro-4,4,5,5-tetramethyl-1,2,3-dioxaphospholane (TMDP).[88, 150, 237]

13C NMR: approximately 150 mg of lignin was dissolved into 450 μl DMSO-$_{d6}$, followed by the addition of 60 μl of a solution of chromium(III) acetylacetonate (50 mg/ml) in DMSO-d6 as relaxation reagent and 15 mg of trioxane as internal standard.[88, 257]

HSQC NMR (Heteronuclear Single Quantum Coherence): 30 mg dried lignin powder was dissolved into 500 μL DMSO-d6. These lignin solutions were thoroughly mixed until no solid was left in the solution and transferred into a 5 mm NMR tube for immediate analysis.

3.12.1.2 Sample analysis

For ^{1}H, ^{31}P, and ^{13}C NMR, the spectra were acquired using Bruker Avance NMR (300 MHz) at 25 °C equipped with a BBO probe. HSQC NMR spectra were acquired using Bruker Avance Bruker AVANCE III (600 MHz) at 25 °C equipped with a cryoprobe. The specific acquisition parameters were indicated as below:

^{1}H NMR: these parameters were applied: relaxation delay 10 s, 30° pulse width, acquisition time 1.3 s, and scan number 256.

^{13}C NMR: an inverse-gated decoupling sequence was applied with parameters: relaxation delay 2 s, acquisition time 1.4 s, pulse length 8.15 μs, 90° pulse angle, and scan numbers 20,000. Signals were calibrated using DMSO as a reference (δ=39.5 ppm). The relative concentration of functional groups is presented per 100 aromatic units. This was achieved by integrating the aromatic regions (100-160 pm) and setting this to a value 600, then all chemical groups would be expressed based on this value.

^{31}P NMR: an inverse-gated decoupling pulse sequence was employed to obtain quantitative 31P NMR with parameters: relaxation delay 5 s, acquisition time1.4 s, pulse length 6 µs, 90° pulse width, and number scan 800. The chemical shift of each phosphitylation product was calibrated with a product of TMDP with water (residual moisture, 2,2' - oxybis (4,4,5,5-tetramethyl-1,3,2-dioxaphospholane), which gave a sharp and stable signal at 132.2 ppm. [165]

HSQC NMR: typically, the ^{13}C-^{1}H spectrum was acquired using Bruker "hsqcetgpsisp 2.2" pulse program with following parameters: matrices of 2048 data points for the 1H and 256 data points for 13C were collected with an interscan delay (D1) of 750 ms, 16 scans, and spectral width from 12.67 to -3.30 ppm for ^{1}H and 210 to -10 ppm for 13C. The obtained spectrum was calibrated using the DMSO-d6 signal (2.50/39.5 ppm). Topspin 3.5 software was used to process the obtained spectrum: Fourier transformation, baseline correction, and calibration. A semi-quantitative analysis of the HSQC spectrum was performed based on previous works. Part of the aromatic spectrum was integrated and defined as the internal standard. For this softwood Kraft lignin, the area of G_2 was incorporated, and the value was set to 100 aromatic units (100Ar). All linkages were calculated relative to 100 Ar.

3.12.2 FT-IR analysis

Sample pellets for transmission FT-IR were prepared by mixing 2-3 mg lignin with 200 mg of dried potassium bromide (KBr). After thorough mixing and compression, lignin pellets were analyzed using a Perkin Elmer Infrared Spectrometer (MA, United States). Spectra were collected with a resolution of 4 cm^{-1} and averaged over 32 scans.

3.12.3 Solubility analysis

5 mg dried samples were weighed in a 1.5 ml vial, following the addition of 500 µL solvent. The mixtures were stirred by a vortex mixer at room temperature and left standing for 1 week to determine the degree of solubility based on the clarity of the solution. (**Figure 23**) Dimethylsulfoxide (DMSO), ethanol, DMF, pyridine, acetone, dichloromethane (CH_2Cl_2), tetrahydrofuran (THF), ethyl acetate, and propionic acid were employed in this study.
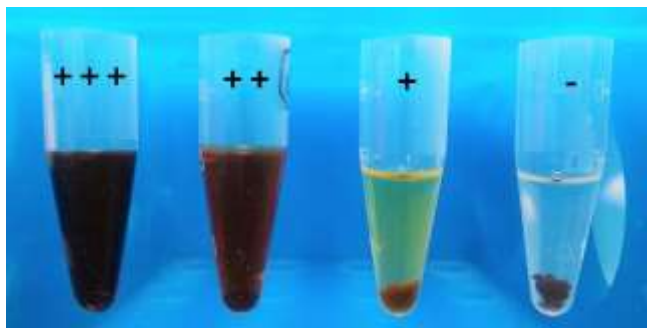
Figure 23 Photo of the represented solubility of lignin in the organic solvent

3.12.4   Molecular weight analysis

3.12.4.1   GPC-dRI analysis

Sample preparation: 5 mg acetylated lignin samples were dissolved into 1 ml anhydrous THF and stored at room temperature for 48 hrs. Lignin samples were then filtrated via 0.45 μm PTFF syringe filters. Polystyrene standards within molecular weight 1.3 kDa, 2.7 kDa, 5.8 kDa, 9 kDa, and 30 kDa were also run to make a standard curve for conventional calibration analysis.

Sample analysis: GPC measurements were carried out using Agilent 1100 GPC equipment (USA) consisting of a pump, an autosampler, and a column oven set at 35 °C. 100 μL lignin solution was injected into the system and fractionated. Three columns (Waters Corp. MA, USA) including Styragel HR4 (5 kDa-600 kDa), HR3 (0.5 k~30kDa), and HR1 (0.1 k-5 kDa) with eluting solvent THF (degassed with helium) at a flow rate of 0.7 ml/min. Fractionated lignins were analyzed with a Wyatt Optilab T-Rex refractive index detector (dRI, USA) with 785 nm at 35 °C. All data were collected and analyzed by Wyatt ASTRA 6.0 (USA).

3.12.4.2   GPC-LS- dRI analysis

Sample preparation: 10 mg acetylated or nonacetylated lignin was dissolved in 1 ml DMSO/LiBr (0.5% w/v) at room temperature overnight. Before the analysis, samples were filtrated using 0.45 μm PTFE filters. PSS standard samples with molar masses of 1.1 kDa, 2.0 kDa, 4.29 kDa, 10 kDa, 29.5 kDa, 63.9 kDa, 145 kDa, and 470 kDa were prepared by dissolving 10 mg PSS in 1 ml DMSO at 50 °C for 48 hrs until they were thoroughly dissolved in the solvent.

Sample analysis: GPC measurements were carried out using Agilent 1100 GPC equipment (USA) consisting of a pump, an autosampler, and a column oven set at 35 °C. 20 µL lignin solution was injected into the system and separated. Two types of PolarGel column (PolarGel M and L, Agilent) were used to fractionate the lignin at 35 °C using DMSO/LiBr (0.5% w/v) as eluent at 0.5 ml/min. The fractionated lignin was then analyzed by multi-angle laser light scattering (MALLS, Wyatt Tech. CA, USA), and the optilab T-rEX differential refractive index detector (dRI, Wyatt Tech. CA, USA). The data were then collected and analyzed by ASTRA 6.0 software. The dn/dc value was calculated through the dRI traces by an on-line method using Astra software.[94]

3.12.5   Thermal Gravimetric Analysis (TGA)

TGA experiments were performed in triplicate using a TA 500 thermogravimetric analyzer (TA Instruments, USA). 15 mg of dried lignin powder was loaded onto a platinum pan and heated to 105 °C, holding for 10 mins to remove residual moisture, and then further heated to 650 °C at a rate of 10 °C/min. All of the samples were analyzed under a nitrogen atmosphere.

3.12.6   Differential Scanning Calorimetry (DSC) analysis

The glass transition temperature (T_g) measurement was measured in triplicate using a TA Q1000 differential scanning calorimeter (TA Instruments, USA). Approximately 5 mg of dried lignin powder was sealed into 40 µL aluminum pans and lids. The sample was analyzed by a 5-cycle, heating-cooling procedure; cycle 1: Ramp was 20 °C/min to 105 °C Isothermal hold for 30 min; cycle 2: Ramp down 10 °C/min to -50 °C; cycle 3: Ramp up 20 °C/min to 180 °C; cycle 4: Ramp down 10 °C/min to -50 °C; cycle 5: Ramp up 20 °C/min to 220 °C; the glass transition temperature was analyzed based on the Cycle 5 heat flow traces.

3.12.7   Thermorheological analysis

Thermorheological analysis was run in a TA Instruments rheometer AR 2000 (USA). Dried and finely ground lignin powder (mortar/pestle) was loaded between two 25-mm diameter stainless steel parallel plates. Samples were heated from room temperature to 150 °C at a rate of 3 °C/min. The normal force was held at 3 N below 100 °C and was weaken to 2 N above 100 °C.

3.13 Characterization of lignin-based polyol and polyurethane foam

The obtained polyurethane foams (PUF) were further cut into cylindrical plates (diameter=12 mm, thickness=5 mm) for density and compression modulus analysis. The density was calculated based on the ratio between the tested volume and weight of PUFs. The compression modulus of the foam samples was tested with a dynamic mechanical analysis (TA Instruments, USA) with a range of force from 0.01 N to 18 N at room temperature. The micromorphology of the lignin-based PU foam was analyzed with scanning electron microscopy (SEM, Hitachi S3000 N). Samples were placed on the conductive tape. After sputter-coating with 15 nm of gold, the images were obtained at an acceleration voltage of 5 kV.

3.14 Preparation of lignin-based hydrophobic coating

400 mg of lignin powder was dissolved into 20 ml THF. The solutions were then transferred into dialysis tubing (cellulose membrane, Sigma-Aldrich) and placed into 1500 ml distilled water for 7 days with slow stirring; the distilled water was changed every 24 hrs. The final concentration for the coating solution was 20 mg/ml.[258]

3.15 Dynamic light scattering (DLS)

After analyzing distilled water as background, 1.5 ml aqueous lignin-particle solution was diluted by 600 ml of distilled water and stirred at 1500 rpm for dynamic light scattering analysis. The data was collected and analyzed with a Mastersizer 2000. Each sample was run in duplicate.

3.16 Characterization of hydrophobic coating

Three types of surfaces were selected for coating analysis: glass, Kraft pulp sheets, and wood (yellow poplar). The glass slides were cleaned by sonication for 30 min to remove contamination, and the surfaces were dried with nitrogen gas. Lignin particle solution was added into an airbrush reservoir for spray coating at a distance of 25 cm. A spin Coater (WS 650, Laurell Technology Corp., USA) was used for spin coating at room temperature. The coated materials were dried under ambient conditions in fume hood overnight. To build the coating, this process was repeated 10 times for both spin coating and spray coating. 5 μL distilled water droplets were dispensed on different types of treated surfaces from a height of 2mm. The contact angle was recorded using a highspeed camera and analyzed by Drop Shape Analyzer (DSA) 1.9 software.

Chapter 4: Uniform chemical functionality of technical lignin using ethylene carbonate for hydroxyethylation

4.1 Introduction

Hydroxyalkyl lignin derivatives offered the opportunity to create reactive segments for step-growth polymers where the aliphatic hydroxyl groups served as a handle for further modification. Due to the drawbacks of traditional routes, recent work has moved from hydroxyalkylation with alkyl oxides or organohalides to carbonates such as ethylene carbonate (EC), glycerol carbonate, and propylene carbonate (PC) to reactants with unsaturated groups like diallyl carbonate, or methylation with dimethyl carbonate (DMC).[128, 136, 259, 260]

Comparing with traditional alkylene oxide compounds, these carbonate compounds, including EC and PC, are attractive substitutes because they have low odor level, low evaporation rate, low toxicity, and high boiling/flashing point.[149, 239] However, caution is required when using such reagents with lignin, as these reactions are temperature dependent, which may also cause structural changes during reactions at elevated temperatures with alkaline catalysts. For example, a recent study used different types of carbonate compounds with reactive conditions near 170 °C and 1, 8-diazabicyclo-undec-7-ene (DBU) as a catalyst. At 170 °C, near pulping conditions, it opens the possibility of lignin modification and significant lignin structural changes at this temperature, which resulted in a significant increase in molecular weight and PDI.[260] These drawbacks would restrict their further application in copolymerization with other monomers.

In the current study, our hypothesis is that if we investigated a range of reaction conditions (time, temperature, catalyst type, catalysts loading, solvent presence) to make lignin with more uniform chemical functionality and enhanced thermal stability, we may minimize additional lignin structural changes and co-polymerization during the hydroxyalkylation.

4.2 Results and Discussion

4.2.1 Acetone fractionation of Kraft lignin

Kraft lignin has non-uniform reactivity and two methods were used to enhance its uniformity. Following previous work by Cui et al., organic solvent fractionation was used to obtain more homogeneous Kraft lignin with lower polydispersity. For this study, acetone extraction was used

for isolation of lower molecular weight fractions of Kraft lignin from hardwood and softwood sources. Softwood Kraft lignin (SKL, Indulin AT) was less soluble in acetone yielding 35% after recovery, while 69% of the hardwood Kraft lignin (HKL, Fibria Innovation) was dissolved, **Table 5**. Analysis of the acetone soluble fractions relative to the parent batch of lignin revealed a greater amount of free aromatic functional groups, as detected via ^{31}P NMR (**Table 5**). While softwoods do not have a syringyl component, a significant portion of the lignin had condensed lignin structures at the ortho carbon, while the total aromatic OH content was 5.53 mmol/g for the softwood compared to 4.87 mmol/g for the hardwood sample (**Table 5**). These values were approximately two times greater than the aliphatic hydroxyl functional groups. In addition, the acetone fraction had a lower molecular weight and PDI. These data were similar to those reported by Cui et al. for acetone soluble softwood Kraft lignin (ASKL).[28]

Table 5 Characterization of softwood Kraft lignin (SKL, Indulin AT) and hardwood Kraft lignin (HKL, Fibria Innovation) and acetone soluble fraction

	Yield/%	AlOH /(mmol/g)	ArOH /(mmol/g)	COOH /(mmol/g)	Total OH/ (mmol/g)	Mn /(g/mol)	Mw /(g/mol)	PDI	T_g/°C
SKL		2.39	4.01	0.46	6.40	1132	4572	4.04	149
ASKL	34.94	2.01	5.53	0.49	7.54	862	1615	1.87	86
HKL		2.26	4.46	0.40	6.72	1309	4719	3.61	132
AHKL	69.46	1.74	4.87	0.52	6.61	1247	2755	2.21	122

4.2.2 Reaction conditions for the hydroxyethylation of Kraft lignin

The hydroxyethyl derivatization of lignin using ethylene carbonate (EC) was systematically studied utilizing alkaline catalysts. Clements discussed the potential reaction conditions and mechanism using carbonate compounds in the reactions with aromatic hydroxyls, aliphatic hydroxyls, and carboxylic acids, which all can be found on technical lignin to various extents.[149] The possible reactions noted in **Figure 24** accounted for, 1) phenolate and carboxylate attack of the cyclic carbonate, with CO_2 off-gas and 2) deprotonated AlOH groups reacting with the carbonyl carbon in EC to possibly form polycarbonate linkages.
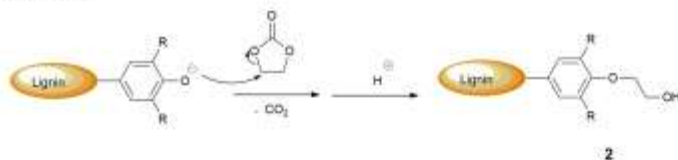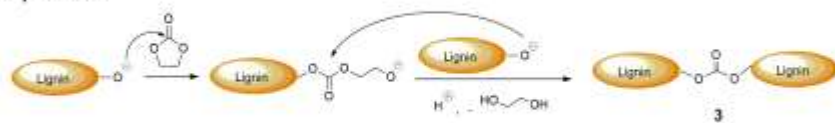
Figure 24 Possible reactions between EC and deprotonated carboxylic acid, aromatic hydroxyl, and aliphatic hydroxyl groups in lignin that produces a mixture of hydroxyethyl lignin compounds 1 and 2, carbonate compounds 3, and polyether copolymers 4. Reprinted with permission from ref. [150]. Copyright 2018 American Chemical Society

As noted in the polymer industry, EC has been widely used to modify carboxylic acid and phenol compounds with alkali catalysts under temperature ranges (100 - 150 °C).[149, 239] Therefore, hydroxyethyl reactions of the lignin were studied for the catalyst and reaction conditions (time, temperature, and solvent). The catalysts Na_2CO_3 (pKa=10.25), K_2CO_3 (pKa=10.25), and NaOH (pKa=15.60), had differences in their basicity and were used for the deprotonation of the aromatic hydroxyl groups on lignin.[143] With these catalysts, initial reaction conditions were established at 120 °C for 20 hrs with excess EC relative to the aromatic content in DMF as a solvent used for comparison purposes (Figure 25 a).
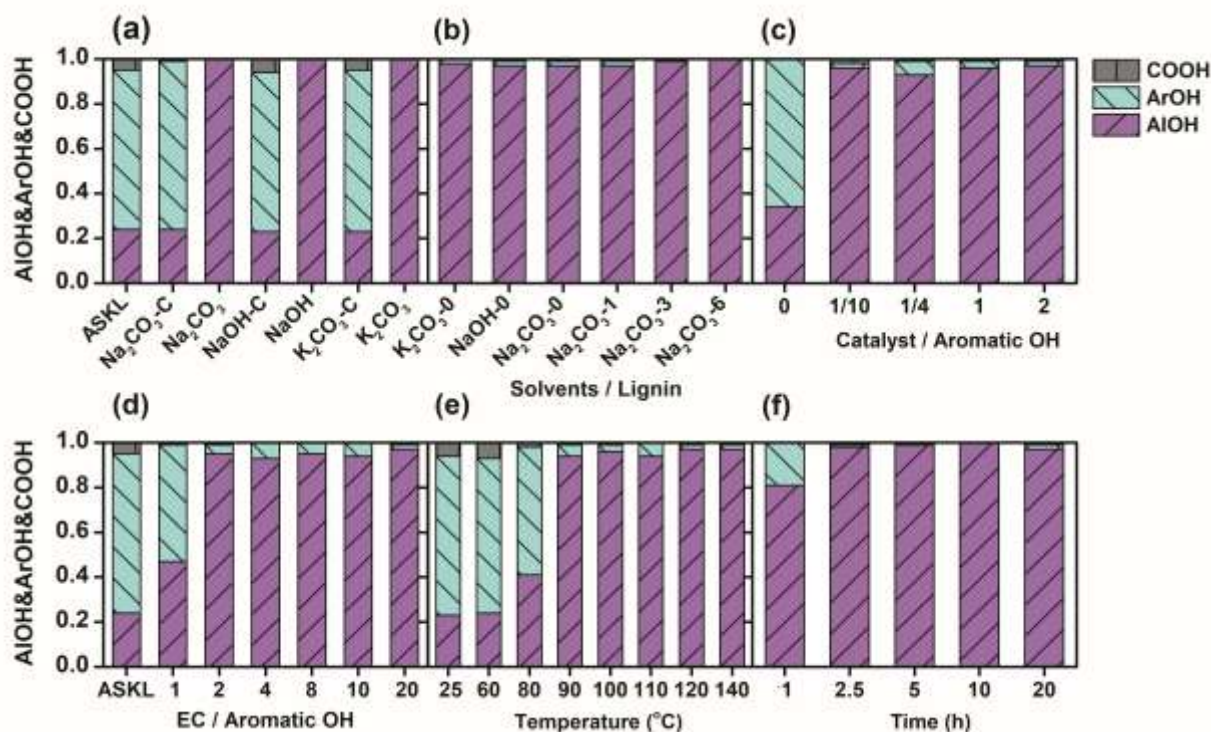
Figure 25 Functional groups of acetone soluble softwood Kraft lignin considering six factors including: the different types of catalysts (a); the ratio of solvent (ml) to lignin (1g) (6, 3, 1, & 0) (b); catalysts loading to phenolic OH (c); ethylene carbonate (EC) to phenolic OH ratio (d); effects of temperature on the reaction at 20 hrs (e); and time on the reaction at 120 °C (f); initial conditions in (a): temperature=120 °C, time=20 hrs, EC/Aromatic OH=20, Alkali/Aromatic OH=2; -C, controlled reaction conditions without adding EC; b different amount of solvents(-6, 1 gram mixing with 6 ml DMF); c,d,e, and f adopting Na2CO3 as catalysis without the addition of DMF. Reprinted with permission from ref. [150]. Copyright 2018 American Chemical Society

The quantitative ^{31}P NMR spectrum can characterize different types of hydroxyl groups in lignin. As shown in **Figure 25 (a)**, ArOH was readily converted into hydroxyethyl ethers using "control" conditions of 20 eq. of EC and 2 eq. alkali at 120 °C for 20 hrs in DMF. This reaction resulted in lignin containing over 95% of AlOH groups for all the catalysts utilized. In addition, deprotonated carboxylic acids on the lignin also reacted with ethylene carbonate (**Figure 24**), achieving high substitution of this functional group, too. Negligible differences were detected in the derivatization of the lignin, as all catalysts were effective in hydroxyalkylating lignin at conditions of 120 °C and 20 hrs. This result was different from Over et al. and Kühnel et al., which required TBAB and DBU as alkaline catalysts for the reaction to proceed with carbonates used in their studies.[260] The

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alkaline carbonate catalysts used in the current study have lower cost and toxicity than these compounds and satisfy requirements of green chemistry.

In a control reaction without ethylene carbonate, there was a slight change in ArOH content, with a reduction of free aromatic groups. The ArOH groups were decreased from 5.98 to 4.32 mmol/g, accompanied by the reduction of 5-substituted ArOH groups from 2.01 mmol/g (ASKL) to 1.41 mmol/g. These changes suggested that the alkaline catalysts at 120 °C may have led to potential polymerization through ArOH, indicating that lignin was very sensitive to structural modification when utilizing alkaline catalysts and heat for derivatization.[261]

A series of additional hydroxyethyl lignin reactions were performed to optimize reaction conditions which included the quantities of DMF, alkali, and ethylene carbonate content relative to the ArOH concentration in the lignin, and temperature/time. Complete substitution of the ArOH occurred with and without the presence of the additional solvent (**Figure 25b**). In so doing, excess solvent recovery was avoided during this reaction. Moreover, the yield increased for the DMF solvent-free conditions from 60% to 80%, which was attributed to the loss of hydroxyethyl lignin in the recovery and purification stages when using DMF. The comparison among these three catalysts without the addition of DMF showed that the total OH (4.85 mmol/g) and the percentage of AlOH group (97.3%) for Na_2CO_3 were similar to K_2CO_3 (4.60 mmol/g, 97.6%) and NaOH (4.81 mmol/g, 96.2%). Essentially, the catalyst type did not have a significant impact on this reaction and the additional solvent is unnecessary for the hydroxyethyl reaction.

The catalyst loading had a minimum impact on the etherification of ArOH and COOH groups (**Figure 25c**). Complete substitution occurred for a range of conditions when the catalyst amount was twice the number of ArOH group content down to a level when the catalyst content was cut down to one tenth of the lignin ArOH group content. For the latter, the percentage of AlOH group content was nearly 97%. Overall, the smallest addition of the catalyst was enough to deprotonate the ArOH groups on lignin for the reaction. In the absence of catalyst, the control reaction revealed the ArOH groups did not change, indicating the need for the catalyst for conversion of the ArOH into AlOH.

Since ethylene carbonate can be the solvent and reagent at the same time during the reaction, we were able to remove DMF from the reaction scheme. By reducing the EC amount from 20 e.q. to 2 e.q., the percentage of AlOH group content remained over 90%. (**Figure 25d**); however, an obvious reduction of AlOH content occurred when the EC/ArOH was decreased to 1 e.q. Noteworthy, it was observed that a relatively low amount of ethylene carbonate led to high solvency of the lignin. Previous research indicated the complete liquification of biomass at relatively low temperatures demonstrating high solvency of biomass in alkyl carbonate compounds.[240] The reaction time was shortened to 2.5 hrs with an additional amount of EC at 120 °C (**Figure 25f**).

The temperature of the reaction had a significant impact on the lignin structure as the total hydroxyl content decreased as a function of temperature (**Figure 26**). Further, **Figure 25e** showed that the significant changes in the hydroxyalkylation reaction occurred when the temperature increased from 80 °C to 90 °C. The percentage of AlOH group content increased from 41% to 93% with the reduction of total hydroxyl group from 5.82 mmol/g to 4.74 mmol/g. Above 90 °C, there was a nearly complete substitution of ArOH groups with only minor modification of total hydroxyl groups for samples reacted in a range from 90 to 120 °C (5.02 mmol/g, **Figure 26**). Reactions that occurred above 120 °C, showed significantly lower AlOH group content; from this observation higher temperatures also caused side reactions, that would lead to condensed structures. This crosslinking reaction had been further revealed in the following results on gel permeation chromatography analysis.
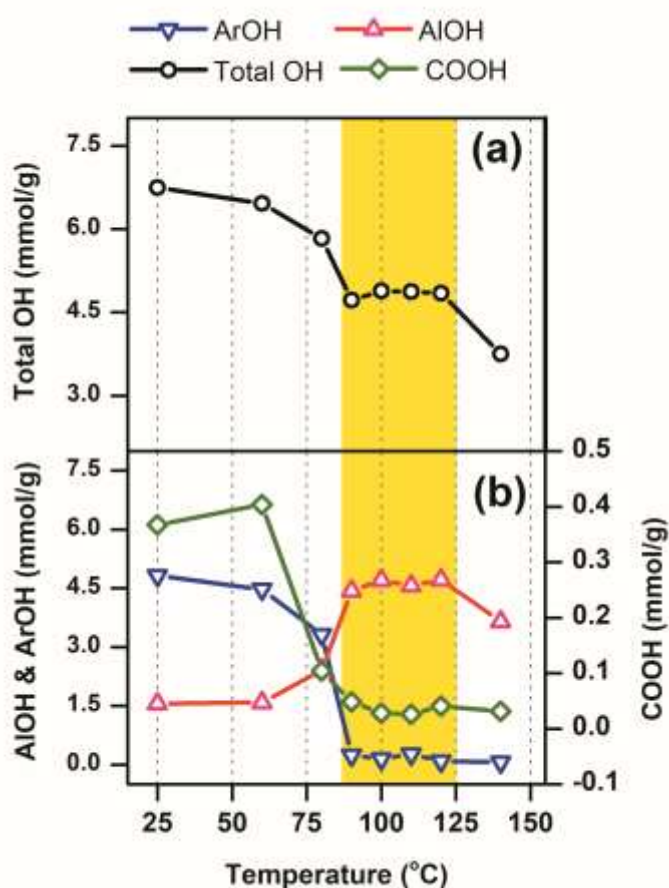
Figure 26 Impact of temperature on total OH, AlOH, ArOH, and COOH for the hydroxyethyl ASKL; Reaction conditions: Time=20 hrs, EC/Aromatic OH=20, Na2CO3/Aromatic OH=2; Reprinted with permission from ref. [150]. Copyright 2018 American Chemical Society

Further, these reaction conditions were investigated for a hardwood lignin substrate (acetone soluble hardwood Kraft lignin, AHKL). The AHKL had a lower substitution of the aromatic groups compared with ASKL when using the same conditions of the softwood lignin. Therefore, complete substitution required longer reaction time or higher reaction temperature to complete the reaction. This result may be explained based on the structure of hardwood lignin that contained syringyl units (**Table 1**) and thus had additional steric hindrance arising from the additional methoxy group near the phenolic during the reaction with ethylene carbonate. As a result, the reaction conditions were modified for the lignin type or source.

4.2.3   Gel permeation chromatography analysis

Acetylated lignins (ASKL and AHKL) and hydroxyethyl lignin (**Table 6**) with different reaction conditions were dissolved in THF and analyzed for molar mass. Hydroxyethyl lignin for both hardwood and softwood lignin showed a shift to higher molecular weight versus the lignin precursor (**Figure 27**). Lignin molecular weight values, M_n, M_w, and polydispersity (PDI), were calibrated based on a series of polystyrene standards. After modification, lignin had higher PDI, and this value increased with the temperature and reaction time indicating the sensitivity of Kraft lignin to this reaction. The outcome suggested that a narrower distribution of molecular weight required lower reaction temperatures for lignin modification.
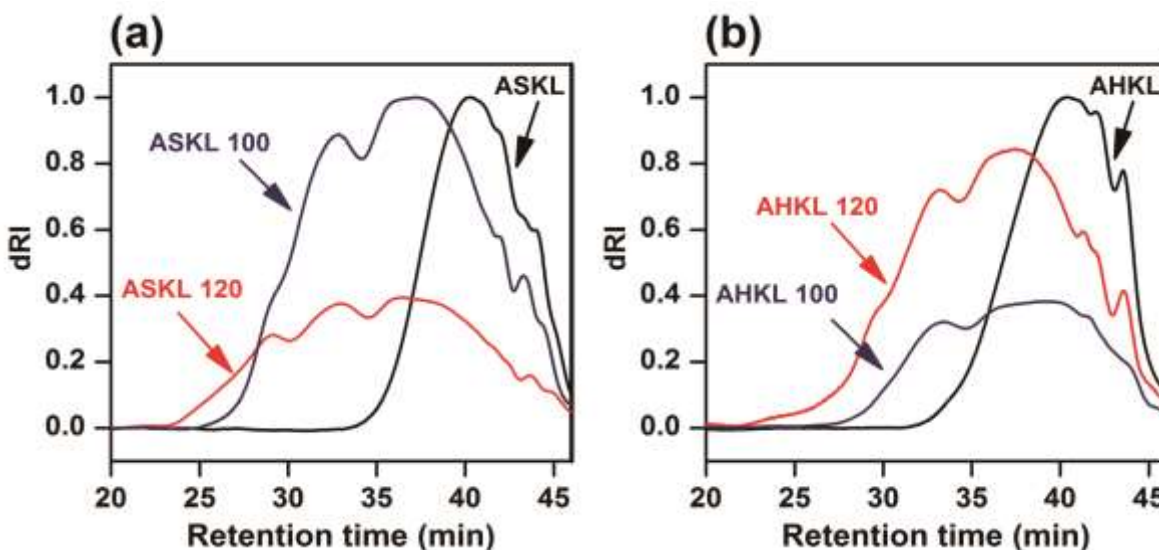
Figure 27 GPC traces of softwood (a) and hardwood (b) lignin before and after hydroxyethylation with different temperatures (100 or 120 °C). Reprinted with permission from ref. [150]. Copyright 2018 American Chemical Society

Table 6 Change of chemical structure and molecular weight with different lignin resources and reaction conditions

No.	Reaction condition	AlOH /(mmol/g)	ArOH /(mmol/g)	COOH /(mmol/g)	Mn /(g/mol)	Mw /(g/mol)	PDI
ASKL							
HE_ASKL	100 °C /5hrs, 4 EC, 0.25 Na$_2$CO$_3$	4.76	0.22	0.04	1996	12780	6.40
HE_ASKL_1	120 °C /20hrs,	4.62	0.14	0.04	1676	20630	12.31

No.	Reaction condition	AlOH /(mmol/g)	ArOH /(mmol/g)	COOH /(mmol/g)	Mn /(g/mol)	Mw /(g/mol)	PDI
RHE_ASKL	2 EC, 0.25 Na$_2$CO$_3$ 170 °C /3hrs, 10 EC, 0.25 K$_2$CO$_3$	nd	nd	nd	nd	nd	nd
AHKL							
HE_AHKL_1	100 °C /20hrs, 4 EC, 0.25 Na$_2$CO$_3$	3.86	0.17	0.06	1604	8888	5.54
HE_AHKL	120 °C /20hrs, 4 EC, 0.25 Na$_2$CO$_3$	4.09	0.42	0.05	1572	15660	9.95
RHE_AHKL	170 °C /3hrs, 10 EC, 0.25 K$_2$CO$_3$	nd	nd	nd	nd	nd	nd

As indicated earlier, the increased temperature led to structural changes in the modified lignin with a reduction in the overall hydroxyl content. A loss in total hydroxyl content would be an indication that the AlOH content will react with the EC by transesterification or polymerization reactions (**Figure 24**). Further, with lignin in alkali, free radical reactions may have also occurred through phenoxy radicals reacting with other lignin segments at open ortho positions on adjoining aromatic rings. Hence, the temperature was a highly important factor to control lignin derivatization without significant lignin co-polymerization with polycarbonate segments and lignin cross-linking.[26]

4.2.4 Impact of modification on the structure of lignin

4.2.4.1 Quantitative 13C NMR analysis

From the ^{13}C NMR spectrum of acetylated lignin samples (**Figure 28**), we distinguished the different hydroxyl groups in the resulting lignin. Similar to ^{31}P NMR analysis, the AlOH group (Peak 1 and 2) increased with the corresponding reduction of ArOH (Peak 3 and 4) for the samples after hydroxyethylation (**Figure 26 and Table 7**). Also, the total hydroxyl group content diminished for both modified ASKL and AHKL as previously noted above with ^{31}P NMR analysis. Additionally, an unexplained phenomenon was observed, the secondary AlOH groups (Peak 2) were also modified as shown the emergence of a new peak 5 (77 - 72 ppm).
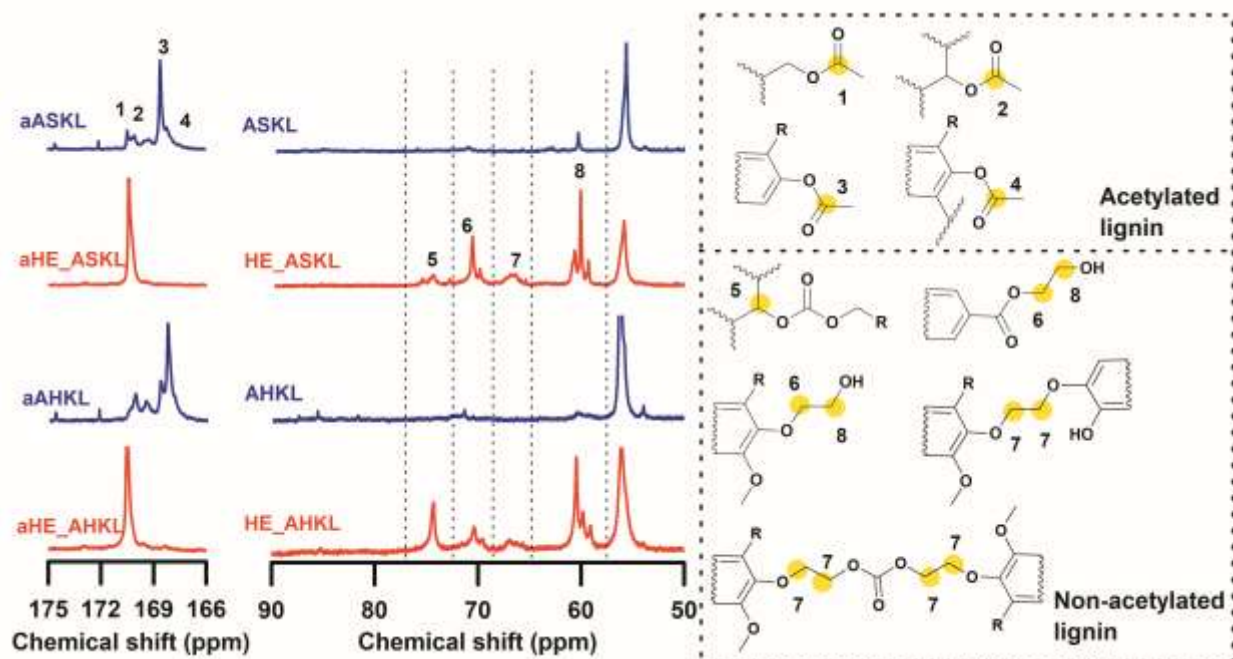
Figure 28 ^{13}C NMR spectra of lignins before and after hydroxyethyl reactions; in DMSO-d6 (δ=39.5 ppm) for both nonacetylated (ASKL, HE_ASKL, AHKL, and HE_AHKL) and acetylated lignin (aASKL, aHE_ASKL, aASKL, aHE_AHKL). Reprinted with permission from ref. [150]. Copyright 2018 American Chemical Society

Noteworthy, the increased amount of primary AlOH groups, 48 per 100 C_6 units (Peak 1, **Figure 28**), was lower than the reduction of ArOH groups, 60 per 100 C_6 units (peak 2, **Figure 28**), after the hydroxyethyl reaction for both hardwood and softwood Kraft lignins. This difference in AlOH group content when accounting for the substitution of the ArOH groups was suggested to arise from the reaction of lignin into compounds like 3 or 4 in **Figure 24** during the modification and/or lignin condensation reactions. The substitution of AlOHs can create carbonate linkages, which would lead to a decreased total hydroxyl group content and an increased molecular weight. Peak 7 was related to the formation of carbonate bonds between AlOH groups and ethylene carbonate during the hydroxyethylation process (compound 3 and 4 in **Figure 24**). Further, the peak clusters in a range from 155 to 154.4 ppm revealed carbonyl signal from compounds 3 and 4 in **Figure 24**. The existence of these carbonate groups had also been shown by the FT-IR spectrum, since a distinctive increase in absorbance for the carbonyl peak ν=1748 cm^{-1} after hydroxyethyl reaction was observed.

Table 7 Quantitative ^{13}C NMR analysis of major functional groups in softwood and hardwood lignin before and after hydroxyethyl reaction including acetylated and non-acetylated lignin (per 100 Ar)

Peak No.	Assignment	Peak range[ppm]	ASKL	HE_ASKL	AHKL	HE_AHKL
	Acetylated Lignin[a]					
1	AlOH primary	172-169.8	20	68	18	66
2	AlOH Secondary	169.8-168.9	15	4	15	5
3	ArOH 5-free	168.9-168.3	42	1	22	2
4	ArOH 5-substituted	168.3-166	19	0	42	1
	Total AlOH	172-168.9	35	72	32	71
	Total ArOH	168.9-166	61	1	64	3
	Total OH	172-166	96	73	96	75
	Non-acetylated Lignin					
5	-$\underline{C}$H(-R)- O-C=O-	77-72[b]	10	31	19	42
6	-O-$\underline{C}$H$_2$-CH$_2$-OH	72-68	9	55	17	33
7	-O-$\underline{C}$H$_2$-$\underline{C}$H$_2$-O-C=O, Ar-O-$\underline{C}$H$_2$-$\underline{C}$H$_2$-O-Ar	68-65	4	31	8	19
8	-O-CH$_2$-$\underline{C}$H$_2$-OH	65-58	21	88	32	85
	Co-polymerization[c]			0.18		0.11
	Degree of condensation		57	76	38	56

[a] the acetylated lignin sample were used to analyze the hydroxyl group of lignin, [b] unknown compounds may contribute to this peak area, [c] co-polymerization=1/2×peak 7 / peak 8

Further evaluation of the degree of carbonate linkage formation was found as follows: a range of 72 – 58 ppm showed new peak clusters (peak 6 and 8) appearing after the modification for both hardwood and softwood lignin. These two peaks corresponded to the hydroxyethyl carbons in the resulting lignin. The peak clusters labeled as peak 6 appeared with greater intensity (68 - 65 ppm) in the modified softwood lignin than clusters in the modified hardwood lignin. This difference may partly arise because of structural differences between hardwood lignin and softwood lignin. The peak clusters 8 (65 - 58 ppm) represents the C_γ of the side chain in unmodified lignin, which directly relates to the native primary AlOH groups. The peak of C_γ will change depending on the chemical structure of the original compounds. By comparing peak 7 and peak 8, the carbonate carbon was identified and related to the amount of primary AlOH groups to determine the degree of co-polymerization. Since the ratio was 0.18 (HE_ASKL) and 0.11 (HE_AHKL), (**Table 7**),

there had been limited co-polymerization between modified lignin and ethylene carbonate (compound 4 in **Figure 24**) with our optimized conditions. This result was quite different from the traditional ethylene oxide modification of lignin in which ethylene oxide reacts with itself to form polyethylene oxide chains.[244]

The degree of condensation of lignin after the modification was one of the primary reasons for the increased molecular weight. The degree of condensation was calculated based on the formulation by Balakshin et al.[91] After the modification, the degree of condensation increased, and the hydroxyethylated softwood lignin had a higher degree of condensation than that of modified hardwood lignin (**Table 7**). Most likely syringyl units found in hardwood lignin prevented the condensation of lignin at the open C_5-position. This data agreed with changes in the molecular weight (**Figure 27**). Overall, ethylene carbonate was used to create hydroxylethylated derivatives that contain nearly only primary hydroxyl groups—this result contrasted with the starting material that had carboxylic acids, secondary hydroxyls, and phenolics. Hence, ethylene carbonate is a unique reagent to create lignin with uniform chemical functionality and limited co-polymerization.

4.2.4.2 FT-IR analysis

ASKL and AHKL before and after hydroxyethylation were analyzed using FT-IR and the spectra were depicted in **Figure 29** allowing the comparison of the optimized reaction conditions to the higher temperature reaction at 170 °C. Generally, ASKL and AHKL had similar FT-IR spectra, except the stronger syringyl C-H at $v=1120$ cm^{-1} in AHKL. For all lignin samples, the broad peaks from 3200 - 3700 cm^{-1} is O-H stretching with hydrogen bonding. Significant sp3 C-H stretching in alkyl groups ($v=2926$ cm^{-1}) was also observed for the modified lignin samples. This signal was greatly enhanced for samples reacted at 170 °C. As found in the NMR spectra after modification, a distinctive increase in absorbance for the carbonyl peak $v=1748$ cm^{-1}, demonstrated the carbonyl involvement in the reaction mechanism. In other words, deprotonated lignin or hydroxyethyl lignin had formed a carbonate interchange with EC by attacking the carbonyl group of EC (**Figure 24**, compound 3 and 4). This signal was much more evident in the high-temperature reaction at 170 °C. In addition, a change of stretching of aryl C-O at a cluster of peaks from $v= 1270$ cm^{-1} to 1250 cm^{-1} and the stretching of alkyl C-O at $v=1170$ cm^{-1} to 1020 cm^{-1}, compared to unmodified lignin, confirmed the formation of aryl-alkyl ethers in the hydroxyethyl lignin. The C-O in phenolic

groups disappeared at ν=1200 cm^{-1} after the hydroxyethyl reaction. Overall, these results supported the previous quantitative conclusion that phenolics were converted into AlOH by the modification of EC with the formation of carbonate and ether bonds, with more copolymerization of EC when conducted at higher conditions.[262]
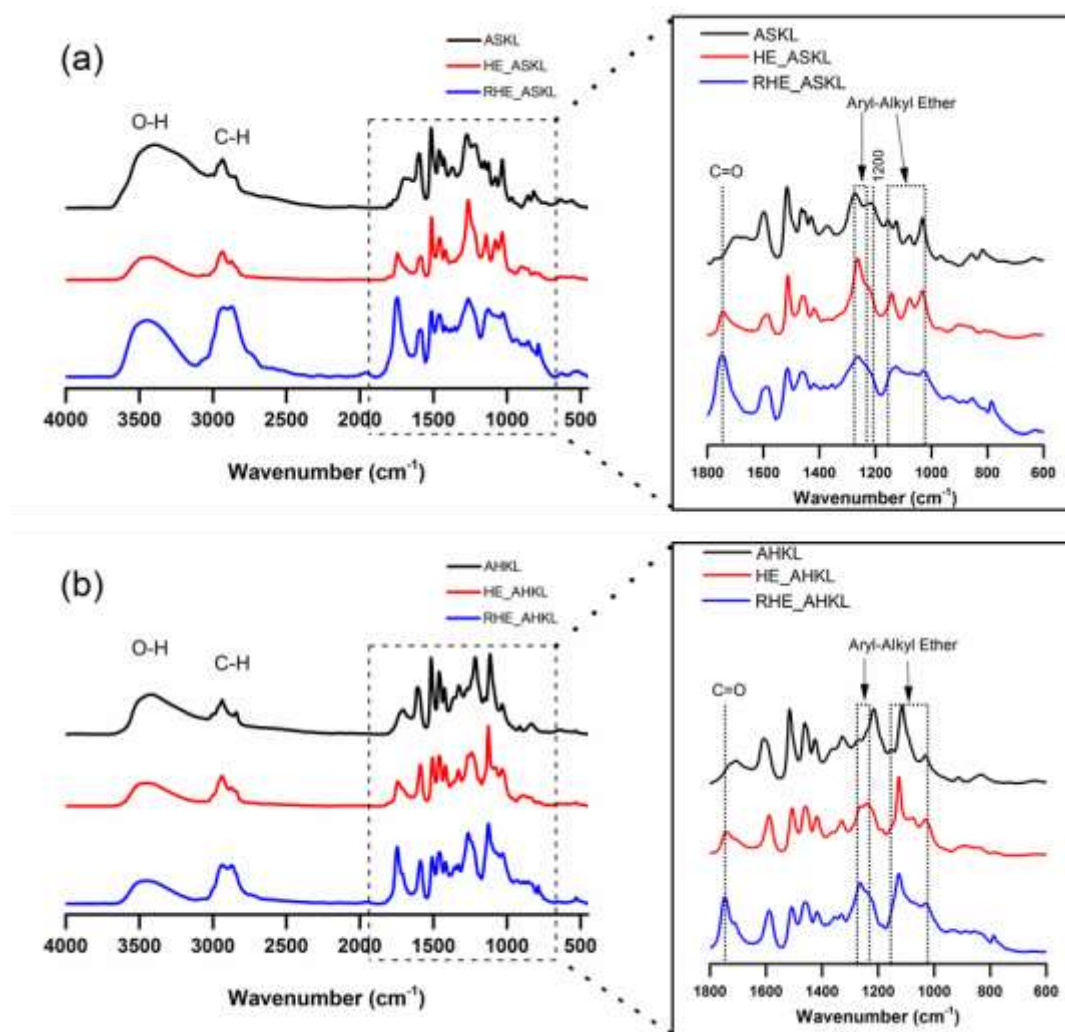
Figure 29 FT-IR spectra of softwood (a) and hardwood (b) lignin before and after hydroxyethylation at optimized (HE_) and higher temperature reference (RHE_) conditions. Reprinted with permission from ref. [150]. Copyright 2018 American Chemical Society

4.2.5   Solubility analysis

In view of greener advances, the solubility of lignin would impact the following preparation of lignin-based plastics involving chemical modification, polymerization, and copolymerization.

Further, the structure of lignin influences their solubility in different types of solvent with varying solubility parameters. According to the Hanson solubility parameter theory, the Hildebrand Solubility Parameter (δ-value) has been separated into three different components: dispersion, polar, and hydrogen bonding components.[115] Schuerch et al. found that the higher hydrogen bond capacity of the solvent made positive impacts on the lignin solubility, while the increased molecular weight of lignin would limit lignin dissolution.[263]

Table 8 showed the δ-value of different solvents and their dissolving ability for different types of lignin, based on solvent clarity. (**Figure 23**) Moreover, the acetone purification enabled isolation of lignin with a δ-value close to acetone and thus lignin readily dissolved in DMF, pyridine, and THF. After the hydroxyethyl reactions with optimized conditions, softwood and hardwood lignin had slightly lower solubility in ethanol, acetone, and THF in comparison original Kraft lignin. Overall, the hydroxyethyl lignin had a slight change in its solubility in these organic solvents, which is in agreement with our previous conclusions that there was derivatization rather than co-polymerization during the modification. Interestingly, for the solvent with the lowest δ value used, propionic acid, showed enhanced solubility for the modified lignin which is relevant for the esterification of lignin described below.

Table 8 Solubility analysis of lignin before and after hydroxyethyl reaction in different organic solvents

	δ-value (MPa$^{1/2}$)	ASKL	HE_ASKL	RHE_ASKL	AHKL	HE_AHKL	RHE_ASKL
DMSO	26.4	+++	+++	+	+++	+++	+
Ethanol	26.0	++	+	+	++	+	+
DMF	24.7	+++	+++	+	+++	+++	+
Pyridine	21.9	+++	+++	+	+++	+++	+
Acetone	19.9	+++	++	+	+++	++	+
CH$_2$Cl$_2$	19.8	+	+	-	+	+	-
THF	18.6	+++	++	+	+++	++	+
Ethyl Acetate	18.6	+	+	-	+	+	-
Propionic acid[a]	14.5	+	++	+	+	++	+

[a] lignin without acetone purification were adopted;

4.2.6   Thermal properties of lignins

The thermal stabilities of unmodified and hydroxyethylated lignin were analyzed by TGA under a nitrogen atmosphere. The $T_{D5\%}$ (the temperature with 5% degradation) of softwood and hardwood Kraft lignin occurred at 213 °C and 218 °C (**Table 9**). After hydroxyethylation, $T_{D5\%}$ of ASKL and AHKL shifted to 251 °C and 273 °C, respectively. ASKL and AHKL had a higher weight loss rate at a range from 200 to 450 °C compared to the modified samples. Below 300 °C, about 15% weight of original lignin was lost due to the degradation of thermally sensitive groups with the increased temperature. From this result, it is clear that after the hydroxyethyl reaction, lignin became more thermally stable as less than 10% weight loss occurred below 300 °C, which stability is critical when processing thermoplastic materials at elevated temperature.

Table 9 Thermal properties of lignin before and after hydroxyethylation at optimized (HE_) and higher temperature reference (RHE_) conditions

	ASKL	HE_ASKL	RHE-ASKL	AHKL	HE_AHKL	RHE_AHKL
$T_{D5\%}$/°C	213±2	251±1	293±11	218±2	273±2	300±0.30
T_{g_DSC}/°C	86±2	73±4	31±7	122±9	108±5	43±4
$T_{g\_G'}$/°C	99	81	<25	129	112	49
$T_{g\_G''}$/°C	101	88	<25	145	114	57
$T_{g\_tan\delta}$/°C	120	139	52	163	174	95

Lignin can be potentially used as thermoplastic materials, dependent upon its glass transition temperature (T_g). In this study, DSC and thermo-rheological analysis were used to obtain the T_g of lignin before and after hydroxyethylation. Based on the thermal scans, there were clear endothermic changes in the baseline for all lignin samples, allowing the determination of the T_g by DSC. Comparing the parent materials after annealing treatment, hardwood lignin had a T_g of 128 °C which was greater than softwood lignin (T_g of 88 °C). While methoxy groups usually decreased the T_g, the hardwood had higher molecular weight than ASKL, which can impact the chain mobility. After the hydroxyethyl reactions, both types of lignin had a slightly lower T_g, which may have arisen from the additional bulking from the ethylene groups. [264]

Parallel plate dynamic rheological analysis was used to investigate the change of mechanical properties, including storage modulus (G'), loss modulus (G"), and tan δ, as a function of temperature (**Figure 30**). With a normal force applied to the sample during the temperature ramp, there was densification of the material with a response seen as an increase in G'. When the samples reached their T_g there were nearly 2 orders of magnitude decrease in storage modulus with continued heating. The unmodified lignin had a higher T_g than the hydroxyethylated lignin (**Table 9**). The onset of G' decrease was similar in value to the DSC data for these lignin samples. The peak of tan δ values for both hydroxyethyl lignin derivatives was lower than the parent lignin. The temperature range width of the transition for the softwood was slightly wider than the unmodified lignin, indicating a broad relaxation profile. Total tan δ profiles for both samples of the hardwood Kraft lignin were above the testing conditions of the experiment, however, the hydroxyethyl derivatives had a significant shoulder on the peak. This shoulder or wider peak temperature ranges may belong to the wider distribution of polymer's molecular weight, in agreement with GPC results (**Figure 27**).
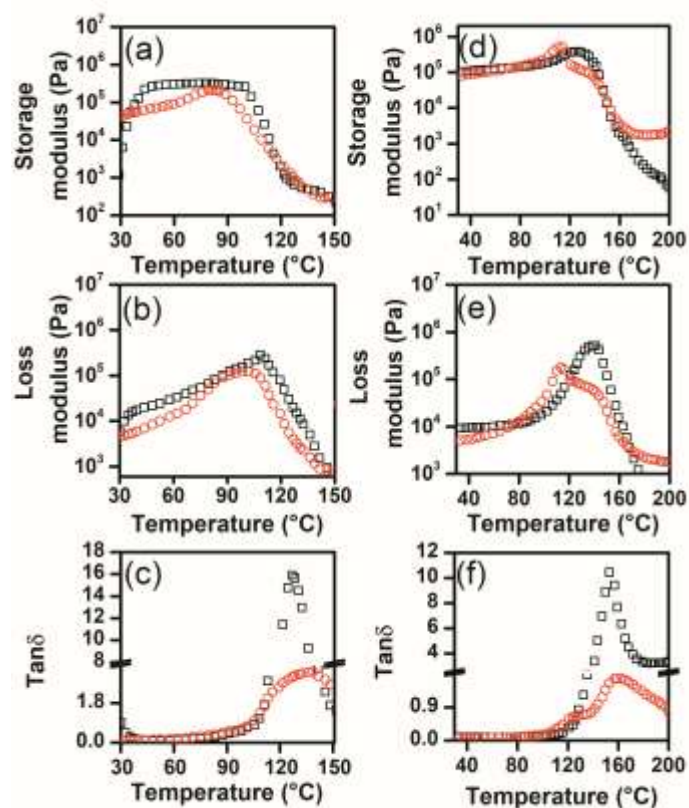
Figure 30 Storage modulus (G', a ASKL, b AHKL), loss modulus (G'', b ASKL, d AHKL), and tanδ (degrees, a ASKL b AHKL) of lignin before (black square) and after hydroxyethyl reaction (red cycle). Reprinted with permission from ref. [150]. Copyright 2018 American Chemical Society

4.2.7   Comparison with reference conditions

Based on the above discussion, this hydroxyethyl reaction was robust enough to adopt the low amount of catalysts and ethylene carbonate without adding additional solvent. However, this reaction was temperature-sensitive, because of the co-polymerization or transesterification with ethylene carbonate under high temperature. We minimized these reactions to prepare hydroxyethyl lignin derivatives by adopting a lower reaction temperature range from 90 to 120 °C. Previous researchers had developed hydroxyalkyl lignin by reactions with ethylene carbonate and propylene carbonate (PC) with temperature 170 °C. Results showed that ArOH groups were converted with 10 e.q. EC or PC at 170 °C for less than 3 hrs, but also resulted in a significant increase in molecular weight and its distribution, and undesirable changes to hydroxyl content.[137, 260] Herein, those reference conditions were also adopted in the synthesis of the hydroxyethyl lignin for ASKL and AHKL, relative to the optimized conditions of this current study. Compared with untreated lignin,

the hydroxyalkyl reaction at 120°C caused lignin to become a lighter tan color in its dry powder form. The 170 °C reference conditions resulted in lignin as a dark-colored solid that appeared with a wax-like texture (**Figure 31**). For both ASKL and AHKL, these modified lignins under high temperature showed much lower solubility in all solvent. (**Table 8**) The lower solubility made the lignin difficult for further evaluation, processing or modification.
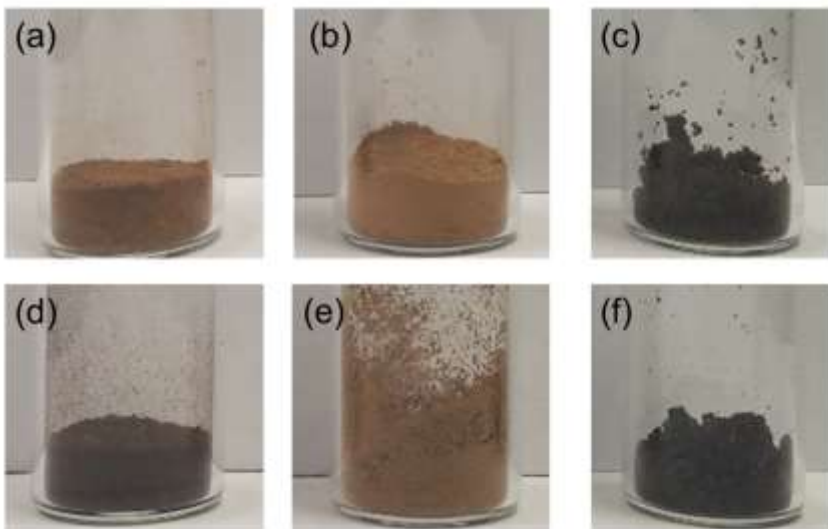
Figure 31 Photos of lignin before and after hydroxyethyl reaction. (a) ASKL; (b) HE_ASKL; (c) RHE_ASKL; (e) AHKL; (e) HE_AHKL; and (f) RHE_AHKL

In addition, these lignins have higher thermal stability, but much lower glass transition temperatures, near room temperature because of the higher number of aliphatic groups. These characters arise partly because of the co-polymerization or transesterification between modified lignin and ethylene carbonate under high temperatures. Moreover, the FT-IR spectrum (**Figure 29**) showed an obvious increase in the carbonyl peak (v=1748 cm^{-1}). In summary, the temperature is highly important to distinguish between lignin derivatization and lignin co-polymerization with polycarbonate segments on the lignin.

4.3   Conclusion

1) Ethylene carbonate, as greener reagent with lower toxicity and higher stability (boiling point=243 °C), was reacted with lignin aromatic hydroxyl groups and carboxylic acids to form hydroxyethyl lignin. In this chapter, the hydroxyethyl reaction conditions and reagents were

studied for lignin aromatic hydroxyl conversion, while limiting the change in total hydroxyl content.

2) Optimized reaction conditions for softwood Kraft lignin led to 95% conversion of ArOH into primary hydroxyalkyl ethers (90% for hardwood Kraft lignin) with a total hydroxyl content of 5.02 mmol/g (4.56 mmol/g hardwood Kraft lignin).

3) Further, ^{13}C NMR analysis was utilized to reveal that the alkyl carbons of the derivatives corresponded with the phenolic ethers, indicating there was mainly derivatization and not polymerization of the ethylene carbonate at the optimized conditions. Further, the lignin derivatives were more thermally stable compared to the unmodified analog, while hydroxyalkylation at optimized conditions caused a slight decrease in T_g relative to the unmodified sample.

4) Finally, hydroxyethylation using ethylene carbonate with common catalysts may serve as a robust route to create lignin with uniformity, avoiding carcinogenic reagents typically used in these reactions; however, reactive conditions should be carefully selected with technical lignin in order to minimize structural changes to the lignin.

Chapter 5: The structure-property relationship of lignin-based rigid polyurethane foam

5.1 Introduction

Polyurethane foams are produced by the condensation reaction between a "polyol" and an isocyanate compound.[184] Though industrial technical lignin can be treated as a kind of polyol due to its abundant hydroxyl groups, it is difficult to use these lignin resources directly to make polyurethane foam. Besides the problems we discussed in chapter 1, several other issues will further prevent this application 1) due to the high glass transition temperature (T_g=90 - 160 °C), lignin at room temperature are solid particles, which cannot react with isocyanate thoroughly or homogeneously; 2) lignin has limited solubility or dispersibility in polyols;[265] and 3) the low reactivity of aromatic hydroxyl groups with isocyanate groups.

Many researchers have followed two routes to utilize lignin as polyol for PU foams: 1) modify the lignin to derivatize the ArOH by esterification or etherification to improve their reactivity with isocyanate; or 2) although ineffective, simply mix low levels of lignin with traditional fossil-based polyol.[187] In chapter 4, we developed hydroxyethyl modification to obtain lignin derivatives with uniform hydroxyl groups, containing 90% aliphatic OH groups. In tandem, propylene oxide which has been used throughout the literature was also utilized to modify the ArOH of lignin at room temperature to obtain hydroxypropyl lignin (HPLignin).[255]

Lignin has different miscibility with polyols, dependent upon the plant origin and isolation methods.[266] Organosolv lignin is extracted by the aqueous alcohol under high temperature, so it has enhanced solubility with polyether polyol relative to Kraft lignin.[266] However, the adoption of an organic solvent requires significant capital investment and operating costs in this process. As a result, using low-quality biomass resources such as bark that has lignin content as raw feedstock can potentially reduce the cost of organosolv lignin production. **Appendix B** showed that the organsolv process can extract high yield crude lignin from both pine bark and oak bark. These crude lignin contains a higher amount of polyphenolic compounds and organic acid with lower molar mass. So, it potentially has good mixability with the polyol.

Five types of lignins were used for polyurethane foam production: softwood Kraft lignin (SKL), hydroxypropyl SKL (HPSKL), and hydroxyethyl SKL (HESKL), organosolv pine bark crude lignin (PBL), and organosolv oak bark crude lignin (OBL) were prepared and characterized by ^{31}P NMR, ^{13}C NMR, and gel permeation chromatography (GPC). These lignin resources were then mixed with a polyester-based polyol to make a PU foam, followed by the characterization of the foam's properties. Our goal was to understand the structure-property relationship of lignin-based PU foam; this may instruct the way to "design" or select lignin to make more superior foam materials.

5.2   Results and Discussion

5.2.1   Reactivity of lignin with isocyanate

The isolation of technical lignin using aqueous alkali or acid by the degradation of ether bonds such as β-O-4 will lead to the formation of ArOH groups (directly) and COOH groups (indirectly). These functional groups can all react with the isocyanate functional group. However, they have different relative reaction rates due to their different nucleophilicity. As a control, softwood Kraft lignin (SKL) was initially reacted with phenyl isocyanate. After the reaction, revealed in the ^{13}C NMR spectrum, aliphatic hydroxyl groups (AlOH) and aromatic hydroxyl groups (ArOH) formed new peak clusters in 148.4 – 149.6 ppm and 152.4 – 152.8 ppm, respectively (**Figure 32, a**). By integrating these two peaks, we could calculate the ratio of AlOH/ArOH (1.03) in carbomated lignin, which is higher than the original SKL 0.81, indicating the higher reactivity rates of AlOH groups with isocyanate relative to ArOH. ^{31}P NMR spectrum showed a small amount of ArOH groups in carbamated SKL (**Figure 32, b**). The high reactivity of AlOH groups with isocyanate was due to its stronger nucleophilicity than the carboxylic acid and aromatic alcohols. An earlier study showed that the relative reaction rate of primary AlOH groups is 2 - 4 fold higher than that of COOH and secondary AlOH group, and more than a thousand fold greater than that of ArOH groups.[267] Therefore, if we can modify the lignin so it contains a higher amount of AlOH groups, it may improve performances of the resulting polyurethane foam.
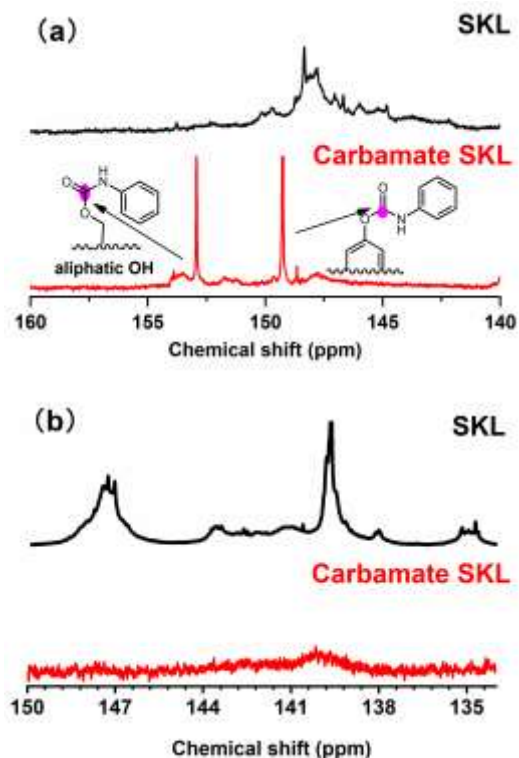
Figure 32 ^{13}C NMR spectrum (a) and 31P NMR spectrum (b) of SKL before and after carbamylation

5.2.2 Hydroxyalkylation of lignin derivatives

The chemical modification of lignin, such as oxypropylation and hydroxyethylation with ethylene carbonate, allows the modification of the ArOH groups to AlOH groups. Oxypropylation was extensively studied by Glasser and his co-workers, who used propylene oxide to modify the ArOH groups of lignin in aqueous alkali.[145, 146] Depending on the reaction temperature, hydroxyalkylation either resulted in liquified oxypropylated lignin polyols or hydroxypropyl lignin derivatives (HPLignin). The high reaction temperature ($> T_g$ of lignin) also may cause depolymerization or polymerization with itself, which may prevent understanding the structure-property relationship of the derivatized lignin when used in materials. So, in the current study, the derivatized reaction under room temperature was employed to keep the Kraft lignin structure unmodified as much as possible. The hydroxyethyl reaction, developed in chapter 4, was another method to obtain hydroxyethyl lignin (HELignin), which contained a higher amount of AlOH groups. (**Figure 33**)
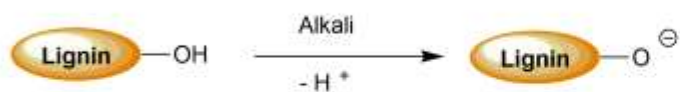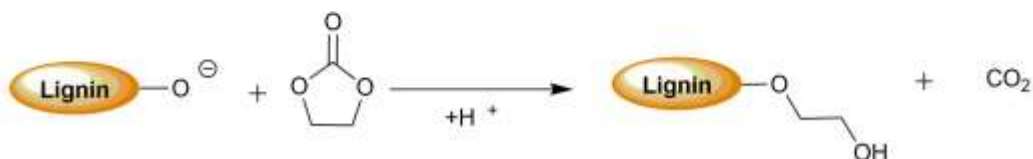
Figure 33 Reaction scheme of hydroxypropyl and hydroxyethyl reaction

^{31}P NMR was used to analyze both HPLignin and HELignin, which had increased content of AlOH groups (AlOH, 150-145 ppm) corresponding with a reduction or disappearance of aromatic OH groups (ArOH, 144-136 ppm). (**Figure 34, a**) Noteworthy, the HPLignin still contained a trace amount of ArOH and a higher amount of COOH groups. Also for this sample, there were two peaks in the AlOH regions, where the right peak belonged to AlOH groups from the extended oxyalkylene ether. Further, quantitative results were tabulated in **Table 10** and revealed that HPLignin had 5.80 mmol/g AlOH groups and HELignin contained 3.01 mmol/g AlOH groups. The total OH groups of HPLignin (7.15 mmol/g) is much higher than the total OH groups of HELignin (3.31 mmol/g).

Table 10 Characterization of softwood Kraft lignin (SKL), hydroxypropyl SKL (HPSKL), hydroxyethyl SKL (HESKL), organosolv pine bark lignin (PBL), organosolv oak bark lignin (OBL)

	^{31}P NMR (mmol/g)				^{13}C NMR (100 Ar)						GPC		
Lignin	AlOH	ArOH	COOH	Total OH	AlOH Primary	AlOH Secondary	ArOH C5-Sub	ArOH C5-Free	Total OH	ArH	Mw /(KDa)	Mn /(KDa)	PDI
SKL	2.40	4.00	0.46	6.40	32	15	31	27	107	217	3.26	0.75	4.33
HPSKL	5.80	1.35	0.57	7.15	78	16	8	11	114	220	7.17	1.48	4.85

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	^{31}P NMR (mmol/g)				^{13}C NMR (100 Ar)						GPC		
Lignin	AlOH	ArOH	COOH	Total OH	AlOH Primary	AlOH Secondary	ArOH C5-Sub	ArOH C5-Free	Total OH	ArH	Mw /(KDa)	Mn /(KDa)	PDI
HESKL*	3.01	0.30	0.05	3.31	-	-	-	-			15.81	1.47	10.77
OBL	2.28	4.44	0.35	6.72	29	37	60	31	157	217	3.04	0.91	3.34
PBL	2.73	4.16	0.92	6.89	42	40	54	30	166	226	2.04	0.48	4.23

* this lignin has low solubility in the DMSO solvent

(a)
Aliphatic OH
Aromatic OH
COOH
SKL
HPSKL
HESKL
150
145
140
135
Chemical shift (ppm)
(b)
HESKL
MeO
DMSO-d6
HPSKL
SKL
1
2
3
4
5
172
170
168
166
Chemical shift (ppm)
90
80
70
60
50
40
30
20
10
Chemical shift (ppm)
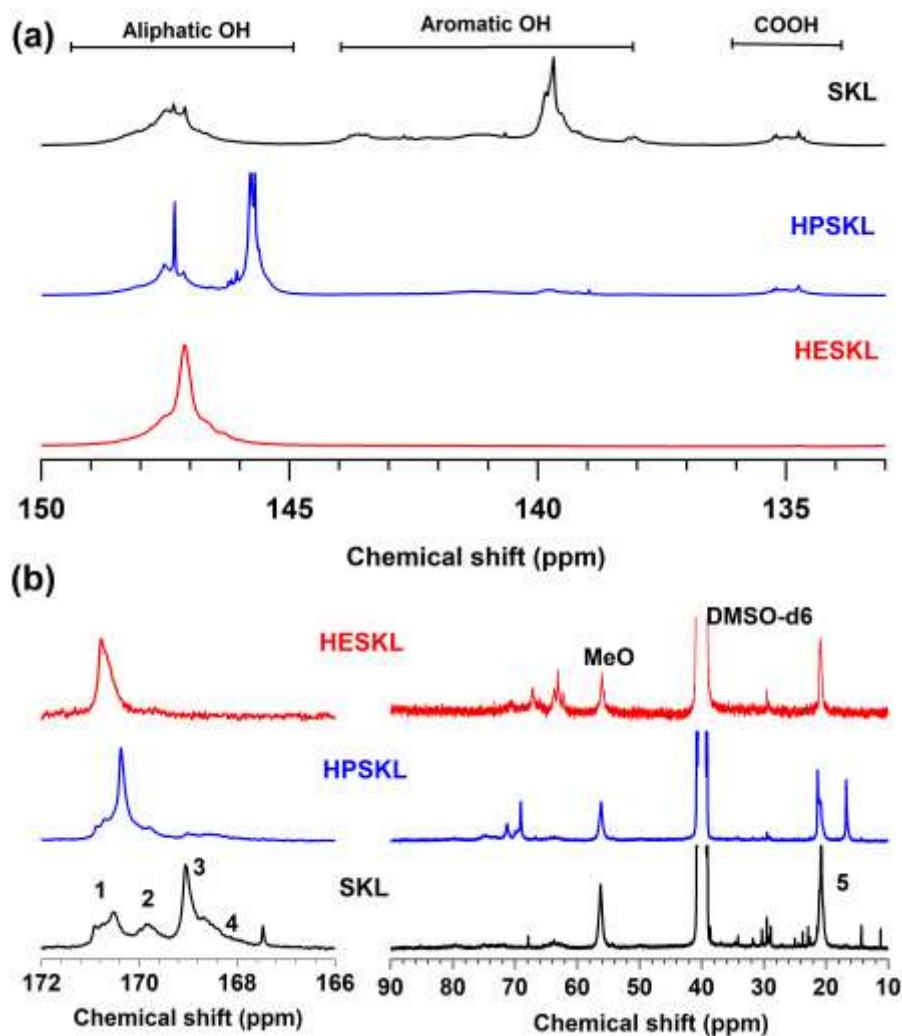
Figure 34 ^{31}P NMR spectrum (a) and ^{13}C NMR spectrum (b) of acetylated softwood Kraft lignin (SKL), acetylated hydroxypropyl SKL, and acetylated hydroxyethyl SKL

^{13}C NMR was also used to analyze acetylated lignin. The acetylation could distinguish, or tag different types of hydroxyl groups in lignin. As shown in ^{13}C NMR spectrum (**Figure 34**), the

primary AlOH (172 – 169.7 ppm), secondary AlOH (169.7 - 169), ArOH 5-Sub (169 – 168.3 ppm), and ArOH 5-free (168.3 – 166 ppm) were identified in the SKL. After the modification, HELignin only contained primary AlOH groups, while the HPLignin mainly contained secondary AlOH groups. For the hydroxypropyl reaction, the deprotonated phenolic ion in lignin, under alkali conditions, could attack the carbon in the epoxy ring of the propylene oxide via an SN_2 reaction mechanism. As the 2-propyl oxide ion had higher stability than 1- propyl oxide ion, the resulting lignin would contain a higher amount of secondary AlOH group than the primary AlOH group; the derivatized secondary AlOH (22 - 18 ppm) was obviously higher than the derivatized primary AlOH (18 - 15 ppm) shown in **Figure 34, b**. ^{13}C NMR ArH spectral regions for the lignins were similar for the hydroxypropyl lignin and SKL, indicating that a few condensation reactions occurred during the modification.

Due to the addition of hydroxyalkyl groups, molecular weight traces of HELignin and HPLignin shifted to shorter elution times (higher Mw) after the modification. HELignin has a larger molar mass and broader molecular weight distribution than other types of lignin. (**Figure 35**) This issue most likely arose because of side reactions such as condensation reactions of inter-lignin moieties (see **Chapter 4** for full discussion). Overall, both hydroxypropyl and hydroxyethyl processes could successfully modify the ArOH groups of lignin to produce derivatized lignin with a higher amount of AlOH group.
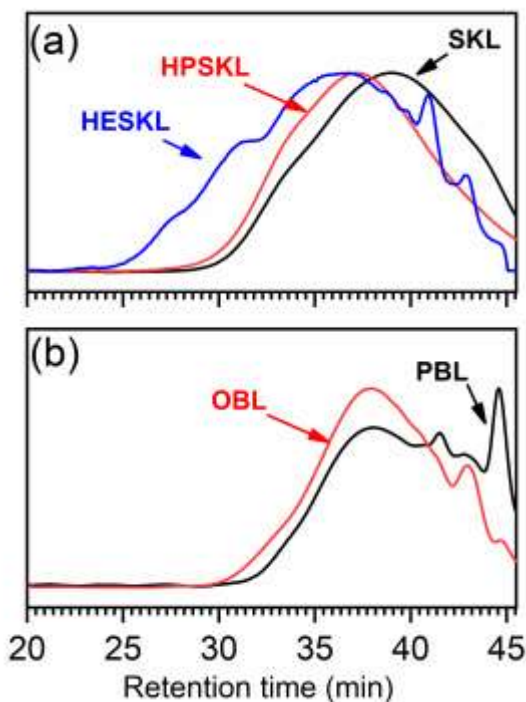
Figure 35 Gel permeation chromatography traces of acetylated lignin including softwood Kraft lignin (SKL), hydroxypropyl SKL (HPSKL), hydroxyethyl SKL (HESKL), organosolv pine bark lignin (PBL), and organosolv oak bark lignin (OBL)

5.2.3   Organosolv bark lignin

Besides chemical modification, a series of technical lignins with slightly different structures and functionality have been developed recently, especially using the organosolv process.[115] Previous studies found that organosolv lignin-based PU foams had better performances than Kraft lignin-based PU foams.[266] In this study, the ethanol-water organosolv process (1% sulfuric acid) was applied to extract crude lignin compounds from pine bark and oak bark, which is an underutilized biomass resource.

Different from both the softwood lignin (Kraft and PBL), the OBL contained syringyl OH groups, as it originated from hardwood species (**Figure 36 a**). Quantitatively ^{31}P NMR showed that OBL contained 6.72 mmol/g of total OH groups, and PBL had 6.44 mmol/g of total OH groups. Their AlOH/ArOH ratios (OBL, 0.65 and PBL, 0.66) were close to SKL (0.64). PBL had a higher amount of COOH groups than other types of lignin resources, due to extractive compounds such as fatty acids found in bark (**Appendix B**). ^{13}C NMR analysis (**Appendix B**) further confirmed the

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extractive compounds (polyphenolics) and suberin-derived organic acid in extracted PBL. These low molar mass extractive compounds lead to the formation of a sharp peak at the end of elution during molecular weight analysis (retention time 40-45 min). OBL and PBL have lower molecular weight and a more narrow MW distribution than SKL. (**Figure 35**)
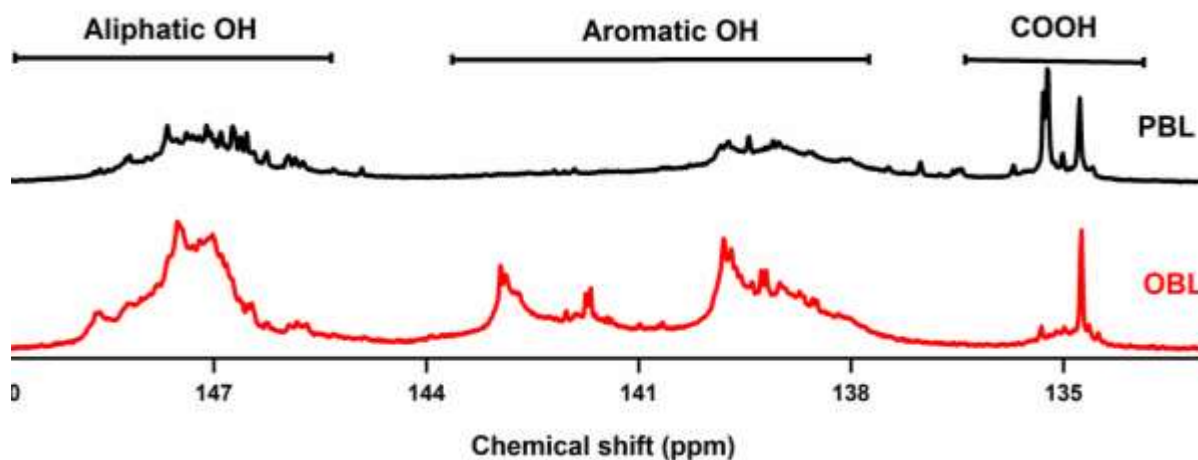
Figure 36 ^{31}P NMR spectrum of organosolv pine bark lignin (PBL) and organosolv oak bark lignin (OBL)

5.2.4 Blends of the lignin-based polyol mixture

For the polyurethane foams, the different lignins were mixed at different portions of the polyol in order to substitute a certain portion of the polyol, while still maintaining adequate performance. For this system, the lower viscosity of the resulting lignin-polyol mixture indicated a higher amount of polyol as the addition of lignin impacted the viscosity of the system. Generally, the viscosity of polyol must be lower than 300 Pa·s to form good foams when reacted with polyurethanes.[187] Higher viscosity will lead to incomplete mixing resulting in the heterogeneous distribution of catalysts, blowing agents, and surfactants.[266] As a result, the obtained PU foam would have a non-uniform cellular structure. The addition of lignin increased the viscosity of resulting lignin-polyol mixture (SKL, modified SKL, PBL, and OBL), but in all cases, they were lower than 300 Pa·s. (**Figure 37**) However, the different types of lignin-polyester polyol mixtures had quite different viscosity values. When 10% lignin (wt) was added into the polyol, the viscosity increased 2 - 4 fold, while the PBL-polyol mixture had the lowest viscosity. Noticeably, the viscosity of HPSKL and HESKL was significantly lower than SKL when the lignin content increased to 18% and 25%.
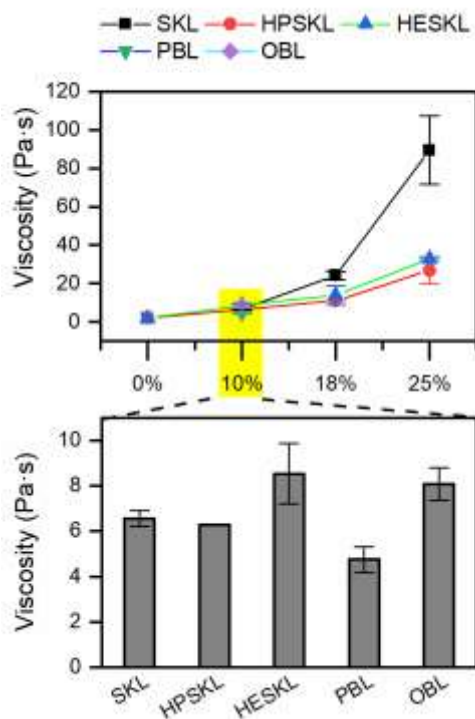
Figure 37 Viscosity of lignin-polyester polyol mixture within different types of lignin including organosolv oak bark lignin(OBL) organosolv pine bark lignin (PBL), hydroxyethyl lignin (HELignin), hydroxypropyl lignin (HPLignin), and the increasing amount of lignin

5.2.5   Lignin-based polyurethane foam

The above different types of lignin-based polyols were further reacted with pMDI to produce polyurethane foams. One observation was that the resulting foam had different colors dependent on lignin resources (**Figure 38**). Most of the foams appeared uniform at a lignin loading level of 10% lignin in polyol by weight. If the lignin concentration was further increased, the SKL-based PU foam became very brittle and did not form a PU foam, most likely due to the low relative reactivity rate of ArOH and COOH functional groups on lignin. HESKL and HPSKL could still make quite uniform PU foams, even when the concentration of lignin was increased to 18%. Their micromorphology showed the microscale cell structure formed in the polyurethane foam and some of the lignin foams, but it was difficult to see a well-developed cell structure in SKL-based PU foam (**Figure 38**).
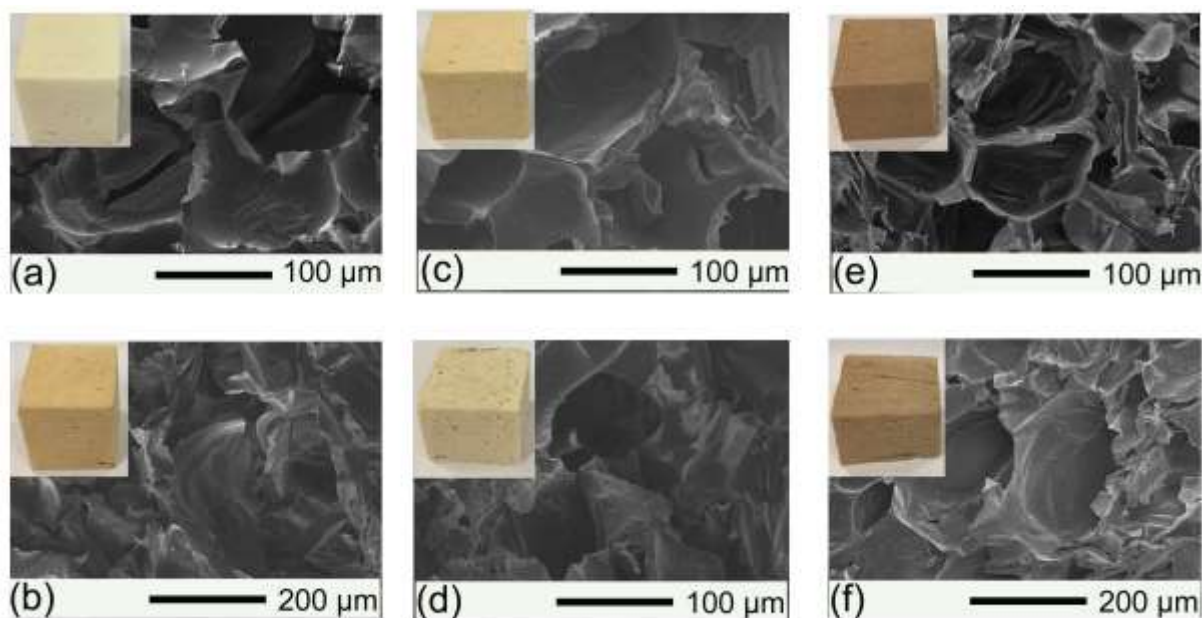
Figure 38 Macro - and micro- morphology of lignin-based polyurethane foam; (a) PU, (b) 10% SKL-PU foam (c) 10% HPSKL-PU foam, (d) 10% HESKL-PU foam, (e) 10% PBL, and (f) 10% OBL

5.2.6   Density analysis of lignin-based PU foam

In comparison with the original rigid PU foam, the addition of lignin lessened the density of PU foam from 0.1 g/ml to 0.08 g/ml for SKL and modified SKL and 0.9 g/ml for organosolv bark lignin. (**Figure 39**) This was desirable as the lower density means the reduced weight of PU foam for packaging or insulation. The density of HPSKL based foam is higher than HESKL based foam, since the HPSKL contains higher total hydroxyl groups and contains both primary AlOH and secondary AlOH group with more branching points. With an increasing amount of HESKL and HPSKL, the resulted related PU foam had larger variability of density, as increased viscosity may have caused a heterogeneous distribution of reagents and catalysts.
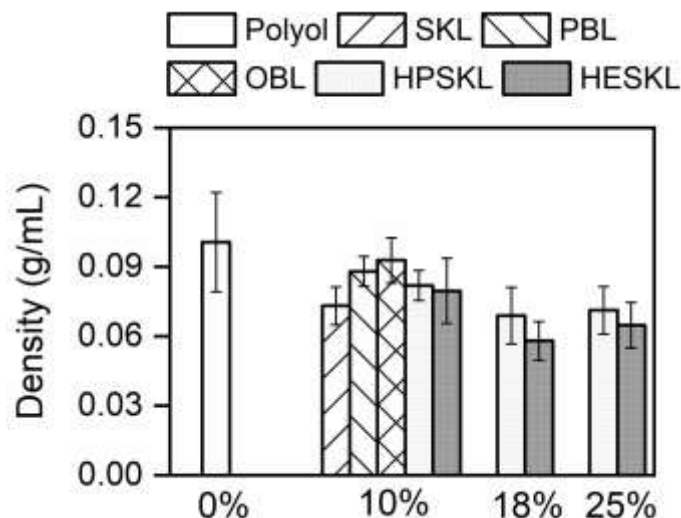
Figure 39 Density analysis of PU foam and lignin-based PU foam (softwood Kraft lignin, SKL; organosolv pine bark lignin, PBL; Organosolv oak bark lignin, OBL; hydroxypropyl SKL, HPSKL; hydroxyethyl SKL, HESKL)

5.2.7 Compressive modulus analysis of lignin-based PU foam

The aromatic polyester polyol (Stepanpol PS-2352) was designed for the preparation of rigid PU foam due to its rigid aromatic backbones and thus has high compressive strength (2 MPa). The addition of 10% lignin weakened the compressive modulus and increased the flexibility of the resulting lignin-based PU foam (**Figure 40**), due to the formation of nonuniform cellular structure (**Figure 38**). Noteworthy, different types of lignin had quite different compressive modulus. As expected, the organosolv lignin and modified lignin had a higher compressive modulus than SKL due to their better dispersibility and higher reactivity of the lignins.
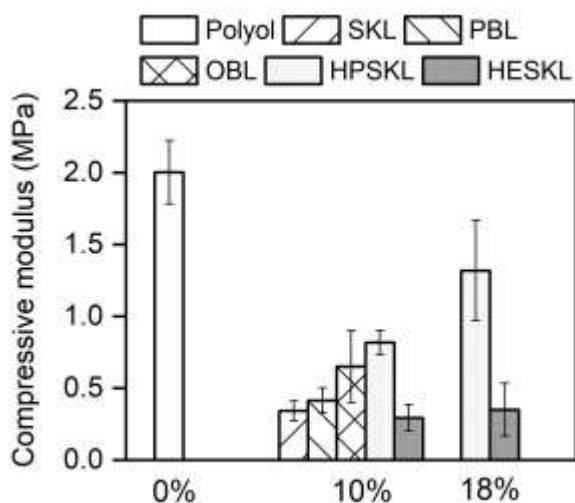
Figure 40 Compressive modulus of PU foam and lignin-based PU foam (softwood Kraft lignin, SKL; organosolv pine bark lignin, PBL; Organosolv oak bark lignin, OBL; hydroxypropyl SKL, HPSKL; hydroxyethyl SKL, HESKL)

5.2.8 The structure-property relationship of lignin-based PU foam

The viscosity, density, and compressive modulus of foams were compared with different lignin attributes from the five different lignin sources as shown in **Figure 41**. Surprisingly there was a relationship between the viscosity and carboxylic acid content of the lignin. As the polyester polyol was mainly synthesized from an aromatic carboxylic acid and diol, ester linkages on the polyol may provide a similar environment to help dissolve the lignin with a higher amount of carboxylic acid due to the improvement on their intermolecular interactions and lead to better miscibility. The increasing amount of AlOH may enhance the dispersibility of lignin as well, as HELignin- and HPLignin- polyol had a much lower viscosity than SKL-polyol at increasing addition amount (**Figure 41 a**).
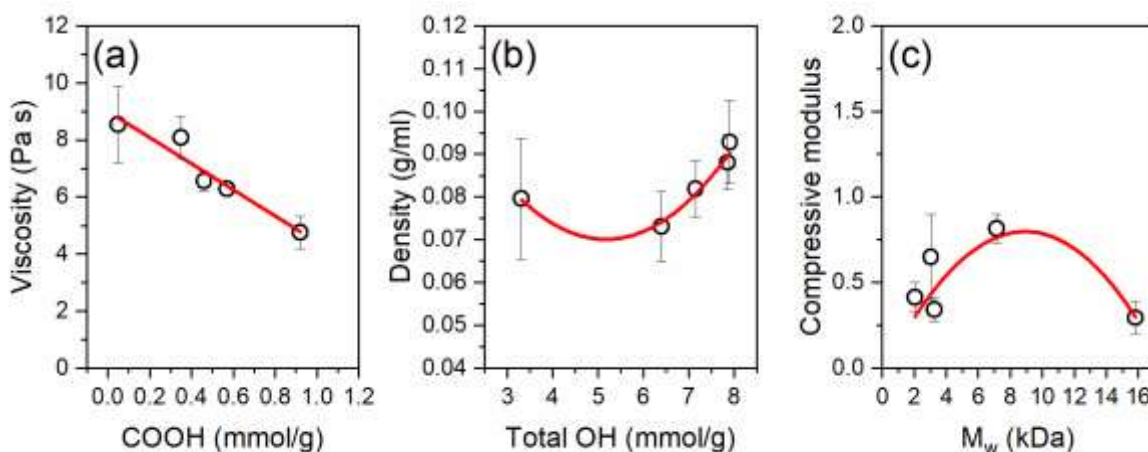
Figure 41 Correlation between the structure (functional groups) of lignin and the properties of resulting polyol (lignin/polyol: 1/9) and PU foam (lignin/polyol: 1/9); (a) carboxylic acid (COOH) groups and viscosity, (b) density-total OH groups, and (c) compressive modulus and molar mass

Except for the HESKL, the increased amount of total hydroxyl groups and molar mass in lignin will raise the density and compressive modulus of resulting PU foam. The random distribution of hydroxyl groups as handles will lead to more connections in the PU foam, which may increase the density and thus the compressive modulus of resulting PU form. The HESKL behaved differently, partly because of the broad molar mass distribution. Some of the modified HESKL had a large molar mass and were not dispersed effectively in the polyol. This failure to mix created some unreacted zones appearing as dark specks belonging to the modified lignin; these fragments impacted the density and compressive modulus (**Figure 38, d**).

In a short summary, the mixability and dispersibility of lignin in polyol was mainly impacted by their chemical functionality and molecular weight. The rule of thumb for "like dissolves like" or the difference in solubility parameters (enthalpic component) combined with the effects of molecular weight (entropic component) could be used to explain the miscibility of the lignin with the polyol. A higher amount of COOH and AlOH were essential to improve the miscibility of lignin in the polyol. The total number of hydroxyl groups and molar mass will impact the density and compressive modulus of the resulting foam. The lignin, within more "superior handles" (AlOH), was preferred to be mixed with the polyol to obtain PU foam with comparable performance. Of course, the backbone structure of lignin would have a direct relationship with the

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final properties of PU foam, but from this work, it is clear the importance of the accessible hydroxyl groups for forming a good foam.

5.3   Conclusion

1) In this chapter, a series of different types of lignin, including softwood Kraft lignin, hydroxypropyl SKL, hydroxyethyl SKL, and orgnanosolv bark lignin (pine bark and oak bark) were prepared to make PU foams.

2) The reaction between the phenol isocyanate and SKL showed that the carbamylated reaction had a higher selectivity toward the AlOH than ArOH.

3) Moreover, an increasing amount of functional groups, such as carboxylic acids and aliphatic hydroxyl groups, improved the dispersibility of lignin in the aromatic polyester polyol.

4) The addition of lignin weakened the density and compressive modulus of final PU foam. This result was mainly impacted by the total hydroxyl groups and the molar mass of the lignin. A suitable selection of lignin resources is vital to realize the control of the final properties of PU foam.

5) Further, the hydroxy alkylation of lignin provides for better properties of PU foams when compared to the unmodified lignin. For processes such as hydroxyethylation with ethylene carbonate, reaction conditions must be developed to limit the high molecular weight derivatives that are difficult to dissolve in the polyol.

Chapter 6: Real-time monitoring of the hydroxyethyl reaction

6.1 Introduction

As discussed in **chapter 1**, greener organic carbonate compounds including dimethyl carbonate,[135, 136] diallyl carbonate,[128] ethylene carbonate,[150] propylene carbonate,[137, 151, 259] glycerol carbonate,[33, 260] and vinyl ethylene carbonate[138] have been studied to modify or functionalize polyphenolic compounds such as lignin and tannin.[33, 259, 260] The modified lignin contains over 80% of aliphatic hydroxyl groups with enhanced thermal stability and slightly lower glass transition temperature. These modified lignins, such as hydroxyethyl lignin using ethylene carbonate, had benefits for direct esterification with the target of degradable plastics and hydrophobic coatings.[165, 250]

However, past studies showed that the modification using cyclic organic carbonates was sensitive to reactive conditions, including catalysts, temperature, time, and the type of lignin resources. Longer reaction time or higher temperature caused the crosslinking of lignin, which reduced the hydroxyl groups in modified lignin and significantly enhanced its molecular weight. (**chapter 4**)[150] This outcome means excess reaction time or heat will cause unexpected structural changes, limit solubility, and decrease yields. Finally, side-products will make negative impacts on the quality of lignin derivatives, especially physical properties. We potentially can minimize those side reactions by better controlling the reaction time and temperature. Another route involves highly selective catalysts such as DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) to replace the carbonate salt.[151] However, different types of lignin will require different reaction conditions no matter the catalyst type. For example, hardwood lignin required longer reaction times than softwood lignin for equivalent levels of modification owing to the structural hindrances of the second methoxyl group near the phenolate ion. (**chapter 4**) So, considering there are multiple different types of lignin resources, it is unimaginable to optimize the reaction conditions for all those lignins. Also, choosing toxic amide compounds (DBU) as catalyst will cause environment issues considering the need for separation and recovery.

A simple yet effective method to avoid this issue is to monitor the reaction *in situ* to limit side-product formation. Hence, real-time monitoring, aimed at controlling conditions, can enhance yields to make a more uniform product. From this standpoint, it is one of the 12 fundamental green

chemistry principles.[38, 268] By this technique, we can better control the quality of final products, minimize the waste side products, increase the flexibility of the reaction by monitoring product formation (**Figure 42**).[40] This advance can reduce the workload for optimizing the reaction conditions of different types of lignin resources and account for any variations in temperature control. This monitoring is important since mass and heat transfer will play a vital role in obtaining high-quality products, and natural materials like lignin have inherent variability. The real-time monitoring of this reaction requires choosing a suitable process analytical technique. There are several in-situ spectroscopic tools, including NMR,[269] UV,[270] Raman,[271] and infrared[272, 273] to analyze the functional groups. Though these methods will provide qualitative trending and quantitively assessment of the reaction, these *in-situ* spectroscopic have an issue by the contamination from other reaction reagents. Also, it can be costly to apply these detectors for lab-based experiments.
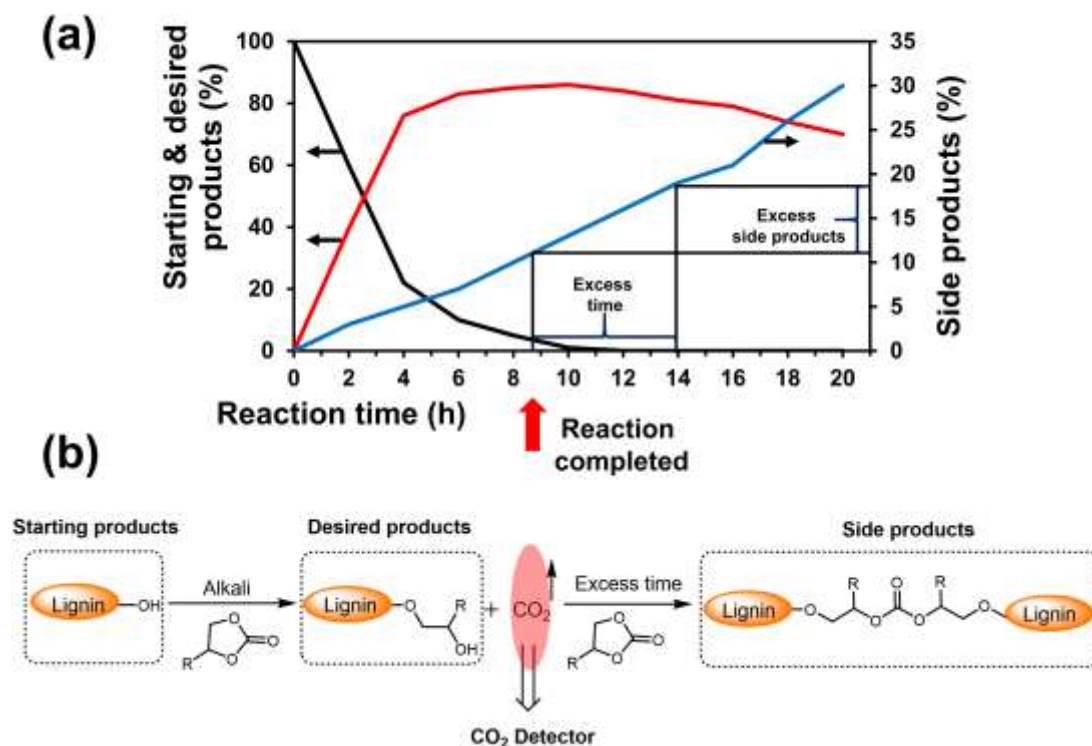
Figure 42 (a) Reaction and analysis of a process that generates the desired product and an undesired side product (b) the hydroxyalkylation of lignin using cycle carbonate

Fortunately, hydroxyethylation of lignin with cyclic organic carbonates will produce carbon dioxide (CO_2) gas in stoichiometric yield. The volume of gas can be readily measured using lab-designed equipment (**Figure 22**). In this reaction, CO_2 was the main gaseous product by the nucleophilic reaction of phenolic ion or carboxylic ion with ethylene carbonate (**Figure 42**). In theory, the production of 1 mole of CO_2 means 1 mole of aromatic hydroxyl groups and carboxylic acid groups are modified during this reaction. Therefore, the amount of CO_2 can serve as a detector to aid in the real-time monitoring of the reaction. Our hypothesis was that the correlation between the amount of CO_2 and the degree of hydroxyethylation of the lignin can be used to control the reaction and stop it prior to by-product formation. We studied the hydroxyethyl reaction using ethylene carbonate as solvent and reagent to modify the softwood Kraft lignin (Amillan A), which was isolated from the LignoForce process. In so doing, we have added insight into the by-product formation during this lignin derivatization method, providing perspective on the robustness of this method to make uniform functional groups on lignin derivatives.

6.2   Results and Discussion

6.2.1   The accuracy control of this equipment

To realize the real-time monitoring of the reaction, our goals were to ensure that the produced CO_2 was only from the side reactions and the resulting collected CO_2 can be accurately measured in our laboratory set-up. Under certain conditions, the degradation of EC can also produce CO_2, which will impact the accuracy of a real-time monitoring system. Several factors were considered to avoid this degradation of ethylene carbonate during the reaction. Water, especially alkaline water, can initiate the hydrolysis of ethylene carbonate to produce CO_2 gas and ethylene glycol.[274, 275] Hence, anhydrous conditions were essential for this system. Also, for the initiation of the reaction, the hydroxyl ion is a stronger nucleophilic reagent than both the phenolic ion and carboxylic ion. Because of this issue, catalyst selection was important, making it critical to adopt carbonate salts as catalysts to reduce the degradation of EC. [274, 276, 277] This aspect was verified in control experiments, mixing ethylene carbonate and Na_2CO_3, producing a negligible amount of CO_2 at 120 °C for 4 hrs. Also, in the reaction medium with lignin, part of these salts may be neutralized by the carboxylic acid or phenolic functional groups, avoiding the initiation of EC degradation. Finally, under alkaline conditions, high-temperature (170 °C) can also lead to the self-copolymerization of EC to produce additional CO_2.[278] Therefore, by removing the water, using

carbonate salts in small quantity relative to the lignin, and reacting at relatively lower temperature (<150°C), we can limit CO_2 to the reaction between lignin and EC rather than the degradation or self-polymerization of EC.[279]

A simple and accurate way was required to measure the volume of CO_2 during the hydroxyethyl reaction using a water displacement method .[280] This method was developed in the 18th-century[281], and still widely used to record the generated gas such as oxygen and hydrogen during chemical reactions.[282, 283] Carbon dioxide has a solubility of 1.45 g/L in aqueous water, so an excessive amount of CO_2 was dissolved into the water (**Figure 2**) to ensure saturated conditions. All the connecting ports were carefully sealed to minimize potential leaking. The reactor was pre-purged with a nitrogen atmosphere to dry the sample and prevent the backflow of water vapor causing the degradation of ethylene carbonate. The pressure of collected gas in the cylinder was approximately equal to the atmospheric pressure (Vancouver, BC). It is worth to metion that the impacts from the buoyancy pressure of the water in the cylinder, the slow leakage of CO_2 gas for extended time periods (>6 hrs), and the water partial vapor pressure may slightly affect the gas pressure in the cylinder with around 3% change. Here, we didn't consider about these impacts.

6.2.2 The evolution of CO_2 during the hydroxyethyl reaction

Based on our previous study, 100 °C, and 120 °C were selected for the hydroxyethyl reaction. After the deprotonation using carbonate salt, the anions from the carboxylic acid and aromatic hydroxyl groups can attack the ethylene carbonate to form hydroxyethyl groups and produce CO_2 gas. (**Figure 42**) The volume of CO_2 increased with longer reaction time and a higher temperature (**Figure 43a**). This observation was in agreement with our previous result that the degree of modification increased with reaction time and temperature. The maximum amount of CO_2 was around 97 ml per one g of softwood Kraft lignin at 120 °C after 6 hrs, under these selected conditions.
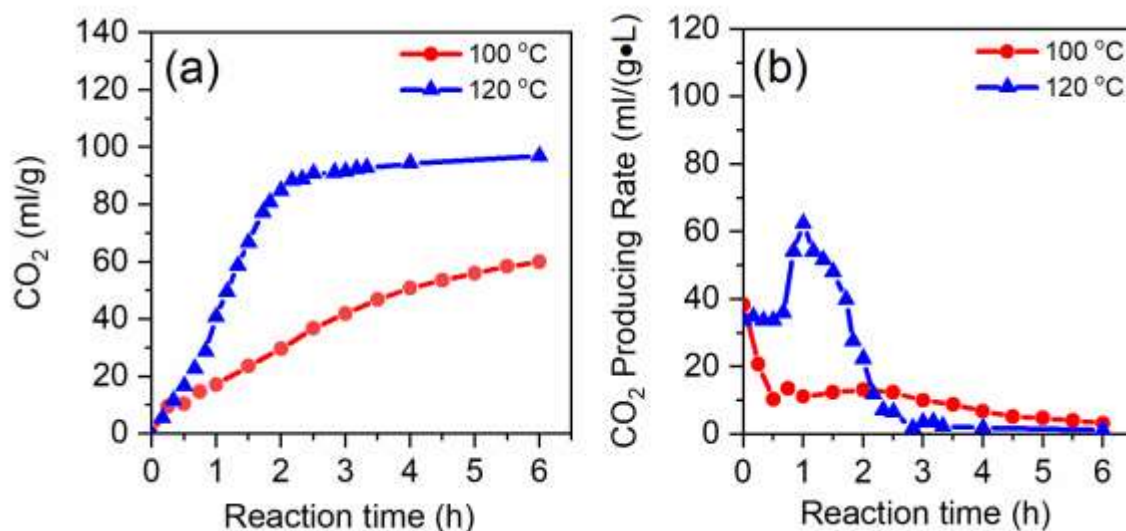
Figure 43 Volume of collected CO_2 with different hydroxyethyl conditions (a) and the CO_2-producing rate (b);

The CO_2-production rate was also calculated (**Figure 43b**). At 120 °C, the rate decreased after one hour, most likely due to the lower concentration of reactive groups. Noteworthy, the gas-production rate after 2 hrs at 100 °C also decreased, although there are still had many ArOH and COOH groups (**Figure 45**). This result may have occurred because of the side reactions, such as condensation, increasing the molecular weight of lignin and further reducing the transport of lignin in the ethylene carbonate solution.

6.2.3 The change in hydroxyl groups of lignin

The main objective of the hydroxyethyl reaction is to convert ArOH and COOH into AlOH. The change of these OH groups in lignin represented the degree of modification. ^{31}P NMR technique was utilized to characterize the different types of hydroxyl groups. The spectra of modified lignin (**Figure 44**) showed an apparent reduction of both ArOH and COOH peaks with an increasing amount of CO_2. When the volume of CO_2 reached 86 ml/g, we can clearly see the disappearance of ArOH and COOH peaks indicating a thorough modification of these two functional groups.
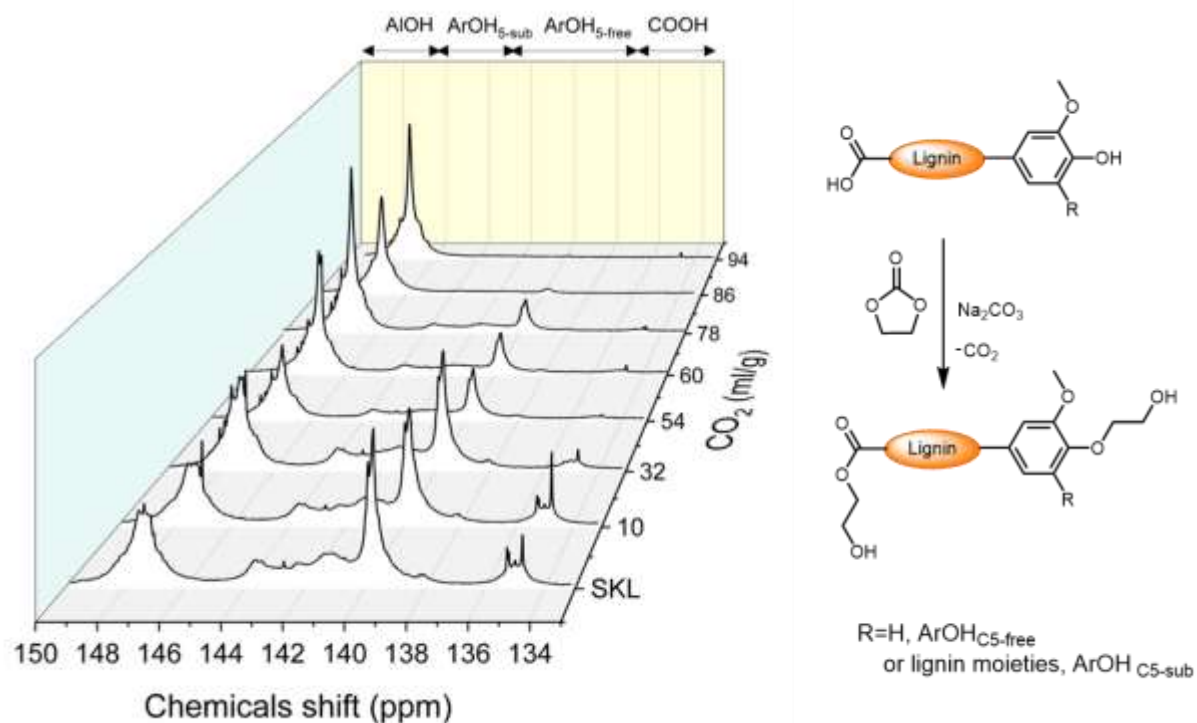
Figure 44 ^{31}P NMR spectrum of lignin with the generation of different amount of CO_2 during the hydroxyethyl reaction; aliphatic hydroxyls groups (AlOH), aromatic hydroxyl groups (ArOH) including C_{5-free} and C_{5-sub}; carboxylic acid groups (COOH)

Quantitative results showed that the amount of CO_2 had a linear correlation with the sum of ArOH and COOH (R^2=0.98, **Figure 45a**). Based on our knowledge of the system, this result means the derivatization of these functional groups is the main factor driving the production of CO_2. The amount of CO_2 also has a high correlation with AlOH groups when the CO_2 reached 78 ml/g at 120 °C. The maximum amount of AlOH groups was 4.30 mmol/g and their ratio with total OH groups 88%. After that, the AlOH groups decreased to 3.5 mmol/g, though the ArOH groups kept reducing and the AlOH/Total OH increased to 91%. This result is because the formation of carbonate linkages was more than the hydroxyethyl modification of ArOH groups (**Figure 24**). Hence, by monitoring CO_2 production, there was a time in the reaction when additional reaction time negatively impacted the formation of free hydroxyethyl groups.
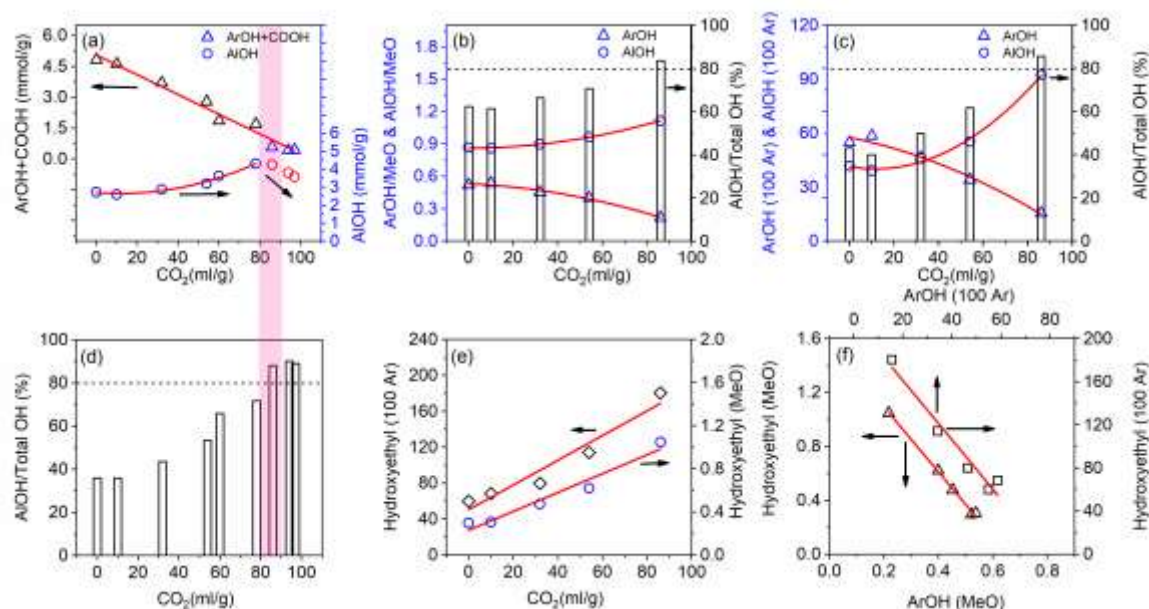
Figure 45 Correlation analysis between the produced amount of CO_2 and degree of modification (a and d, ^{31}P NMR; b, ^{1}H NMR; c, ^{13}C NMR), aliphatic hydroxyl groups (AlOH), aromatic hydroxyl groups (ArOH), carboxylic acid groups (COOH); hydroxyethyl groups based on ^{1}H (○), and ^{13}C NMR (◊) results; the correlation between hydroxyethyl groups and ArOH groups based on ^{1}H NMR (▲) and ^{13}C NMR (□)

Further, the total OH groups of resulting lignin (CO_2=86 ml/g) were 4.81 mmol/g, which was significantly lower than unmodified SKL (7.54 mmol/g). One of the main reasons is the addition of hydroxyethyl groups will increase the molar mass of lignin when accounting for the mass of the functional group. It means that one-gram of derivatized lignin would have less molar amount of hydroxyl groups, which will lead to an underestimation of the actual OH groups. A simple example to clarify this statement is the modification of phenol using ethylene carbonate. Phenol (M=94 g/mol) contains 10.60 mmol/g ArOH groups. Hydroxyethyl phenol (M=138 g/mol) has 7.24 mmol/g of hydroxy groups, which is 32% lower than phenol.

Therefore, it is necessary to have other ways to confirm those changes on the hydroxyl groups of lignin quantitatively. The acetylation can tag the ArOH and AlOH groups of lignin with acetyl groups. This modified lignin then can be characterized by ^{1}H NMR and ^{13}C NMR semi-quantitatively, even without adding additional chemicals as an internal standard. For ^{1}H NMR the proton in the methoxy group can be used as an internal standard as this functional group should not be impacted by the reaction conditions; while the carbon signal from the aromatic group can

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be used as an internal standard for ^{13}C NMR. All of their spectra showed the reduction of ArOH groups and increasing of AlOH groups with the production of CO_2. (**Figure 46 and 47**)
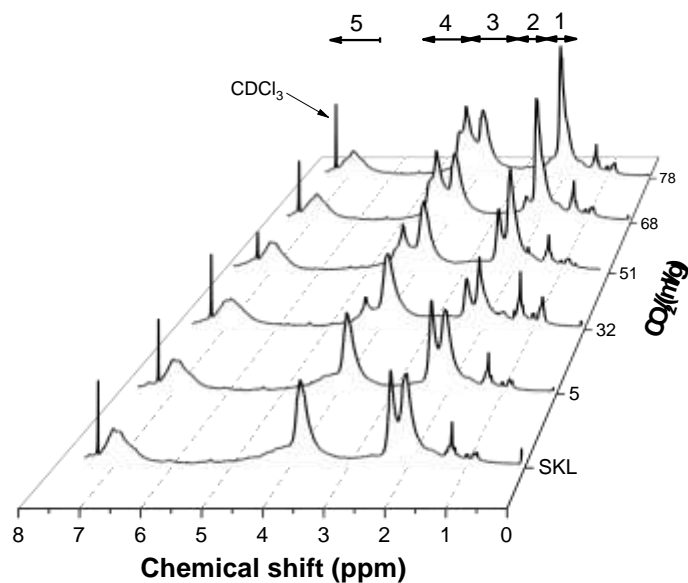
Figure 46 ^{1}H NMR spectrum of hydroxyethyl lignin within different amount of CO_2
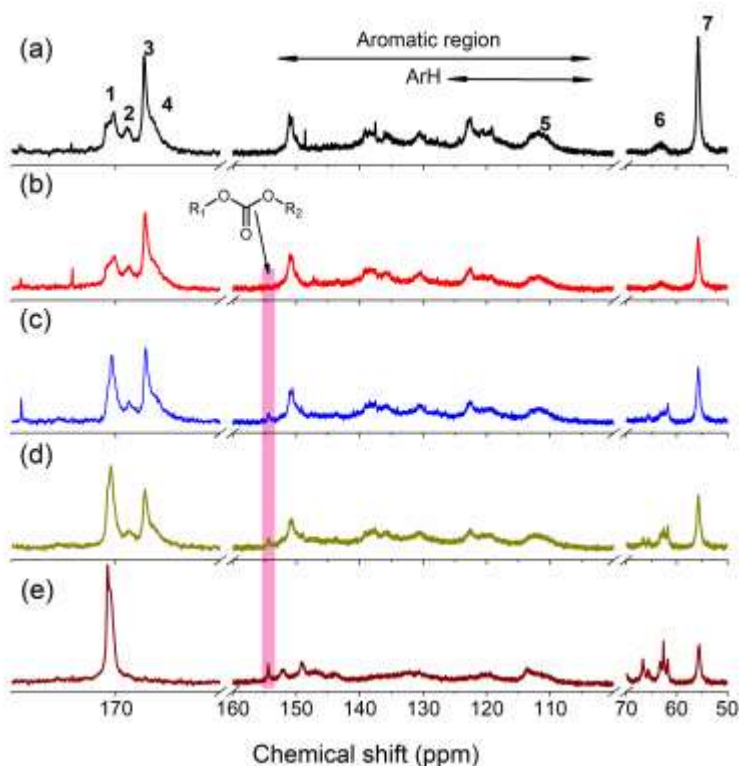
Figure 47 ^{13}C NMR spectrum of hydroxyethyl lignin within a different amount of CO_2; (a) unmodified SKL; (b) CO_2=10 ml/g; (c) CO_2=32 ml/g; (d) CO_2=54 ml/g; (e) CO_2=86 ml/g

Similar to ^{31}P NMR results, quantitative ^{1}H NMR and ^{13}C NMR results showed the amount of CO_2 had a high correlation with ArOH groups (R^2=0.99) and the AlOH groups (R^2=0.99, **Figure 45 e** and **f**). Also, the addition of hydroxyethyl groups had a linear correlation with the CO_2 volume (R^2=0.94) and the amount of ArOH groups (R^2=0.98). (**Figure 45 g**) These findings suggest the reduction of ArOH groups had a direct relationship with the hydroxyethyl reaction rather than self-condensed reactions such as 4-O-5 bonds. These pieces of evidence supported our hypothesis: if one functional group (ArOH or COOH groups) was modified, it accompanied by adding one hydroxyethyl group and producing one CO_2. So, the amount of CO_2 was an efficient detector to monitor the hydroxyethyl reaction.

6.2.4 Other side reactions during the hydroxyethyl reaction

Noteworthy, the reduction of ArOH was slightly greater than an increased amount of AlOH groups (**Figure 45 b and c**). The newly formed aliphatic hydroxyl ion will further copolymerize with EC

by carbonate linkages without forming new hydroxyl groups. The potential copolymerization mechanism is the transesterification between aliphatic hydroxyl ions and ethylene carbonate (**Figure 48**). In modified lignin, the ^{13}C NMR spectrum showed that the carbonated linkages (155-160 ppm) became more evident with the increasing amount of CO_2. (**Figure 47**) [149] Further, we used this hydroxyethyl reaction to modify a model phenolic monomer, phloretic acid, that contained both a phenolic and carboxylic acid group. After the modification, the derivative also showed the carbonate linkage in the ^{13}C NMR spectrum. All ArOH groups and COOH groups were modified as seen by the shift of COOH peak (peak 7) and phenolic carbon (peak 8, **Appendix A2**). The newly formed hydroxyethyl groups appeared from 75 – 55 ppm. It was noteworthy that the integration value of peak 2 was higher than the value of peak 1 due to the formation of carbonate linkages.
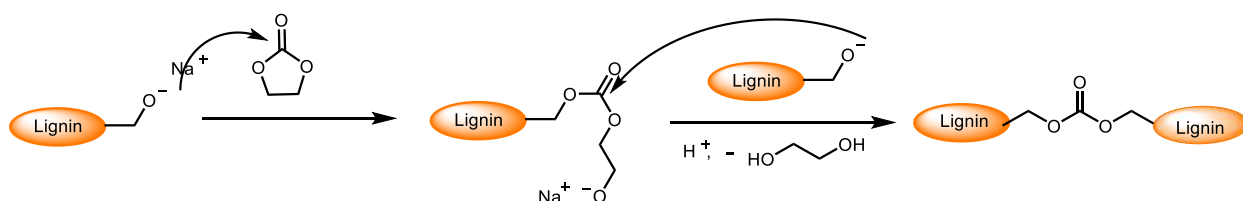
Figure 48 Reaction scheme of self-copolymerization
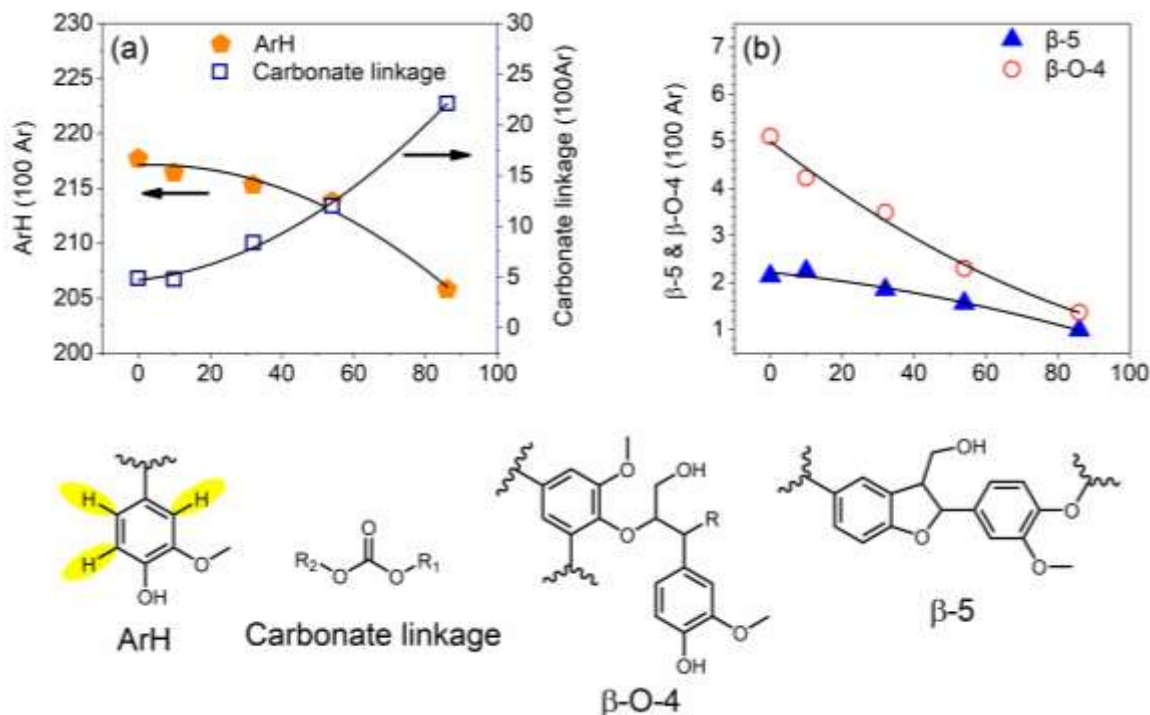
Figure 49 Correlation analysis between amount of CO₂ and the major linkages during the modification, including (a) aromatic hydrogen (or condensed reaction) and carbonate linkages based on 13C NMR results, and (b) β-o-4, β-5 based on HSQC NMR results

^{13}C NMR and HSQC NMR are powerful techniques for the characterization of major linkages (C-C condensed linkages and β-O-4, β-β linkage) in the resulting lignin.[284] The decreased amount of aromatic hydrogen as determined with NMR suggested the formation of inter- or intra-molecular condensed linkages of lignin during the modification (**Figure 49a**). [285] (**Figure 50**) Unfortunately, none of these linkages is distinguishable from the ^{13}C NMR and HSQC NMR spectrum due to the overlap from other groups. However, there was evidence implied that the breakage of sulfur bond and/or α-ether bond occurred to form carbanion and its conjugated compounds, quinone methides, under the high-temperature alkaline condition.[285] The reduction of β-5 (α-o-4) linkages (**Figure 49b**) and carbohydrate compounds supports the breakage of an α-ether bond. After the hydroxyethyl reaction, there was a strong odor in the reaction vessel, which may belong to the hydrogen sulfide in the CO₂ saturated water. This result suggested the partial removal of the hydrogen sulfide ion during the modification. Of course, the radicals may be alleviated and promote the formation of the phenolic oxide radicals, as the lignin dissolved in EC with the increased temperature.[286] These unstable phenolic oxide radicals would further copolymerize with

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its conjugate compounds increasing the molecular weight of the derivative. Besides these condensation reactions, the lignin also undergoes some degradation as the reduction of native β-O-4 linkages occurred during the reaction (**Figure 49c**). The degraded lignin compounds from reactive quinone methides under these alkaline conditions, following by additional condensation reactions.

(a)

(b)
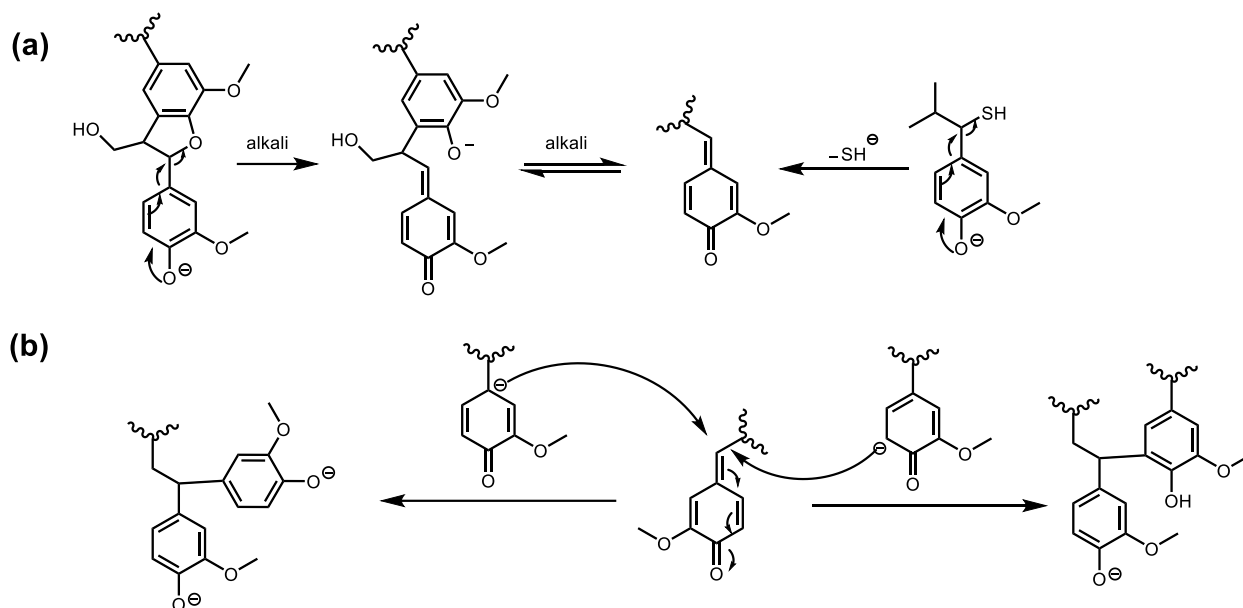
Figure 50 Potential reaction mechanism of degradation and condensation during the hydroxyethyl reaction, (a) the formation of quinone-methide, (b) the potential condensed reaction;

6.2.5   The molecular weight of modified lignin

The molecular weight of modified lignin using organic carbonate was always 2 to 50 times larger than unmodified lignin.[33, 151, 260] The molecular weight of acetylated lignin was detected by multi-angle light scattering (785 nm), equipped with a concentration detector (dRI). The light scattering traces for the modified lignin showed a bimodal peak. The sharp peak near 20 min becomes more evident during the modification. For the lower molecular weight section at higher retention times, there was a clear shift to the high molecular weight sections with an increasing amount of CO_2 (**Figure 51**).

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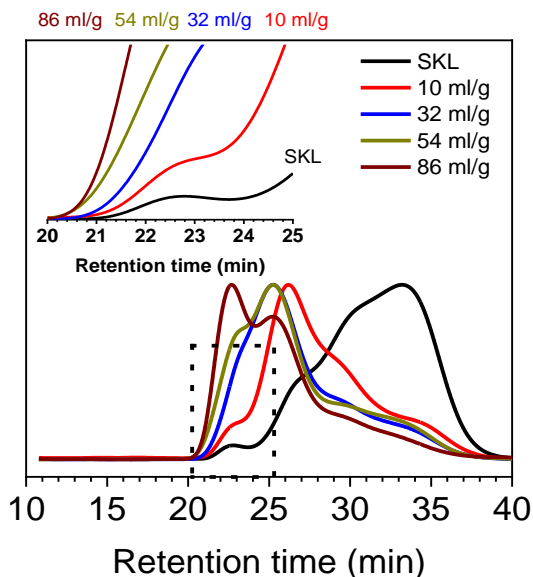
Figure 51 GPC-MALS traces of lignin before and after the hydroxyethyl reaction with different amount of CO_2

The absolute molar mass of lignin was characterized based on the light scattering data. By using an online method, the dn/dc value was calculated based on the dRI data and has a range of 0.05 - 0.14. The acetylated SKL has a weight average molecular weight of 28.3 KDa with the polydispersity index 3.7 (PDI). After the modification, the weight average molecular weight (M_w) rises up to 278.5 kDa (86 ml/g) with an increasing amount of CO_2. Further, the conventional calibration using poly (styrene sulfonate) (PSS) as standard was adopted to analyze the molecular weight changes based on the dRI traces. The molecular weight and polydispersity were all significantly higher than unmodified lignin due to the side reactions including intermolecular copolymerization and condensation.

6.2.6   The predictive model of the hydroxyethyl reaction

As discussed above, the hydroxyethyl reaction was always accompanied by side reactions and thus requires *in-situ* monitoring to avoid extensive crosslinking. The amount of CO_2 has a more direct relationship with the modification than the reaction temperature and time. We thus can build a simple predictive model to control this hydroxyethyl reaction based on the above data. By using the ideal gas law equation (**Equation 7**), the volume of CO_2 could be converted to the molar amount. The theoretical molar amount of CO_2 was calculated based on the change of COOH and ArOH groups under different reaction conditions (**Equation 4**) Also, as another model,

hydroxyethyl derivatization was applied to phloretic acid. The volume of CO_2 produced was collected and measured. **Figure 52** showed a high linear correlation (slope=0.749, intercept=0.327, $R^2 = 0.99$) between the theoretical amount of CO_2 and the actual amount CO_2.
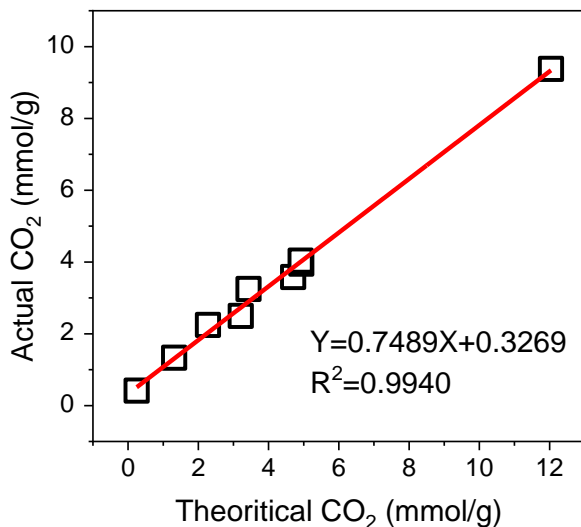
Figure 52 Linear correlation between the actual amount of CO_2 and the theoretical amount of CO_2 based on the grams of starting lignin

Based on this experimental relationship, we can potentially predict the final volume of CO_2 when the hydroxyethyl reaction reached the expected level. In order to calculate the theoretical amount of CO_2, the ArOH groups and COOH groups, before and after the hydroxyethyl reaction, were analyzed by ^{31}P NMR; the weight change during the modification should be considered as well; We assumed that the molar amount of ArOH and COOH groups equaled to the sum of molar amount of these groups in modified lignin and the molar amount of produce CO_2;

$$m \times [N]_u = (m + 44 \times \frac{m \times [N]_{tg}}{1000}) \times [N]_m + m \times N_{tg} \qquad (4)$$

Further, the theoretical molar amount of CO_2 can be calculated (**equation 5**);

$$N_{tg} = \frac{[N]_u - [N]_m}{\frac{44[N]m}{1000} + 1} \qquad (5)$$

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m, the weight of inputting lignin (g); $[N]_u$, the molar amount of ArOH+COOH groups in untreated lignin, (mmol/g); $[N]_{tg}$, the theoretical molar amount of gas (mmol/g); $[N]_m$ the molar amount of ArOH+COOH in modified lignin, (mmol/g);

The actual amount of CO_2 has a linear correlation with the theoretical amount of CO_2 (**equation 6**):

$$N_{ag} = 0.7487 \times N_{tg} + 0.3269 \qquad (6)$$

$[N]_{ag}$, the actual amount of CO_2, (mmol/g)

The molar amount of CO_2 can be converted to volume for specific weight amount of lignin based on the ideal gas law (**equation 7**):

$$PV = nRT \qquad (\mathbf{7})$$

P, the atmosphere pressure (102.2 kPa, Vancouver local); V, the volume of CO_2 (ml); R, the gas constant (8.314 J/(mol·K)); T (K), the absolute temperature (room temperature is 296.15 K); N, the molar amount of CO_2 (mol)

$$V = \frac{m \times N_{ag} \times R \times T}{P} = 24.09 \times m \times N_{ag} \quad (8)$$

By combining equation (6), (7) and (8), we can generate the equation below (9) to predict the actual amount of CO_2; V is the predictive volume of CO_2, ml;

$$V = \frac{1.804 \times 10^4 \times m \times ([N]_u - [N]_m)}{44 \times [N]_m + 1000} + 7.875 \times m \quad (9)$$

To further prove the accuracy of this predictive model, softwood Kraft lignin from another recovery method was exploited for this hydroxyethyl reaction. The aromatic hydroxyl groups and carboxylic acid groups of SKL-BC were characterized by ^{31}P NMR in advance ($[N]u=4.75$

mmol/g). As discussed above, a thoroughly modified SKL may lead to significant side reactions, increase the molar mass, and weaken the solubility of lignin (**Table 8**). We targeted an amount of CO_2 (89 ml/g), which would have the number of $[N]_m$ to be 85 to 90% substitution level. After the modification, the number of $[N]_m=0.57$ mmol/g (degree of substitution=88%) was measured by ^{31}P NMR of resulting lignin and the related theoretical amount of CO_2 was predicted to be 81 ml/g. This small variance (9% difference) means this predictive model can be applied to the other types of lignin resources. The variance may belong to the instrument errors from unstable temperature and pressure when collecting CO_2 with our homemade device, along with a slight deviation during the quantification of functional groups on lignin. Here, we provided a simple and relatively accurate way to realize the real-time monitoring of this hydroxyethyl reaction for the lab-based experiments. In the future, more advanced on-line equipment such as near-infrared detector or electrochemical mass spectrometry[274] can be adopted for measuring the amount of CO_2 to realize industrial-scale control.

6.2.7 Economic analysis of this modification using organic carbonate

The modified lignin has shown advances as a building block for polyesters and potentially polyurethanes if crosslinking can be limited.[250] Thus hydroxyethyl derivatives may be more valuable than unmodified lignin for polymeric applications. Besides the production of modified lignin, this process will produce another valuable industrial product, high-purity CO_2. For the recovery of Kraft lignin, CO_2 is the major chemical to acidify black liquor and precipitate the lignin. Actually, over 50% of the recovery cost of lignin is from the consumption of CO_2.[114] Utilizing the CO_2 to coagulate the lignin is a necessary step for all those recovery techniques on the market.[113, 114, 287] Therefore, we tried inputting CO_2 produced from the hydroxyethyl reaction into the black liquor (**Figure 53**). The pH value of black liquor was reduced from 13.5 to the required value of 9.3 to coagulate the lignin. Most lignin resources in black liquor can be recovered by further compressing. Theoretically, without considering additional solvent, 1 kg ethylene carbonate was able to modify 2.27 kg softwood Kraft lignin, which can recover 1.25 kg lignin is for the LignoForce process.[113] The produced CO_2 during the modification is enough to precipitate those lignin resources. The excess amount of high purity CO_2 as renewable resources can be converted into high-value chemicals such as organic carbonate[288] and organic acid[289]. (**Figure 53**)
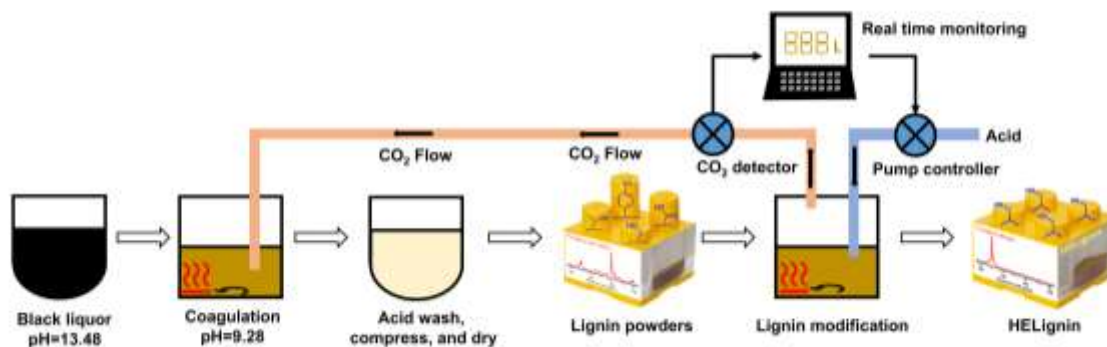
Figure 53 Integration of the lignin recovery process with this real-time monitoring modification process.

After washing the hydroxyethyl lignin with acidic water, collected supernatants were analyzed by ^{1}H NMR. The spectrum shows that it mainly contains ethylene carbonate and ethylene glycol with a ratio of 4 to 1. It means most of the unreacted ethylene carbonate can be recovered by removing the water or the excess ethylene carbonate can be converted to ethylene glycol by just adding the alkali water in the system. The latter route is more advanced than the traditional way of using ethylene oxide, which is toxic and will produce more side products.[290]

Overall, this hydroxyethyl reaction can realize real-time monitoring by measuring the amount of CO_2 during the reaction. By this technique, we can increase the flexibility of reaction conditions of large-scale productions and provide consistent products. Potentially, we would be able to modify different types of lignin resources with appropriate reaction times and temperature by quantifying the ArOH and COOH groups. This result would significantly reduce the workload for the optimization of reaction conditions, but more importantly better monitor large scale reactions where heat and mass transfer issues must be taken into account. This hydroxyethyl modification can potentially be integrated into the pulping industry, cut the overall cost for recovery, and help provide high-value products, including uniform technical lignin (contains 88% AlOH groups), high purity CO_2, and ethylene glycol. Moreover, organic carbonate like ethylene carbonate would be considered a carbon storage chemical.[241] Masahiko and his collaborator developed a series of ways to synthesize cyclo carbonate compounds from diol and carbon dioxide.[291] Utilizing this type of compound will help reduce the carbon emission for the pulp industry, which potentially can realize negative carbon emission.[292]

6.3 Conclusion

1) Process analytical technology is essential for the next generation factory to control the quality of the final products. In this chapter, we developed lab-designed equipment to measure and monitor the produced volume of CO_2 during the hydroxyethyl reaction of lignin with ethylene carbonate. The accuracy of this real-time monitoring equipment was further discussed.

2) A linear correlation between the chemical structure and the amount of CO_2 was found. Besides the hydroxyethyl reaction, a close examination of the condensation and copolymerization reactions of modified lignin were discussed, which can lead to a significant increase in molecular weight.

3) By using the volume of CO_2 as a detector, we can better control the quality of lignin (minimize those side reactions) and shorten the excess time to increase the process flexibility. A predictive model was built to reduce the workload for the optimization of different types of lignin resources.

4) Finally, we proposed a kind of modification technique to help pulp companies, not only to obtain more uniform lignin and high-value chemicals but also cut the overall lignin recovery cost and the emission of CO_2.

Chapter 7: A simple route to synthesize esterified lignin derivatives

7.1 Introduction

Esterification, a prototypical derivatization technique for biopolymers, is a more than 100-year-old technology applied to biobased materials to make them processable and useful.[293] With some of these esterification methods, derivatized lignin was used for analysis, as well as the preparation for useful thermoplastic and thermoset materials.[23] As discussed in **chapter 1**, most methods report on the esterification of lignin with anhydrides and acyl chloride, which are usually performed in homogeneous solutions with added catalysts. Anhydrides are very reactive and will modify both aliphatic and aromatic hydroxyls in lignin, albeit at slightly different rates on the lignin. Another derivatization route used acyl chlorides to engineer the thermal properties of lignin allowing the resulting derivatives to be blended with traditional synthetic materials such as polypropylene and polystyrene or degradable polymers such as PLA.[31, 102, 161] The drawback to these reactions using anhydride and halogenated compounds is three-fold; the first is the production of waste due to the reagent combined with the drawback of using a toxic solvent and catalyst, especially halogenated-based compounds. Further, the separation of toxic solvents and catalysts makes these reactions have a higher cost and environmental impact, which is more difficult for industrial adoption. In addition, both anhydride or acyl chlorides cannot fully modify the lignin efficiently when working with longer chain organic acids.[31] Therefore, these methods cannot satisfy the requirements of green chemistry and do not work efficiently.

Comparing esterification routes, the simplest approach may be Fisher esterification reacting carboxylic acid compounds with alcohols in the presence of strong acid used as catalysts.[294, 295] This approach allows the use of reagents such as short-chain organic acids or longer chain fatty acids that can be liberated from industrial crops such as done for the production of biodiesels.[296] While this esterification route is simple, there has been limited work in the literature of creating lignin esters utilizing this approach. This issue arises for two simple issues that plague lignin utilization: mixed functionality of technical lignin and structural modification (crosslinking) of lignin when exposed to acid and heat.[297, 298] For the former, when organic acids are reacted with lignin, the differences in reactivity of phenolics and aliphatic hydroxyls lead to only partial esterification. This issue could be addressed by the hydroxyalkylation of phenolics creating ether

derivatives that have terminal AlOH.[150] Moreover, removing ArOH groups prevents condensation under high temperatures that form typically through reactive quinone methide intermediates in acidic environments.[26] As such, removing the acid catalyst for lignin modification may limit side reactions previously reported.[82, 299] In previous research, Persson et al. adopted lactic acid as a catalyst to selectively modify the primary AlOH in carbohydrate compounds using ε-caprolactone. Due to higher acid strength, the lactic acid can efficiently catalyze this ring-opening esterification. [300] Our simple hypothesis is that even without additional acid, higher temperatures would remove the side-product of water and then promote the esterification reaction of lignin using aliphatic acid as solvent, reagent, and catalyst.(**Figure 54**).
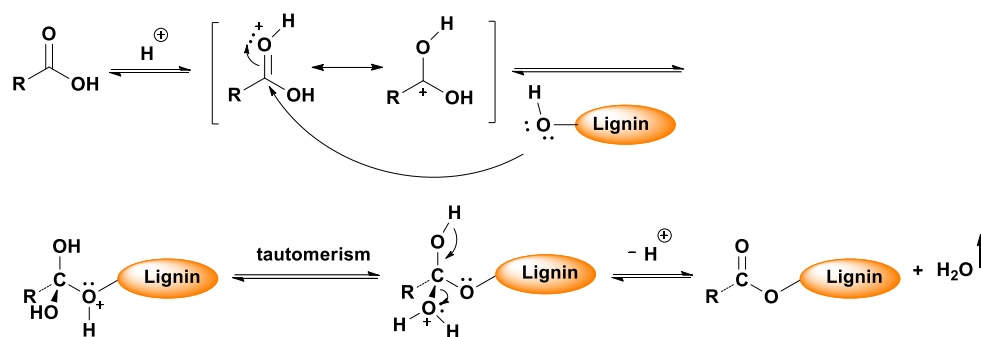
Figure 54 Reaction mechanism of direct esterification (Fischer esterification)

In this chapter, we performed this simple reaction to obtain esterified lignin using organic acid as solvent and reagent, but without adding strong acid. Both softwood Kraft lignin (SKL, Biochoice, Domtar Corp.) and organosolv hardwood lignin (OSHL, Fibria Innovation) were used as starting materials. Hydroxyethyl lignin derivatives were also adopted to ensure the complete esterification. We performed a systematic study to make a series of lignin ester derivatives yielding a high degree of substitutions and showcased how both the degree of substitution and reagent impacted the properties of the lignin derivative. In this way, a simple route to lignin esters addressed many drawbacks that surrounded the derivatization with a focus on the green advance; the aliphatic acid usually will have low volatility and can be used as both a safe solvent and reagent. Moreover, this greener procedure (low environmental factor (E-factor) with a higher atom economy) would be more economically and environmentally friendly for the preparation of lignin-based materials designed for applications such as biobased polyesters or hydrophobic coatings.

7.2 Results and Discussion

7.2.1 The catalyst-free esterification of SKL and OSHL

As control experiments, both softwood Kraft lignin (SKL-BC) and organosolv hardwood lignin (OSHL, Fibria) without modification or fractionation were reacted with propionic acid. These two types of lignin had different properties considering molecular weight, chemical structure, and thermal properties (**Table 11**) because of the isolation methods and their origin. Propionic acid was selected to modify the lignin initially, due to its boiling point (b.p.=141.2 °C), low volatility, better solubility in water, and dissolution ability for lignin.[150] Our previous results showed that the organic acid was a good solvent for modified lignin, especially hydroxyethylated lignin.[150] Further, the higher temperature improved the acidity of propionic acid, thus offered more free hydrogen ions (lower pKa value) to help the protonation of carboxyl groups to make them more electrophilic (**Figure 54**).[301, 302] Therefore, this system only contained lignin and the additional propionic acid without mineral acid catalyst, thus excess reagent could be easily recovered after esterification without any further purification required to recycle the reagent.

Table 11 Quantitative ^{31}P NMR analysis, molecular weight, and the glass transition temperature (T_g) of softwood Kraft lignin (SKL), propionate SKL (PSKL), hydroxyethyl SKL (HESKL), organosolv hardwood lignin (OSHL), propionate OSHL (POSHL), and hydroxyethyl OSHL

	AlOH (mmol/g)	ArOH (mmol/g)					COOH (mmol/g)	M_w (KDa)	M_n (KDa)	PDI	T_g/°C
		S	5-Sub	G	H	total					
SKL	1.52	n.a.	1.68	1.48	0.33	3.49	0.45	6.50	0.95	6.82	143.0
PSKL	0.30	n.a.	1.36	1.45	0.24	3.05	0.46	4.82	1.75	2.76	117.9
HESKL	3.48	n.a.	0.25	0.14	0.03	0.42	0.04				
OSHL	1.97	2.34	0.34	1.10	0.29	4.07	0.32	2.81	0.76	3.67	117.5
POSHL	0.54	2.08	0.32	0.95	0.25	3.60	0.18	5.47	1.65	3.30	103.3
HEOSHL	4.30	0.08	0.08	0.04	0.21	0.41	0.02				

With the excess propionic acid serving as a solvent, the reaction temperature and time were studied for this reaction. For the temperature, our hypothesis was that the temperature range (b.p. of water

≤ reactive temperature ≤ b.p. of organic acid) would make side product of water that would evaporate and move the reaction equilibrium to the desired direction. However, the upper-temperature range would possibly impact the stability of lignin leading to structural C-C linkages forming on the lignin.[26, 297] Therefore, a milder temperature of 120 °C for 24 h without adding additional strong acid was used as an initial condition. At this condition, the vapor pressure of propionic acid, 74.1 – 85.5 mm Hg, was lower than water (over 658 mmHg).

^{31}P NMR analysis (**Figure 56**) showed that the catalyst-free esterification successfully modified the aliphatic OH groups in lignin for both SKL and OSHL without the additional strong acid. (**Figure 55**) After the esterification, the AlOH groups (δ=150-145 ppm) in SKL and OSHL decreased from 1.52 to 0.30 mmol/g and from 1.97 to 0.54 mmol/g, with a degree of substitution of 80% and 72%, respectively (**Table 11**). The ArOH and COOH groups only had a slight reduction. The ^{13}C NMR spectrum showed the same conclusion that the AlOH groups were selectively esterified by propionic acid with the formation of aliphatic ester groups (δ=174-172 ppm) after the reaction and the formation of aliphatic carbon chains (δ=28-26 ppm and δ=10-8 ppm) in propionic groups (**Figure 57**). Two peaks appeared in the OSHL after the esterification. This result suggested that both the primary aliphatic OH group and secondary aliphatic OH group could be esterified by this method. Overall, similar to traditional esterification of lignin using acyl chloride[31] or anhydride compounds[32], this reaction showed high selectivity toward aliphatic OH groups compared with aromatic OH and COOH groups.
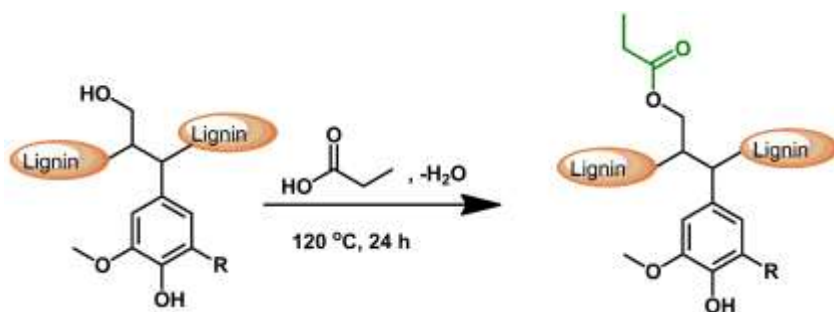
Figure 55 Reaction scheme between lignin (SKL and OSHL) and propionic acid; (R = H, OCH₃, or lignin moieties).
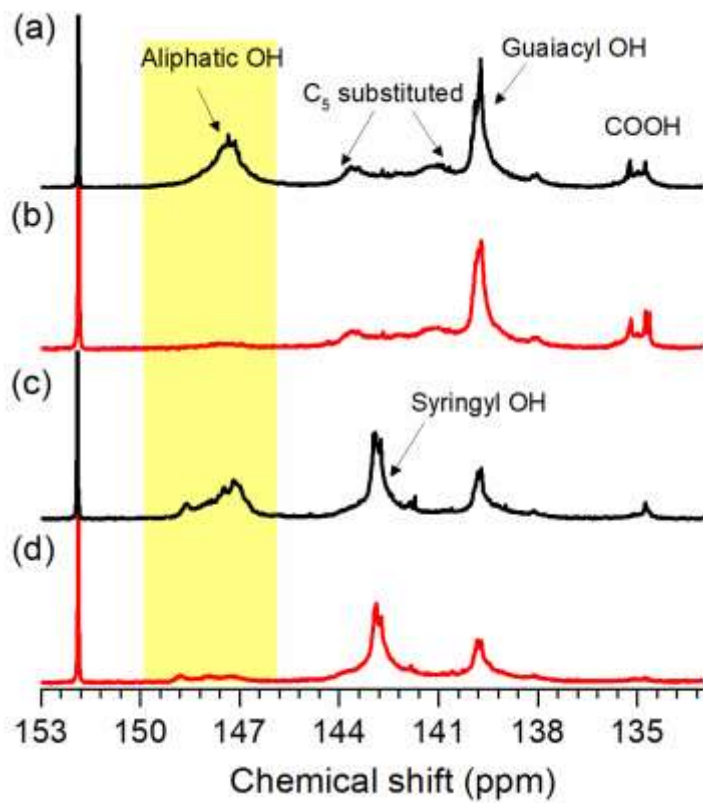
Figure 56 ^{31}P NMR spectrum of SKL (a), propionated SKL (b), OSHL (c) and propionated OSHL (d)
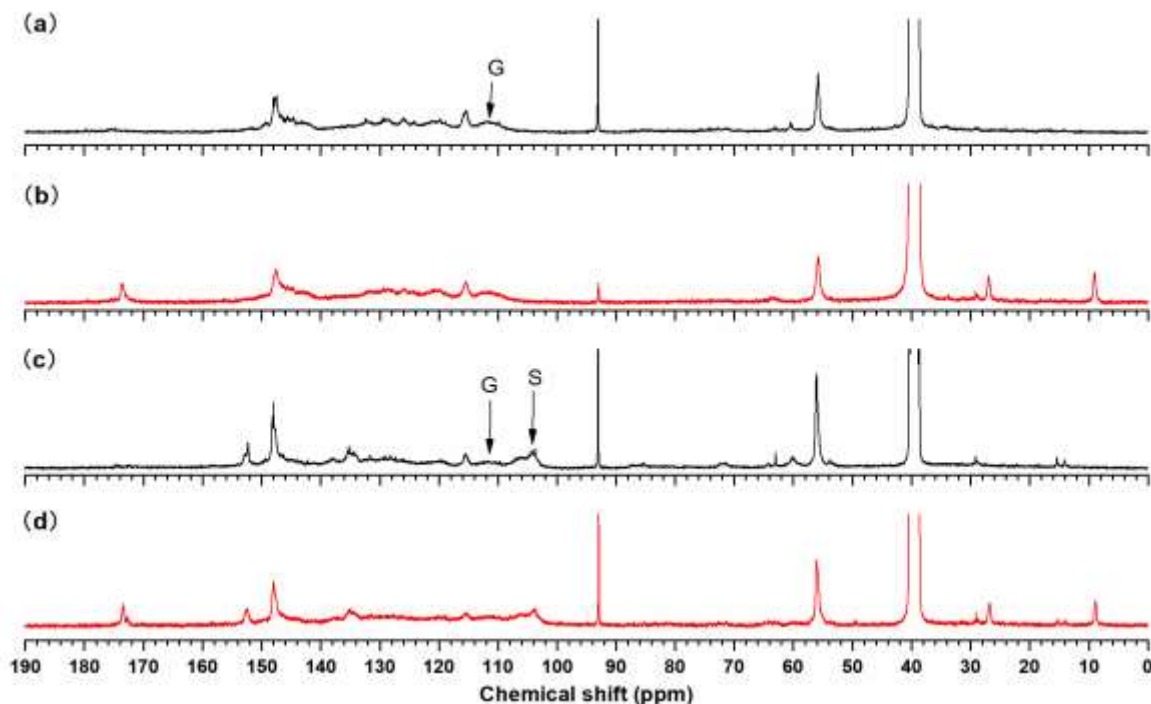
Figure 57 ^{13}C NMR spectrum of SKL (a), propionate SKL (120°C, 24 h, b), OSHL (c), and propionate OSHL (120 °C, 24h, d)

The SN$_2$ reaction played a dominant role in this catalyst-free esterification route (**Figure 54**) where the aliphatic oxygen served as a nucleophilic reagent to attack the carbonyl carbon and form a tetrahedral intermediate under acidic conditions. After the tautomerism and the removal of water under high temperatures, the lignin ester was formed. However, the phenolates were a relatively weaker base than alkoxide.[303] It was thus more difficult to form ester bonds with ArOH groups. In previous research, Appendino et al. esterified aliphatic hydroxyls in polyphenols using the Mitsunobu reaction, where the aliphatic OH group in phenolic alcohols were selectively modified by carboxylic acid groups in phenolic acids, leaving the ArOH groups unmodified.[304] In a similar fashion, Koivu et al. also found the longer chain chloride compounds prefer to modify the AlOH groups.[31]

Moreover, ^{13}C NMR and GPC results showed that minimum side reactions had occurred during the modification process. As shown in **Table 12**, the major repeat units (guaiacyl and syringyl units) and functional groups (methoxy groups) were determined based semi-quantitative ^{13}C NMR normalized per 100 aromatic units. These moieties have minimum changes during the

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esterification process for both SKL and OSHL. The degree of condensation (DC), the relative number of C-C linkages arising in technical lignin, was also calculated based on Balakshin et al.'s method.[91] Results showed that this quantity of linkage was stable in this process (**Table 11**). The molecular weight analysis revealed that propionate SKL and OSHL have similar molecular weight traces when compared with untreated SKL and OSHL samples. (**Figure 58**) As a conclusion, this catalyst-free esterification could selectively modify the aliphatic OH group without causing degradation and polymerization under the conditions used in the study.
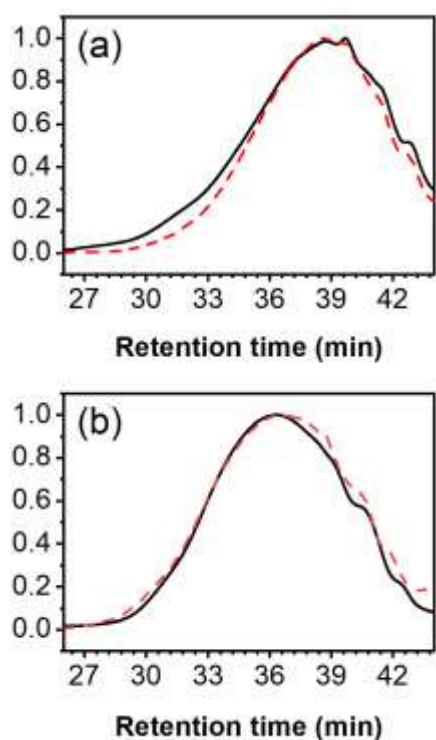
Figure 58 Molecular weight traces of SKL (a) and OSHL (b) before (dark line) and after (red dash) esterification using propionic acid at 120 °C for 24 h

The T_g of the substituted lignin was determined by measuring the middle point of the baseline shift in the third cycle of the DSC traces. Partially esterified softwood and hardwood lignin (**Table 11**) showed a decreased T_g by 26 °C (SKL) and 15 °C (OSHL), because of the reduction of AlOH content. This substitution weakened the inter hydrogen bonding network which is an important factor impacting the rheology of lignin. Overall, the catalyst-free esterification was shown to

selectively modify the lignin with higher reactivity toward AlOH groups than ArOH and COOH groups with modest shifts in the T_g.

7.2.2 Hydroxyethyl lignin (HELignin, contains 90% aliphatic OH)

In order to obtain thoroughly esterified lignin, first hydroxyethyl lignin derivatives were synthesized modifying both SKL and OSHL in order to obtain lignin, containing only aliphatic OH groups.[150] In this reaction, hydroxyethyl lignin (HELignin) was prepared by using ethylene carbonate as both solvent and reagent. The deprotonated aromatic OH groups and COOH served as nucleophiles and reacted with the methylene carbon in ethylene carbonate releasing CO_2 as a by-product. (**Figure 59**) After the modification, HElignin had a more uniform chemical structure (3.48 mmol/g, 88% AlOH group in HESKL and 4.30 mmol/g, 91% AlOH group in HEOSHL) (**Table 11**). ^{13}C NMR spectrum also showed an emerging peak cluster 3 (61.5-58 ppm) belonging to the hydroxyethyl group (Ar-O-CH$_2$-CH$_2$-OH, **Figure 60 a** and **d**).

These reactions slightly weakened the hydrogen bonding network of lignin and slightly changed the thermal mobility (the reduction of T_g in **Table 11**). However, there was an increase in weight average molecular weight, during hydroxyalkylation under alkaline conditions at high temperatures (**Table 12**). Yet, HELignin had better solubility in propionic acid and better thermal stability with increasing temperature than unmodified lignin making them an interesting precursor for this catalyst-free esterification route.[150]

Table 12 The chemical structure, molecular weight, and glass transition temperature (T_g) of esterified HESKL and HEOSHL with different reaction conditions

No.	Lignin	Temp /time	DS/%	G /100Ar	S /100Ar	MeO /100Ar	DC /100Ar	M_w /KDa	M_n /KDa	PDI	T_g/°C
	HESKL										
(a)		untreated	-	78	n.a.	69	73	8.8	0.92	9.70	121.7
(b)		90/24	61	76	n.a.	68	64	8.2	2.28	3.60	63.8
(c)		120/48	91	77	n.a.	65	68	9.4	2.33	4.05	48.9
	HEOSHL										
(d)		untreated	-	54	37	101	47	14.9	2.72	5.45	101.6

No.	Lignin	Temp /time	DS/%	G /100Ar	S /100Ar	MeO /100Ar	DC /100Ar	M_w /KDa	M_n /KDa	PDI	T_g/°C
(e)		90/24	53	51	36	97	47	16.5	3.77	4.37	77.4
(f)		120/48	87	51	36	97	48	18.8	4.03	4.68	54.4

7.2.3 Catalyst-free esterification of HELignin using propionic acid

Propionic acid was reacted with HElignin at a temperature in the range of 90-120 °C for 24-96 h. The degree of substitution (DS) and the chemical structure of HElignin before and after esterification were semi-quantitatively analyzed by ^{13}C NMR (**Figure 60**). After the initial hydroxyalkylation, the peak cluster 3 (δ=61.5-58 ppm, **Figure 60 a** and **d**) in HELignin formed for both SKL and OSHL. Once the OH groups were modified, the peak cluster 3 was significantly diminished within the emergence of peak cluster 4 downfield (δ=65-61.5 ppm) for the (Ar-O-CH$_2$-CH$_2$-O-CO-R) (**Figure 60**). Based on these two peaks, the DS of esterification within different reaction conditions were determined. A higher temperature and longer time resulted in a high DS. The highest DS was 91% (HESKL) and 87% (HEOSHL) at 120 °C for 48 h based on semi-quantitative ^{13}C NMR analysis. Further evidence in ^{13}C NMR was seen upfield with the aliphatic carbons (CH$_3$, peak clusters 2, δ=10–8 ppm) and downfield with the carbonyl carbons (peak cluster 1, δ=175-170 ppm), which indicated the success of modification via catalyst-free esterification.
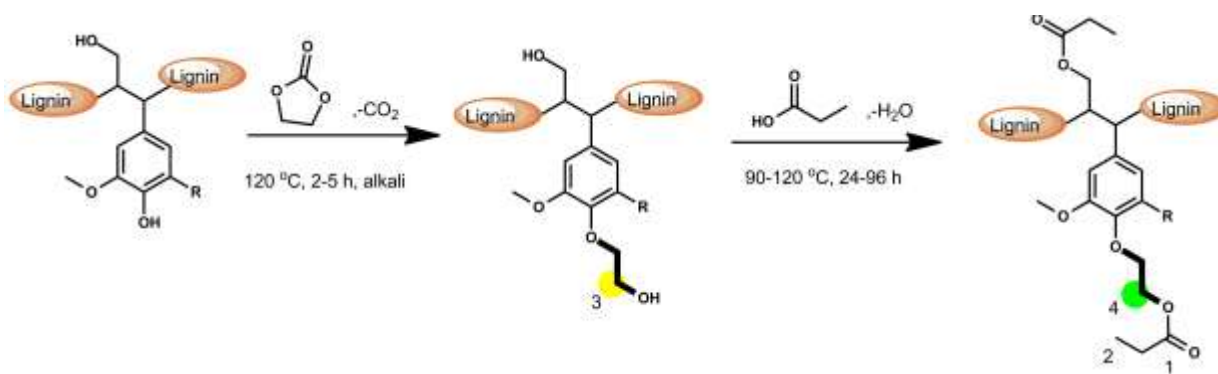
Figure 59 Reaction scheme of catalyst-free esterification

$$DS = \frac{Peak\ 4}{Peak\ 3 + Peak\ 4} \times 100\%$$
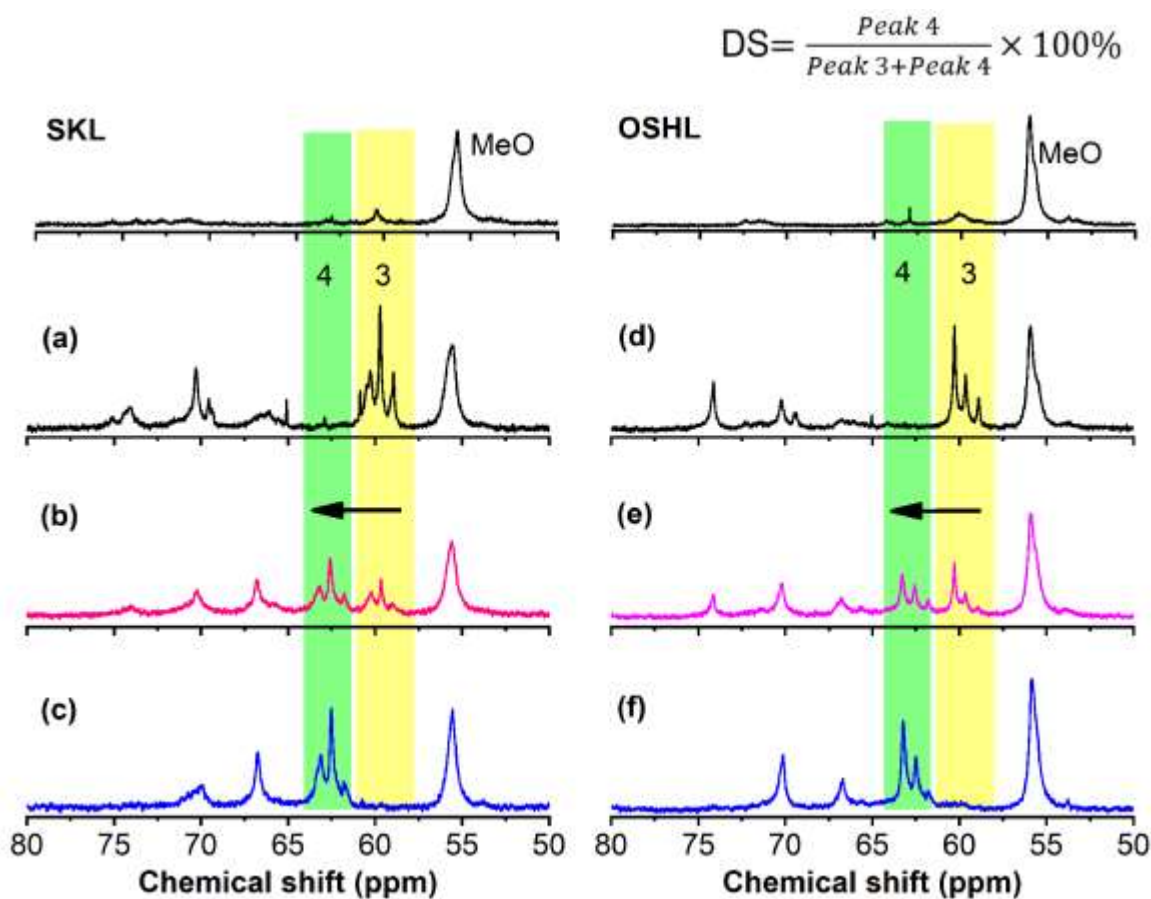
Figure 60 ^{13}C NMR spectrum of HESKL (a, b, c) and HEOSHL (d, e, f) before and after direct esterification using propionic acid with different reaction conditions; (a) HESKL, (b) HESKL- 90 °C-24 h, (c) HESKL-120 °C-48 h, (d) HEOSHL, (e) HEOSHL- 90 °C-24 h, (f) HEOSHL-120 °C-48 h.

On the other hand, the major repeat units, functional groups, and chemical linkages in lignin including guaiacyl (G) and syringyl (S) content, methoxyl (MeO), and the degree of condensation (DC) (**Table 12**) were calculated using ^{13}C NMR normalized per 100 aromatic units.[91] For both HESKL and HEOSHL, these repeat units and linkages were similar before and after esterification with different conditions. These results were in line with ^{31}P NMR results for the esterification of unmodified lignin (**Table 12**). This analysis revealed the lack of obvious side reactions during this esterification. This result was different than previous results, working on the surface modification of cellulose, albeit a different biopolymer, that had included strong mineral acid as catalysts. The strong acid had caused the degradation of cellulose chain during esterification.[299, 305] For lignin, the aromatic OH groups with strong acid conditions may induce polymerization or condensation

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in organic acid under high temperature.[298, 306] This was further discussed in Chapter 8. Moreover, using hydroxyalkylation to modify the aromatic OH group improved the thermal stability of lignin under these conditions.[150]

After the modification, the M_w had increased for both HESKL and HEOSHL with different reactive conditions, but a more uniform molecular weight distribution was obtained (**Table 12**).). A higher DS for the esterified products led to a higher M_w with a decreased polydispersity index (PDI) by shifting the curve. (**Figure 61**) However, it was worth mentioning that esterified HESKL at 90 °C for 24 h (DS=61%) had a lower solubility in THF than thoroughly esterified lignin (DS=91%). Thus, the obtained GPC results only represented the soluble portion of the partially substituted lignin. Based on comparison to the higher substituted materials, the low solubility resulted from mixed functionality at shorter reaction times. Overall, the increased molecular weight and improved solubility in THF indicated the success of the catalyst-free esterification reaction.
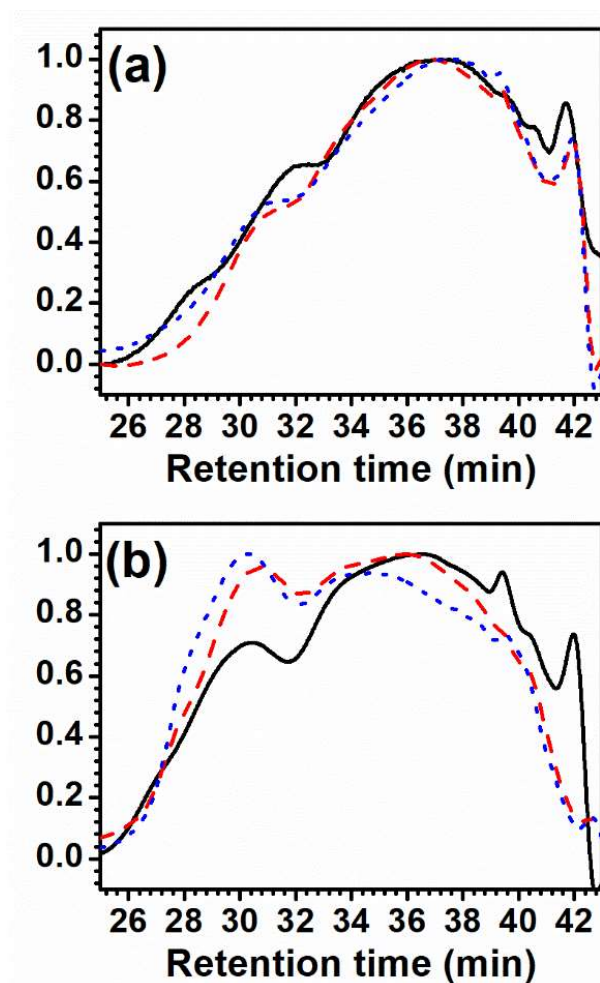
Figure 61 Molecular weight races of HESKL (a) and HEOSHL (b) before and after direct esterification using propionic acid with different reaction conditions; HELignin (dark solid line), 90 °C 24 h (red long dash line), 120 °C-48 h (blue short dash line)

This esterification with propionic acid also caused a significant reduction of the T_g of modified lignin. **Table 12** showed that the esterified lignin had a lower T_g (48.9 °C, HESKL and 54.4 °C, HEOSHL) than HELignin and the esterified PSKL and POSHL lignin (**Table 11**). The reduction in T_g was because the esterification of all hydroxyl groups removed the inter- and intra- hydrogen bonding capability of lignin. As a result, the weaker intermolecular bonds allowed more mobility of lignin macromolecules at elevated temperatures.[31]

A series of different reaction conditions were further studied (**Figure 62**). Manipulating the temperature and time, resulted in control of the DS for both HESKL (**Figure 62a**) and HEOSHL

(**Figure 62b**). Differing levels of DS were directly related to the thermal mobility of lignin. As shown in **Figure 62c**, the DS had a linear relationship with the T_g of lignin for both SKL and OSHL (R^2=0.98). This controllable T_g would provide an opportunity to prepare lignin-based thermoplastic materials; since the T_g impacts the ability to blend lignin with other polymers[157] and may further tune low T_g thermoplastics for applications where heat deflection is critical.[307]
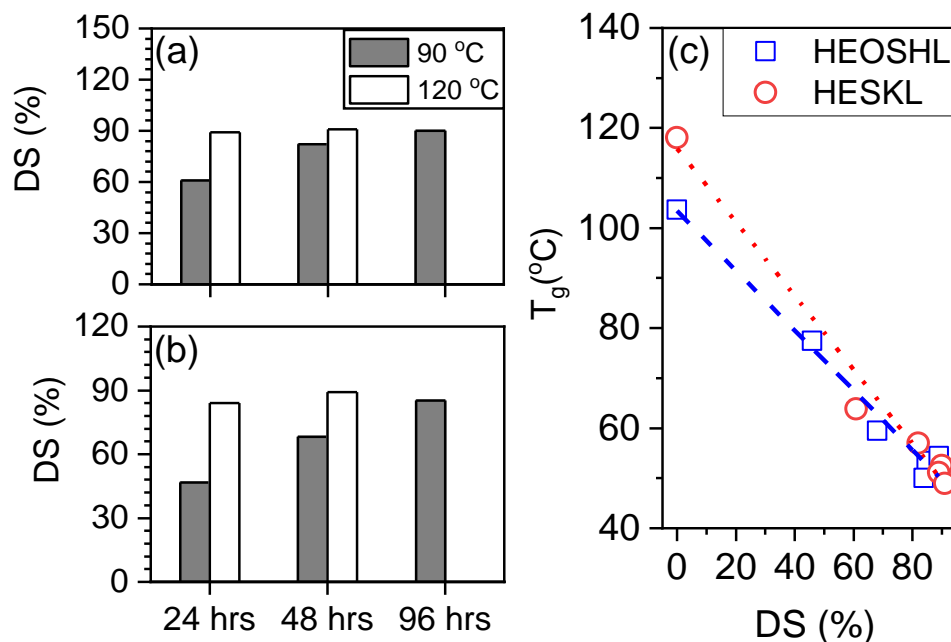
Figure 62 Degree of substitution (DS) of HESKL (a) and HEOSHL (b) and the correlation analysis between the DS (%) of esterification and Tg of esterified lignin Reprinted with the permission from ref. [165] Copyright 2019 Royal Society of Chemistry

7.2.4   Catalyst-free esterification of HELignin using longer chain organic acid

Longer chain carbons such as valeric acid (C_5), octanoic acid (C_8), and unsaturated oleic acid (C_{18}) were also utilized as both reagent and solvent to modify HESKL and HEOSHL. As found above, the temperature controlled the DS and the resulting glass transition of lignin. A higher temperature of 160 °C was used in order to improve the acidity of the solvent and reduce reaction time, since the longer chain acid had larger pKa values (C_5=4.84, C_8=4.89, C_{18}=9.85) and thus a low acidity.[302] The semi-quantitative ^{13}C NMR analysis showed that all these longer chain acids could successfully modify both HESKL and HEOSHL with DS in a range from 77%-85% (**Figure 63**). The emerging peaks clusters 1 and 2 in **Figure 63** further indicated the formation of esters on the

lignin. Moreover, the unsaturated bond in oleic acid was retained after the modification, which may offer more "handles" for further reactions of the lignin.[138, 166, 308]

Table 13 showed that the M_w of esterified HELignin increased with the length of the carbon chains. Since THF was used to extract modified lignin, unmodified HELignin with large M_w might be selectively removed during the extraction procedure as an artifact. Therefore, valerate HELignin (C_5) had slightly lower M_w than propionate (C_3) HELignin, which was purified by extraction with water. The PDI of valerate was lower than acetylated and propionate HELignin, which would further reduce with increasing carbon length. Hult et al. had a similar conclusion by using lauroyl chloride to obtain esterified lignin with narrow molecular weight distribution.[160] This result was most likely an artifact of the isolation procedure because the ethanol washing procedure removed the low molecular weight portion of the lignin. The other reason is that the longer chain acid modification most likely prevented the formation of lignin aggregation during analysis, as lignin aggregation plagues molecular weight determination.[24] In agreement with our previous research, M_w traces of HELignin showed two sections: larger M_w lignin and low M_w lignin (**Figure 64**). After the modification by longer chain acids (C_{18}, C_8, C_5), the traces of HEOSHL moved to a shorter retention time (larger M_w part) with a reduction of PDI, and thus more uniform lignin was obtained after the esterification (**Figure 64**). For HESKL, an increase of M_w was revealed for the longer retention times with the longer carbon chain ($C_{18} > C_8 > C_5$) of the reagents, but the larger M_w shoulder of the elution profile for oleate HESKL was muted. Again, this may be an artifact of the procedure when washing in THF.
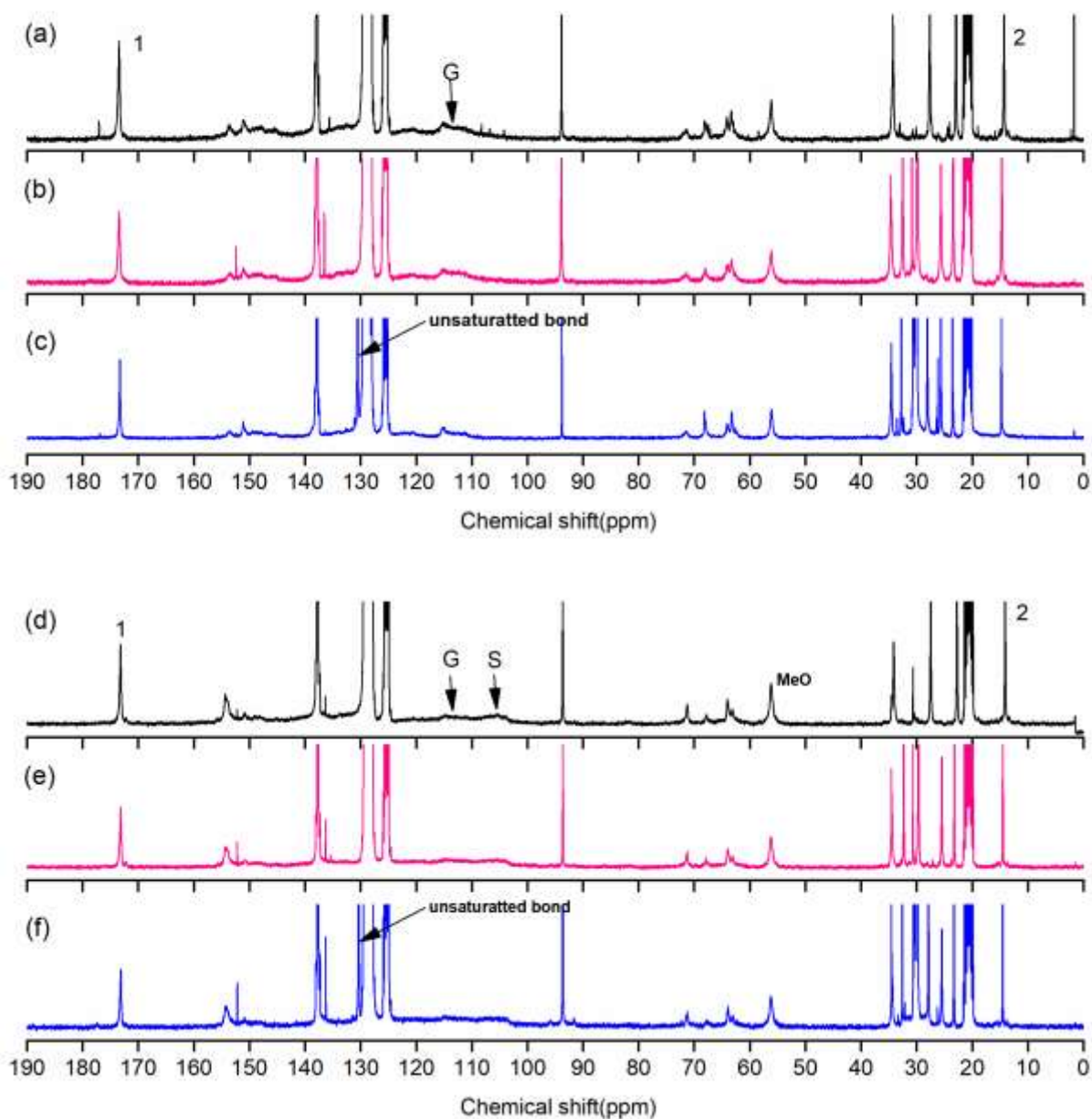
Figure 63 **^{13}C NMR Spectrum of esterified HESKL: (a) valerate HESKL, (b) octanoate HESKL, (c) oleate HESKL; and esterified HEOSHL (d) valerate HEOSHL, (e) octanoate HEOSHL, (f) Oleate HEOSHL.**

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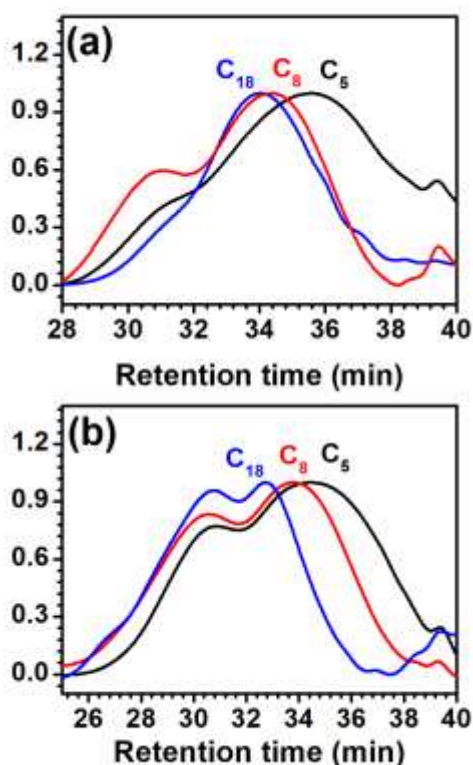
Figure 64 Molecular weight traces of different esterified lignin, (a) HESKL (b) HEOSHL, oleate (C_{18}), octanoate (C_8), valerate (C_5)

The T_g of esterified HELignin decreased with the increasing length of the aliphatic chain bonded to the lignin (**Table 13**). HESKL and HEOSHL had T_g=121.7 °C and T_g=101.6 °C, respectively. After the esterification, the T_g of HELignin was decreased all the way down to 3 °C (oleate HESKL) and 18.1 °C (oleate HEOSHL) for the longest chain in this study. In general, the T_g of lignin was impacted by variables such as rigid condensed aromatic backbones and strong intermolecular hydrogen bonding.[145] After the esterification, the hydrogen bonds were replaced by bulky, lower strength intermolecular dispersion bonds. As a result, the lignin chains, even with the rigid backbones had mobility at room temperature. The longer aliphatic chain would have also increased the free volume and thus further reduced the T_g of esterified lignin.

Table 13 Molecular weight and glass transition temperature (T_g) of valerate, octanoate, and oleate HELignin

No.	Lignin	Acid / Temp./Time	M_w/(KDa)	M_n/(KDa)	PDI[c]	T_g/°C
	HESKL					
(a)		Valeric (C_5) /160°C /24 h	8.0	2.8	2.86	34.0
(b)		Octanoic (C_8) /160°C /24 h	14.4	7.32	1.96	15.9
(c)		Oleic (C_{18}) /160°C /24 h	10.6	7.44	1.42	3.0
	HEOSHL					
(d)		Valeric (C_5) /160°C /24 h	14.2	6.82	2.09	36.8
(e)		Octanoic (C_8) /160°C /24 h	16.9	9.81	1.72	24.5
(f)		Oleic (C_{18}) /160°C /24 h	23.0	17.1	1.34	18.1

7.2.5 The preparation of clickable lignin by esterification

Inspiring by natural chemical synthesis, Sharpless and his coworkers described a strategy to synthesize small products with heteroatom links (C-X-C) in 2001.[309] They termed this reaction approach as "click chemistry" with a set of stringent criteria. The reactive route should have a thermal dynamical driving force greater than 20 kcal·mol^{-1}. It is thus a nearly perfect "spring-loading" reaction and can be finished rapidly. Other criteria are included in the 12 principles of green chemistry such as high yield, mild reactive conditions, a low amount of benign byproducts, high selectivity, and tolerance to functional groups.[309] Because of these greener merits, these routes are recently used to prepare a set of polymeric materials with widespread applications.[310]

For proceeding lignin-based material, introducing click-able groups can improve the reactivity of lignin for synthesizing advanced plastic materials.[311] The esterification or etherification using halogenated compounds are always adopted to introduce click-able groups in lignin.[132, 247, 311] For example, Habibi and his coworkers firstly introduced maleimide groups in lignin and then polymerized with polyfunctional thiols. [247] The resulting plastic materials contained 30%- 40% lignin and showed noticeable thermal and mechanical properties. However, the utilization of toxic halogenated compounds was not very efficient and significantly increased the E-factor of the system with issues on separation at the end of the reaction.

In replace of these routes and improve the reactivity of lignin, the catalyst-free esterification routes were adopted to prepare click-able lignin building blocks by introducing alkene and alkyne groups. Acrylic acid and propiolic acid were used as solvent, reagent, and catalyst to modify the hydroxyethyl softwood Kraft lignin (HESKL). The ^{13}C NMR spectrum (**Figure 65)** showed the shift of AlOH during the esterification. The DS (%) of acrylic acid esterified HESKL and propiolic acid esterified HESKL was calculated as 50% and 90%, respectively. In the NMR spectra, peak 1 in the acrylic acid esterified HESKL (**Figure 65 c**) in part belongs to the radical reaction between the unsaturated bond and water during purification. In the future, an inert solvent should be adopted to avoid side reactions, recover the acrylic acid, and separate the lignin from resulting mixtures. Surprisingly, the introduction of alkyne groups showed high selectivity and efficiency without any side reactions (**Figure 65 d**). It is reasonable as alkyne-based click polymerization methods are more powerful and are able to react in aqueous phase solvents.[312] As far as reported, this approach was the first time to introduce the alkyne functional groups in lignin with such a high degree of substitution. In the future, more advanced plastic materials such as hydrogels, resins,[247] and ion trapping materials[313] can be prepared from these materials for wide application.
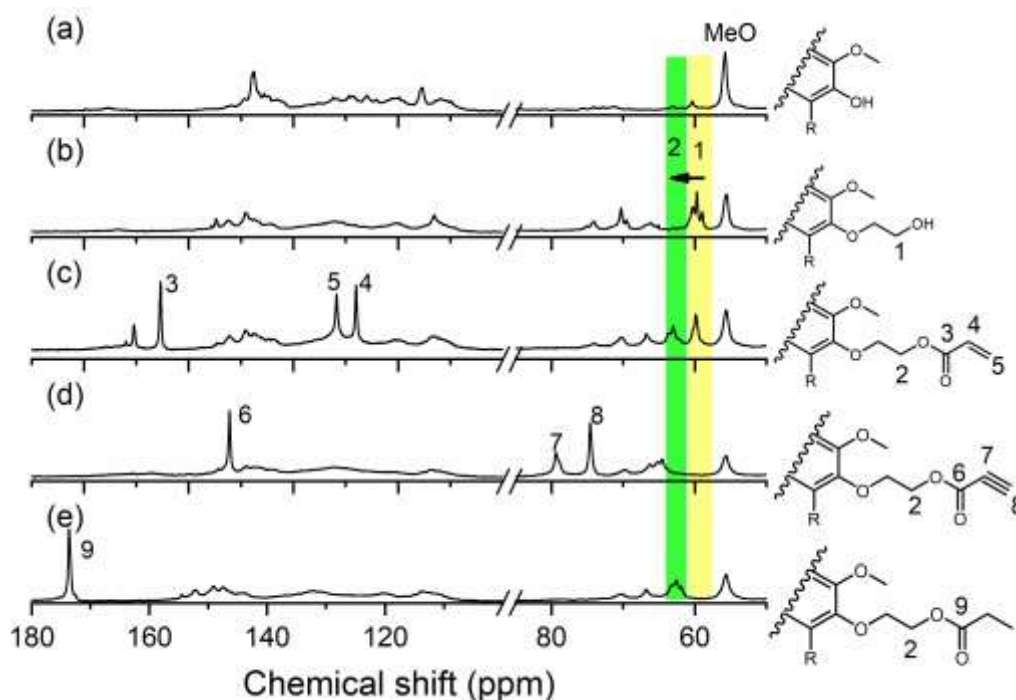
Figure 65 ^{13}C NMR spectrum of softwood Kraft lignin (a), hydroxyethyl lignin (b), and esterified hydroxyethyl lignin with –ene (c) and –yne groups (d), and esterified lignin with propionate groups using one-pot process (e)

7.2.6   One-pot process to synthesize esterified lignin derivatives

The catalyst-free esterification has high selectivity towards the AlOH of technical lignin. In advance, the hydroxyethyl reaction was necessary to obtain uniform technical lignin (contains 80% of AlOH). (**Figure 59**) Doing this two-step reaction in a one-pot without isolating or purifying the intermediate (hydroxyethyl lignin) will definitely reduce the overall cost, time, and labor.[39] Theoretically, the excess EC and catalysts in the first step will not inhibit the following esterification when we add an excess amount of propionic acid. The real-time monitoring technology developed in **chapter 6** was adopted to help us evaluate the endpoint of hydroxyethyl reaction in order to add the organic acid. It was also an excellent way to control the quality of hydroxyethyl lignin without significant crosslinking. After the modification with propionic acid, the ^{13}C NMR spectrum of the resulting lignin showed the degree of substitution (DS) of modified lignin was 91%. (**Figure 59 e**). This result showcases how the catalyst-free esterification is robust enough to thoroughly esterify the newly formed hydroxyethyl groups in lignin in a one-pot process.

Besides reducing overall costs, doing this two-step reaction in one-pot has additional benefits. Firstly, these two reactions have a similar reactive temperature (90 - 120 °C). We thus do not require additional time to change the temperature of the reactor. Secondly, adding organic acid to neutralize the alkali (carbonate salts) quenches the hydroxyethyl reaction promptly to minimize the reaction of EC copolymer formation. Thirdly, the excess EC in the hydroxyethyl reaction may play a role of cosolvent in the following esterification to prompt the reaction at the beginning. A control reaction without adding lignin was run with ethylene carbonate and propionic acid. **Figure 66** showed that the ethylene carbonate has lower reactivity with the propionic acid at 24 hrs, suggesting a limited reaction between these compounds under neutral conditions. After 48hrs reaction, 50% of EC was converted into ester compounds: ethylene propionate.
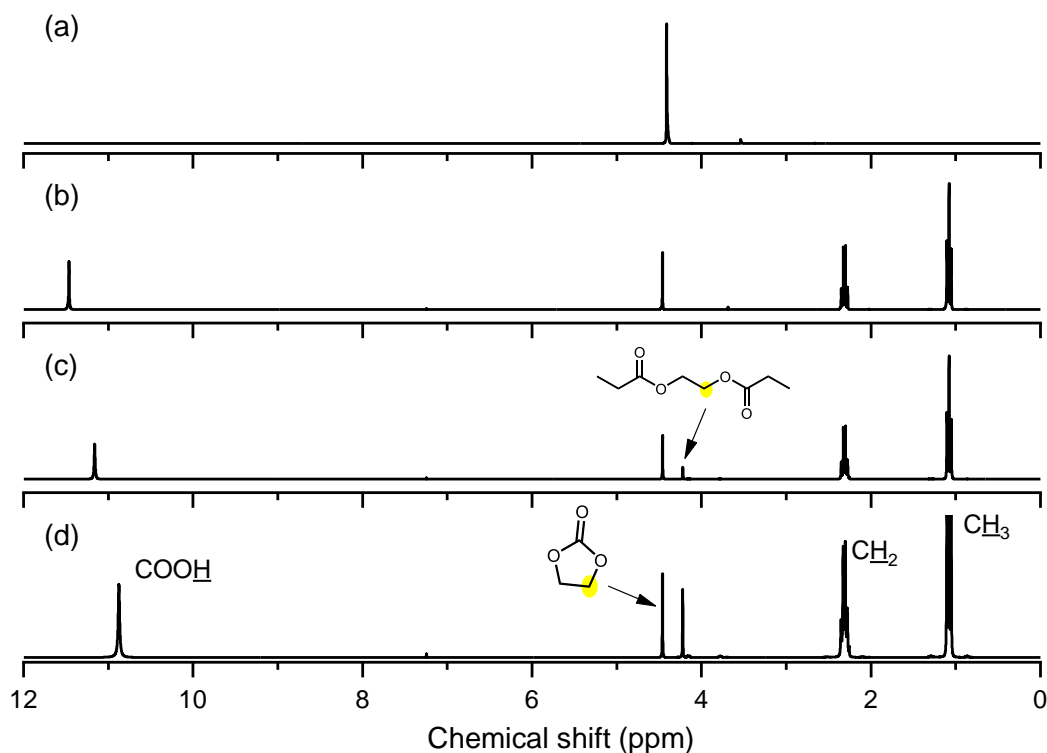
Figure 66 ¹H NMR spectrum of EC (a), EC/acid mixture (b), EC/acid at 120°C for 24h (c), EC/acid at 120 °C for 48h (d)

7.2.7 Greener metrics of the catalyst-free esterification

Using anhydride compounds and acyl chloride reagents with different length of aliphatic chains or functional groups, researchers were able to develop different types of lignin esters to engineer the thermal properties of lignin,[31] along with compatibility in biodegradable polymers,[157, 159] and solubility in monomers.[32] Further, esterified lignin could copolymerize with compostable polyesters through transesterification.[107] Unfortunately, using these traditional chemical esterification routes may cause the lignin-based materials to be less economically and environmentally beneficial. In this study, we developed greener direct esterification (catalyst-free esterification) to modify technical lignin including organosolv hardwood lignin and softwood Kraft lignin. Hence the study replaced toxic compounds in traditional esterification routes avoiding anhydride and acyl chloride compounds. To further evaluate these different esterification methods and show the greener metrics of our route, we highlighted many of the green chemistry principles developed by Anastas and Warner[38] applied to lignin esterification (**Figure 67**). In the past

decades, these principles have been widely used in chemical synthesis,[213] the pharmaceutical industry,[209, 314] materials preparation,[220, 315] and environmental protection.[208]
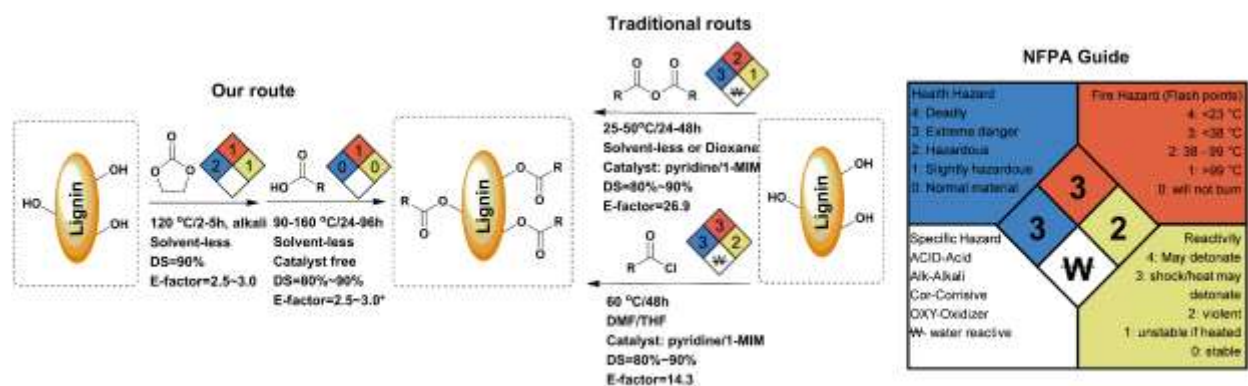
Figure 67 Greener metrics of our two-step route to obtain esterified lignin.

Considering the principles of green chemistry, there were two measurable factors developed including atom economy (AE)[212] and environmental factor (E-factor)[214] to help us calculate whether their reaction had a green advance. For AE, the molecular weight of the starting materials is important, however, lignin as a macromolecule is difficult to obtain absolute molecular weight.[168] This issue impacts the calculation of AE (**Equation 1**), but a rough calculation can be made considering the by-product. For example, the esterification using propionic anhydride, propionyl chloride, and propionic acid will produce by-products: propionic acid (74 g/mol), hydrogen chloride (36.5 g/mol), and water (18 g/mol), respectively. The catalyst-free esterification potentially will have much higher atom economy than the other two methods, due to the fact that water has the lowest molar mass. Even considering the side products CO_2 (44 g/mol) during the hydroxyethyl reaction, our route is still lower than anhydride route. On the other hand, the hydroxyethyl reaction could be replaced by hydroxypropylation using propylene oxide (carcinogenic compound) to obtain lignin only containing aliphatic OH groups without producing side products, if the atom economy was the only metric.[244] However, the AE is further removed from practical conditions, since it does not consider the utilization of solvent and catalysts. Different from AE, the calculation considered the utilization of reagent, solvent, and catalyst during the reaction (**Figure 67**).[43, 214] The two-step esterification route had an overall E-factor (2.5-3.0) for the first step and 0.9-1.5 for the second step. By combining these two reactions together,

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the final E-factor was 3.4-4.5, which is 70%-80% lower than traditional routes noted in **Figure 67**. Noteworthy, we did not consider the production of wastewater in these reaction comparisons. For traditional esterification routes, the utilization of toxic reagents, even carcinogenic halogenated compounds, or water-reactive anhydride compounds will cause a serious issue on waste-water treatment. Therefore, the E-factor with water for routes using anhydride and halogenated compounds will be greater than the number in **Figure 67**. The catalyst-free esterification can be finished in the one-pot process, which will help us reduce the consumption of water for the recovery and further reduce the E-factor.

The reagent safety and solvent utilization were other important considerations for green chemistry.[232] To dissolve lignin, traditional routes generally will use toxic solvent such as dioxane,[32] pyridines,[31] dimethylformamide,[175] or tetrahydrofuran[163]. As we said earlier, DMF was widely used in the textile industry has been banned in Europe and will be banned in China in the near future.[234] In our two-step catalyst-free esterification route (**Figure 67**), the reagents were used as solvents and those reagents have low environmental impacts considering flammability, reactivity, healthy, and water reactivity. Our THF washing of the lignin was only performed for analytical purposes which can be avoided in industrial settings. Moreover, reagents we used were renewable, which was another principle for green chemistry. Ethylene carbonate could be synthesized from the reaction using renewable compounds: ethylene glycol and carbon dioxide;[241] although the industry still uses epoxides and phosgene.[238] Further, organic acids generally can be extracted from renewable plant resources. For example, oleic acid occupies the largest proportion in olive oil, pecan oil, and canola oil composition.[296]

Lastly, this catalyst-free esterification route was highly efficient to modify the aliphatic OH groups in lignin without causing significant side reactions. The drawback of the reactions is the high temperature; however, certain biocatalysts have been demonstrated to be useful in the catalyst-free esterification of diacids and diols providing a route to make these processes greener,[316] which will be utilized in future studies to reduce the energy consumption in these reactions. In summary, this two-step catalyst-free esterification is a simple and robust route to make esterified lignin useful in polymer blends that satisfies many green principles.

7.3   Conclusion

1) Traditional esterification routes using anhydride and acyl chloride compounds to modify lignin are unsustainable considering the requirements of greener chemistry. In this chapter, we developed a catalyst-free esterification route to modify softwood Kraft lignin (SKL) and organosolv hardwood lignin (OSHL) and hydroxyethyl modified lignin using organic acid as solvent, reagent, and catalyst.

2) Results showed that this reaction successfully modified the aliphatic OH group in the lignin, keeping the aromatic OH and COOH groups intact, without causing any side reactions. After the modification, the partially esterified lignin had a lowered T_g.

3) To develop thoroughly esterified lignin, the hydroxyethyl reaction with ethylene carbonate was used to obtain hydroxyethyl lignin (HELignin, about 90% aliphatic OH group). Subsequent catalyst-free esterification successfully modified nearly all the aliphatic OH groups in HElignin for both SKL and OSHL with a high degree of substitution (91% and 87%) at 120 °C.

4) By changing the reaction condition, the DS was controlled and as a result the T_g of lignin was modified; the work showed the DS and T_g have a high linear correlation for the propionate derivatives.

5) The longer chain organic acids including valeric acid (C_5), octanoic acid (C_8), and oleic acid (C_{18}) were also used for the catalyst-free esterification at a higher temperature 160 °C for 24 h. All of these reactions were efficient at substituting hydroxyl groups with a DS: 77%-85%. The longer the aliphatic chain of organic acid, the higher the molecular weight and the substitution modified the T_g of lignin, down to 3 °C.

6) By using unsaturated organic acids such as acrylic acid and propiolic acid, we can introduce clickable -yne and -ene groups in lignin with a DS 91% and 50%, respectively.

7) Further, a one-pot procedure was successfully applied on the esterified lignin which showed a high degree of substitution resulting in a uniform lignin ester.

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8) Overall, this two-step reaction was more efficient to obtain thoroughly esterified lignin and satisfy many greener metrics than traditional methods.

Chapter 8: Aqueous dispersions of esterified lignin particles for hydrophobic coatings

8.1   Introduction

In nature, trees with protection from external factors can survive hundreds of years. For example, phloem tissue serves as protection from fungi spores and bacteria; a significant fraction of this phloem composition is suberin, a polymeric compound that is a combination of aromatic and aliphatic structures.[317] Further, on external surfaces such as leaves, a variety of long-chain aliphatic organic compounds in epicuticular waxes imparts hydrophobicity to its surfaces. These highly structured waxes with microscale roughness and nanoscale textures can create superhydrophobicity on the leaves of plants where water can roll off the surface as found with the lotus leaf.[318] Hence, the use of aliphatic carbon chains is a simple approach to make highly hydrophobic materials.

Recently, this method was recreated utilizing biopolymers such as cellulose, [319] waxy,[320, 321] and lignin[159] to produce hydrophobic coating materials. Geissler et al. developed superhydrophobic coating materials from stearic esterified micro-cellulose particles. Results showed that the micro-/nano scale particle geometries could significantly improve the hydrophobicity of the surface and develop self-cleaning properties, mimicking the lotus leaf. Forsman et al. adopted aqueous waxy particle dispersion by the layer-by-layer technique in replace of poly-L-lysine to improve the hydrophobicity of cellulosic fibers.[321] Hult et al. determined that esterified lignin showed improved water-proofing for the paper board.[160] Lignin derivatives have also been used to coat wood surfaces to improve hydrophobicity as exhibited with weakened wettability measurements.[322] For these samples, the esterification process was shown to increase the hydrophobic nature of lignin. Halogenated or anhydride compounds were adopted in this process with either partial and full conversion of lignin into its esterified form as discussed in Chapter 1.[31] These methods were performed under standardized conditions requiring solvent, which increased the environmental factor (or E-factor) with potential to cause negative environmental issues due to the use of toxic halogenated and anhydride compounds.

In order to avoid these problems, the catalyst-free esterification was developed in chapter 7.[165] Working from this approach, softwood Kraft lignin (extracted from LignoForce system)[113] was

modified by ethylene carbonate to obtain lignin only containing aliphatic hydroxyl groups.[150] Then oleic acid was utilized as both solvent and reagent to realize the catalyst-free esterification of hydroxyethyl lignin derivatives. This technique created both an aromatic and aliphatic component that was a simplified model of suberin material, found in bark, for the protection of wood. The obtained esterified lignin was then prepared as aqueous micro-lignin particles via dialysis to use as a hydrophobic thin coating for wood-based materials. In most cases, short-term storage needs or temporary protection during construction requires a low-cost treatment solution for lumber or composite panels. Hence a low-cost and "green" hydrophobization agent would enhance the protection of these materials from water.

8.2   Results and Discussion

8.2.1   A two-step route toward esterified lignin

SKL contains different types of hydroxyl groups, which were reported to have different reactivity for esterification.[32] In chapter 7, it showed that the direct esterification, using organic acids as solvent and reagent, could successfully modify the aliphatic OH groups.[165] Therefore, the hydroxyethylation with ethylene carbonate as both solvent and reagent was used to convert the aromatic OH groups into aliphatic OH groups (**Figure 68**), to improve the relative reactivity of lignin towards organic acids.[150] The exact values of each type of OH groups before and after the hydroxyethylation were reported in **Table 14**. For the hydroxyethyl lignin, the amount of AlOH increased from 2.07 mmol/g to 4.27 mmol/g, while the amount of total OH group decreased from 6.45 mmol/g to 5.03 mmol/g. The significant reduction of the ArOH (0.69 mmol/g) indicated that HELignin had a more uniform chemical structure with 82% of the ArOH and 88% of the COOH converted into AlOH groups.

Table 14 Characterization of original lignin and hydroxyethyl lignin (HELignin); For 13C NMR, the aromatic carbon region (160 - 100 ppm) was set as 100 Ar.

	AlOH (mmol/g)	ArOH (mmol/g)	COOH (mmol/g)	Total OH (mmol/g)	DS /%	M_w/ kDa	M_n/ kDa	PDI	T_g (°C)
Lignin	2.07	3.87	0.56	6.49	-	6.184	1.366	4.53	165.1
HELignin	4.27	0.69	0.07	5.03	83	8.468	1.258	6.73	120.1
Oleate HELignin	-	-	-	-	88	7.53	2.927	2.58	8.1
Oleate HELignin (1% acid)	-	-	-	-	89	7.096	0.815	8.71	2.7
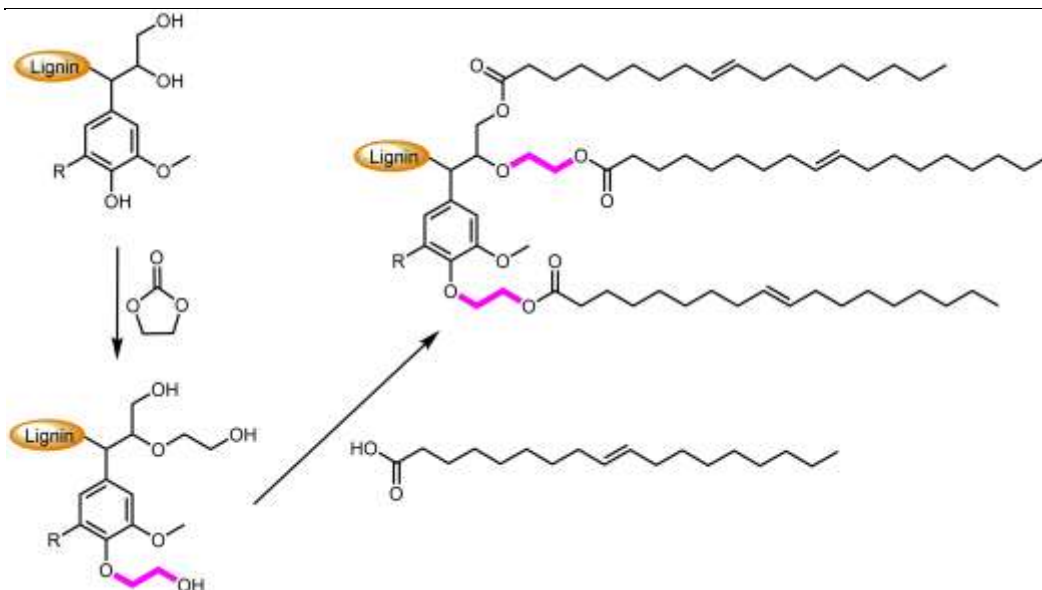
Figure 68 Reaction scheme of two-step esterification for the preparation of oleate hydroxyethyl lignin.

To achieve a lignin sample with hydrophobic characteristics, oleic acid was used to modify the aliphatic OH groups in lignin. Oleic acid was reported as a major component in plant oils potentially serving as abundant resources for making renewable materials.[323, 324] In order to obtain esterified lignin, high-temperature reactions were required to promote the esterification process and providing enough hydrogen ions. To make a comparison, the Fischer esterification process which used 1% H_2SO_4 (98% conc.) as catalysts was also performed at the same temperature and reaction time. Based on ^{13}C NMR spectrum, the degree of substitution (DS) for these two types of esterification routes was calculated based on the change of AlOH groups (*peak cluster 1*: 61.5-58 ppm, **Figure 69**), which was formed during the hydroxyethylation.[91] After the esterification, the *peak cluster 1* disappeared, and the shielding of the additional ester group formed a new peak

region (*peak cluster 2*: 65 – 61.5 ppm, **Figure 69**). The degree of substitution (DS) for the esterification reaction was analyzed utilizing these peak structures: DS=peak 2/ (peak 1+peak 2). The DS for the esterification with and without 1% H_2SO_4 were 89% and 88%, respectively (**Table 14**). Noteworthy, peak 2 in **Figure 69D** (with H_2SO_4) had different peak shapes with *peak cluster 1* in **1A** and *peak cluster 2* in **69C**. This indicated that the addition of H_2SO_4 may have caused side reactions including the degradation of linkages or further condensation of lignin.
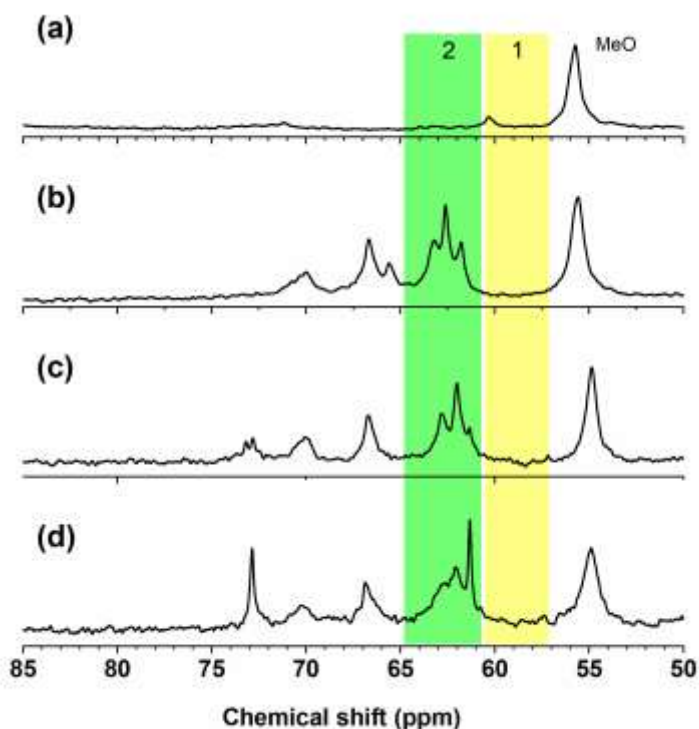
Figure 69 ^{13}C NMR spectrum of (a) Lignin, (b) Acetylated hydroxyethyl lignin, (c) oleate hydroxyethyl lignin, and (d) oleate hydroxyl lignin with 1% H2SO4 (w/w).

After the hydroxyethyl reaction, the FT-IR spectrum showed that modified lignin had slight changes on Aryl-Alkyl ether bond and carbonyl groups (C=O, 1800 - 1600 cm^{-1}). (**Figure 70**) Overall, there were few changes in the HELignin, as the hydroxyethyl reaction only selectively modified theArOH groups without causing obvious side reactions. Confirming this change, FT-IR analysis is a useful method in revealing a change in hydroxyl stretching associated with these hydrophilic functional groups. In the spectrum, there was evidence of the efficiency of our direct esterification (catalyst-free esterification) toward the hydroxyl groups in HELignin, as illustrated

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by a clear reduction of the hydroxyl group (O-H stretching, 3650 – 3200 cm^{-1}) absorbance. Further, there was evidence of the alkyl chains (C-H, 3200 - 2800 cm^{-1}) and carbonyl linkages (COOR, 1800-1700 cm^{-1}). (**Figure 70**)
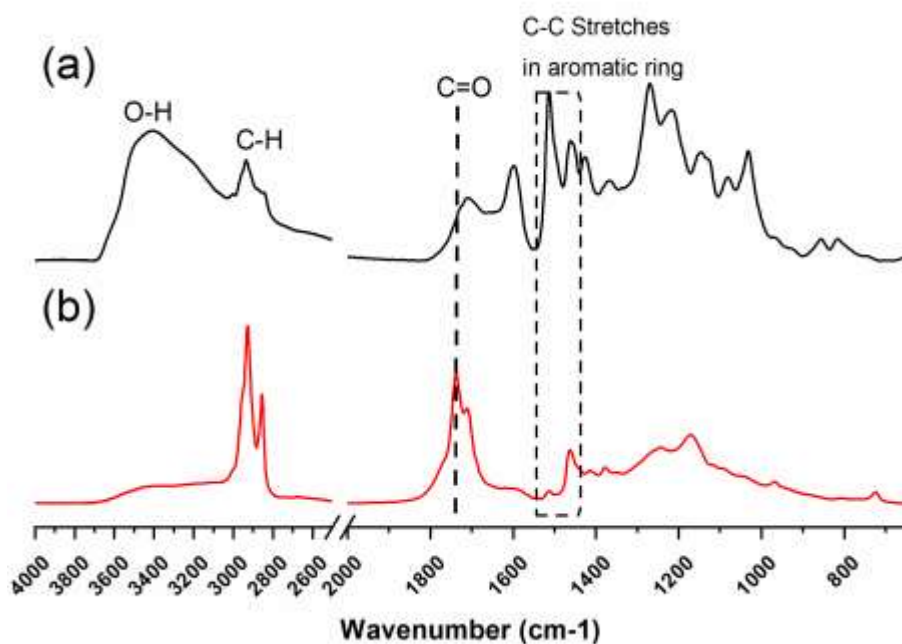
Figure 70 FT-IR spectrum of (a) Lignin, (b) oleate-ethyl lignin

8.2.2   Molecular weight analysis of esterified HELignin

The molecular weight was analyzed with gel permeation chromatography (GPC) as shown in **Figure 71**. In agreement with our previous research on other lignin sourced materials, the HELignin had a slightly larger molecule weight (M_w) and a wider polydispersity index (PDI). In addition to the hydroxyethyl groups on lignin, an increase in the degree of condensation was found arising from heating lignin in an alkaline environment as discussed in **chapter 4** and **5**. After the catalyst-free esterification, GPC analysis revealed that oleate HELignin with added acid catalyst had a much wider distribution of molecular weight and the traces had multiple peaks due to side reactions such as the condensation or degradation of ether bonds (**Figure 71**). As such, the lignin with acid catalyst was not further considered for the formulation of the hydrophobic coating. The esterified lignin via direct esterification without acid catalyst had a GPC trace revealing a more

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uniform molecular weight distribution than the other types of lignin. (**Table 14**) However, the reduction of molecular weight for this lignin may be an artifact of the washing procedure to prepare materials for analysis.
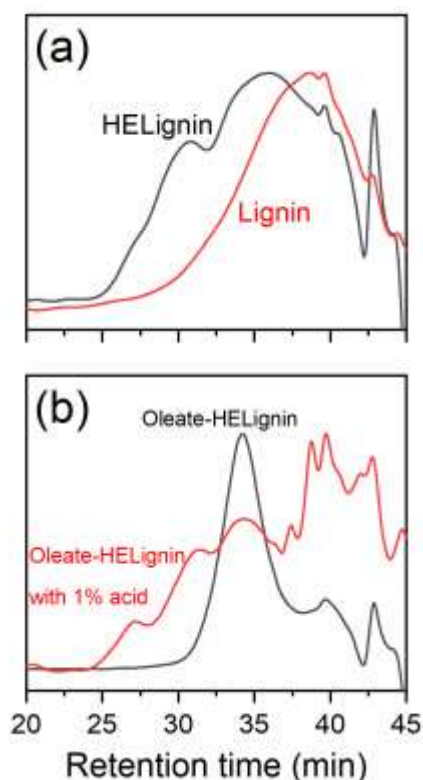
Figure 71 Molecular weight traces of (a) Lignin, Hydroxyethyl lignin (HELignin) and (b) oleate HELignin, oleate HELignin with 1% H_2SO_4 acid.

8.2.3   Thermal properties of esterified HELignin

The thermal properties of lignin before and after modification were also analyzed utilizing differential scanning calorimetry (DSC). The glass transition temperatures (T_g) were detected based on the heat flow baseline shift after the third cycle in a heat-cool-heat program. By derivatizing the sample, the T_g was decreased from 165.1 °C (SKL) to 120.1 °C (HELignin). This reduction was larger than previously reported hydroxyethylated lignin samples that had first undergone acetone fractionation.[150] The HELignin contained a higher amount of hydroxyethyl groups, which potentially would provide additional bulking to the lignin structure, reducing the T_g further. The ethyl-oleate derivative had a significant change of T_g before and after the reaction;

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reducing the T_g from 120.1 °C down to 8.1 °C or 2.7 °C (1% H_2SO_4 as catalyst). (**Table 14**) This result occurred because the esterification reaction had significantly decreased the amount of aliphatic OH groups (more than 4 out of 5 hydroxyl groups were modified with the long carbon chains), which directly weakened the intra- and inter- molecular bonding network and caused an increase in free volume. Hence, the alkyl chains created bulky side-groups that enhanced the inner plasticization of the lignin derivative. The change on the T_g of esterified lignin was similar with the previous report that used halogenated compounds to obtain a series of lignin with different carbon chain lengths. The T_g of esterified lignin was reduced with increasing carbon chain length and the degree of substitution.[31]

8.2.4   Aqueous lignin particle solution

Research into lignin-based particles[325] is of growing interest from emulsions[326] to surfaces coating[327]. Lignin as amphiphilic compounds could form colloidal spheres by self-assembling during the solvent exchange.[328] Adding additional fatty acid chains would improve the hydrophobic properties of these spheres and may further promote the formation of colloidal spheres. The aqueous lignin micro-particles were prepared by the dialysis bag solvent exchange method, developed by Österberg and her co-workers.[329] We hypothesized that these colloidal spheres, once coated on the surface, may form a film similar to the microstructure of the surface of the lotus leaf.

As such, the particle size distribution of this aqueous lignin particle will make significant impacts on the final hydrophobic properties. Dynamic light scattering was used to characterize the particle size of the dispersion after controlled precipitation. **Figure 72** showed the distribution of particle sizes of SKL and the oleate HELignin derivative. The particle size for SKL had a large distribution in a range from 200 nm up to the maximum detectable range. This large range of particle sizes may be related to the swelling of the lignin via the available hydroxyl groups. The lignin formed large particles and was precipitated due to the aggregation with itself after extended storage. Conversely, the esterified lignin particle solution formed a steady dispersion with a particle size centered at 2 μm. Surprisingly, the dispersion was stable for more than one week without precipitation. As a comparison, Monica and her collaborators adopted a natural carnauba waxy to

prepare an aqueous hydrophobic coating solution.[330] During this process, ZnO or TiO2 were required to improve the stability of aqueous particles.
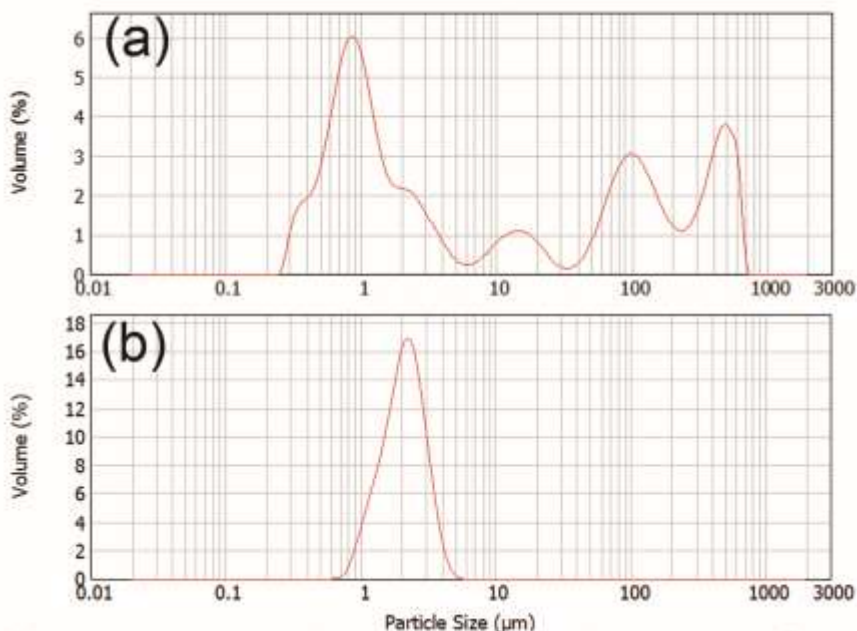
Figure 72 Dynamic light scattering traces of aqueous lignin particles (a) and aqueous oleate hydroxyethyl lignin particles (b)

8.2.5   Contact angle analysis

The target application of this lignin-based material was to serve as a sprayable water-based renewable material coating for forest-based products, which is critical in construction and packaging.[322] Wood-based products like wooden timbers can biodegrade in high-moisture environments due to the attack of fungi, following depolymerization of the polysaccharides into simple sugars.[331] For wood materials, loss of mass by just a few percent caused significant impacts on the toughness of wood.[322, 332] Hence, durability impacts the overall performance and moisture exposure can occur in service or during handling and storage at the construction site.

To illustrate the change in coated surface behavior, the wettability of the modified surface was investigated using a static contact angle test. Bleached Kraft pulp sheet stock, wood, and glass were selected as the test substrates to investigate the hydrophobicity of the coatings consisting of the lignin-oleate microparticles. The oleate esterified HELignin suspension was sprayed onto the various surfaces utilizing an airbrush. Multiple coating cycles were used to form a uniform layer.

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However, uniformity was difficult to achieve on the non-porous surface. Spin coating was also adopted to form a uniform layer on the surface of the target materials.

Figure 73 showed that the coating suspensions would increase the hydrophobicity for all three types of material surfaces for both spray and spin coating. The lignin ester deposited on the glass slides had a contact angle 110° (spray) and 95° (spin), while uncoated samples had an angle of 39°. The aqueous lignin particle solution was applied to two common wood-based products which included a solid wood block of yellow poplar and a Kraft pulp sheet. For the solid wood, the contact angle increased from 68° to 147° (spray) and 137° (spin) after coating with the lignin derivative. This value is more than 20° and 10° greater than previously reported values for organosolv hydrophobized lignin esters on poplar.[322] For the pulp sheet, the contact angle increased significantly from 80° to 122°(spray) and 123°(spin). One observed phenomenon is that the water droplets disappeared in 10 seconds for uncoated pulp, while the water droplets on the coated materials were stable after more than 2 min. Further, the initial contact angles of the lignin oleate ester coated handsheet were similar to reported values for coated filter paper or coated commercial paper board with suberin-like lignin ester derivatives[333] or tall oil lignin ester derivatives,[160] respectively. In these cases, the process required the dissolution of the lignin derivative into acetone and application to the substrate with an organic solvent. In contrast, spraying or spinning from an aqueous suspension avoids potential VOCs during the application process.
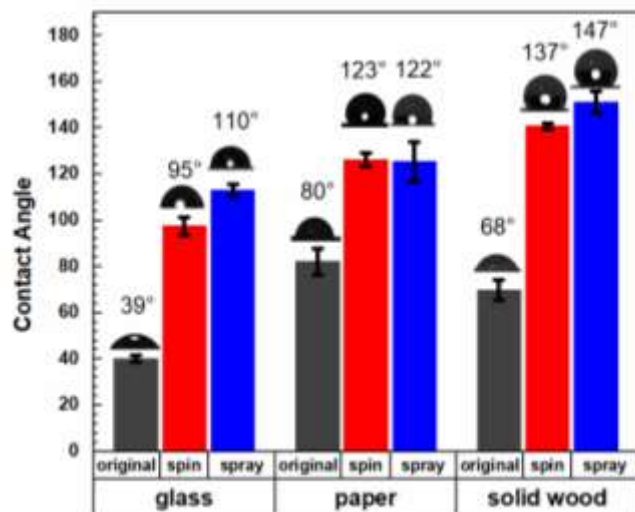
Figure 73 Contact angles of spray or spin coated surface of glass, paper, and solid wood using aqueous oleate hydroxyethyl lignin particle

8.2.6   Micromorphology analysis of aqueous lignin coating

The morphology of coated surfaces was analyzed by scanning electron microscopy (SEM) and atomic force microscopy (AFM); the roughness of surfaces contributes to the hydrophobic properties of waxy coating materials. **Figure 74 (b)** showed that the coated surface of pulp boards had a more "uniform" surface than the uncoated pulp board (**Figure 74 a**) because the merging of these lignin particles would form a film (**Figure 74 c**) to cover the surface. The AFM showed similar morphology (**Figure 74 e and f**), as particles merged into clusters, seen as linkages amongst droplet islands. This phenomenon resulted from the fact that the samples were stored at room temperature and the coating material has a low glass transition temperature (T_g=8.1 °C).
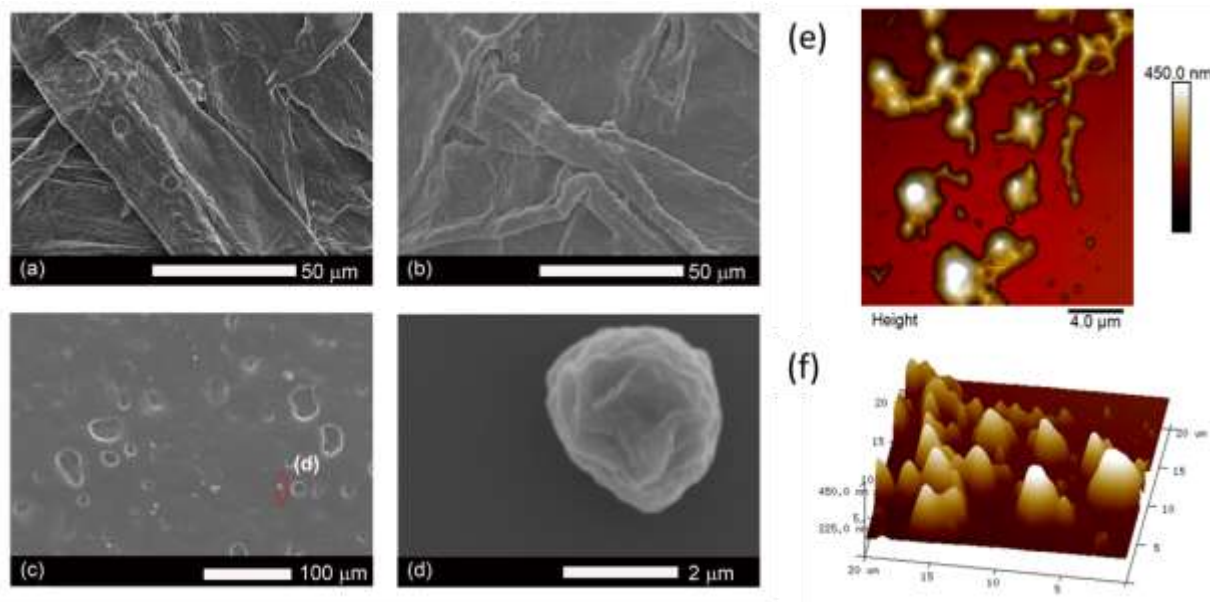
Figure 74 SEM photos of pulpboard (a), coated pulpboard (b), coated glassware (c), lignin microparticles (d), and AFM photos of coated glassware (e and f)

At room temperature, the coated lignin particles can soften and relax to the structure of the surface. Similar to latex coatings, once the water has evaporated, those lignin micro particles merged into larger structures, even films at room temperature. Due to the coverage of these hydrophobic lignin particles or films, the coated surface demonstrated improvement on their hydrophobic properties. However, the surface did not retain the microstructured roughness from the dispersed compounds. Hence the roughness resulted from the substrate below the lignin film, which would explain why the smooth glass surface had the lowest contact angle. In future, the large molar mass of lignin or ZnO[330] potentially can be used to improve the stability of lignin particles under the high temperature. On the surface of films, there was still a small fraction of lignin particles not fully relaxed (**Figure 74 d**); the diameter for these particles was around 2 µm. This result was in agreement with our previous dynamic light scattering data (**Figure 72**).

8.3   Conclusion

1) In this chapter, a nature-inspired lignin-based hydrophobic coating material was developed by esterification of lignin with a plant-based fatty acid. The ArOH were first hydroxyethylated using ethylene carbonate and subsequently, the AlOH were esterified with oleic acid. Reaction

conditions with and without added strong acid as a catalyst provided a derivative with high substitution levels;

2) Utilizing the oleate ethyl-lignin derivative without added acid, lignin micro-particle suspensions were then prepared by controlled precipitation using a dialysis tube. The oleate HElignin particle showed a particle size centered at 1μm.

3) By spray or spin coating, this aqueous lignin particle solution could successfully improve the hydrophobic properties of solid wood and pulp paper with a contact angle above 120°.

4) The low glass transition of the lignin derivative provided the ability of the microparticles to transform on the surface, a dynamic process, conforming to the inherent surface roughness.

5) This renewable coating material helps to advance the field of simple methods to utilize technical lignin in relevant applications for packaging and construction material protection.

Chapter 9: Conclusion and future work

Catalyzed by the increasing pace of consumerism, plastic materials derived from fossil fuels were so successful in the last 70 years that they have become embedded in the fabric of modern society. Yet these materials have limited degradability that has led to a significant pollution problem.[7,334] While policy-based approaches are critical to address end-of-life disposal for plastic waste,[334] we can also create more sustainable polymeric materials from utilizing modern carbon (plant feedstocks) forming compostable materials.[335, 336] Addressing this issue, kraft lignin derived from the second-largest amount of naturally occurring biopolymer on earth, lignin, was investigated in this dissertation as a promising avenue to solve problems of sustainable materials development.[14] Currently, the largest amount of lignin is produced by the pulp and paper industry. Technical lignin from these sources have complicated structure with various functional groups, a wide molar mass distribution, and thermal instability when heated at industrially relevant polymeric processing temperatures. As a result, lignin has uneven reactivity and poor performance when added into other polymeric systems. Additionally, past approaches for lignin derivatization utilized malignant chemistry not suitable for scale-up that had a large environmental footprint during processing. This dissertation research identified a safe-compound, ethylene carbonate, for use to create a technical lignin with greater uniformity by the selective reaction of the phenolic groups and carboxylic acids. In so doing, the reaction with ethylene carbonate produced lignin with predominately one type of functional group that had potential to enhance the thermal stability. However, many questions needed to be addressed to understand how to drive the reaction towards a uniform lignin derivative instead of a co-polymer with carbonate linkages which was previously produced in the literature. Underlying this thesis was the focus on green chemistry attributes during derivatization in order to judge the modification route. The resulting hydroxyethyl lignin (HElignin) had a uniform chemical structure (containing more than 80% of aliphatic hydroxyls, AlOH) and enhanced thermal stability. **In Chapter 4**, we optimized the reaction conditions and found that increased temperature (>120 °C) led to the unfortunate reduction of aliphatic hydroxyl groups as a result of the crosslinking with excess ethylene carbonate and lignin.

Due to the addition of aliphatic hydroxyl groups, the HELignin showed improved miscibility with polyester-based polyols used in polyurethane foams (**Chapter 5**), in comparison with original lignin. Combining polyols with hydroxypropyl lignin and organosolv bark lignin, the structure-

property relationship was studied and showed that the functional groups including carboxylic acids and total hydroxyl groups (including the amount of different type of hydroxyl groups), and molar mass will make significant impact on the viscosity of polyol, foam density and compressive modulus of resulting materials. This work provided a novel route for future research using a controlled esterified hydroxyethyl lignin polyol; this could include the possibility of preparing copolymers using lignin, glycerol, and and di-acids with lipase as catalysts. In such a system, a new type of lignin-based polyol would have a significantly lower T_g, and higher hydroxyl content, which would help avoid the utilization of petroleum-based polyols for lignin-based PU foams.

However, due to the complicated structure of lignin and its sensitivity with reaction conditions, it was critical to adopt methodology for controlling the hydroxyethylation reaction. In **Chapter 6**, an in-situ analytical process was developed based on monitoring the amount of CO_2 produced during the reaction of the ethylene carbonate with the phenolate or carboxylate ions on the lignin. By using the volume of CO_2 as a detector, we had better control of the quality of the lignin derivative (minimizing side reactions) and shortened the excess reaction time to increase the process flexibility. A predictive model was built to reduce the workload for the optimization of different types of lignin resources. Finally, we proposed a type of modification system to help pulp companies, not only obtain more uniform lignin and high-value chemicals but also reduce the overall lignin recovery cost and the emission of CO_2. In the future, this in-situ monitoring technique may be applied to different types of hydroxyalkylation reactions as there a variety of different cyclic carbonates with various reactivities that would produce CO_2 as a by-product.

As esterification can tailor the properties of lignin for specific applications, a significant scientific advance of this dissertation was developing a direct esterification process of HElignin (**Chapter 7**). In substitution of traditional esterification routes using anhydride and acyl chloride compounds, we developed a catalyst-free esterification route to modify the hydroxyethyl lignin with a high degree of substitution (>80%). For this set of reactions, the organic acid was used as the solvent, reagent, and catalyst. By changing the reaction condition, the DS was controlled and as a result, the T_g of lignin was modified based on the degree of substitution. Further, different types of organic acids, including valeric acid (C_5), octanoic acid (C_8), oleic acid (C_{18}), and unsaturated organic acids such as acrylic acid and propiolic acid were reacted with the lignin the research revealed

efficient at substitution of hydroxyl groups with a DS: 50%-85%, which was higher than typical substitution levels with organic acid chlorides. By using these organic acids, we could engineer the properties of the resulting lignin (T_g) and introduce clickable -yne and -ene groups into the lignin. Further, a one-pot procedure was successfully utilized for a sequential reaction of hydroxyalkylation and esterification of lignin, which showed a high degree of substitution. Overall, this two-step, one-pot reaction was more efficient to obtain thoroughly esterified lignin and satisfy many greener metrics of lignin modification than traditional methods.

Further, **Chapter 7** provided a promising route for the creation of lignin derivatives. Based on this chapter, several new ideas and promising methods were developed to utilize technical lignin. Besides the modification of lignin, fractionation was another important strategy to improve the characterization of lignin and obtain more uniform materials. By adopting the catalyst-free esterification route, the esterified technical lignin could thoroughly dissolved into organic acid reaction medium. One area of future work is to isolate lignin with specific molar mass by downward fractional precipitation by adding specific amounts of non-solvent, like water to precipitate lignin of specific attributes. By thorough characterization of these lignin fractions using NMR, GPC, and molecular modelling, a deeper understanding of lignin's chemical structure and conformation can be derived. From this standpoint, future work would include preparing a type of polymer alloy by blending the fractionated esterified lignin (high molecular weight) with aliphatic polyesters. These polyesters make an important contribution to the biodegradable plastic materials market. With a better understanding of the structure-property relationship, this may help researchers overcome the poor mechanical properties of those lignin-based materials. The addition of clickable functional groups in lignin also provided a route to prepare more advanced bioplastic materials such as hydrogel, block-copolymers, and recyclable polymers.

In chapter 8, a nature-inspired lignin-based hydrophobic coating material was developed by esterification of lignin with a plant-based fatty acid (oleic acid). The free phenolics were first hydroxyethylated using ethylene carbonate and subsequently, the aliphatic hydroxyls were esterified with oleic acid. Reaction conditions with and without added strong acid as a catalyst provided a derivative with high substitution levels; utilizing the oleate ethyl-lignin derivative without added acid, lignin micro-particle suspensions were then prepared by controlled

precipitation via dialysis. The oleate HElignin particle showed a particle size centered at 2 μm. By spray or spin coating, this lignin aqueous solution improved the hydrophobic properties of solid wood and pulp paper with a contact angle above 120°. The low glass transition temperature of the lignin derivative provided the ability of the microparticles to transform on the surface, a dynamic process, conforming to the inherent surface roughness. This renewable coating material helped to advance the field to utilize technical lignin in relevant applications for packaging and construction material protection. In the future, the oleate ethyl lignin building blocks could be used as a precursor to making a variety of materials by further modification of the unsaturated bonds.

From these studies, several routes guided by green chemistry principles were created for new lignin derivatives. The resulting processes had a lower environmental factor compared to traditional modification routes and resulted in a lignin material with little side-product formation, controlled physical properties and uniform chemical functional groups. In this dissertation, these materials were explored for their use in rigid polyurethane foams and as hydrophobic polyester coatings. Future work with these materials will involve melt-processing with biodegradable plastics to form lignin bioplastics as well as advance materials such as block-copolymers and hydrogels for multifunctional responsive materials.

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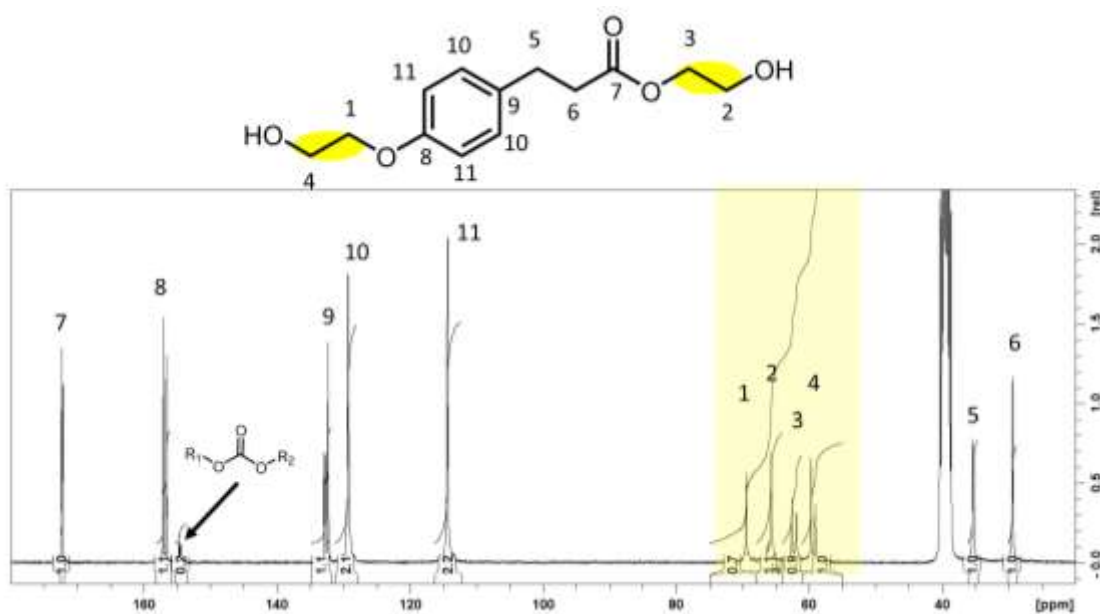
Appendices

Appendix A

A.1   The design of CO2 collecting and measuring equipment
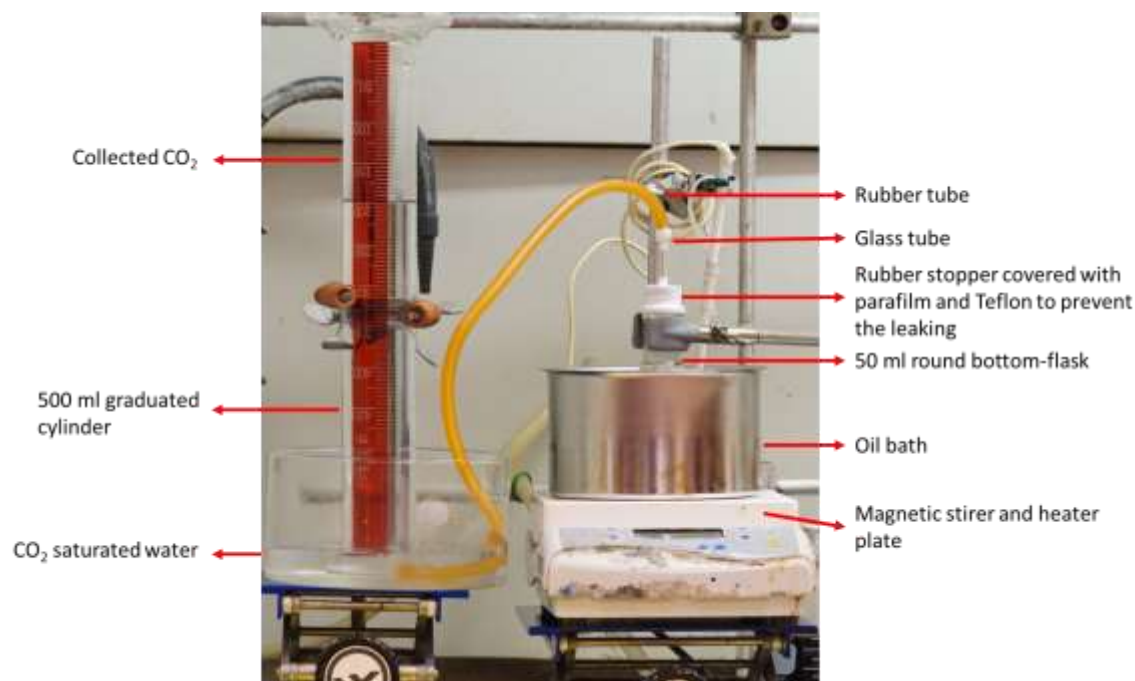
A.2 ^{13}C NMR spectrum of hydroxyethyl phloretic acid

Appendix B Valorization of bark using ethanol-water organosolv process: isolation and characterization of crude lignin

B.1   Introduction

The outer portion of woody-plants, bark, forms a remarkable barrier against fungi and insects, as well as serves as a key component in regulating moisture.[337] While known for its protection, certain species such as cherry demonstrate surprising mechanical properties due to its hierarchical structure.[338] Composition of bark is dependent upon species of woody plant but contains a higher amount of extractives such as tannins and fatty acids, along with suberin and minerals.[337] When trees are processed for lumber and pulp, the bark is stripped away from the log and either utilized in value-added applications such as mulch or is burned for energy recovery. Owing to its multi-functionality of serving as a barrier and conductor of fluids, it contains typical structural polymers found in the xylem. Hence it also contains high levels of potential extractives along with useful polysaccharides, lignin, and suberin.[337] Based on the above characteristics, it is clear that bark is a different feedstock filled with valuable components for the preparation of renewable materials and chemicals if it could be processed efficiently.[339] Previous approaches have shown that bark can be converted into various value-added materials such as nanocellulose,[340] epoxy,[341] and polyols[342].

While research into bark utilization is growing, few published works described the properties of the lignin fraction in the bark and their potential utilization. Renewable lignin resources have gained increasing attention as an alternative resource in replacing fossil-based compounds.[14, 23, 27, 343] Different from traditional Kraft and sulfite pulping using aqueous alkali or aqueous acid, the organosolv process utilizes organic solvents such as alcohols,[344] ketones,[345] or even organic acids[346] to treat the biomass at 90 °C – 200 °C in the presence of organic acid or mineral acid catalysts. Due to the mild reactive conditions and high selectivity of organic solvent in dissolving lignin, the resulting organosolv lignin has a series of merits: sulfur-free, more homogeneous chemical structure, lower molecular weight, lower glass transition temperature (T_g), and less contamination.[244] As a result, organosolv lignin typically outperforms other lignins in similar applications; for example, it has better compatibilities with polyols,[266] polyesters[347] and can be used for applications in foams and bioplastics, respectively. Currently, this process still has limited

competitiveness in the market since the utilization of organic solvent will increase energy consumption and capital expenditure.[115]

Therefore, utilizing low-cost feedstock like bark may enhance economics if there was an economically compelling reason to do so. Karnaouri et al. using the organosolv process (ethanol/water) combining with a steam explosion to treat bark, following with the characterization of the chemical structure of lignin.[86, 348] However, these studies mainly focused on converting the treated bark residue to sugar and neglected the valuable application of extracted compounds in the liquor section. In this chapter, both pine bark (PB) and oak bark (OB) were treated using an ethanol-water organosolv system to extract valuable crude lignin compounds. We hypothesized that the organosolv processing could help realize the valorization of bark resources, by extracting high-valuable lignin, removing part of extractives that have high hydroxyl content A simple two-level factorial design with Design Expert 8.0 was adopted to study the impact of temperature, ethanol concentration, and solid loading on the solubilization of bark and the yield of crude lignin. Then, ^{13}C NMR and HSQC NMR spectrum were further used to characterize the major composition and chemical structure in the resulting crude lignin.

B.2   Results and discussion

Compositional analysis of bark resources

Besides common compounds such as polysaccharide, lignin, extractives, and ash in xylan, bark tissue was expected to contain extra compounds including polyphenols and suberins compounds with the number of extractives, lignin, and ash higher than values typically found in xylem due to its protective function for wood.[337] The original bark resource contained 34.3% (PB) and 31.0% (OB) of extractives, 30.1% (PB) and 30.5% (OB) of lignin, 13.1% (PB) and 10.5% (OB) of glucan, 9.6% (PB) and 9.6% (OB) of other sugar content derived from hemicellulose, with a level of 6.93% (PB) and 5.83% (OB) ash contents. The extractive and lignin components were higher than the results of Miranda et al [349] and Ruiz-Aquino et al.,[350] most likely because the suberin content may be depolymerized and combined with phenolic extractives with the reaction conditions.

The compostional change during the organosolv processing

The complicated composition may limit the valorization of bark resources. As such, one of the hypotheses in this study is that the organosolv process (ethanol-water) can lead to the fractionation of bark resources by isolating extractives and lignin compounds from the resources simultaneously. At the same time, we may obtain extractive and lignin less bark residue for more valuable applications such as biofuel. (**Figure 75**)
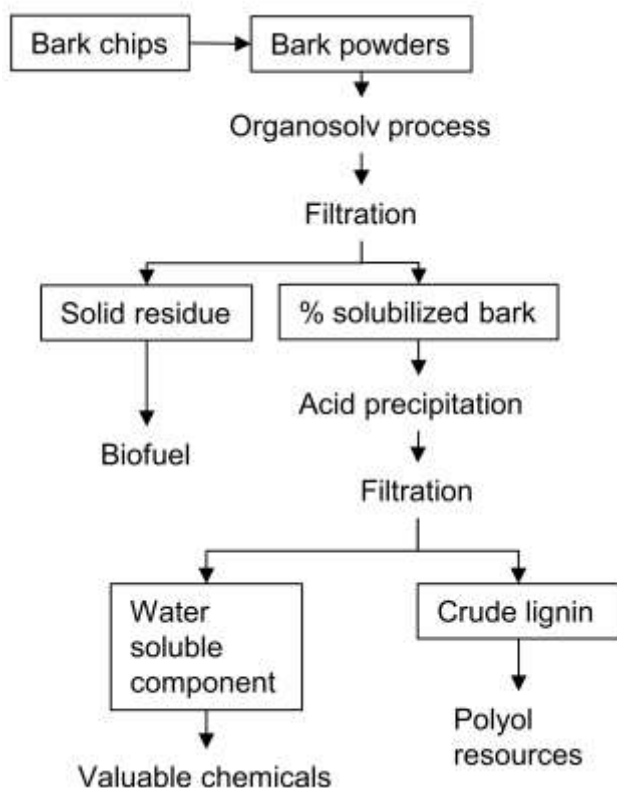
Figure 75 Promising route for the valorization of bark resources including biofuel, chemicals, and materials.

For the organosolv conditions, Zhang et al. summarized the reactive conditions and found that the ethanol-water (50 – 80%) solvent was always adopted to treat different types of biomass using sulfuric acid (catalyst, 1% wt to biomass) at a high temperature (140- 210 °C).[115] Increasing temperature will lead to an increased yield of resulting lignin, but this will also cause the condensed reaction of isolated fragments.[76] The softwood contains guaiacyl units (G) and p-hydroxyphenyl units (H), while the hardwood also contains syringyl units (S).[351] The aromatic ring of S was substituted by two methoxy groups, which would have limited condensation reactions at this

position on the aromatic ring.[82] As the condensation will cause negative impacts on the yield and chemical structure of lignin, we adopted a slightly lower temperature to treat pine bark (softwood, 165 °C, 60%, 60 min, and 1% acid) than oak bark (hardwood, 180 °C, 60%, 60 min, and 1%).

We initially put 100 g pine bark and oak bark in the reactor and finally recovered 56 g (PB) and 47 g (OB) of solid residue after filtration and purification. **Figure 76** showed that the major component in the solid bark residue changed significantly. These solid residues contained lower amounts of extractives than the original bark; as 25 g (PB) and 24 g (OB), extractives were removed from the solid residue during the organosolv process. An obvious reduction of extractives and hemicellulose components occurred since the aqueous ethanol dissolved degraded compounds at high temperature with an acid catalyst. As a result, the weight percentage of carbohydrate compounds in pine bark and oak bark residue had increased.
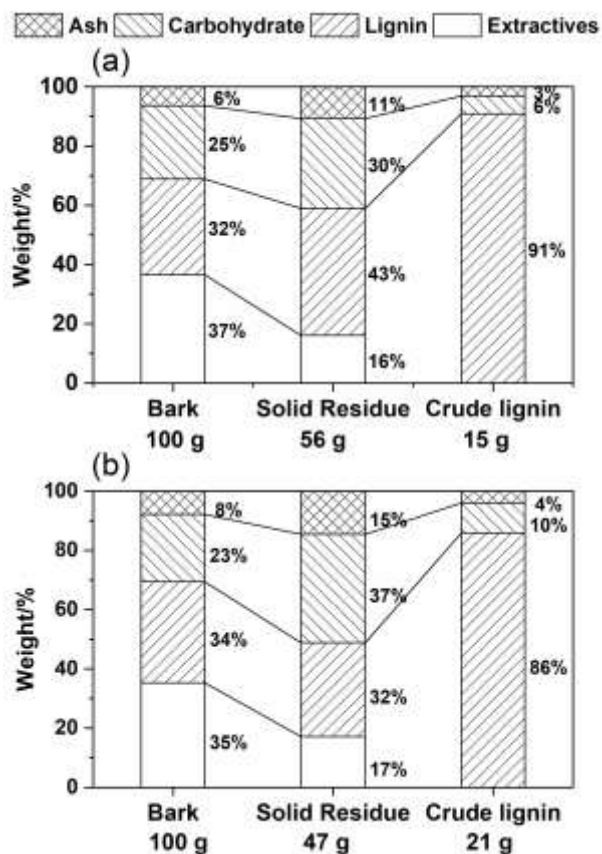
Figure 76 Changes of compositional analysis during the ethanol-water organosolv process for both oak bark and pine bark (reactive conditions) (a) pine bark (165 °C, 65% ethanol concentration, and 0.075 g/ml) and (b) oak bark (180 °C, 65% ethanol concentration

After the organosolv pretreatment, 46 g of pine bark and 53 g of oak bark (**Figure 76**) has been dissolved into the supernatant, which is higher than previous methods,[348] indicating the high efficiency of this organosolv process to isolate various compounds from bark resources. For the black liquor after removing ethanol, a traditional coagulation process, pouring the liquor in acidic water, was adopted to recover the crude lignin compounds. (**Figure 75**) Within select conditions, 15 g and 21 g solids (crude lignin) were precipitated from pine bark and oak bark liquors, respectively. Around 30 g of bark (water-soluble compounds, **Figure 75**), belonging to the low molar mass oligomers or chemical monomers such as flavone derivatives, terpenes, and non-structural sugars compounds,[337, 352] were dissolved in the aqueous solution, which required more studies in the future.

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For the recovered solids from the supernatant, the klason crude lignin was the predominate component at 12 g (pine bark) and 17 g (oak bark) besides carbohydrate and ash. The amount of klason crude lignin is higher than the calculation, based on the composition of solid bark residue before and after the organosolv process, showed that 6 g pine bark lignin and 17 g oak bark lignin were removed, due to the mixed extractive, suberin, hemicellulose, and their degraded compounds.

Overall, the organosolv process was an efficient way to dissolve around 50% of bark resources, which may contain valuable products, if proper fractionation methods were adopted. The increased concentration of carbohydrate content in the resulting solid residue provides more valuable products for biorefinery.[348] The E-factor analysis reveals that waste produced per unit mass of product were greater in case of oak bark compared to pine bark as a feedstock.[353] Hence, solvent recovery and the complete utilization of isolated fractions of bark resources are critical to ensure that the process has a low environmental footprint.

Impacts of reaction conditions on lignin yield and solubilization of bark

To study critical factors on the solubilizatoin of bark and yield of crude lignin, we adopted a two-level factorial design to study the impacts of different reaction conditions including temperature (°C), ethanol concentration (%), and solid loading (S:L, g/ml).

Table 15 The organosolv process conditions on the solubilization of bark (%) and the yield of organosolv pine bark crude lignin (PBL) and organosolv oak bark crude lignin (OBL)

No.	Temperature (ºC)	Ethanol Concentration (%)	S:L (g/ml)	Solubilization (%)	Yield (%)
PBL					
1	180	70	0.05	46	17.42
2	180	50	0.05	40	11.20
3	150	50	0.05	27	9.59
4	180	50	0.1	36	8.69
5	150	50	0.1	28	10.65
6	180	70	0.1	43	18.11
7	150	70	0.05	38	9.54
8	150	70	0.1	41	13.48
OBL					
1	165	70	0.025	44	14.37
2	165	50	0.025	48	15.70
3	165	50	0.05	42	17.41
4	195	50	0.05	49	13.92
5	195	70	0.025	53	20.93
6	165	70	0.05	34	16.03
7	195	70	0.05	49	21.33
8	195	50	0.025	52	16.05

The solubilization of bark resources (%) indicated the efficiency of the organosolv process for bark resources, which was in a range from 27%-46% for PB and 34% - 53% for OB. The crude lignin yield (without ash) was in a range from 8.69% to 18.11% (PB) and from 13.92% to 21.33% (OB) with selected conditions (**Table 15**). Generally, the amount of ash content in the bark was 10% higher than wood.[337] These ash compounds were also extracted and mixed with the organosolv bark lignin during the organosolv process. The selected reaction conditions had subtle impacts on their concentrations in the lignin. The obtained crude lignin yield was thus recalculated by removing ash contents (**Table 15**).

The analysis of variance (ANOVA) showed that the ethanol concentration (%) and temperature (°C) had more significant impacts on the crude lignin yield and solubilization of bark than s:l. The increased temperature with high ethanol (%) will improve the yield of crude lignin and the solubilization of bark (**Figure 77**). Pan et al. studied the impacts of temperature (160 °C - 215 °C) on the delignification of hybrid poplar. The maximum yield and solubilization of bark were obtained as the temperature went up to 195 °C. Meanwhile, the increased ethanol (%) from 50% to 70% improved the solubility of the component in bark, especially extractive and suberin comounds, but higher than that will lead to the solubility reduction of lignin due to the solvent parameter changes.[76, 354]
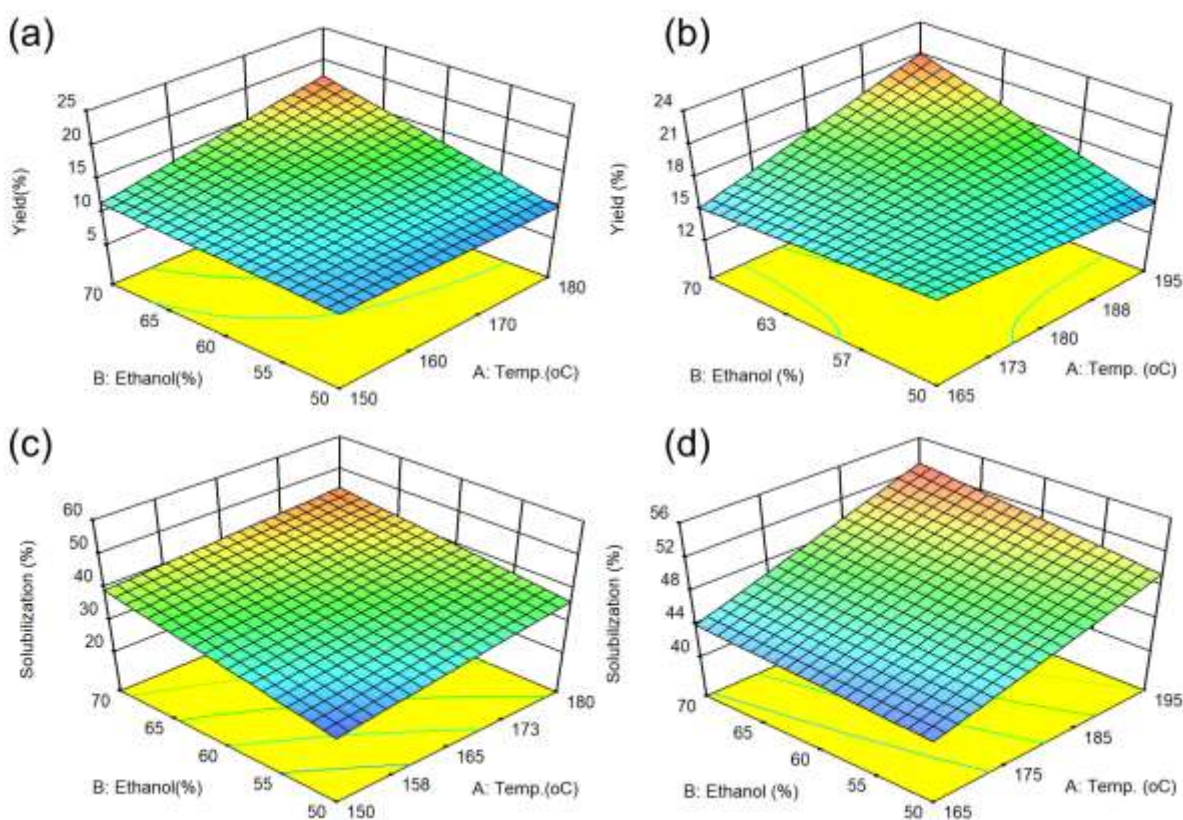

Figure 77 Interactive impact plots of temperature and ethanol concentration on the yield of crude lignin (a, organosolv pine bark crude lignin; b, organosolv oak bark crude lignin) and solubilization of bark (c, pine bark; d, oak bark)

By adopting a design of experiments approach, models were built to predict the crude lignin yield and % solubilization of bark under different experimental conditions (**Table 16**). The center point condition was performed to further indicate the accuracy of models. The variance between predicted values and actual values were around 15% (**Table 16**). With the same reaction condition (160 °C and 60 % ethanol, the solid loading was not involved), oak was more readily solubilize and had a higher yield than pine bark. Lignin in the hardwood generally has higher β-ether reactivity and a higher concentration of readily hydrolyzable α-ether linkages than lignin resources in softwood.[67] Besides, syringyl units in the hardwood are limited to undergo condensation reactions during the organosolv process. Shimada et al. studied model compounds showed that the reactivities of guaiacyl carbocations were higher than syringyl carbocations to form condensed bonds with anionic aromatic ring sites. Based on the reactivity, it was suggested that the condensation reaction was partially responsible for the low efficiency of the solubilization of bark using softwood as feedstock. [298] It is clear that softwood bark behaves similar to softwood xylem during the organosolv pulping.

Table 16 Models of crude lignin yield with the selective range of reactive conditions

Response (% bark)	Equations[a]	R^2	Predict value/%	Actual value/%	Variance /%
Crude lignin yield (Pine bark)	$12.85+1.39*A+1.99*B+1.53*AB$	0.84	12.34	14.86	16.96
Solubilization (Pine bark)	$37+3.5*A+5*B-A*B$	0.97	37.00	44.00	15.90
Crude lignin yield (Pine bark)	$17.43+1.41*A+1.52*B+2.10*A*B$	0.92	17.34	20.09	13.69
Solubilization (Oak bark)	$47.5+4*A+1.25*B+0.5*A*B$	0.99	47.25	53.00	10.84

A = temperature, (1, -1, or 0); B =ethanol concentration (%), (1, -1, or 0); AB = the interactive impacts of temperature and ethanol concentration, (1, -1, or 0);

The structural analysis of crude lignin

In this study, we mainly focused on the characterization of isolated crude lignin. Quantitative ^{13}C NMR (**Figure 78**) and HSQC NMR (**Figure 79**) spectra are excellent methods to analyze the chemical structure and major composition of crude lignin directly. As a comparison, milled pine lignin (MWL-Pine) and milled oak lignin (MWL-Oak) were used to represent the chemical structure of native lignin. (**Table 17**)[87] The acetylate process was performed as a duplicate for the ^{13}C NMR quantifications of fundamental units and hydroxyl groups of crude lignin.
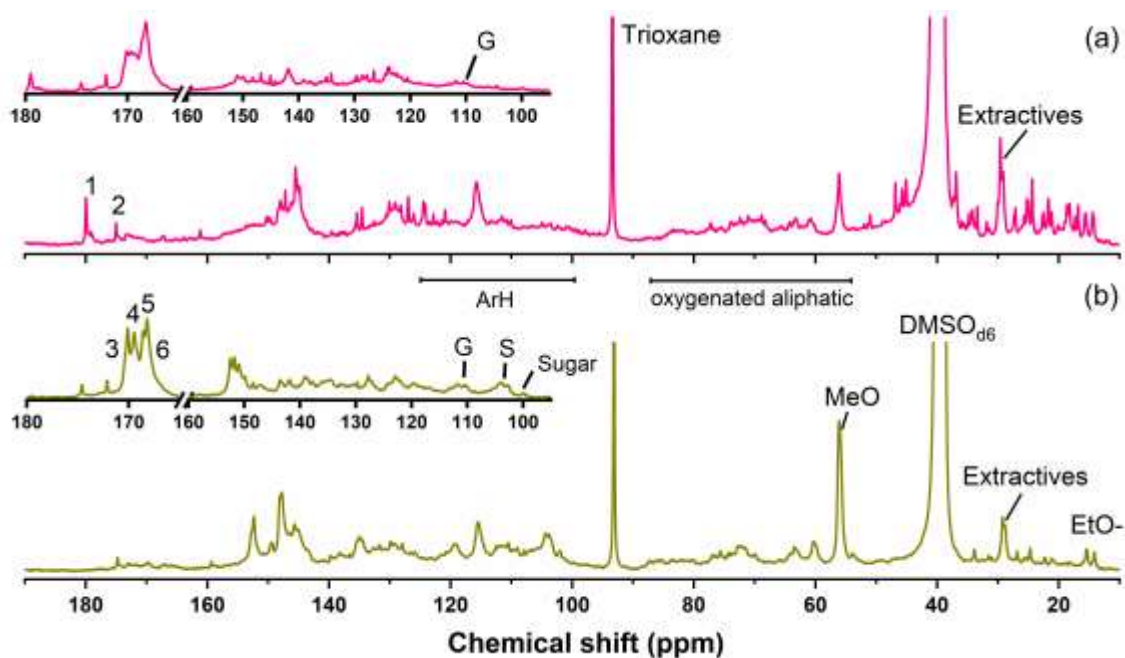

Figure 78 ^{13}C NMR spectrum of organosolv crude lignin, (a) pine bark (PBL, 165 °C, 65%, and 0.075 g/ml) and (b) oak bark (OBL, 180 °C, 65%, and 0.0375 g/ml)

The spectrum of crude lignin showed the fundamental lignin units guaiacyl (G) and syringyl units (S), though their amounts are lower than MWL. The native bark lignin normally has a lower amount of methoxyl groups than native wood lignin due to the low enzyme reactivity of methylation in the bark cell. [87] [89] As such, the methoxy group content (MeO, 58-54 ppm, **Table 17**) in the crude lignin was lower than MWL. Also, the demethylation during the organosolv process will lead to the reduction of methoxy groups.[89] PBL was lower than OBL since lignin from the hardwood sample contained syringyl units (**Table 17**).

Table 17 Quantitative structural analysis of milled pine lignin (MWL), milled oak lignin (MWL), organosolv pine bark lignin (PBL, 165 °C, 65% and 0.075 g/ml), and organosolv oak bark lignin (OBL, 180 °C, 65%, and 0.0375 g/ml) (Per 100 Ar)

Functional groups	Chemical shift (ppm)	MWL-Pine[89]	PBL	MWL-Oak[91]	OBL
G	114-108	99	72	30	42
S	108-102	n.a.	n.a.	64	24
X*	86.8 (δC)/5.49 (δH)	n.a.	4.0	n.a.	n.a.
EtO-	16.5-13	n.a.	15	n.a.	9
Methoxy content	58-54	97	35	169	82
Aliphatic OH	172-168.7	107	67	132	74
Aromatic OH	168.7-166	33	91	29	79
Total OH	172-166	140	158	161	153
ArH	125-102	253	226	211	217
DC	200+G-ArH	43	46	20	25
β-5*	86.8 (δC)/5.49 (δH)	10	5	3	3
β-β*	85.1 (δC)/4.63 (δH)	4	2	6	3
β-O-4*	70.9 (δC)/4.77 (δH)	42	11	60	12
Stilbene*	125.6 (δC)/6.97 (δH)/	n.a.	12	n.a.	`~1
Sugar	102-98	n.a.	7	n.a.	9
Polyphenolics*	94.9 (δC)/5.9 (δH)	n.a.	12	n.a.	n.a.
Unsaturated fatty acid*	129.1 (δC)/5.70 (δH)	n.a.	16	n.a.	3
Rosin acid*	120.1 (δC)/5.3 (δH)	n.a.	27	n.a.	~1

G, guaiacyl units; S, syringyl units; X, cinnamyl acid; EtO-, extractives; ArH, aromatic hydrogen; DC, degree of condensation; *quantitative HSQC NMR analyzed results;
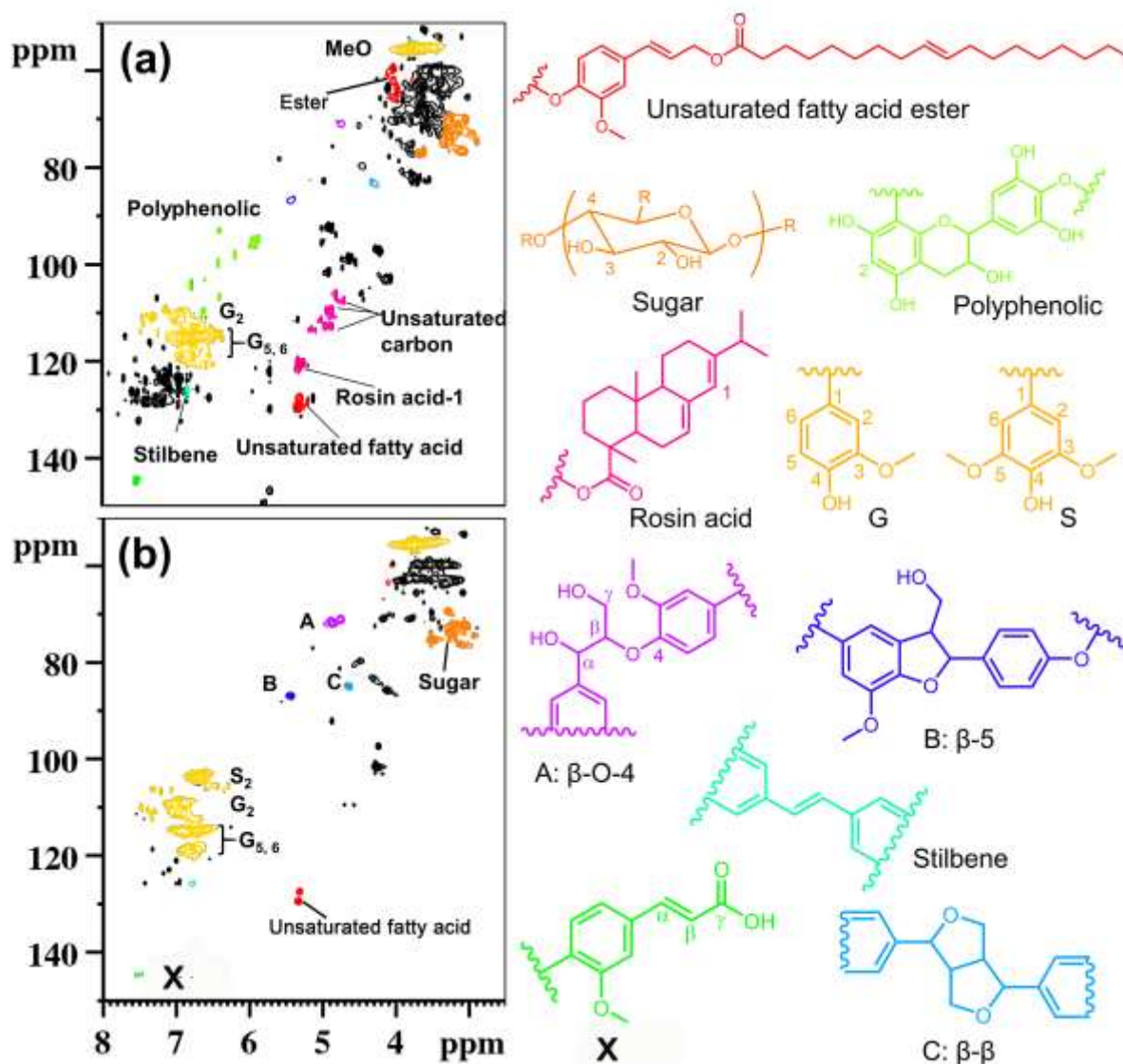
Figure 79 HSQC NMR spectrum of organosolv bark crude lignin, (a) pine bark (PBL, 165 °C, 65% and 0.075 g/ml) and (b) oak bark (OBL, 180 °C, 65%, and 0.0375 g/ml)

Organosolv pretreatment of wood generally includes two steps during the delignification: (1) lignin is depolymerized via the breakage of α ether bonds, following with the breakage of β ether bonds under higher temperature; (2) the polymerization or condensation of benzyl cations under acidic conditions, as those degraded aromatic monomers will become ionic compounds and easily react with other monomer/oligomers from lignin, polyphenols, and carbohydrates by condensation or copolymerization.[66] The native lignin linkages including β-O-4, β-β, and β-5 were tabulated in

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Table 17. The reduction of these linkages in the crude lignin (PBL and OBL) indicated the breakage of the β-O-4 bond during the isolation. In line with the previous organosolv treated wood lignin,[89] the excess amount of carbon-carbon linkages (degree of condensation, DC) and an increased amount of aromatic hydroxyl groups were formed or produced during the organosolv process.

These increased amounts of ArOH also belong to the polyphenolic compounds. As shown in the HSQC NMR spectrum, the extractive compounds, including polyphenolic compounds such as condensed tannins, rosin acid, and suberin-related compounds (unsaturated fatty acid ester) were blended or reacted with the resulting crude lignin. PBL contained a greater amount of these compounds than OBL as additional peaks appeared in the spectrum. These spectra also revealed that sugar compounds in both OBL and PBL. (**Figure 78** and **Figure 79**) As such, it is in agreement with the compositional analysis that the PBL, relative to the oak bark, had a greater mixture of lignin and extractive compounds and suberin. Besides those extractive compounds, other unsaturated linkages or groups including stilbenes and cinnamyl acid end groups (X) were found in the extracted OBL and PBL. Overall, the higher percentage of lignin related fundamental units and linkages reflected that the major component of crude lignin belongs to the lignin, especially for the OBL.

B.3   Conclusion

In summary, the organosolv process was used to treat pine bark and oak bark to fractionate the bark and extract crude lignin. Given temperature (°C), ethanol concentration (%), and solid loading (s: l, g/ml), predictive models on the solubilization of bark and crude lignin yield were built within the experimental range. The maximum solubilization of bark was 46% (PB) and 53% (OB), and the maximum yields of crude lignin were 18.11% (PB) and 21.33% (OB), respectively. Further analysis of resulting crude lignin by ^{13}C NMR and HSQC NMR showed that extracted compounds mainly contained lignin, accompanied by polyphenolic, extractives, suberin, and a low amount of carbohydrate, especially for the organosolv pine bark crude lignin (PBL). Extracted bark lignin would be used as polyol for polymeric materials such as rigid polyurethane foams and polyesters.