

Proceedings

Finnish Training School for LignoCOST CA17128

Chemical structure and selected applications of lignins

June 20-23, 2022

Åbo Akademi University (ÅAU), Turku, Finland



Patrik Eklund | Chunlin Xu (eds.)

Luyao Wang (Technical editing & text formatting)

Preface

In June 20-23, 2022 approximately 60 scientists from 12 different countries gathered for the Lignin Training School for LignoCOST CA17128 at Åbo Akademi University, Turku, FINLAND. The organizing committee consisted of Prof. Chunlin Xu, Dr. Patrik Eklund, Dr. Anna Sundberg, Dr. Lucas Lagerquist, and M.Sc. Luyao Wang from the Faculty of Science and Engineering at Åbo Akademi University and Monika Österberg from Aalto University. The program was focused on the chemical structure and selected applications of lignin. Lectures on topics such as fractionation and purification, characterization, chemical modification, and applications of lignin were given by 10 invited trainers as well as by the local organizers. In addition, the program included lab demonstrations, a poster session, social events, workshop/groupwork and an excursion to CH-Bioforce pilot plant in Raisio, Finland. Some of the lab demonstrations were based on the outcome from the Business Finland funded project ‘Novel Fiber Surfaces Functionalized by Lignins Refined and Engineered from Finnish Biorefinery Processes (LigninReSurf)’ targeting to develop high performance copolymers and materials based on lignins from Finnish biorefinery processes, part of activities in ExpandFibre ecosystem. The atmosphere was relaxed and there were fruitful discussions between all the participants. In this proceeding we have collected the poster as well as the mini-review papers from the groupwork. We would like to thank all the participants, trainers as well as Dr. Ted Slaghek and Dr. Richard Gosselink for making this training school possible, and LignoCOST for financial support.

Patrik Eklund and Chunlin Xu.

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Tour and Social Event



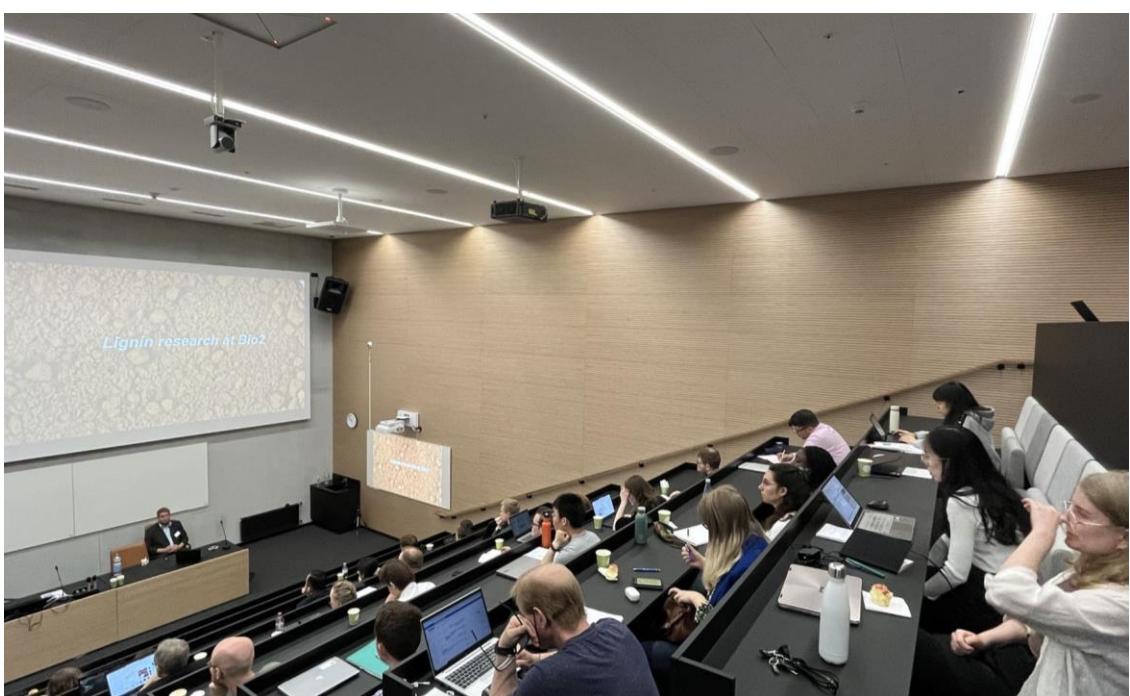
Turku Cruise boat Rudolfiina



Turku Cruise boat Rudolfiina



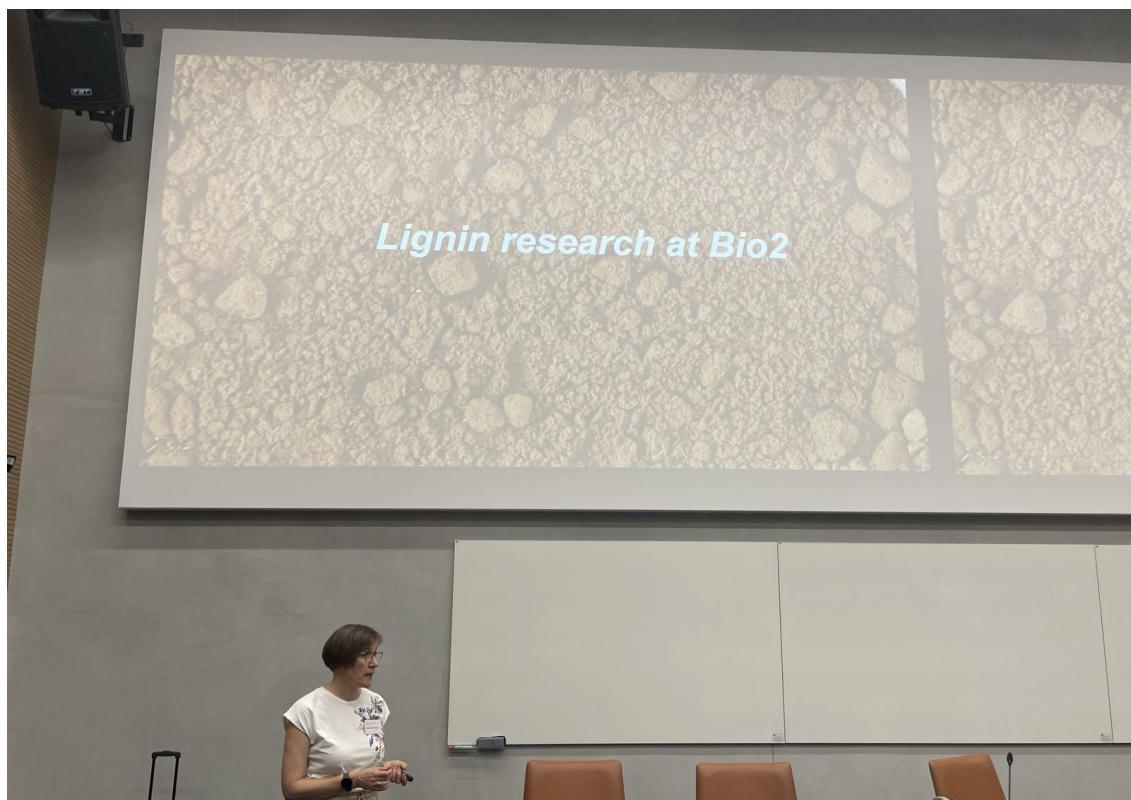
Opening of the Finnish Training School for LignoCOST CA17128



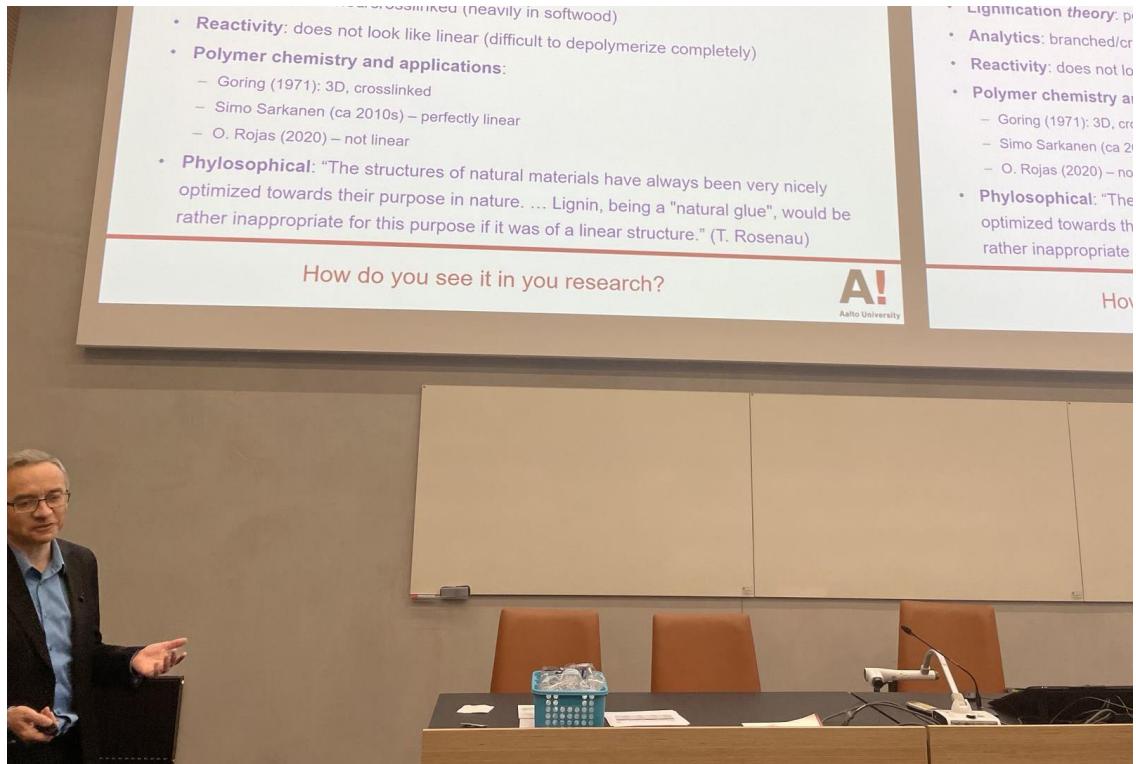
Participants



Presentations of local organizers, Åbo Akademi University (Patrik Eklund & Chunlin Xu)



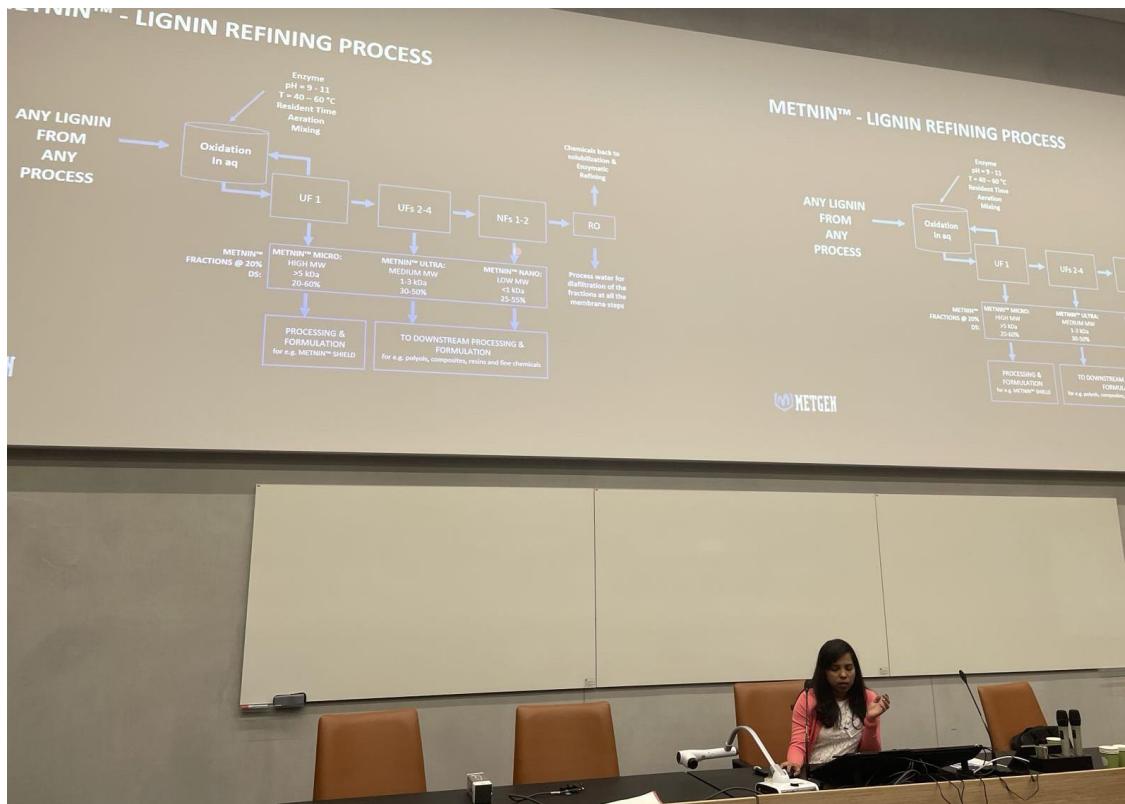
Presentations of local organizers, Aalto University (Monika Österberg)



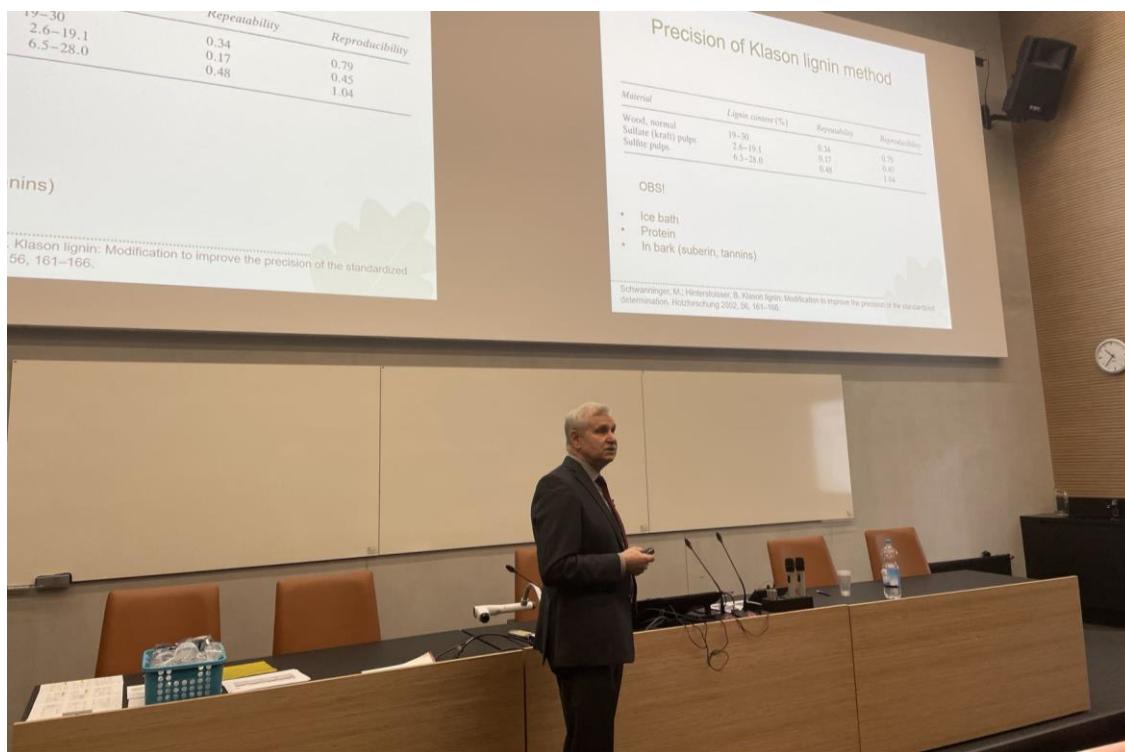
Lignin-first vs other technologies: Prof. Mikhail Balakshin (Aalto)



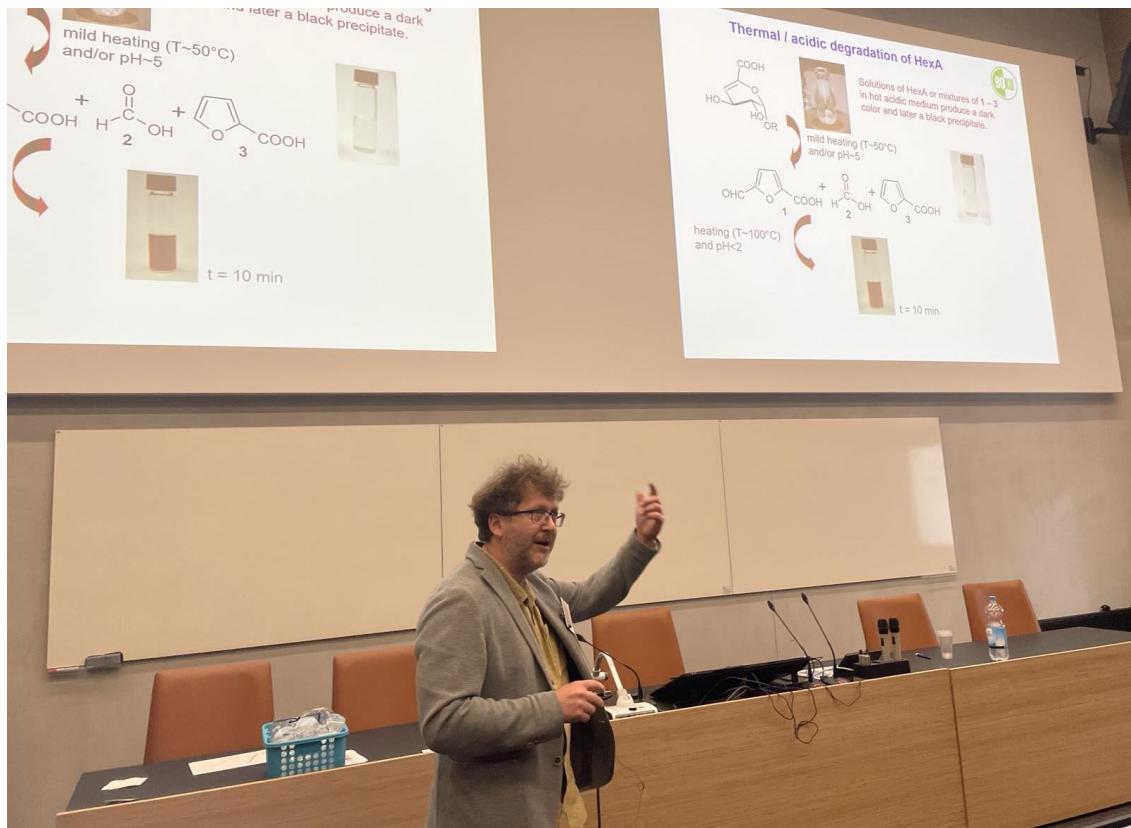
Chemical structure by NMR: Dr. Ewelyn Capanema (RISE)



Biorefinery fractionation & purification: Industrial approaches: Metgen concept: Liji Sobhana, Metgen



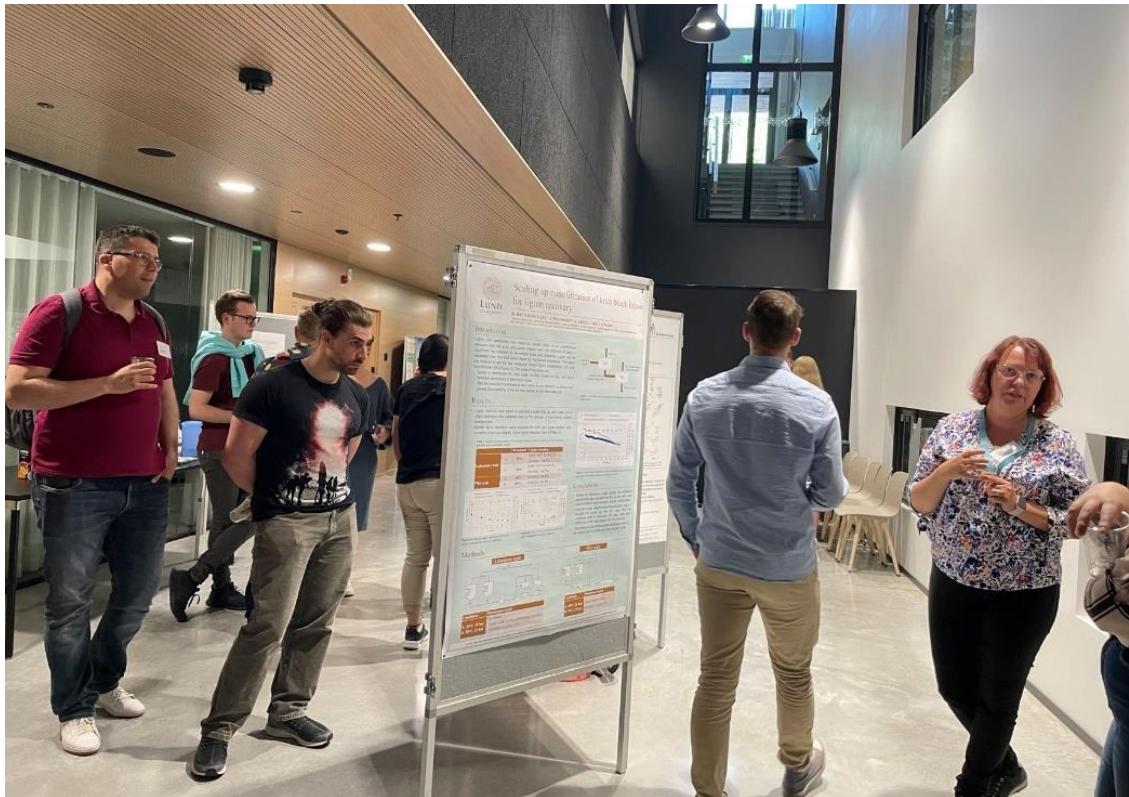
Classical wet-chemical methods for lignin analysis: Dr. Andrey Pranovich (ÅAU)



New methods in understanding aging/chromophore chemistry: prof. Thomas Rosenau (BOKU, AUS)



Lignin carbonization: prof. Michael Hummel (Aalto)



Poster Session



Lab demonstration



Introduction to CH Bioforce fractionation technology: Dr. Lari Vähäsalo



Excursion to CH Bioforce pilot plant

Programme

Monday June 20, 2022: 9:00- 17:00

Welcome and introduction

- 9:00 - 10.00 Presentations of local organizers, Åbo Akademi University (Patrik Eklund & Chunlin Xu) and Aalto University (Monika Österberg) including lignin activities
10:00- 11.30 Presentations by each participant (2 slides and 2 mins each)
11:30 - 12:00 Initialization of group work (with 5 credits option)
Mounting of posters
12:00 - 13:30 Lunch

Biorefinery fractionation & purification

- 13:30-14:30 Lignin-first vs other technologies: Prof. Chunlin Xu, (ÅAU), Dr. Patrik Eklund (ÅAU), Prof. Mikhail Balakshin (Aalto)
14:30-15:00 Industrial approaches:
Cellunolix concept: Timo Leskinen, St1
Metgen concept: Liji Sobhana, Metgen
15:30-16:15 Fractionation/Purification of lignin, case studies: Lucas Lagerquist and Luyao Wang
16:00-17:00 Lab tour at Aurum building

Tuesday June 21, 2022: 8:15 – 16:30

Characterization of lignin

- 8:15-9:30 Chemical structure by NMR: Dr. Ewellyn Capanema (RISE, SE)
9:30-10:30 SEC/MALLS with some 2D-SEC and functional dispersity distribution and speed analysis methods: Prof. Antje Potthast (BOKU, AUS)
10:30-11:30 Classical wet-chemical methods for lignin analysis: Dr. Andrey Pranovich (ÅAU)
11:30-13:00 Lunch
13:00-14:00 New methods in understanding aging/chromophore chemistry: prof. Thomas Rosenau (BOKU, AUS)

Lab demonstrations

14:00-16:00

Introduction 30 min

NMR: Lucas Lagerquist

- sample preparation, ^{31}P , HSQC and ^{13}C NMR

HPSEC: Luyao Wang

- Sample preparation, data interpretation

3D printing: Andrey Pranovich

- Filament preparation, printing

Poster session with refreshments

18:45 Dinner: cruise boat Rudolfiina

Wednesday June 22, 2022: 9:30-17:00

Modification for applications

9:30 - 10:30 LNPs: prof. Monika Österberg (Aalto)

10:30-11:30 Lignin carbonization: prof. Michael Hummel (Aalto)

11:30-13:00 Lunch

13:00-13:30 Lignin as macromonomers, polymer blends and co-polymers: Dr. Patrik Eklund (ÅAU)

13:30-14:00 Catalytic lignin depolymerization: prof. Henrik Grenman (ÅAU)

14:00-15:00 3D printing: prof. Chunlin Xu (ÅAU)

Workshop/group work

Thursday June 23, 2022: 9.00-13:00

Excursion

9:00 -9:45 Introduction to CH Bioforce fractionation technology: Dr. Lari Vähäsalo

10:00- 12:00 Excursion to CH Bioforce pilot plant

12:00 End of the workshop

Review Articles

Fractionation and purification, Industrial new biorefinery concepts for the production of lignin

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Abstract

Lignin is a highly abundant natural polyphenol. Because of plastic waste and rising carbon dioxide emissions, the general public increasingly desires to move away from fossil-based materials, and lignin could play an important role due to its abundance. However, the lignin that is available from today's pulp mills and biorefineries is structurally heterogeneous and difficult to use. There has therefore been much discussion about altering the pulping process or increase valorization efforts to improve lignin's quality. As consequences, the review will firstly summarize the recent developments of pretreatment process of biomass and purifying lignin to enhance the quality of downstream product, such as steam-explosion pretreatment, ultrasonic and solvent extraction, dialysis, hot water treatment, base hydrolysis followed by acid precipitation, acid hydrolysis, and biological purification. In addition, the fractionation of lignin is highlighted, the fraction of lignin with improvement in homogeneity will be reviewed by some well-known techniques: sequential solvent or pH-dependent precipitation, and membrane filtration. Lignin particles have also become increasingly interesting in the research community due to their applicability in aqueous systems without the need for solvents, and the preparation of lignin particles are also discussed. A brief discussion on applications for different types of lignin and lignin-fractions is also included to present the benefits and importance of fractionation methods in practice. In the end, the market and economic feasibility will decide on how lignin is used, which is why techno-economic aspects are important and are also discussed.

Introduction

About 70% of all harvested forest biomass is currently incinerated for energy production around the world [1]. Although energy production from burning biomass is certainly more environmentally friendly compared to burning fossil-based raw materials, other renewable energy sources, such as wind, solar, wave, and geothermal energy do not produce any greenhouse gas emissions and are therefore "greener". For the environment's sake it would be better to utilize biomass in solid applications, as it would contribute to decreasing the carbon dioxide levels in the air.

Lignin, which is the second most abundant natural polymer in the world, belongs to the large fraction of wood biomass that is not utilized in solid applications at this time. About 70 – 100 million metric tonnes of lignin is incinerated annually, and only ca. 2 – 5 % of this lignin is utilized in applications such as asphalt-or cement-filler or the production of aromatic

chemicals [2]. There are a number of reasons for this. Firstly, lignin has a rather high calorimetric value when incinerated, and is therefore quite suitable as raw material for incineration. Secondly, and more importantly, lignin is highly heterogeneous, poorly water soluble, has a dark color that is not suitable in many applications, and has a limited amount of reactive groups that can be used for chemical modification, depending on the delignification method [3]. Global warming and plastic pollution have nevertheless initiated a need to increase the use of renewable raw materials, which has led to a new interest in research on lignin-modification and applications.

To address the challenges in the applicability of lignin, new biorefining strategies such as the *lignin first approach* has been suggested. In general terms, the lignin first approach aims to protect the lignin from unpredictable condensation reactions by stabilizing reactive intermediate lignin molecules, which hinders them from reacting and polymerizing with other lignin molecules. The lignin valorization is thus considered already in the design phase [4]. Organosolv-type delignification processes are generally more suitable for the lignin first approach compared to the globally more common kraft delignification process [5]. However, most of the global pulp mass is delignified using the kraft process. It may therefore be challenging to implement lignin first approaches in existing biorefineries and pulp mills, and the production of new facilities requires large investments. As long as the value of lignin is uncertain, *i.e.*, there are few successfully demonstrated value-adding applications, such investments are unlikely. Hence, it is important to find ways of applying the currently available lignin while also solving process-related challenges that have hindered lignin from being applied in the past. This strategy will likely require the use of post-pulping purification and perhaps fractionation of the lignin. These processes will create new types of lignin depending on the wood source, purity, and fractions, and while creating new possibilities also creates challenges. There is no doubt that depending on the origin of biomass and the processes it has undergone, each technical lignin possesses distinguishable properties from each other that need to be considered individually in terms of lignin valorization [6,7]. This text will review various methods for the isolation, purification, and fractionation of lignin, and discuss how these methods affect the lignin chemically. The text will then demonstrate the importance of understanding these effects to find the most suitable application for various lignins. The market size and economic outlook of lignin will also be discussed, to give an overview of current trends and future possibilities in this field.

Principles of Lignin Purification and Fractionation

The presence of undesired compounds in technical lignin, known as impurities, are mostly from the nature of lignin-carbohydrate complexes and the biomass pretreatment process. The so-called purification of lignin means removing as much as possible of sugars, ash, inorganic compounds (e.g., Na₂S and NaOH), and proteins (mostly from ethanol process lignins by fermentation) from technical lignin [6,7]. In most cases, these impurities in technical lignin show its negative impact on later application in making carbon fibers [8,9], lignin-phenol-formaldehyde (LPF) resins [10,11]. Sometimes, the concern about inorganic impurities, acting as catalysts, especially for synthesis of phenolic resin [11] or composite material [12] were also reported. There are several ways to improve the purity of technical lignin, for instance, hydrothermal pretreatment of biomass by steam-explosion; ultra-sonic/solvent extraction, dialysis, hot water treatment; alkaline hydrolysis-acid precipitation, acid hydrolysis; and biological purification that will be discussed in this review study [11,13–15]. These methods

could be simply grouped as pretreatment of biomass and post-treatment of lignin, respectively.

Steam-Explosion Pretreatment of Biomass to Improve Purity of Lignin

The biomass pretreatment process aims to disrupt the recalcitrance of lignocellulosic matrix that improves the fractionation efficiency of biomass into its constituents with high yields and purities. There are some suggested criteria for how to reach the optimal results: (i) avoid as much as possible degradation of carbohydrates, (ii) ability to enhance hydrolysis efficiency, (iii) less production in inhibitor for enzymatic hydrolysis, (iv) high yield recovery of lignin for other application, and (v) cost-effective [16]. Among pretreatment methods (categorized as physical, chemical, hydrothermal, biological), steam-explosion technique turns out to be the most popular and effective way that meet most of the qualities (such as, low energy consumption, less in the usage of chemicals, cost-effective, high efficiency in disrupting the lignocellulosic network) and belongs to hydrothermal group [17].

The principle of steam-explosion method is to treat biomass under high constant pressure, under elevated temperature for a short period of time, and then depressurized instantaneously to breakdown the cell wall due to decompressive explosion [17]. The steam-explosion derived-corn stalk resulted the high purity of liquor lignin under alkaline extraction condition [11]. Specifically, optimal condition was reached at high constant pressure (1.8 MPa), operated at 195°C, and kept for 5 mins before depressurizing, after that the pretreated biomass was washed by distilled water for three times to remove the water-soluble hemicellulose. Subsequently, the obtained liquor lignin was dried in a forced-air oven at 55°C for 48 hours. The resulted lignin with 90.92% of purity and a significant improvement in purity by reducing up to about 40% of carbohydrates content, compared to reference sample, was reported [11]. Another method for steam-explosion pretreatment, without operating at high temperature, started with immersion of non-food biomass (e.g., corncob) in a diluted sulfuric acid (0.5% w/w) for 10 hours, followed by steam explosion operating at 1.5 Mpa for 5 minutes. After that the dried residue from diluted acid steam explosion (DASE) was extracted by ethanol aqueous (20/80 v/v) at 160°C for 120 min. The combination of DASE together with liquid hot pressured alcohol extraction showed a high purity of recovered lignin up to 91.20%, and less than 2.50% of impurities [18].

Lignin Purification Methods

In addition to pre-treatment of biomass, the quality of technical lignin could also be improved by shifting the focus to the workup procedure of downstream products. The term describes these protocols known as lignin purification techniques. Due to the abundance of Kraft lignin among others [19], one research group have reported different ways to remove as much as possible the impurities from Kraft lignin in which one of them was hot water treatment process was optimistic for up-scaling [13]. This comprehensive work paid attention to dialysis, hot water treatment, ultrasonic extraction, and Soxhlet-extraction techniques. The general results showed that ultrasonic extraction using a binary solvent system of ethanol/acetone (9:1), and dialysis followed by hot water treatment at 220 °C were the two best combined protocols to remove impurities (less than 3% remained), however, a partial condensation took place in the core structure of purified lignin [13]. Other than that, with the same focus on Kraft lignin, a research group leading by Tang. T investigated a new eco-friendly treatment by using *Pseudomonas fluorescens* [15]. This species has been studied as one of the best cellulolytic

bacteria that could selectively degrade cellulose and hemicellulose [20]. The bacteria can produce cellulolytic enzyme that particularly cleaving carbohydrate polymer chains into free sugars and use it simultaneously as their carbon source [15]. As the results, after enzyme treatment, the total carbohydrates content was drastically reduced 70% for acidic Kraft lignin, and 57% for alkaline Kraft lignin [15]. Later, Tang. T *et al* has successfully applied this bio-cleaning process to get purified lignin with enhancement in their electro spinnability property that affordable to produce carbon fiber for removal of methylene blue from wastewater [9].

Nowadays, hydrolysis lignin is also becoming more and more popular source of technical lignin [19], however, it inherently contains high contaminants from carbohydrates that limit their utilization. It is thus a reason to shift scientists' attention towards finding a solution for purifying hydrolysis lignin. One of the most recent research projects suggested two simple and effective ways to deal with upgrading hydrolysis lignin from hardwood containing from 10 to 15% of polysaccharide, were (i) alkaline hydrolysis-acid precipitation, and (ii) acid hydrolysis [14]. In the first approach, it was reported that the effect of alkaline concentration on the quality of lignin was not pronounced as much as variation in the operating temperature, whereas the influence of solid-volume ratio in the reaction cocktail showed a slight negative correlation impact on the polysaccharide content. The second investigated method was hydrolysis by sulfuric acid in various concentrations, temperatures, and times that generally showed the lowest impurities in the leftovers (below 3%) [14]. Furthermore, from the economic and industrial point of view, their conclusion clarified that the acid hydrolysis purification protocol was promising with the possibility to obtain high yield of purified product over 95%, compared to alkaline hydrolysis simultaneously acid precipitation with maximum yield 50% [14].

Utility of Inorganics in Lignin

Despite all efforts to find an optimal condition for purification of lignin, from chemistry point of view, inorganic impurities present in technical lignin are somehow useful for later application due to its possible catalytic activities. Interestingly, X. Bai and his team showed the results that could surprise readers about metal impurities in technical lignin were not as always as harmful as they were for some applications [12]. Indeed, their case study presented that the best thermal stability and tensile strength of composite material was made from polylactic acid (PLA) and organosolv lignin with 4% metal elements (e.g., Al, Ca, Fe, Mg, P, S, Na, and K) [12]. Nevertheless, inorganic contaminants were not a big concern by mean of neither harmful nor useful in the synthesis of phenolic resin [11]. By considering these results, the direct usage of technical lignin without any purification will be cost saving for biorefinery processes.

Lignin Fractionation Methods

As it has been discussed, the inherent inhomogeneity of technical lignin tightly correlates with its high polydispersity in molecular weight and creates bottlenecks in biorefineries, specifically for lignin valorization. In fact, the effect of molecular mass on physical/chemical properties as well as structural information of lignin mixture has been extensively studied and clarified [21–23]. In other words, the narrower molecular mass distribution obtained, the more uniform lignin mixture is. Before using lignin as starting material for any target application, it is thus plausible to increase the homogeneity of lignin solution by means of

narrowing the dispersity of molar mass. This methodology is used for lignin fractionation and commonly adopted by three approaches: sequential solvent fractionation [24–26], pH-dependent precipitation [27,28], and membrane-assisted filtration methods [29–31]. An illustrative animation describes the ideas behind these processes presenting in **Figure 1**.

Solvent Fractionation

Among other techniques, organic solvent precipitation method is mostly used to fractionate the crude lignin into more homogeneous fractions with the controlled qualities, able to be used for further application or valorization [24,32]. Hansen suggested three solubility parameters of a solvent: dispersion force, polar interaction, and hydrogen bonding that could relate to the dissolution of the polymer [33]. Based on this theoretical approach, the solubility experimental data used eight solvents from different groups (e.g., alcohol, ketone, and ester) showed a strong linear correlation between the polarity values and their ability to dissolve softwood Kraft lignin [24]. Moreover, a combined computational and experimental study was carried out the results that the solvent polarity strongly affects the solubilization of hardwood Kraft lignin and resulted in soluble/insoluble fractions with different average molar mass [24,25]. From the understanding of how organic solvents affect the recovery of lignin fractions with different molecular weight, the solvent fractionation process is well established by adjusting the solvent polarity to separate the crude lignin into several fractions with controllable molecular property. In fact, the process could be categorized into two types: single solvent for one-step extraction, and multiple/mixture of solvents for sequential fractionation.

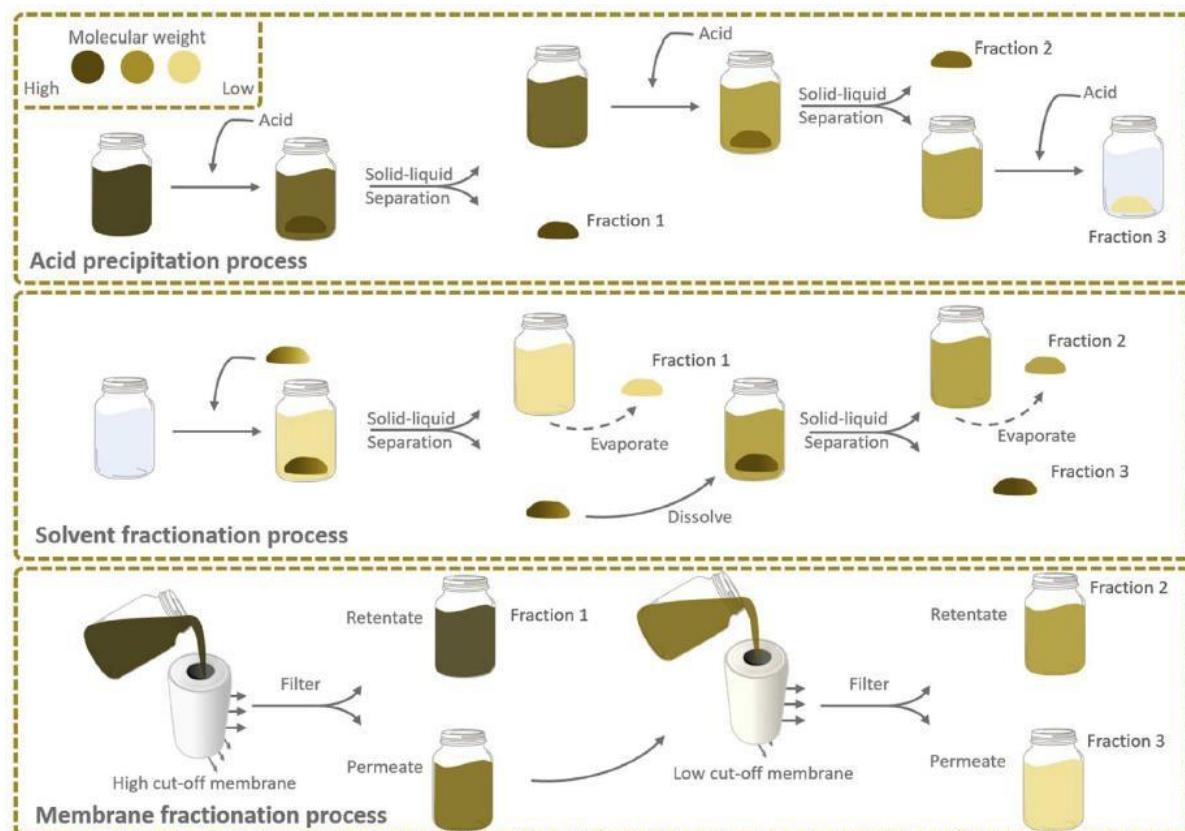


Figure 1. The illustration of three common methods of lignin fractionation: pH-dependent precipitation, solvent fractionation, and membrane filtration to fractionate crude lignin into different fractions with controllable molecular weight [21].

The single solvent used in one-step extraction is carried out by dissolving lignin to get soluble and insoluble parts separately. This protocol is straightforward and efficient. Recently, the method has been used to investigate the real interaction between solvents (e.g., ethanol, acetone, diethyl ether and hexane with the polarity values: 8.8, 10.4, 2.9, and 0, respectively) and lignin during the dissolution process [25]. In conclusion made from computational calculation and experimental data, the polarity value of solvent showed a positive linear correlation with the yields of soluble lignin, which have lower and narrower molecular weight distribution compared to the parent lignin and the insoluble parts. Another investigated nine organic solvents varying from polar to non-polar (polar protic: methanol, ethanol, propanol; polar aprotic: acetone, ethyl acetate, dichloromethane; non-polar solvent: diethyl ether, hexane, petroleum ether) and the relation in structure property of corresponding lignin fractions (reported in **Table 1**) [26].

Table 1. The summary of properties of soluble and insoluble fractions of hardwood Kraft lignin (from Eucalyptus chips) after one-step treatment with nine different organic solvents [26].

	Homogeneity ^a	Hygroscopic Stability	Antioxidant Capacity	Thermal Stability ^b	Ash Content
<i>Soluble fractions</i>					
Methanol	+	+	+	=	+
Ethanol	+	+	+	+	++
2-propanol	++	+	+	+	++
Acetone	+	+	+	=	++
Ethyl acetate	+	+	++	+	++
Dichloromethane	+	+	++	=	++
Diethyl ether	++	+	++	=	++
<i>Insoluble fractions</i>					
Methanol	-	-	-	-	-
Ethanol	-	-	-	-	-
2-propanol	-	=	-	-	-
Acetone	-	-	-	-	-
Ethyl acetate	-	=	+	-	-
Dichloromethane	-	=	=	-	-
Diethyl ether	=	=	+	=	=
Hexane	=	=	+	=	=
Petroleum ether	=	=	+	=	=

^a Reduced Mw distribution and polydispersity; ^b According to T_{max} value; - Deteriorate; = No improvements; + Improvements; ++ Remarkable improvements.

Although the single-step extraction is advantageous to get improvement in homogeneity of lignin, it is impossible to get more than two fractions with a distinction of molar mass. Therefore, solvent sequential fractionation approach is preferable to obtain more than two batches with narrower molecular weight distribution. One of the most recent studies successfully applied this methodology by setting up a solvent system with an increase in solubility power (*i*-PrOH < EtOH < MeOH) to get homogeneous lignin fractions with narrower molar mass distribution and an increase in average molecular weight [34]. Even though the results showed the lignin fractions obtained with well-defined properties, the impurities and sugar contents were highly found in MeOH-soluble fraction, which caused a lower capacity in water resistance of lignin-phenol-formaldehyde wood adhesive [34]. It is no doubt that using several solvents for sequential extraction is efficient in terms of refining lignin, however, less environmentally friendly, and highly cost are the two main disadvantages of this method.

Therefore, another perspective in the stepwise precipitation process is to apply a mixed solvent system, containing good and anti-solvents in which a gradient concentration in one phase will adjust the polarity factor that is efficient in lignin refining process [21]. As it has been reported, this application was successfully carried out by using a mixture of a green solvent derived from sugar, γ -valerolactone (GVL) and water with a gradual decrease of GVL content in aqueous phase (40%, 30%, and 5%) to reduce inhomogeneity of enzymatic hydrolysis lignin [34]. As the results, lignin fractions obtained with narrower molar mass with a decrease in average molecular weight when there was less amount of organic phase. From the green chemistry point of view, the process was considered greener because it used only one organic solvent, and an addition to that point is GVL was highly recovered (up to 95%) from the mixture with water of 5% and induced the same extraction efficiency as the new solvent mixture [34].

pH-Dependent Precipitation

Acid precipitation method is the second common approach to separate lignin into more homogeneous fractions (**Figure.1**) [21]. The process firstly starts to dissolve lignin in strong base medium and subsequently adding acid (H_2SO_4 and HCl are usually used) to adjust the solution's pH, leading to aggregation of lignin colloids due to the happening of neutralization of their negative charge on the surface [27]. Therefore, the relationship between pH value and lignin fraction properties is strongly correlated. From the practical results, it showed that at higher pH, the fraction with higher molecular weight obtained, and vice versa [27]. On the other hand, lignin fractions from sugarcane bagasse extracted at pH = 9, 7, 5.3, and 0.3 (by using sulfuric acid) showed a distinction in terms of chemical properties [28]. Particularly, those precipitated at higher pH 5 significantly differed from the acidic fractions in carbon, oxygen, and hydrogen contents. Additionally, the syringyl fragments were largely precipitated at pH 5 rather than pH 9, it was thus reported higher ratio of S/G in lignin's precipitate at pH 5 [28].

Membrane-Based Filtration

Among other techniques, the membrane technology offers a sufficient procedure to get homogeneous lignin fractions in biorefineries by mean of using semipermeable polymeric or ceramic-based membrane that could separate a mixture of crude lignin into several identified fractions according to the target molecular weight (**Figure.1**) [21]. It is suggested that using ceramic membrane is preferable to polymer due to the high resistance to pH, it thus allows direct filtration of Kraft lignin liquor without any pretreatment [29]. The membrane-based filtration method is outstanding among others due to its capable of operating continuously, less usage of hazardous chemicals (strong base/acid), low energy consumption, and the high flexibility in combination with other fractionation methods [21]. The most common set up for this procedure is sequential filtration with different molecular weight cutoffs. In the study conducted by C. Huang, before starting the membrane-assisted fractionation, Kraft lignin from black liquor was precipitated at pH 2 to 3 and the solid residue was suspended in acetic acid to lower the viscosity of the solution [30]. Subsequently, sequential ultrafiltration was applied with membrane cutoff 5 kDa and 3kDa to obtain three fractions with molecular weight 7010 (F1), 3540 (F2), and 1890 (F3) (g/mol), respectively. In the same publication, the application in preparing composite material by blending three different obtained fractions together with

Polyethylene showed that F3 with the lowest molecular weight gave better mechanical performance due to the higher affinity with polyethylene.

One of advantages in using membrane-assisted filtration is its ability to combine with other fractionation techniques to improve performance in refining lignin. For instance, one research from Allegretti combined organic solvent extraction with the assistance of Soxhlet system, directly followed by membrane ultrafiltration [31]. Particularly, the initial softwood Kraft lignin was extracted by Soxhlet system for 8 hours, using 2-butanone (MEK) as solvent and the soluble part dissolved in organic phase was then submitted to the downstream sequential ultrafiltration with 5 kDa, and 2 kDa cutoffs. In this study, it was noticed that the choice of MEK was highly considered because it gave high yield of extraction, and the low viscosity was beneficial in filtration technique to avoid membrane clogging.

Lignin Particles

The use of lignin as water-dispersible particles is an alternative to fractionation or modification, such as depolymerization. The major benefit of lignin particles in comparison to regular lignin is that they can be used in water-based applications without solvents. They can be used for Pickering emulsions that could be used for cosmetics or biomedical applications [35,36], in composite materials [37], coatings [38], adhesives [39], or shape retention agent in hydrogels for tissue engineering [40]. Lignin particles can be either irregularly shaped or spherical, depending on the precipitation method. The acidification of alkaline lignin solutions leads to irregularly shaped particles, while solvent switching most often leads to spherical particles [41–43]. Solvent switching has some advantages. Firstly, the spherical shape provides increased colloidal stability [44], and the solvent switching provides excellent control over the size and surface charge [42,43]. Large-scaled production of lignin particles has been studied, and the process can be done in an economically feasible manner [45]. This section will briefly illuminate solvent switching to synthesize lignin particles to give an understanding of some important factors that affect their properties.

Preparation and Properties of Lignin Particles

Solvent switching relies on precipitating a dissolved polymer from a solution by adding an anti-solvent or decreasing the solvent : anti-solvent ratio. For lignin, the most usual solvent is a mixture of either acetone or tetrahydrofuran and water. Common water:solvent ratios are 1:3 w/w [37,42]. Other solvents, such as dimethyl sulfoxide also work [46]. Ethanol can also be added, which allows the main organic solvent (acetone or tetrahydrofuran) to be reduced, and leads to smaller particle size [43]. The solution is then added to about 1.8 – 2 times the solution's weight of water, which acts as an anti-solvent and initiates the precipitation [42,43,47]. The anti-solvent can also be added slowly, which seems to work better for organosolv lignin [48]. The particle size depends on the solvent system, concentration of lignin, the anti-solvent addition speed, the amount of anti-solvent, the lignin's molecular weight and chemical structure (mainly number of hydroxyl groups and ratio between different hydroxyl groups). The polydispersity is affected by the lignin's heterogeneity, and fully monodisperse particles can be made using fractionated lignin [49]. Multiple mechanisms for the precipitation has been suggested. It is widely accepted, that the precipitation begins from the most hydrophobic lignin, and ends with the smallest and most hydrophilic lignin fraction [50]. Because of this, the surface of lignin particles are hydrophilic, and interacts well with

water and hydrophilic polymers [37]. Co-precipitating lignin and a hydrophobic molecule, such as medicinal agents, leads to the formation of hybrid particles with a lignin surface and a core of lignin and the hydrophobic substance. This can be used to create capsules for drug delivery or e.g. phase change materials [51,52].

Lignin particles are usually between 100 – 500 nm in size and have a zeta potential of ~ -40 mV [42,43,49,53]. The surface charge can nevertheless be modified reversed by the adsorption of cationic polymers, such as polyelectrolytes, proteins or cationized lignin [42,54,55]. Cationic lignin particles has some utility in emulsions [35,55]. It has also been shown, that cationic lignin particles can be used to remove viruses from water, which makes them useful for water purification as well [56]. Lignin particles can also be infused with silver particles, which give them antibacterial properties [41,57,58]. Lignin particles can also be cured using epoxies. This allow them to be used as adhesives [39] or mechanically durable protective coating [38].

Properties and Applications of Different Lignins and Lignin Fractions

As we have mentioned, lignin is very underutilized at the moment, mainly because applications where lignin provides significant improvement in performance, or at least does not reduce performance significantly, are rare. However, the reason to valorize lignin instead of using it to produce energy is to reduce fossil-based materials and increase bio-based materials in solid applications, which means that such applications have to be found. To find applications where lignin can contribute positively, it is important to understand how the properties contribute to performance. We have already concluded that fractionation can be used to retrieve lignin fractions of different molecular size, but fractionation also separates lignin according to chemical properties [49]. In additions, there is often a correlation between molecular weight and chemical property. For example, small lignin molecules have a higher weight-proportion of polar end-groups (often phenol groups) in comparison to very large lignin molecules [59–61]. This means, that the smallest lignin fraction often is the most polar, and vice versa, and that all fractions in essence differ in chemical properties. It is important to understand how these properties will affect the performance in certain applications. In this section, we will discuss a few applications and the lignin type and fraction that would be most suitable in these applications to give a brief demonstration of the effect of lignin fractions on the performance of different applications.

Additive in Plastics and Composites

There are some challenges regarding the use of lignin in polymer blends. It tends to aggregate within the blend, and lead to brittleness and weak strength. This type of aggregation often occurs due to hydrogen bonding of polar structures within a non-polar matrix. It would be expected, that a less polar lignin fraction would experience less problems of this sort. Indeed, it has been shown that composites of poly-(butylene adipate-co-terephthalate) and acetone-soluble lignin fractions of softwood and hardwood kraft lignin and soda grass lignin had better tensile properties compared to those of composites with raw lignin [62]. However, in the case of lignin and poly lactide copolymers, there were no significant differences in tensile strength in different fractions [63].

Lignin-based fibers can also be used in composites, similarly as synthetic fibers are used today. The lignin fraction has tremendous effect on fiber properties. It has been shown that fibers

from water-insoluble kraft lignin fractions have better mechanical properties than fibers from water-soluble lignin fractions [65]. In another study, it was also observed that fibers from acetone-soluble kraft lignin were hydrophobic, compared to fibers from non-acetone soluble kraft lignin which were very hydrophilic. However, the fibers from acetone-insoluble lignin were more thermally stable [66]. In the case of pH fractionation, it has been shown that the fibers from the alkaline lignin fraction (soluble at pH > 10) had significantly higher mechanical properties than other fractions (insoluble at pH < 10) [67]. The fibers' surface properties are important to take into consideration when using fibers as reinforcing agent in composites. Good fiber-matrix interactions lead to better load-transfer in composites, and therefore increases strength [68]. By choosing the lignin fraction according to the desired polymer matrix, vice versa, the strength of the overall composite can likely be optimized.

Additive in Adhesives

Adhesives are in many ways similar to plastics and composites, with some differences. The performance depends on the adhesive's ability to penetrate and interact with its substrate as well as its strength. Therefore, the molecular size plays a role in a slightly different way. Ghorbani et al. observed that phenol-formaldehyde adhesives containing kraft lignin had a better lap shear strength than those containing straw or grass soda lignin. The authors concluded that this likely is because the kraft lignin had a significantly higher amount of free phenolic groups than the other types of lignin. These groups are more reactive with formaldehyde compared to substituted aromatic groups [64]. It has also been observed, that the propanol-soluble lignin fraction performed better in phenol-formaldehyde adhesives than other fractions (ethanol- and methanol-soluble fractions) for the same reason [34].

Solt et al. [69] examined the use of fractionated softwood kraft lignin in phenol-formaldehyde adhesives. They fractionated using ethanol and water into three fractions; soluble in 80% ethanol, soluble in 50% ethanol, and completely insoluble. When addressing the solubility, we will describe it as water-solubility, as the fractionation was based on increasing the water content. They found that low molecular weight lignin had a higher solubility in solutions with high water content. The water solubility also correlated positively with the number of phenolic groups. Here, the authors saw no significant differences in adhesive strength. However, parameters such as viscosity and condensation times were also different for the lignin-phenol-formaldehyde resins depending on which lignin fraction that was used (lower molecular weight caused a prolonged condensation time), which makes it difficult to determine the exact reason for the performances in adhesives.

Lourençon et al. [70] presented a similar approach, where lignin hardwood kraft lignin had been precipitated based on solubility in decreasing pH. Their results showed that the best bonding strength was achieved with lignin that precipitated at lower pH (3 – 7) compared to that which precipitated at higher pH (9). The authors did not speculate about possible reasons for the differences, but one possible reason is the lower molecular mass for lignin fractions that precipitated at lower pH. The most significant chemical difference between the lignin fractions was the higher phenolic content (especially syringyl and condensed guaiacyl units) for the lignin that precipitated at lower pH. However, when combining the observations with those made by e.g. Ghorbani et al. [64], it seems like the amount of phenolic hydroxyl groups does have a significant effect on adhesive strength.

Raw Material for Tailored Lignin Particles

The size of lignin particles can be important in certain applications, and homogeneity can be crucial in e.g. medicinal applications. The basics of lignin particle preparation has already been discussed, but this section will briefly discuss how the significance of the lignin fraction on the particles' properties and characteristics. As mentioned, it has been speculated, that the most hydrophobic lignin fractions aggregate first, and therefore creates the core of lignin particles, while the most hydrophilic lignin coats the surface, thereby increasing stability in aqueous media. Lignin's heterogeneity has therefore not been regarded as a problem in the preparation of lignin particles. In fact, it has been seen as an important factor to be able to produce stable particles. It has nevertheless been shown that by using fractionated lignin, completely monodisperse particles can be prepared [49]. The stability of particles from fractionated lignin has not been evaluated systematically, and would be a valuable research subject for future studies. It has nevertheless been established that the size and properties of lignin particles depends on the lignin fraction (chemical properties), the anti-solvent addition speed and concentration.

Good solubility in aqueous media usually leads to increased particle size. This is because hydrophilic structures enable the lignin to interact favorably with aqueous media. This delays particle formation and increases the particles' porosity. Poor solubility on the other hand, causes the lignin to precipitate quickly and pack tightly to avoid the media [71, 72]. The amount of phenolic and carboxylic groups is therefore an important factor, that usually correlates with molecular weight. This is partially because small molecular weight lignin contains a larger ratio of phenolic end-groups to total molar mass compared to large molecular sized lignin. There is nevertheless still some uncertainty regarding the effect of carboxylic groups. On one hand, large amounts of carboxylic groups increase the lignin's ability to interact with water, which seems to lead to larger and more porous particles [71 – 74]. On the other hand, carboxylic hydroxyl groups are responsible for creating the electrical double layer that is needed for the particles' stability [42, 50]. The inner morphology of the particles is also affected by the lignin fraction. For example, hydrophobic lignin and high-molecular weight lignin can be used to create hollow particles with slow anti-solvent addition. It is believed that the hollowness forms as the most hydrophobic lignin, in the initial stages of particle formation, traps the original solvent to avoid interactions with water. When the water content increases, the solvent-filled lignin particles burst due to the osmotic pressure, creating a pierced hollow sphere [73 – 75].

The recent findings on how the properties of lignin particles are affected by the lignin's chemical properties and characteristics are important, because they can lead to new high-value applications in fields like optics [76], medicine [77], and cosmetics [54].

Lignin Market Review

As a major renewable source of aromatics lignin will play an important role in the change from fossil world to sustainable bioeconomy [78]. From the market perspective the industrial lignins are typically divided into four categories by production method.

- Ligno-sulphonates derived from sulphite pulp mill sidestreams
- Kraft lignins derived as a side process of a kraft pulp mills

- Organosolv lignins
- Others

Industrial lignins can also be divided into different categories by the end use: macromolecule, aromatic or others [79].

The global lignin market size was estimated USD 954.5 million in 2019. According to some sources it is expected to expand at 2.0% in terms of revenue, from 2020 to 2027. The dominant quality in the markets is lignosulphonate with more than 85% market share and most of the rest is kraft lignin. The reports show that even though sulphur-free organosolv-based lignins are much in focus in research, their share in the global lignin markets is almost non-existing [80]. The biggest growth driver is anticipated to be the increasing demand for lignin in animal feed and natural products. Lignin-based macromolecules play an important role also in development of eco-friendly bitumen, biofuels and bio-refinery catalysts, the factor that likely supports the market growth. Growing demand for concrete admixtures and adhesives and binders coupled with increasing investments in infrastructure development is expected to fuel the market growth. In the near future no major changes in the lignosulphonate markets could be seen as the product is based on the side stream of sulphite pulp production. For the kraft lignin the changes are easier to make from the production side as basically all kraft pulp mills can extract part of their black liquor as a lignin product. If the prices of the lignin rise, it is possible that lignobost type extraction becomes more common.

Expansion Possibilities and New Technologies

The success of the new product development is a key for market expansion. If the new products with high hopes like anode material for batteries or carbon fibers made from lignin make the commercial breakthrough then the possibilities are somewhat unlimited and this could change for example the way of operations in the kraft pulp mills. If the price of the kraft lignin is high enough, the processes will be optimized to secure the lignin quality and production level. Lignobost process is best applicable to the mills where recovery boilers are a bottleneck. In these cases there are possibilities to increase the pulp production too. However the changes in the chemical and energy balance need to be taken into account as lignin itself is a valuable source of bioenergy. Stora Enso has announced the feasibility study of industrial scale lignin based anode material facility [81]. A big question for the kraft lignin is how much the sulphur content and other typical features like smell affect to the end products.

For the organosolv lignin there has not been that many industrial scale plants, only pilot and demo scale facilities, even though the lignin quality has been tested a lot and the technology family is considered widely to be one of the most interesting biorefinery options in the future [82]. Some market research reports predict a big growth for sulphur-free and organosolv-lignins in the future based on the potential increase in the manufacturing of carbon fiber, activated carbon, vanillin, phenol derivatives and phenolic resins [81]. Interesting industrial scale facility is announced to be built by using the formic and acetic acid based technology developed by Chempolis. The facility will be built in India and the raw material will be bamboo [83].

Lignin should be important side product from the wood-based biorefineries where the main product is bioethanol for traffic applications. The St1-facility in Kajaani, Finland is using

cellunolix-technology in their facility that uses softwood sawdust as a raw material. Not surprisingly lignin condensation has caused major problems for the facility and because of that the operational efficiency was poor. According to update during Lignocost-summer course the only way to utilize lignin still is to burn it in the biomass boiler [84]. There are other new technologies for biomass separation and extraction that produce high quality sulphur-free lignin. Dawn technology by Dutch company Avantium is regarded one of the most promising one. A business model is based on the utilization of agricultural and forest residues and the products would be sugars, and high quality lignin. The technology could then be connected to bioplastic production. One possible drawback in the technology is the use of strong hydrogen chloride, which possibly could cause some formation of organochloric compounds during the process [85]. Other potential technologies are steam explosion typically connected with organosolv treatment and different technologies based on the use of ionic liquids [86, 87].

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Lignin-based Composites and Blends in Thermoplastics

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Abstract

Biobased thermoplastic composites have emerged as attractive, sustainable materials to replace traditional plastics. In this new frontier of materials science, designing biobased solutions that compete with conventional fossil-based plastics is crucial. Lignin, as the second most abundant biobased material, can be a prominent contender for high-performance composites due to its multiple functional groups as the active sites for interactions with other compounds. However, the lignin valorization for thermoplastic composites is not yet commercialized on the large scale, most likely due to its complex structural heterogeneity. This review highlights the recent achievements in the utilization of lignin in thermoplastic composites. First, the role of lignin in the thermoplastic composites, either as the main matrix and reinforcing filler or compatibilizers, is discussed. Second, the effect of lignin on the properties of thermoplastic composites is reviewed. Lastly, the potential application of lignin-based composites and their future perspectives are addressed.

Keywords: Lignin, Blend, Functional Filler, Interfacial Mediator, Thermoplastics

Introduction

Currently, composite materials have attracted wide attention due to their excellent mechanical properties¹. A composite is a combination of two or more materials, possessing properties different from those of individual components². Furthermore, reinforced plastic composites are a new type of composite materials, which add high modulus fibers or polymers to the matrix to overcome its thermal instability and low modulus. At present, the raw materials of the traditional thermoplastic materials are petroleum-based materials which are not sustainable and biodegradable, causing an environmental burden with regard to their disposal³. Various biobased materials, including polylactic acid (PLA)⁴, poly(hydroxybutyrate) (PHB)⁵, poly(hydroxyalkanoates) (PHA)⁶, cellulose, and starch⁷, have been studied extensively in thermoplastic application. Although these biobased materials have biodegradable properties, the large demand for these biobased polymers will affect the current food-related raw materials⁸. Meanwhile, a large amount of lignin, as a byproduct with antibacterial, antioxidant, UV-shielding, and high thermal insulation performance, is produced by biorefineries and the paper industries. The presence of lignin in the production of biodegradable thermoplastics is a promising and cost-effective alternative to petroleum-based thermoplastic polymers. Recently, the conversion of lignin into high value-added products has attracted the interest of researchers and factories. Being a type of nontoxic aromatic biopolymer with multiple functional groups (such as aliphatic hydroxyl groups, phenolic

hydroxyl groups, and methoxy groups), lignin has a complex cross-linked structure⁹. These functional groups provide a broad range of chemical modifications. Most importantly, lignin is made up of cross-linked phenylpropane units, which gives lignin its hydrophobicity, specific antioxidant and antibacterial properties, and UV-shielding.¹⁰ Lignin has been combined with a variety of polymers to create compounds for applications with a high added value. Given the tremendous complexity of the lignin structure and its reactivity, efficient blending is frequently challenging to achieve. Due to its wide network of strong intra- and intermolecular hydrogen bonds, lignin exhibits thermoplastic behavior; nevertheless, at high temperatures, it behaves as a thermoset material due to the occurrence of significant cross-linking processes, particularly kraft lignin. Investigating lignin's miscibility with other polymers in depth while keeping an eye on the phases' evolution and compatibility is crucial in this context¹¹. The resulting blends would either create miscible blends or show a phase separation, depending on how well lignin interacts with various polymer matrices. Lignin exhibits a strong affinity for polar polymer matrices because it is a relatively polar polymer with several structural OH groups. Generally speaking, lignins, neat or chemically modified, could be used to perform the following tasks within a blended system: reactive components in the production of a variety of resins (for example, epoxy resins, phenol-formaldehyde resins, and polymers (for example, polyurethanes), nucleating agent, surfactant, UV blocker, thermal stabilizer, flame retardant, adsorbing agent, reinforcing filler in composites, anti-microbial agent¹². The definition and categorization of lignin-based multi-component materials in the literature are inconsistent. The names "blends" and "composites" are sometimes used interchangeably, and the function of lignin itself is frequently ambiguous, ranging from additive or matrix material or from filler and reinforcement. We try to gain a better understanding of these issues in the following sections.

Role of Lignin in Thermoplastic Composites

Currently, industrial lignin is considered a promising raw material for manufacturing thermoplastic matrix composites. The total cost of thermoplastic composites can be reduced by adding low-cost lignin to thermoplastic materials¹³. Lignin is expected to be used as matrix, initiator, and reinforcement filler in thermoplastic composites.

Lignin as the Matrix in the Thermoplastic Composites

Considering that lignin has a melting point between 140 and 160 °C (lower than PLA, which has a melting point between 180 and 210 °C), as well as radical-induced self-condensation between the functional groups at high temperature, it makes a good matrix for thermoplastic biocomposites containing natural-based thermosensitive fillers and reinforcements, like hemp, flax, and wood, to create fully biobased composites or green composites. Results have demonstrated that lignin matrix and natural fibers can be effectively bonded. These composites have mechanical properties that are strongly influenced by the fiber content; however, these characteristics were dramatically diminished above a specific filler content¹⁴. Young et al. develop biobased lignin-co-polyester/amide thermoplastics, showing thermoplastic melt behavior with a lignin content of only up to 20%¹⁵. And the lignin-based copolymers observed that Young's modulus values ranged from 5MPa to 340MPa, which is comparable to natural rubber, while the tensile strengths are lower. Saito et al. prepare lignin-based polyurethane thermoplastics using solvent-extracted lignin from hardwood biomass as raw materials, which possess high lignin contents (65-75%). Results shows the glass transition

temperature and molecular weight were altered through cross-linking with formaldehyde, while formation of a network soft segment formed by cross-linked lignin and diisocyanate-based telechelic polybutadiene¹⁶. In another case, the relationship between molecular structure, properties and feasible lignin-based thermoplastic polyurethanes has been studied. Gouveia chemically modified craft lignin by partially acetylation to reduce reaction sites and avoid the formation of highly cross-linked structures, thus achieving control over the reaction schedule, revealing that the hydroxyl content from the parental lignin could be reduced by half in a controlled manner. Also, lignin-based thermoplastic polyurethane was successfully produced from partially acetylated lignin macromonomer as a polyol, and a stable thermoformable polymer was formed¹⁷.

Lignin as Macromonomer During the Process of Polymerization in the Thermoplastic Composites

The thermoplastic polymer monomer will polymerize with the hydroxyl group of the lignin and grow a polymer chain on the lignin core, which could be achieved by ring-opening polymerization and radical polymerization³. Ring-opening polymerization is a chain polymerization on the lignin core by reacting with the hydroxyl group of lignin, and further ring monomers such as lactide or propiolactone could react to open the ring system. Thermoplastic lignin-polycaprolactone (PCL) grafted copolymer is synthesized by using ϵ -caprolactone (CL) as a reactive solvent, polymerizing CL on the reactive hydroxyl (OH) sites in lignin macromonomers¹⁸. The results show the graft polymerization of CL on LM can be controlled according to the [CL]/[OH] ratio and reaction time, and its molecular weight and grafting degree can be adjusted. Thus, compared with the original lignin, the synthesized lignin-PCL copolymer has enhanced compatibility and thermal stability and exhibits rheological behavior similar to thermoplastics without the need for combustion at high temperatures. Chung et al. show that polylactic acid could be directly grafted onto original lignin (unsulfonated raw kraft lignin) by ring-opening polymerization with the help of an organic catalyst¹⁹. Additionally, the tensile strength and strain of the synthesized material increased by 16% and +9%, respectively.

On the other hand, atom-transfer radical polymerization (ATRP) is a form of controlled reactive radical polymerization that allows for controlled polymer chain length and a higher degree of polymerization, improving the efficiency of grafting and low molecular weight of copolymer²⁰. Liu et al. demonstrate a method for producing a lignin-based macromonomer using butyl methacrylate (BMA) with biobutanol lignin by ATRP, posing a high hardness, T_g , and thermal stability²¹. Also, Washburn et al. prepare a series of kraft lignin graft copolymers via ATRP, with poly (methyl methacrylate), poly (n -butyl acrylate). Kinetic studies indicate that the graft copolymerization proceeded in a controlled/living manner²². Recently, UV cross-linkable thermoplastic lignin graft copolymers were produced via ATRP. Kraft lignin and acryloyl benzophenone comonomer could copolymerize by incorporating a UV-sensitive compound, resulting a polymer network, which the thermal stability and solvent resistance performance.

Lignin as Reinforcement Fillers in the Thermoplastic Composites

The addition of lignin as reinforcement typically lowers the cost and water uptake while increasing strength. Furthermore, because the phenolic hydroxyl groups can scavenge free

radicals, lignin plays an important role in antioxidant properties as a stabilizer. Plasticizers can interact with polymers by substituting for polymer interactions. This phenomenon improves polymer flexibility, mobility, and workability by lowering intermolecular forces, T_g, and the blend's processing temperature. When lignin is added to starch, protein, or polycaprolactone, plasticization occurs. Huang et al. prepared thermoplastic elastomers using enzymatic hydrolysis lignin as the hard plastic phase and polyolefin elastomer (POE) as the rubber matrix²³. The thermoplastic demonstrates lignin has an excellent enhancing effect on POE matrix when the content of lignin is as high as 30 wt%, showing enhanced strength and toughness of the thermoplastic composites. The interface between lignin and elastomer matrix has been constructed by coordination sacrifice bond, which not only facilitated the dispersion of lignin nanoparticles but promoted the interfacial interaction between lignin and elastomer matrix, as well as improved the orientation of chain segments during stretching. Cao et al. adopt a general method combining chemical modification and lignin fractionation to prepare a series of lignin-based fillers (lignin grafted with polymethyl methacrylate, L-G-PMMA). The results indicate the tensile properties of synthetic materials can be adjusted by molecular weight, type and content of S/G units²⁴.

Lignin as Compatibilizer in Thermoplastic Composite

Apart from the role of lignin as the functional filler in the thermoplastic matrixes, lignin has been used as a compatibilizer between natural polar fibers such as cellulose and nonpolar thermoplastic polymers. Inspired by the role of lignin in plant cells as binder, lignin has potential as a coupling agent between reinforced fibers and polymer due to its inherent amphiphilic characteristic and the ability of lignin to form noncovalent interactions with both cellulose and nonpolar polymers such as PCL and PLA^{14, 25,26}. The main driving forces are associated with van der Waals, and hydrogen bonds contributed by abundant phenolic hydroxyl and alkyl groups in lignin. For instance, Wang et al showed that coating cellulose nanofibers (CNF) with lignin can significantly enhance the compatibility of fibers with PLA, resulting in higher tensile strength rather than pure PLA or a simple combination of CNF and PLA²⁷. According to Graupner et al cotton fibers coated with lignin have better adhesion with PLA compared with untreated cotton fiber and PLA. Furthermore, they showed that the addition of lignin increases the specific fiber surface, providing more space for interfacial bonding of fiber and polymer²⁸.

Blending of Lignin with Thermoplastic Polymers

Blending is one of the most convenient approaches to incorporating lignin into thermoplastic matrixes that can commonly proceed via melt or solution blending processes^{14, 29}. In the melt blending, the mixture of lignin and polymers at their melting points turns into films by hot pressing or blowing molding. In the solution blending, first, a suitable solvent dissolves lignin and thermoplastic polymer; second the restraint solvent evaporation converts the dispersion into the homogenous film or spun fiber by solvent casting or electrospinning, respectively. The structural and mechanical properties of blends strongly depend on the fabrication process. Furthermore, the physical and chemical properties of lignin, such as molecular weight, polydispersity, and glass transition temperature (T_g), affect the dispersion of lignin into the thermoplastic matrix and subsequently the final performance of the blend^{30, 31}. The complex structure of lignin arising from substantial intra-and intermolecular hydrogen bonds between functional groups such as carboxylic acids, hydroxyls, and ethers induce self-aggregation

characteristics that deteriorate the interface compatibility of lignin with thermoplastics³². In addition, many functional groups, especially hydroxyls, from irreversible condensation at elevated temperatures, restricting the processability. To uplift the lignin status as an ultimate material platform, its inherent perplexing challenges needed to be addressed in a sustainable and scalable manner. Many studies have shown that the physical or chemical modification of lignin may improve the interfacial compatibility between lignin and thermoplastics as well as the thermal mobility of lignin^{33, 34}. For example, Zhu et al showed that the tensile strength of the PLA/lignin blend significantly improved by using KH550 (3-amino propyltriethoxysilane) and KH560 (γ -(2,3-epoxypropoxy) propyltriethoxysilane) as the interface compatibilizer. In fact, the amine groups in KH550 and epoxy groups in KH560 could effectively interact with carboxyl and hydroxyl groups of PLA and lignin. Chen et al reported that alkylation of kraft lignin using bromododecane improved the compatibility between lignin and polypropylene³⁵. Liu et al showed that grafting of lignin with vinyltrimethoxysilane (VTMS) can improve the compatibility of lignin with polybutylene adipate-co-terephthalate (PBAT) via the formation of network structure in the blend³⁶.

Application of Lignin-Thermoplastic Composites

For packaging and biomedical applications, generated poly(lactic acid) (PLA)/lignin nanoparticle composite incorporating cinnamaldehyde (Ci), showed a higher UV-light barrier property and biodegradable properties^{37, 38}. Furthermore, The biomedical applications of lignin reinforced thermoplastic have recently been investigated in a series of studies, including the development of an additive for tablet manufacturing, 3D printed antioxidant wound dressing and a recent study in which the antioxidant and antimicrobial properties of lignin were used to create completely green composites with polybutylene succinate (PBS)³⁹. Lignin-based composite can also be used to create multipolarity-related products such as emulsions and dispersants; in agriculture for plant and animal nutrition and soil formation; and in high purity applications such as food and cosmetics containing gels or emulsifiers, active substances with antibacterial, antioxidant, and antiviral properties, and in biomedical applications⁴⁰. The well-known and commercially available lignin-based thermoplastics are ARBOFORM® (made of lignin, natural fibers, and additives) and XylomerTM (made of lignin/polymer blends). ARBOFORM® and XylomerTM can both be used to produce materials with desired shapes using the same machinery that is used for petroleum-based thermoplastics. At high lignin concentrations, thermoplastics such as kraft lignin-poly (vinyl acetate), lignin-based polyurethanes, and coconut shell lignin-polyurethanes were produced with relatively high physical and chemical properties⁴¹.

Conclusion and Perspective

The supply of lignin has been abundantly increased due to the development of the paper and biorefinery industries, stimulating the conversion of lignin from low-value waste to value-added products. And lignin is mainly used as the co-polymer with other polymer monomers in thermoplastic composites, including matrix, initiator, reinforcing filler, and compatibilizer owing to its structural heterogeneity and processability. However, the brittleness of lignin-based thermoplastic polymers leads to poor mechanical properties, which limits the utilization of thermoplastic polymers with high lignin content. Therefore, lignin is mainly blended with other polymers or as copolymers in thermoplastic.

Lignin has been the most essential aromatic polymer derived from renewable resources; it has a distinct and complex chemical structure, is plentiful in nature, and does not compete with the food supply chain. Future research will most likely focus on developing nanomaterials for advanced applications (energy storage, thermoelectric devices, biosensors, controlled drug delivery, gene therapy, and theranostic systems). To establish the complex interactions of these newly designed materials with living tissues, to assess targeting cues, and to provide solutions based on controlled release mechanisms, chemical/enzymatic degradation activity under physiological conditions must be tailored, and elimination procedures to avoid tissue accumulation and side effects must be realized⁴². When these principles are founded, lignin is likely to contribute to the advancement of 3D printing and bioprinting technologies. Finally, the chemical and functional versatility of lignin will have a significant influence on its value, requiring specific approaches to processing and chemical modification. The next steps in this direction will involve a better understanding of the structure/property/function interactions in these materials, as well as the potential of tuning the macroscopic properties of the materials via nanoscale control of structure, morphology, and chemistry¹².

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Challenges in Chemical Structure and Molecular Mass Determination of Lignin

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Abstract

Lignin is a complex macromolecule, and its complete structure is yet to be determined. In this mini-review, the advantage and disadvantages of NMR analysis and molar mass determination of lignin are discussed. NMR is a powerful method for investigating the structure of lignin. With ¹H and ¹³C NMR, quantification of hydroxyl groups can be made, however, some derivatization is often required prior to the analysis. ³¹P NMR can also be used for quantifying hydroxyl and carbon groups as well as distinguishing between aliphatic, condensed and uncondensed hydroxyl groups. The development of 2D-NMR has allowed for more accuracy and the possibility of determining the complete structure of lignin in the analyzed sample. The main challenges with NMR are the overlapping of signals and difficulties with quantitative analyses. The most common way to elucidate the molar mass of lignin is by size exclusion chromatography (SEC) coupled with different types of detectors. The most advanced method used for molar mass determination is SEC coupled with multi-angle light scattering (MALS). With SEC-MALS, the absolute molar mass can be determined without the need to use standards. However, the accuracy of this technique is still discussed. As the lignin structure is so complex, several different methods need to be utilized to receive the most accurate characterization.

Introduction

Lignin is the most abundant aromatic polymer on Earth and can be found in the secondary cell walls of plants. It provides the plant with rigidity and contributes to the plant with defense against pathogen invasion.^{1,1} Lignin is an amorphous polymer rich in polyphenolic material generated via an enzyme-mediated dehydrogenative polymerization of the three monomers p-coumaryl (H), coniferyl (G) and sinapyl alcohol (S) (Figure 1).² The alcohols have similar structures, where phenol is connected to a three-carbon chain (C_{α} , C_{β} , C_{γ}) from the C_1 of the ring. The G structure has a methoxy group at C_3 and the S structure has a methoxy group also at C_5 .³ The most abundant interunit linkage in lignin is the alkyl-aryl ether bond (β -O-4) and together with the other common linkages, it is depicted in **Figure 1**.

The amount of lignin in plants varies between species as well as the ratio of H, G and S. In most softwoods, the lignin content is 24-33%, 19-28% in temperate-zone hardwoods, 26-35% in tropical hardwoods and 11-27% in nonwoody fiber plants.⁴ Hardwood lignins contain a similar amount of G and S units, with low levels of H, whereas softwoods usually contain high

amounts of G units, with a low amount of H.³ Hardwood lignin is usually more linear compared to softwood lignin, which is due to hardwood lignin having less C-C interunit linkages, and the higher amount of methoxy groups in the S unit compared to the G unit causes steric hindrance for the lignin chain and less additional linkages are formed.⁵

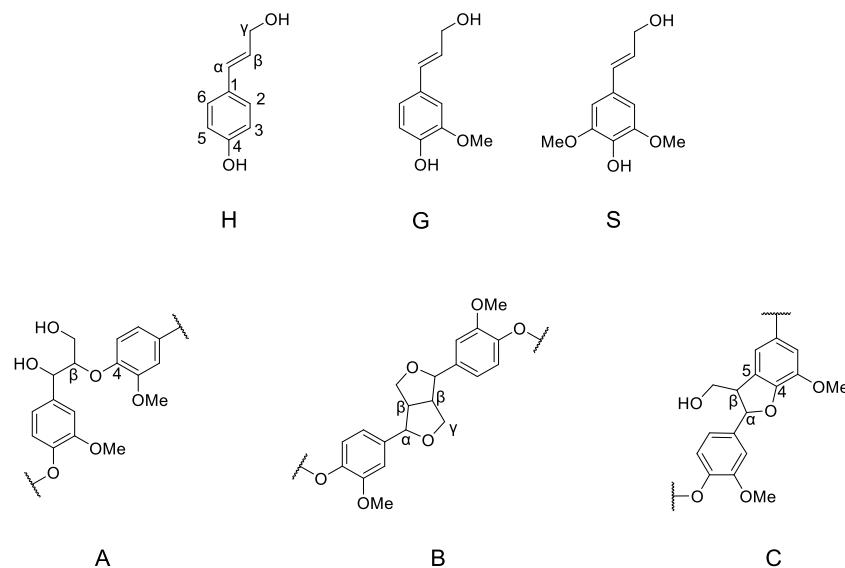


Figure 1. Structures of the monomeric lignin units (H=p-coumaryl alcohol, G=coniferyl alcohol and S=sinapyl alcohol) and interunit linkages (A=β-O-4, B=β-β & α-O-γ and C=β-5 & α-O-4).⁴

Lignin has been considered a by-product and has mainly been used for low-value applications such as low-grade burner fuel. Due to the ever-increasing need for renewable sources to replace fossil-based feedstock, lignin has become an attractive alternative due to the high content of aromatics. To be able to utilize the full potential of lignin, a comprehensive understanding of the structure is needed. However, lignin is a complex polymer and there are many challenges in elucidating its structure, and standard procedures to characterize lignin are still needed. In this review, methods and challenges with characterizing lignin will be discussed, with a focus on NMR and molar mass determination.

Characterization with NMR

To efficiently valorize lignin, a comprehensive structure investigation must be provided. Among the most popular analytical methods of lignin characterization, nuclear magnetic resonance (NMR) spectroscopy takes a leading role in lignin structure development. Throughout the years, NMR spectroscopy has been proven to be both a reliable and effective characterization method in lignin chemistry. Spectroscopic methods outperform degradation methods in terms of lignin analysis as the complete lignin structure can be detected.^{6,7} More importantly, NMR techniques bear higher resolution compared to other presented spectroscopic methods for lignin analysis which include both ultraviolet-visible (UV-vis) and infrared (IR) methods along with Raman spectroscopy. Consequently, a more comprehensive and considerable amount of lignin structural information can be extracted from each single spectroscopic NMR technique.⁷

¹H NMR

At the beginning of the NMR techniques development, proton NMR (^1H NMR) was employed in the majority of lignin samples for reliable and fast structure characterization. Nevertheless, due to the highly complex polymeric structure of lignin and a huge number of protons from arising signals from different lignin subunit structures and interunit linkages, it gets difficult to distinguish the signals properly in the overlapped proton spectrum of lignin.

^{13}C NMR

The breakthrough in lignin chemistry is associated with the development of quantitative ^{13}C NMR spectroscopy. Of particular note is that ^{13}C NMR is a powerful tool in lignin characterization which allows for the detection of a significant amount of lignin polymer structure. To specify, it enabled the possibility to extract the information on the presence of different important units such as condensed and uncondensed aromatic and aliphatic carbons and detect the aryl ether subunits within the molecule.⁷ A more common approach implies the use of ^{13}C NMR only for the investigation of a few specific units.⁸ Another considerable point in ^{13}C NMR characterization is that the poor abundance of the natural ^{13}C isotope decreases the sensitivity of the method and requires a sufficiently long acquisition time and a high concentration of the investigated sample. Even though it allows for improving the sensitivity of the ^{13}C NMR signals, but simultaneously also limits its implementation in a routine lignin characterization analysis. Apart from it, numerous attempts have been conducted to enhance the signal-to-noise (S/N) ratios of the given spectroscopic technique.⁶ Considering everything, a well-established quantitative ^{13}C NMR remains an extremely popular and reliable tool in the structural characterization of lignin as it enables a comprehensive understanding of the changes in lignin structure during pulping and several isolation processes.^{6,7}

Two-Dimensional (2D) NMR

Another major development in lignin analytics underlies in the development of the 2D NMR technique.^{7,9} Nonetheless, it includes experimental accuracy, which is sometimes hard to provide properly. Moreover, the given approach does not allow for an assignment of quaternary carbon.⁷ The popularity of the 2D HSQC NMR technique is predetermined by its unique set of characteristics which allows for providing comprehensive structural data of lignin macromolecule.¹⁰⁻¹² It establishes direct C–H signals simultaneously in two dimensions. Specifically, the assignment of the main lignin building linkages both ether and carbon can be provided by 2D HSQC spectra. Overall, the two regions of the common 2D HSQC lignin spectrum reflect the side-chain detected areas which are placed in the range of $\delta\text{C}/\delta\text{H}=50-90/2.5-6.0$ ppm, while the aromatic-related signals arise within the characteristic region of $\delta\text{C}/\delta\text{H}=100-150/5.5-8.5$ ppm.¹⁰ The former region (side-chain) of the 2D HSQC spectrum is a source of information on the lignin structural linkages (β -O-4, β - β , β -5, etc.).¹⁰

^{31}P NMR Spectroscopy

Phosphorous NMR spectroscopy is a recently developed yet efficient and quick method to quantify various hydroxyl groups in different types of lignins. Additionally, the given spectroscopy technique outperforms all other methods not only in terms of the detection of hydroxyl groups in lignin macromolecule, but it also provides exceptional accuracy along with significant signal resolution.¹⁰ Another valuable characteristic of the ^{31}P NMR spectroscopy is that it enables the detection of the aromatic hydroxyl groups which belong to different lignin

subunits (S, G and H) along with the instant determination of aliphatic hydroxyl groups and carboxyl ones.^{10,13,14}

Challenges with NMR Spectroscopy

The solubility of lignin samples in deuterated solvents can be a limiting factor when performing NMR measurements. This can be avoided by modifying the lignin, e.g., by acetylation, however, it is important to keep the modification in mind when interpreting the data as there might be shifts in the obtained signals.¹⁵ Absolute quantitative data from NMR analysis is difficult to achieve as the measurements are done by relative comparisons of analyses, and absolute values are not obtained.¹⁶ Furthermore, the high variability in the isolation and preparation of lignin samples and the variety in lignin structure depending on the wood source makes it difficult to achieve quantitative measurements. The main challenge with ¹H NMR and ¹³C NMR is the overlapping of signals, which makes it difficult to obtain quantitative data. This is, however, reduced with the use of 2D NMR, as the ¹H is correlated to ¹³C.^{7, 17} Mathematical equations can, in some cases, be utilized to overcome the overlapping, and quantitative data can be obtained.⁷ With ¹³C NMR and 2D NMR, often more than 12h is required for one sample to receive reliable spectra, which makes these techniques rather time-consuming.¹⁷ With the use of a cryoprobe, the analysis time can be considerably shortened.¹⁸ The reproducibility of quantitative ³¹P has shown to be a challenge, especially for less abundant signals, which could be due to the inconsistency of the lignin structure itself.¹⁸

Determination of Molar Mass

Not only the structure of lignin but also the molecular weight of lignin will affect the high-value application of lignin. As an important component of lignocellulosic biomass, many studies have been devoted to the study of the structure and application of lignin. However, the complex structure of lignin makes its structural characterization and molecular weight determination difficult.

Gel Permeation Chromatography or Size Exclusion Chromatography (GPC/SEC) is the primary analytical tool commonly used for polymers, primarily for its quantitative characterization of molecular weight and molecular weight distribution data. Usually, one chromatographic column containing microporous packing materials with appropriate characteristics was used to separate the dissolved samples according to molecular size/volume. Then, appropriate detection instruments were used to analyze the separated samples.

As we all know, biomass lignocellulosic raw materials for obtaining lignin are abundant, including softwood, hardwood and non-wood. From different fractionation processes and different raw materials, we will get different types of lignin. These factors will affect the molecular weight distribution of lignin.¹⁹ It is difficult for us to obtain lignin consistent with the original lignin structure. Typically, the types of technical lignin we get include kraft lignin, lignosulfonates, organosolv lignin and biorefinery lignin.²⁰ This is one of the reasons why lignin molecular weight detection is challenging. Our knowledge of their chemical structures is still partial.

The current basic status of lignin molecular weight determination is shown in **Figure 2**.²¹ Until now, common lignin molecular weight measure methods include Gel Permeation Chromatography (GPC) with a refractive index (RI) detector calculated by standards and Size

Exclusion Chromatography-Multi-Angle Light Scattering (SEC/MALS) without standards. There is an ongoing discussion in the field around the accuracy of these methods and the fact that different methods give different results and that different laboratories obtain different results.

One method is to analyze the Mw after the derivatization of lignin, which is usually done by acetylation. The lignin samples were acetylated to improve their solubility in the subsequent GPC eluent (THF). Acetylation with pyridine and acetic anhydride usually takes a long time (more than 72 h).^{22, 23} Compared to this acetylation method, one acetobromination method was developed to improve the dissolution time. This process was finished in 30 min using acetyl bromide in an excess of glacial acetic acid.²⁴ Of course, lignin can also be dissolved directly in an aqueous solvent without derivatization. For example, lignin can be dissolved in 0.1% NaOH, then diluted with eluent (tris-acetate buffer, 20 mmol L⁻¹, pH 7.4) and injected directly for molecular weight determination.²⁵ Although different attempts have been made to dissolve, it is still a challenge to find suitable standards for the calculation. In particular, the method of derivatization is not applicable to lignosulfonates.

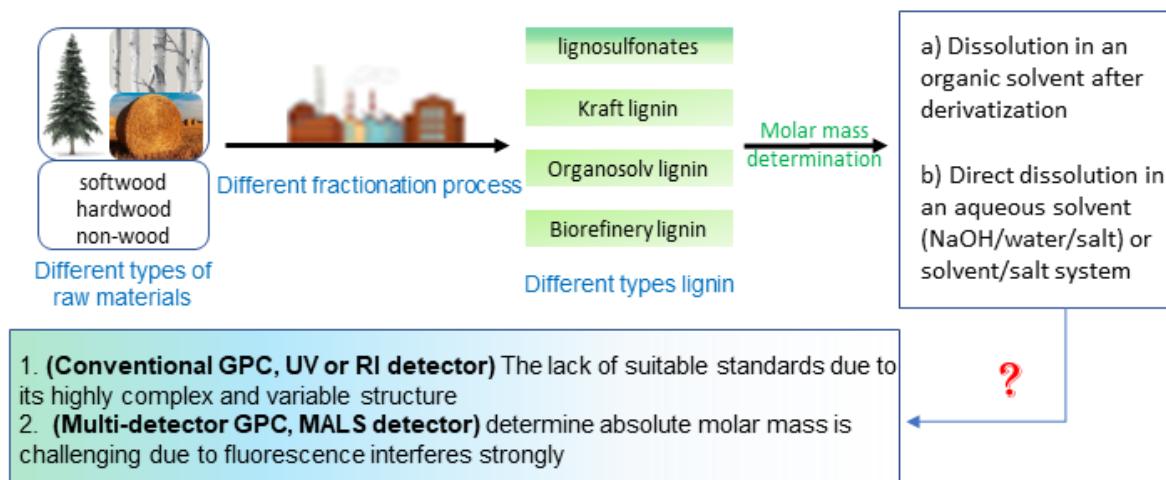


Figure 2. Current Status of Lignin Molecular Weight Determination.¹⁷

The above detection usually uses an ultraviolet (UV) or RI detector, for accurate molecular weight measurements, light scattering detectors are increasingly being incorporated into GPC/SEC systems, eliminating the need for traditional external calibration methods. When a molecule is irradiated with laser light, the intensity of the scattered light is directly related to its molecular weight.²⁶

SEC/MALS method for lignin determination using a light scattering detector no longer requires standards to calculate molecular weight, and typically uses a solvent salt systems (eg. DMSO/0.05 M LiBr, DMF/0.05M LiBr) as the eluent phase. Of course, this method also requires complete dissolution of the lignin sample in order to detect relatively accurate molecular weight distribution values. But in this process, we need to know the corresponding dn/dc value. The dn/dc value depends on eluent solvent viscosity and the purity of lignin samples. If lignin samples have relatively high carbohydrate content, the dn/dc value may be relatively low than high purity lignin. Another challenge is that the fluorescence of the lignin itself can interfere with the detection of the detector. However, for some types of lignin samples, a

fluorescence filter could be applied to the MALS detector to avoid interference. This was however not suitable for lignin samples such as hardwood organosolv lignin and soda straw lignin. Another suggested alternative is to minimize the fluorescence interference could be to use longer wavelengths.²⁷

Other Characterization Methods

Fourier transfer infrared (FTIR) spectroscopy is a rapid technique that gives information on functional groups and their relative proportions in lignin.⁴ Important regions to look for in lignin spectra are 3700-2750 cm⁻¹ and 1800-900 cm⁻¹, which are assigned to OH groups and methyl groups, respectively.²⁸ Furthermore, there is often a sharp band in the region between 1710-1600 cm⁻¹ that is typical for ether and carbonyl groups linked to aromatic groups. Overlapping of bands in FTIR spectra of macromolecules is a limiting factor for obtaining detailed information and is difficult to avoid without implementing mathematical techniques.⁴ Attenuated total reflection (ATR)-FTIR combined with statistical methods, such as partial least squares (PLS) and principal component analysis (PCA) modeling, has shown to be promising in obtaining more detailed sample information, e.g., lignin purity, S/G/H ration, interunit linkages, M_n and M_w.²⁹⁻³¹

Pyrolysis gas chromatography-mass spectrometer (Pyr-GC-MS) has been used for degradation studies and for determining and understanding the monomeric composition of lignin. This method has become a standard for determining the H/G/S ratio of the material.³² However, the most significant limiting factor is the inability to detect structures larger than lignin dimers. With matrix-assisted laser desorption (MALDI), larger fragments of lignin can be measured (up to about 16000 Da).³³ MALDI coupled to mass detectors such as time-of-flight (TOF) can give information on, e.g., average M_w, the number of repeating units within lignin and type of end-groups.³⁴ The sample matrix can interfere with the detection when utilizing MALDI, which complicates the interpretation of the obtained spectra. Silica (TLC grade) has been shown to be compatible with lignin as a MALDI matrix with reduced background noise.³⁵

Conclusion

The characterization of lignin is difficult due to the complexity and the fact that the total structure of native lignin is still unknown. Many powerful methods help us understand lignin and, therefore, increase the valorization possibilities of lignin. NMR is a powerful method that can give structural information and especially the development of quantitative ¹³C was of importance as it allowed for the detection of significant amounts of the lignin polymer structure. Another important technique is the 2D HSQC NMR which allows higher resolution compared to 1D NMR. SEC is the most used analytical procedure for molar mass determination of lignin and the connected detectors are typically RI or MALS. MALS is the most advanced method and does not need a standard for determining the molar mass, however, a dn/dc value is needed which depends on the viscosity of eluent and purity of lignin. Therefore, higher sample purity will give better results. Another challenge that affects the accuracy of the molar mass determination is the interference of fluorescence, which in some cases can be fixed with a filter, however, a solution to completely remove the interference is yet to be reported. As there is no perfect method for characterizing lignin, the best way is to use different complementary types of methods to obtain the most valuable and accurate elucidation. There are limiting factors with each technique such as overlapping, interference with sample

matrices, accuracy and time consumption. As the interest in lignin increases the effort in developing more sensitive and powerful characterization methods rises, the characterization of lignin will become more efficient.

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Methods for Improving the Compatibility of Lignin with Polymer-Covalent Compatibilization and Non-Covalent Compatibilization

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Abstract

Lignin is the cheapest and most abundant aromatic biopolymer. One possible approach toward the high-value-added application of lignin is using it as an alternative for the petroleum-based components in plastics. However, directly blending lignin with polymer is not straightforward because the polarity of lignin molecules usually leads to strong self-interactions. In this scenario, lignin is often modified chemically to be covalently compatible with the polymer matrix *via* various co-polymerization methods. In addition, developing different interactions between lignin and polymer to improve their interfacial adhesion and dispersion in plastics has been studied in the last few decades, and the resulting material was sometimes had superior mechanical properties. Fractionation of lignin structure with defined properties is also a possible way to tailor the interfacial adhesion. In this mini-review, the existing strategies, mainly including covalent and non-covalent compatibilization, for improving the compatibilization of lignin with polymer are presented. In addition, advanced tools, such as three-dimensional (3D) printing, for utilizing lignin blends/composite and future research directions for lignin copolymers are discussed.

Introduction

Due to its functionality and abundance, lignin is receiving increased research attention as we strive to obtain renewable industrial substituents for petroleum-based components. Today, there are several approaches for lignin isolation from lignocellulosic biomass where the industrially established processes are kraft and sulfite pulping. Meanwhile, these processes do not consider lignin as their primary product. Due to the significant modification of the isolated aromatic moieties originating from kraft and sulfite plants, new methods are being developed where a compromise is made in the overall modification of the main constituents of the biomass. Among these are organosolv,¹ while also systems employing deep eutectic solvents and ionic liquids have received attention.^{2,3} All of these offer the potential for less lignin modification relative to its native state. Another factor influencing isolated lignin suitability is the raw material as the original lignin structure is different in hardwoods, softwoods, and herbaceous crops.⁴

Because of the potential different lignin chemistries, their properties in blends and composites will be different.⁵ For example, when producing polyurethanes from hardwood lignins extracted with acetic acid, ethanol or acetone based solvents, the amount of lignin hydroxyls determined the extent of polymer cross-linking, thus directly influence the thermal properties of the obtained polyurethanes.⁶ A certain strategy is to change the extent of secondary bond formations through alkylation or alkoxylation in blends, and therefore the associated thermal response.⁵ Interestingly, when esterifying hydroxyl groups in lignin with dicarboxylic acids, the chain-length of the specific dicarboxylic acid was found to determine the final glass transition of the material due to reduced cross-linking density and enhanced molecular mobility.⁷ Alkylation has also been used to lower the glass transition temperature, meanwhile increases are also reported.⁸ Thus, it is likely essential to consider all potential secondary interactions into account when justifying blend or copolymer miscibility and compatibility. Now, aiming to compose copolymer systems taking all such considerations into account is a daunting task, especially considering the fact that lignin isolates are highly heterogeneous. One of the methods to elucidate the contribution from lignin, is through solvent fractionation. For example, it has been found that upon solvent fractionation of kraft lignins, the fraction containing the fewest native motifs (β -O-4', β -5', and β - β') and low content of aliphatic hydroxyl groups, displayed greater tensile strength and elongation at break when employed in blends with polyethylene.⁹ This fraction also experienced the lowest molar mass which was attributed to better compatibility with polyethylene. This fraction also displayed the lowest glass transition temperature, indicative of an overall low polymer-polymer coherency for lignin, which could be beneficial for specific applications. However, the analyses stop at this point, and it is in general very hard to correlate any other specific, structural factors to properties in polymer blends. An additional approach is to also consider motif compatibility, both lignin-lignin, and lignin-copolymer and copolymer-copolymer compatibility. In addition to the most apparent secondary interactions, one could also account for how segments of aliphatic motifs interact with each other and with aromatic segments. For a long time, it has been evident that aliphatic motifs carry significant bonding potential,¹⁰ as does aliphatic with aromatics, and aromatics.^{11,12}

Based on recent progress, we focus on prospective application of lignin as a macromonomer in the construction of polymers using covalent or non-covalent compatibilization methods in this review.

Covalent Compatibilization

The chemical modification of lignin to functional macromolecules can provide useful handles for covalent integration of lignin with polymer materials. One of the most significant obstacles is the inherent heterogeneity of lignin, which hinder the chemical reactivity and steric accessibility in the process. Lignin fractionation methodologies, e.g., solvent extraction, have been strategically proposed to offer relatively homogeneous lignin fractions, in terms of narrow molar mass dispersity and enriched functional groups for chemical modification and polymerization with high efficacy.¹³ Gioia *et al* fractionated Kraft lignin by using sequential solvent extraction (EtOAc, EtOH, MeOH, and Acetone). The cross-linking efficacy of epoxidized lignin fractions with diamine is higher in low molar mass fractions with more hydroxyl groups, while the fractions with higher molar mass and more stiff interunit linkages retain higher thermo-mechanical properties of thermosetting lignin-containing epoxy resin.¹⁴ Above all,

lignin fractionation method provides a possibility to control lignin on molecular level to tailor the mechanical property of the final lignin composites.

Polymeric modification of lignin *via* graft copolymerization represents an important avenue for improving the compatibilization because this method forms stable covalent linkages between lignin and synthetic functional polymers. Compared with graft-onto method that separately synthesized polymers and lignin are covalently integrated by efficient coupling reaction, significant research attention has been given to the graft-from strategy, where the synthesis of the lignin-macroinitiators is considered to be the most important step to further direct the polymerization of monomers from it.¹⁵ For example, latex films produced by *in situ* lignin-seeded semi-batch emulsion polymerization of butyl acrylate (BA) and methyl methacrylate (MMA), where the lignin macromolecules were functionalized with vinyl groups, exhibited enhanced tack and shear strength that allow for their use in pressure sensitive adhesive applications.¹⁶ Controlled radical polymerization, including atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain-transfer (RAFT),¹⁷ and ring opening polymerization (ROP),¹⁸ can control over the polymerization reaction (e.g., polymer chain length and obtain well-defined structures) as well as the physiochemical properties of the lignin-graft-polymer, which are universal strategies to enhance the material performance and broad the possibility of applications.¹⁹ One of the recent developments in lignin covalent copolymerization is the design of surface-active lignin-based macromolecular RAFT agent to eliminate the use of surfactant. For example, a RAFT agent composed of a hydrophilic polyacrylamide block and a hydrophobic lignin molecular chain can effectively initialize the copolymerization of BA and MMA and provides lignin-based hybrid acrylate resin with a better Young's modulus and tensile strength.²⁰ However, the lignin dosage was limit at only 5% in the acrylate resin.

Non-Covalent Compatibilization

Non-covalent compatibilization is also an effective method to improve the compatibility of lignin with polymers. Non-covalent interactions can be further divided into four categories: electrostatic interactions,²¹ π -effects,²² Van der Waals interactions,²³ and hydrophobic effects.²⁴ The main advantage of this method is that the structure of lignin will not be altered, which will maintain its property and performance. Non-covalent modification of lignin can be achieved by surfactant treatment, polymer winding,²⁵ $\pi - \pi$ interaction, and embedded molecule modification, which will provide modified lignin with improved dispersity in polymer matrix. For example, Jiang *et al.*²⁶ encapsulated lignin with polycation to form positively charged nanoparticles. These nanoparticles can be stably dispersed in NR latex to improve mechanical properties. Then, other researchers have discussed the role of polybutadiene-g-polypentafluorophenylethylene (PB-g-PPFS) as a non-covalent coupling agent between lignin and styrene butadiene rubber (SBR) in the preparation of compounds with high mechanical strength and low viscoelastic loss.²⁷ The PPFs domain in PB-g-PPFS provides an electron defect π ring system, which can couple lignin with rubber through aromatic perfluoropentadiene interaction. The tensile strength was improved by 20% and 10% for compounds of lignin and lignin–carbon black hybrid fillers, respectively. The loss tangent value reduced due to improved filler-rubber interactions promoted by PB-g-PPFS compounds. In recent years, lignin-based coupling agents have gained popularity in the non-covalent compatibilization of lignin. Wu *et al.* prepared solvent-resistant LNPs *via* a combination of lignin solvent fractionation (e.g., sequential EtOH/H₂O extraction) with

hydrothermal treatment-assisted self-crosslinking. The coupling agent, fabricated by grafting D-lactide on the LNPs surface in chloroform (CHCl_3), showed excellent dispersion and compatibility in poly(L-lactide) (PLLA) matrix as estimated by SEM, XRD, and DSC analysis. Consequently, the toughness of the resulted PLLA blends containing 10 wt% LNPs-PDLA coupling agent, in which the lignin is derived from residual lignin after sequential $\text{EtOH}/\text{H}_2\text{O}$ fractionation, reached the highest value among the PLLA materials.²⁸ Importantly, fractionation-dependent LNPs-PDLA coupling agent size can tailor the thermal crystallization and mechanical properties of the PLLA blends, which is beneficial for the specific application.

3D Printing

Additive manufacturing (AM), also known as 3D printing, is a technique to produce objects by building them layer by layer, it can produce more complex parts with lower waste compared to traditional subtractive manufacturing techniques. Lignin is a relatively inexpensive feedstock that could substitute a percentage of currently used thermoplastic polymers, such as PLA and ABS, in fused deposition modeling (FDM).²⁹ In blends of lignin and thermoplastics, the large number of polar functional groups of lignin results in strong interaction between lignin molecules. This makes lignin immiscible with most polymers, as the interaction between lignin and the polymer is much weaker and produces small lignin particles dispersed in the polymer matrix. The lignin polymer blend provides relatively good properties but usually poor deformability. The immiscibility of lignin can be combated by chemical modification, such as copolymerization, where long chains of the polymer is attached to the lignin molecule which reduces the lignin-lignin interaction and improves the miscibility.³⁰ Lignin can also be introduced to stereo lithography (SLA) resins, SLA utilizes light to photopolymerize the resin layer by layer, producing an object. Early test to introduce lignin in resin discovered a couple of problems: dispersion, lignin concentration, crosslinking ability, and material properties. By mixing 1 % Kraft lignin in SLA resin crosslinking degree is reduced by half and ultimate tensile strength reduced by 85 %. This is due to the poor dispersion causing the lignin to settle to the bottom and blocking the light for photopolymerization, the lignin also does not participate in the crosslinked network. By copolymerization of lignin with chains containing acrylate or methacrylate these problems can be solved. Up to 15 % of lignin/methacrylate copolymer can be used in the SLA resin and the ultimate tensile strength is doubled.^{15,29}

Future Research Directions

Lignin nanoparticle (LNPs) surface-initialized co-polymerization would be a promising strategy to further improve the miscibility with polymer and increase the lignin content. LNPs have a large number of surface functional groups (e.g., phenolic hydroxyls, aliphatic hydroxyls, and carboxylic acids) where diverse chemistry can occur and allows the generation of three-dimensional polymeric networks construction. LNPs also possess durable dispersity in water or in certain organic solvent, which can broad the application of lignin to free-radical emulsion polymerization in water medium. Furthermore, lignin also has an amphiphilic structure feature, which can be used as a polymeric surfactant for emulsion polymerization. For example, it has been demonstrated previously that the surface of LNPs can mediate the polymerization process and generate energy dissipative interactions with entangled polymer chains in toughening cellulose-polycaprolactone nanocomposites, polystyrene, poly(vinyl alcohol), pectin-polyacrylic acid hydrogels, etc.³¹⁻³⁴

In the aspect of non-covalent interaction, the structure of lignin can provide good reaction conditions through $\pi - \pi$ interaction or electrostatic adsorption, etc. Through non-covalent bonding, improving the compatibility of lignin with other materials has the advantages of simple reaction steps and simple reaction conditions. Therefore, it is particularly important to study the structure of lignin, for example using small-angle neutron scattering (SANS), establish the relationship between lignin structure and property. Meanwhile, the non-covalent bonding reaction mechanism combined with the relationship between the structure and properties of lignin, and the influence of process conditions on the reaction efficiency is very worthy of further research.

The use of lignin copolymers in AM have resulted in a significant improvement for lignin content and material properties. But research is still needed to fully exploit some of the properties inherent to lignin, such as antioxidative and UV blocking properties. A lot of studies have been targeted at incorporating lignin in extrusion and light polymerization AM technologies, other AM technologies such as selective laser melting (SLM) and material jetting could also benefit from the properties brought by lignin.²⁹

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Recent Progress in Depolymerization of Lignin

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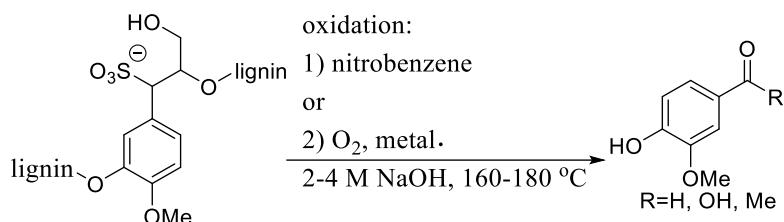
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Abstract

Lignin is one of the most common polymers in the nature and the most abundant aromatic polymer that can be derived from the nature. Due to low reactivity and complex structure direct application for polymeric lignin are somewhat restricted and therefore lignin valorization by depolymerization has gained increasing interest over the years. By depolymerization various small molecular weight hydrocarbons can be derived from lignin example as various aromatic alcohols. In this review novel catalytic methods of lignin depolymerization by oxidative and reductive treatment are summarized alongside different type of industrial processes for mentioned utilization of lignin.

Oxidative Lignin Depolymerization

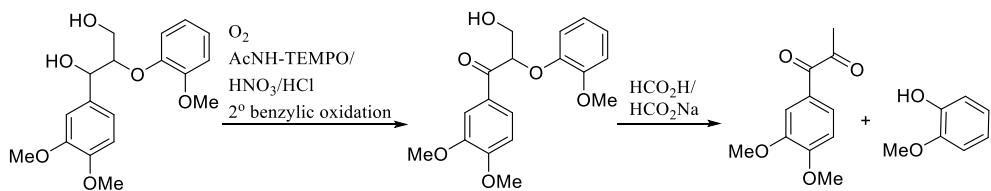
Vanillin is the main phenolic product manufactured from lignin. A representative direct lignin oxidation is the conversion of lignin to vanillin derivatives. Nitrobenzene oxidation [1] of isoeugenol to vanillin was firstly published in 1941. The process occurred under alkali condition at 160-180°C. Nitrobenzene as oxidant led to cleavage of C α -C β bond of β -O-4 units and gave vanillin as major product. The aldehyde yield depends on wood source, softwood can give up to 25-30 wt% of vanillin yield. However, this method was not acceptable for industry since nitrobenzene is an expensive material and the reductant after reaction is difficult to separate. O₂ as an alternative green oxidant [2] with CuSO₄ as catalyst was applied by industry for the production of bio-based vanillin.



Scheme 1. Oxidative depolymerization of lignosulfonate[2].

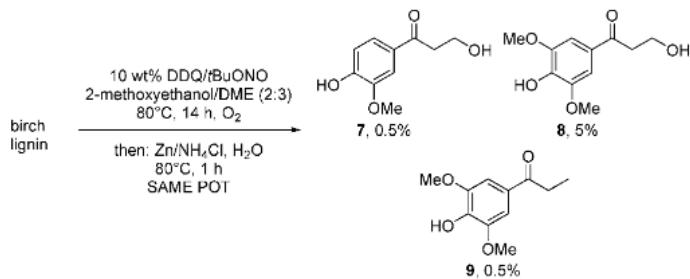
In recent years, a new approach for lignin depolymerization is sequential oxidation-cleavage methodologies [3]. This strategy allows selective oxidation of benzylic or secondary alcohols on β -O-4 structure, then aromatic monomer products can be generated after the second cleavage step.

In 2013, Stahl *et al.* firstly tested various stoichiometric oxidation methods towards β -O-4 dimer model, they found nitroxyl type catalysts AcNH-TEMPO/HNO₃/HCl in the present of oxygen gas [4] gave the best yield on selective oxidation on secondary benzylic alcohol. With the oxidized β -O-4 ketone in hand, the same group developed an aqueous formic acid/sodium formate redox neutral condition [5] for oxidative cleavage. This C-O cleavage method transformed β -O-4 unit into diketone as major product with 96% yield. Oxidized lignin ketone was also tested using this new method, 61.2 wt% of low molecular mass aromatics was obtained in soluble fractions. In addition, different types of lignin were evaluated by this aerobic oxidation-hydrolysis method such as mild acidolysis lignin. S and G derived diketone product was received up to 16.9 wt% after depolymerization, other major products including syringaldehyde, syringic acid and vanillin were also formed.



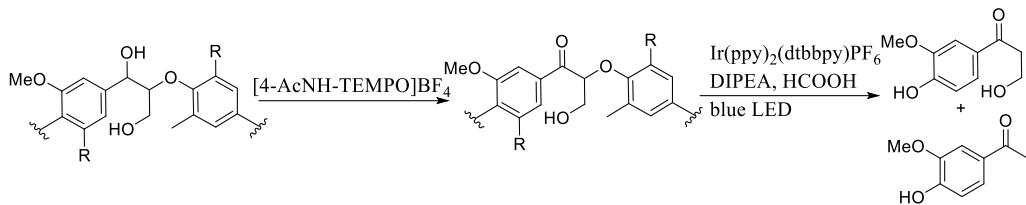
Scheme 2. Chemoselective aerobic oxidation of lignin[4].

DDQ is a common dehydrogenation reagent of benzylic alcohol, Westwood developed catalytic DDQ/tBuONO/O₂ catalytic system [6], this oxidation of β -O-4 models gave high yield and excellent selectivity on benzylic alcohol. In the second step Zn reductive cleavage, 6 wt% of aromatic ketone monomers were isolated. When this method was applied to organosolv birch lignin, the target β -O-4 ketone unit was obtained after determined by HSQC NMR. The oxidation/reduction of birch lignin was conducted in one-pot method, major phenolic monomer **8** product was isolated with 5 wt% yield.

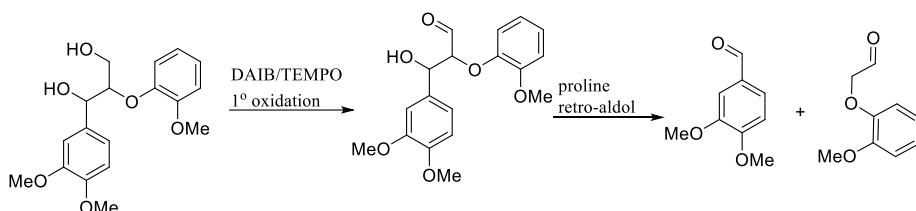


Scheme 3. DDQ/reductive cleavage of lignin[6].

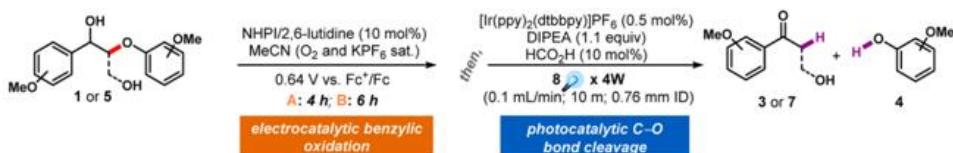
Photocatalysis as environmentally benign method was also taken into account for lignin depolymerization [7]. Stephenson's group revealed using recyclable oxidant [4-AcNH-TEMPO]BF₄ for selective benzylic oxidation. Visible light-mediated C_α-O reductive cleavage was explored by screening various photocatalyst, the reaction carried out under LED irradiation and room temperature, Ir(ppy)₂(dtbbpy)PF₆ was the best catalyst for different β -O-4 models, fragment hydroxyl phenyl ketone and phenol products were obtained in high yield after separation.

**Scheme 4.** Oxidation/photo mediated fragmentation on lignin model[7].

Selective primary alcohol oxidation of β -O-4 was also demonstrated by Bolm and coworkers, they revealed the combination of hypervalent iodine [8] (DAIB)/TEMPO system, which enables chemoselective oxidation of terminal alcohol to aldehyde in 43% yield. This method was extended to the oxidation of organosolv beech lignin. In following cleavage step, DL-proline catalyzed retro-aldol reaction afforded benzylaldehyde and phenol products in high yield.

**Scheme 5.** Hypervalent iodine oxidation/retro-aldol depolymerization[8].

Stahl's group developed electrochemistry-based ACT-TEMPO oxidation [9] of lignin and β -O-4 model. Under basic condition (pH=10), primary alcohol was selectively oxidized to carboxylic acid with 90% yield. In the second step, retro aldol reaction of carboxylic acid containing model occurred under basic aqueous condition, which afforded cleavage and gave aromatic aldehyde as major product. Next, oxidized lignin also enabled C _{α} -C _{β} cleavage by retro-aldol reaction. Under acidic condition, poplar lignin was depolymerized to 30 wt% aromatic monomer compounds. The highest yield was obtained in HCOOH/water=90:10 system.

**Scheme 6.** One-pot electro oxidation/reductive cleavage methodology[9].

Electrocatalytic oxidation/photocatalytic cleavage [10] sequential method was also investigated in lignin depolymerization. Stephenson et al. reported under 0.64V cyclic voltammetry, phthalimide (NHPI) generated N-oxyl radicals combined with 2,6-lutidine in catalytic amount gave the oxidation on secondary benzylic alcohol. After oxidation completed, addition of photocatalyst and DIPEA under photo irradiated flow condition, cleaved ketone as the major product was isolated in high yield accompanied with phenol. Pine lignin was also subjected in this protocol. HSQC indicated oxidation of unit under this catalytic system, GPC and GC-MS revealed monomeric and oligomeric β -O-4 units with lower molecular weight than

native lignin (~43 wt % of oligomeric units, and up to 55 wt % of low molecular weight units) was generated after depolymerization.

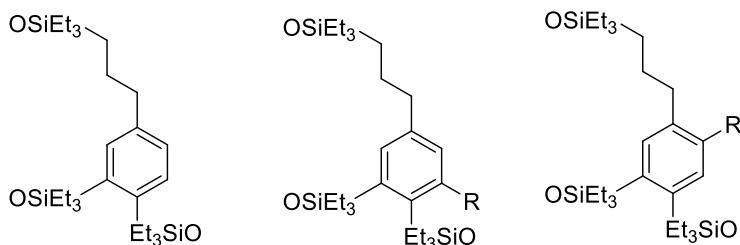
Reductive Lignin Depolymerization

Reductive catalytic fractionation is one of the most promising methods to fractionate lignocellulose. First time reductive treatment of lignin dates to the late 1930s when Harris with his team reacted hard wood lignin with hydrogen in the presence of CuCr catalyst in a relatively harsh conditions to obtain aliphatic compounds [11]. Nowadays there is plenty of different catalyst based on different metal compounds as palladium, nickel, molybdenum, ruthenium, boron and traditional copper alongside with non-metal boron compounds [12].

Different Approaches

Reductive approaches for lignin degradation focus mainly on the production of biofuels using hydrogen gas or hydrogen donor solvents [12]. Reduction of lignin requires catalyst that is capable of selective chain scission of C-O bonds but at the same time one of the biggest issues in reductive methods has been over reduction of the wanted end product especially aromatic compounds for biofuels. PdFe/C catalyst is one of the used ones with high selectivity towards benzene with the capability of not to over reduce and lead to ring opening [13]. Methods utilizing this catalyst tends to provide fairly clean mixtures of alkanes for biofuel applications [14].

In 2015 Cantat and co-workers presented the first reductive depolymerization of lignin with metal-free reaction at room temperature [15]. They used $B(C_6F_5)_3$ as a Lewis acid catalyst and hydrogen and hydro silanes as reductants. In the study they achieved high isolated yields of several aromatic products shown in the scheme below with excellent selectivity. Yields were 7-24% and 0.5-2.4% from the based-on lignin and lignocellulose respectively depending on the wood type.



Scheme 7. Products of metal free reductive depolymerization of lignin.

As it is known, lignocellulose pretreatment causes modifications in the lignin native structure by formation of C-C linkages. To reduce this effect, Luterbacher and co-workers [16] added formaldehyde during biomass pretreatment that resulted to soluble lignin fraction that was then converted to guaiacyl and syringyl monomers by reductive treatment close to theoretical yields. In this method formaldehyde stabilizes native lignin via formation of 1,3-dioxane moiety. After 6h of reductive treatment in 200 °C in the presence of Ru/C catalyst combined yield of monomers was 45% when in comparison without formaldehyde treatment yields with the same monomers were only 7%. When temperature was increased to 250 °C method resulted 78% yield with the same catalyst and reaction time.

One of the most recent innovations in the area was made when Wang and Co-workers invented a catalytic method that enabled to complete removal of oxygen and resulted in complete aromatic hydrocarbons with the yield of 35,5% [17]. Reaction was conducted with direct hydrogenation of organosolv lignin with porous Ru/Nb₂O₅ in 250 °C. In this study catalytic activity was attributed to selective activation and strong absorption of different phenols and synergizing effect of Ru and NbO_x compounds. Aliphatic alcohol moieties of the lignin itself act as a hydrogen donor alongside β-O-4 linkages dehydrogenates by ZnIn₂S₄ forming a "hydrogen pool" where C_β-O bonds underwent hydrogenolysis with hydrogen derived from this pool. These tactics leaded with 71-91% yield of phenols in the conversion of β-O-4 models and 10% yield of p-hydroxy acetophenone derivatives from organosolv lignin.

Batch Type and Continuous Processes for Depolymerization

Previously, most research in lignin depolymerization has been made in batch type processes. Latest interest has been nowadays in continuous type processes [18].

Most of the continuous type process research has been made for plug-flow reactors (PFR). One research deals with continuous stirred tank reactor (CSTR) by Kristianto et al. [19]. At that research, acid hydrolysis lignin is converted into bio-oil. Due to fast heating rate, enhanced bio-oil yield and less solid residue were reached compared to batch-type process. With CSTR process better mixing and controllability can be achieved, compared to PFR-processes. Process provides also less carbon deposits that can stuck into the pipes.

Continuous depolymerization has some advantages compared to batch-type processes. Processing time is shorter with continuous flow reactor. That reduces also energy consumption. Normal processing time is less than 30 minutes for depolymerization. Batch-type process takes more than double the time. Continuous-type process allows also rapid heating and cooling. Some chemical reactions can occur during heating or cooling phase, so time shortening helps to control the process. Fast cooling prevents repolymerization reactions, where complex lignin structures form. Heating can be made fast if output flow is changed to stream going into reactor.

Continuous-type processes are important for future lignin valorization. That also saves energy in sustainable point of view. More research is needed in process development to optimize processes [18].

Technical lignins are complex and heterogeneous. Product mixtures need more processing before utilization. Well-defined fractions have been reached with new membrane separation for depolymerized lignins. Other separation techniques can be acidification, solvent extraction and adsorption. By using membrane, less solvent is needed due to molecular weight separation [20].

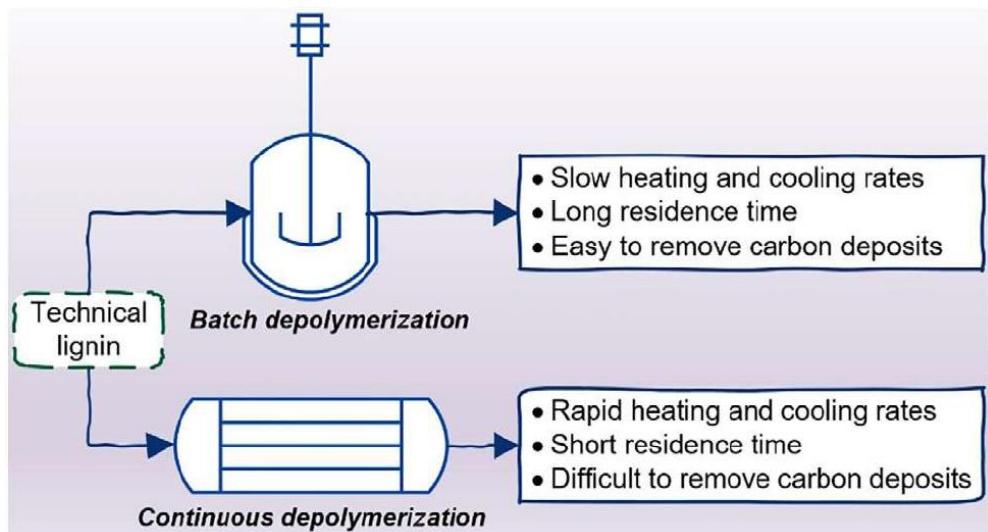


Figure 1. Lignin depolymerization with batch and continuous type reactors [18].

Recycling of catalyst

It is important to separate catalyst from product in product quality and economical point of view. Catalyst reusability has worked with following methods: (a) Separation of a magnetic catalyst by application of magnetic field, (b) Using a microporous catalyst cage, and (c) Liquid-liquid extraction [21].

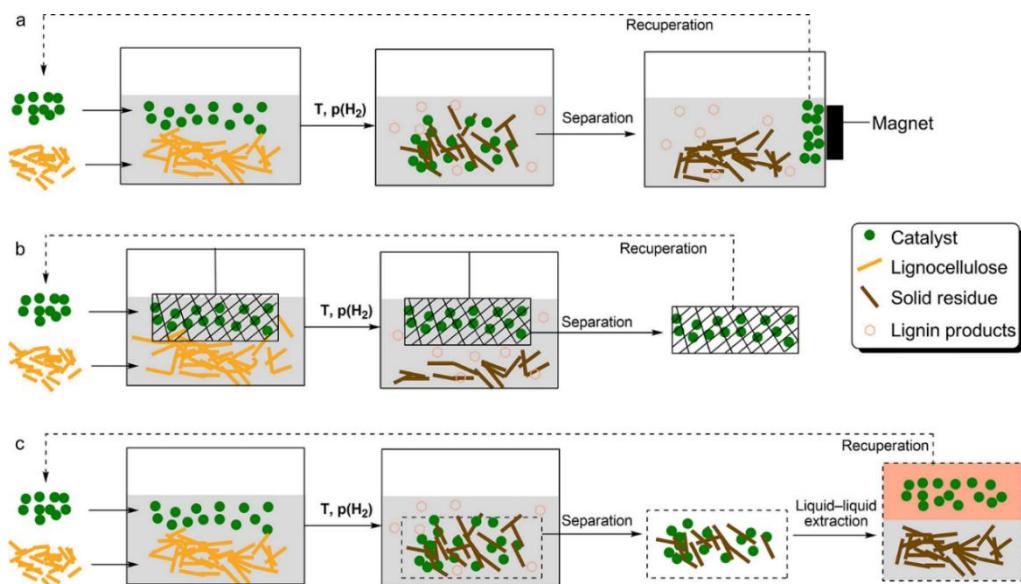


Figure 2. Different catalyst separating technologies [21].

Separation of magnetic catalyst is a simple process. Ni/C catalyst is used as catalyst for smaller fragments, that are converted into monometric phenols. It is highly active catalyst. Ni/C is magnetic, so it can be easily separated by magnet and then reused. Stability and reusability has been mentioned to be good. Raney Ni can be removed with same method [22].

Physical separation of catalyst with microporous gate has been invented by Abu-Omar-group [23]. Ni/C-catalyst and nickel-free cellulose residue were able to keep separated. After every use, ability to use Ni as catalyst, decreased after every instance of usage.

Catalyst extraction from solid residue has been discussed in report of Sels and Co [24]. Ru/C catalyst could be recovered from decane phase. More polar pulp was located at the bottom of methanol phase. Yield was like with fresh catalyst. Only part of catalyst could be recovered (around 30%).

Conclusions

Recently reported lignin oxidation-depolymerization sequential methodologies have received tremendous progress, which gave access to aromatic compounds in a sustainable way. Selective oxidation occurred in either C_α or C_β positions, a variety of cutting-edge synthetic methods were successfully applied to β-O-4 unit oxidation, such as TEMPO oxidation and electrocatalysis. Interestingly, photocatalysis and organocalysis as sustainable method were also applied to the bond cleavage of oxidized carbonyl units (ketone, aldehyde and carboxylic acid). Reactions using birch or poplar lignin high yields results of monomer products demonstrated their potentials to industrial application.

Reductive depolymerization of lignin have a long history all the way from the late 1930s. It has been developed ever since and in the late years new greener and more efficient catalytic methods has been invented. Alongside traditional transitional metal-based catalysts there has been development with metal free catalytic systems based on boron compounds and latest achievements includes also depolymerization with fully oxygen free product pool. Yields close to theoretical ones has been achieved in certain products and future research may be concentrated to systems aiming for different products or making these reactions efficient enough to be used in industrial scale. Batch type-processes has been the most used process method in lignin utilization. Nowadays, new research confirm that continuous-type processes offer more rapid process times, which ensures that non-wanted reactions during heating and cooling remains in minimum. Different catalyst recycling technologies need to be further developed in sustainability and economical point of view.

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Poster Presentations

Smart assembly of wood polymers for advanced materials

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Background

- There is a huge need to replace fossil-based materials with biobased and renewable ones.
- Even fully natural and renewable materials can carry big environmental effects without having a smart strategy and green processing concept.
- Wood-based and agricultural residues coupled with sustainable forest management can be a key to future sustainable development.
- How to get maximum benefit from these valuable resources?



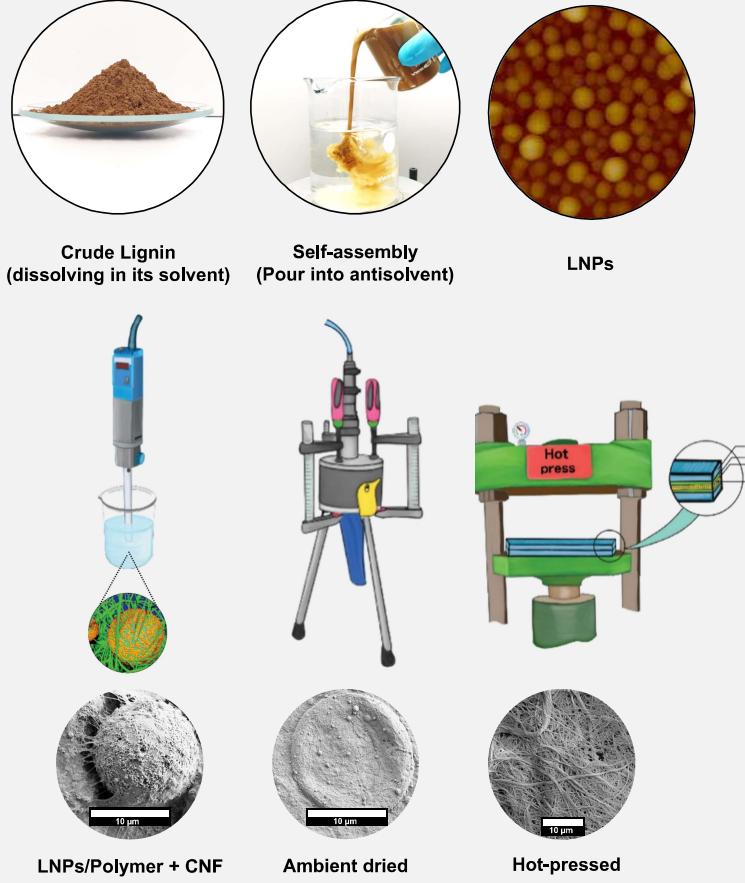
Problem

- Extensive Hydrogen bonding in cellulose induces moisture sensitivity.
- Reducing the mechanical properties of cellulose in the wet state.
- Incompatibility of cellulose with many hydrophobic polymers.
- Surface modifications and chemical grafting of cellulose might reduce the mechanical properties and biodegradability.

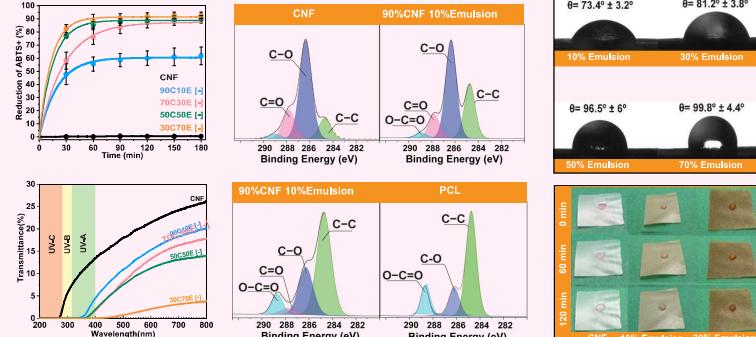
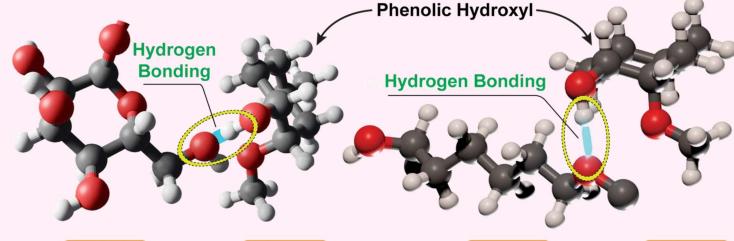
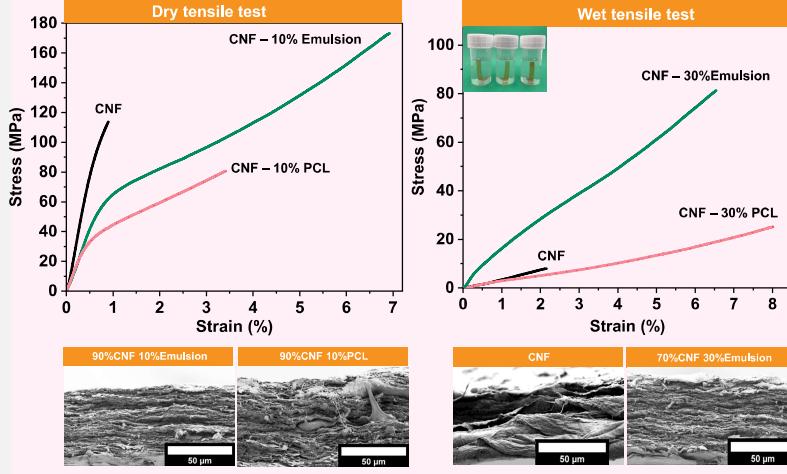
Solution

- Facile interfacial design between composite's components
- Third component as an interfacial mediator between hydrophilic cellulose and hydrophobic polymers.
- Utilizing lignin nanoparticles (LNPs) for stabilizing the hydrophobic polymer emulsion and forming favorable interactions with hydrophilic cellulose

Methodology



Results



Conclusion

- A generic Pickering emulsion strategy for dispersing hydrophobic polymers in hydrophilic nanocellulose
- Multifunctional and waterproof cellulosic composite without any chemical modification
- Avoiding extensive use of chemicals and solvents
- Open avenues for future sustainable development



Effect of wood on the biodegradability of polylactic acid-based composites – Solution to plastic waste?

Joona Kontinen^{1,2}, Kati Meriläinen^{2,3}, Laura Tirkkonen-Rajasalo², Monika Österberg¹

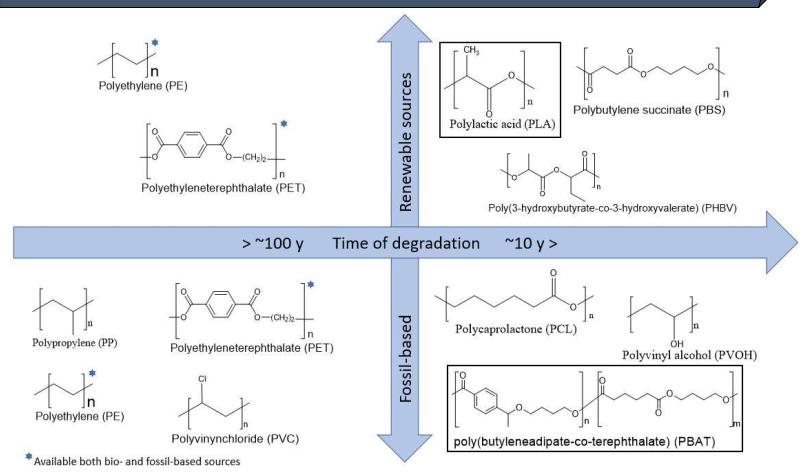
1) Aalto University – School of Chemical Engineering

2) Sulapac Ltd.

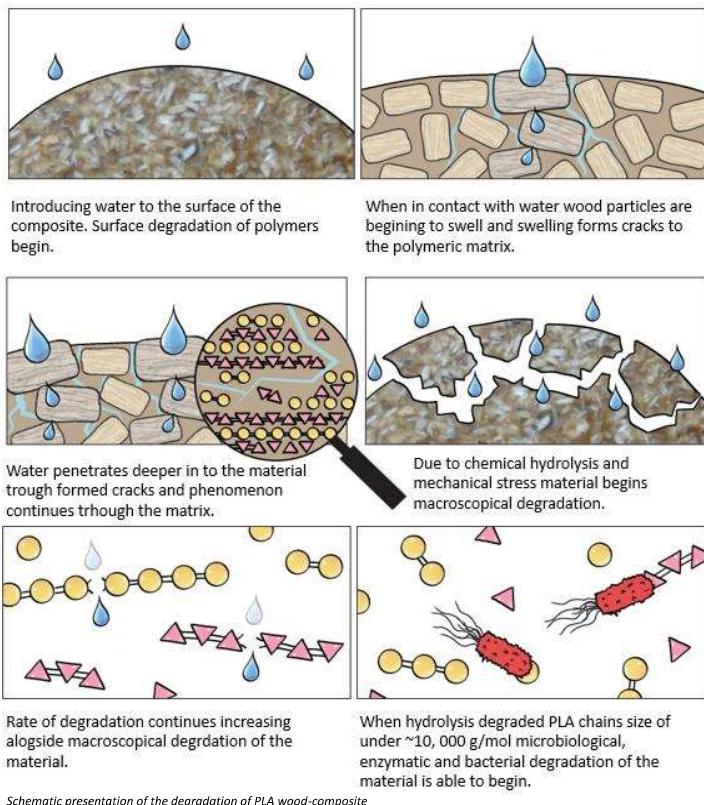
3) University of Helsinki – Faculty of Science

Background

- Based on study conducted by Ellen MacArthur foundation there will be more plastic than fish in the oceans by the year 2050 if nothing changes.¹
- Two problems usually discussed as one
 - Usage of fossil-based resources
 - Accumulation of plastic waste in the oceans
- Three commonly accepted ways of solving the problem
 - Reducing the use of plastics
 - Recycling used plastics
 - Replacing traditional plastics with degradable options

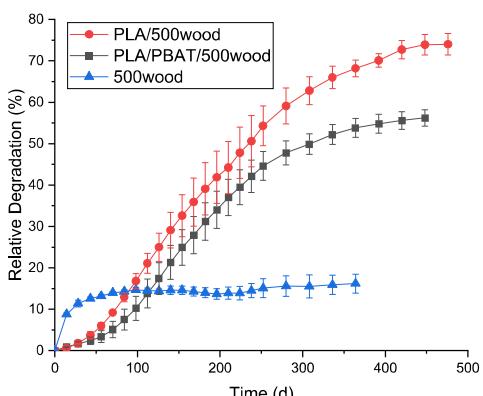


Common industrially used polymers presented as a function of degradation rate and source²



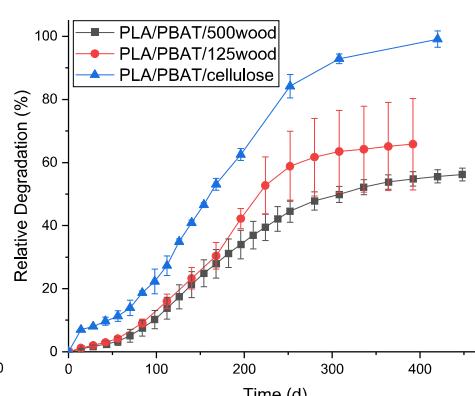
Schematic presentation of the degradation of PLA wood-composite

Marine degradation



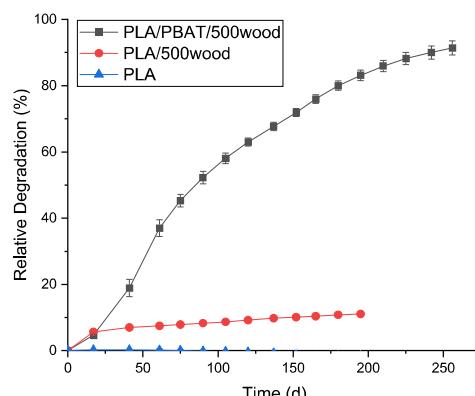
Marine degradation of PLA based wood-composites

Marine degradation



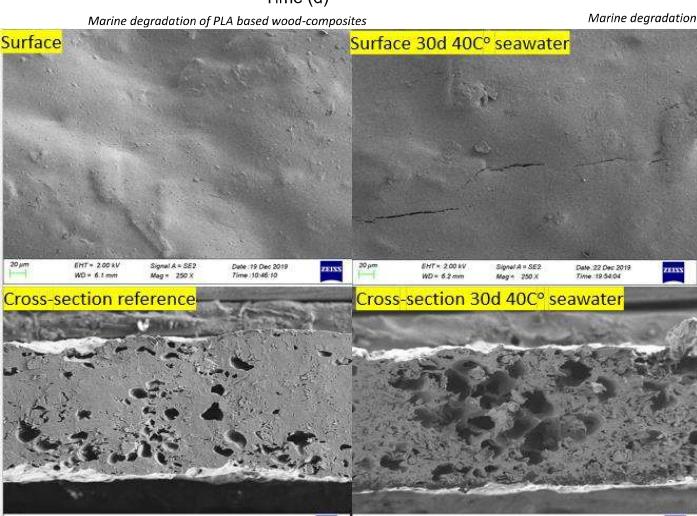
Marine degradation of composites with different fillers

Home compost



Degradation in Home compost environment of PLA based wood-composites

- Studies conducted based on ASTM ISO d6691 and ISO 14855
- Neither PLA nor PBAT is considered as home compostable.³
- In marine environment pure PLA takes decades to degrade.⁴
- Degradation of PLA can be increased in the different magnitude by addition of wood and enable by addition of PBAT.



Sample	Relative degradation (%)	Relative degradation of polymer matrix (%)	Time of the study (d)
PLA/PBAT/500wood	56,2±2,0	64,3±9,3	448
PLA/500wood	80,2±2,6	100,2±10,7	462
500wood	19,2±2,3	-	364
PLA/PBAT/125Wood	69,6±14,5	81,2±19,1	392
PLA/PBAT/Cellulose	99,1±2,6	100,3±3,4	420



What is left?

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Lignin of tomorrow by Stora Enso

Sunila Mill in Kotka, Finland is the world's first integrated lignin extraction plant to produce dry kraft lignin. There are many potential markets for lignin. It is firstly used to replace fossil-based fuel directly in the mill's lime kiln. Mill's CO₂ emissions are cut 40% by using lignin in firing. After processing, lignin can be used in battery material, carbon fiber products, as bio-based binding agent and in many applications to replace fossil-based products. *Finnish training School for LignoCOST CA17128 Anniina Tikkanen, Juha Oksanen Stora Enso*

Sunila Mill, Kotka Finland

Largest kraft lignin extraction plant in the world
Capacity 50 000t/year
Lignin produced at industrial scale since 2015
Lignin is extracted from softwood (pine and spruce)
Technology by Valmet LignoBoost®

Lignin at mill

Reduces recovery boiler load
Increases pulp production, if recovery boiler is bottleneck
Replaces fossil based fuel at lime kiln
Increases evaporation need
Sulphur/Sodium balance

Natural binder Lignin

Polymer of phenylpropane units
Carbon content 60–65% in softwood lignin
High heating value ~26 MJ/kg DS
Lignin is not a by-product, it need to be produced

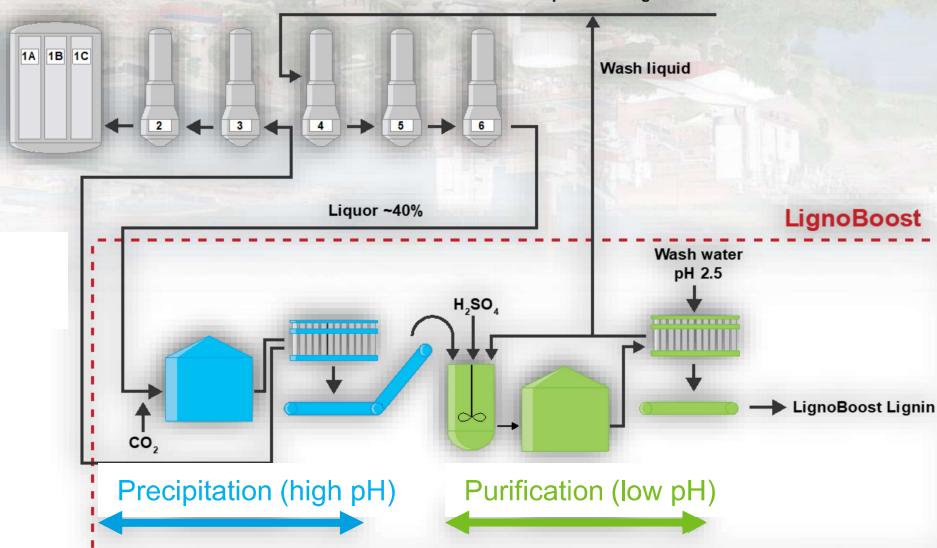
Step 1: Separation

Lignin is separated from mill's black liquor (BL)

Intermediate BL is taken from the evaporation plant

The pH of BL is reduced by using CO₂ and lignin starts to precipitate

Precipitated lignin is separated from BL at the first press filter



Step 2: Washing

Lignin is washed using a low pH solution

Lignin cake from the first stage is re-slurried and the pH lowered using H₂SO₄

The lignin slurry is dewatered in a second filter press

The lignin cake formed is washed for final purification

Lignin Products by Stora Enso

Lignode® hard carbon battery material
NeoLigno® bio-based binding agent
NeoFiber® renewable carbon fiber
Lineo® sustainable alternative for fossil-based products (for example in polymer or asphalt manufacturing)



Renewable



Bio-based



Made from sustainably managed forests



Fossil-free



Lignin (Stora Enso)

Lignin is separated from wood during the production of cellulose fibers.

Hard carbon powder (Stora Enso)

The lignin is refined into a fine carbon powder, which serves as an active material for the negative anode of the lithium-ion battery.

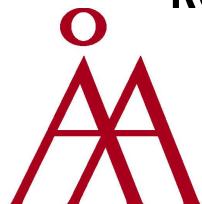
Hard carbon electrode

The hard carbon powder is then used to produce electrode sheets and rolls

Battery

Finally, the hard carbon electrodes are combined with positive electrodes, separator, electrolyte, and other components into a lithium-ion battery.

RUTHENIUM-CATALYZED TRANSFER HYDROGENATION PROCEDURE FOR SELECTIVE MODIFICATION OF HYDROXYL GROUPS IN LIGNIN MODEL COMPOUNDS



Veronika D. Badazhkova, Risto Savela and Reko Leino

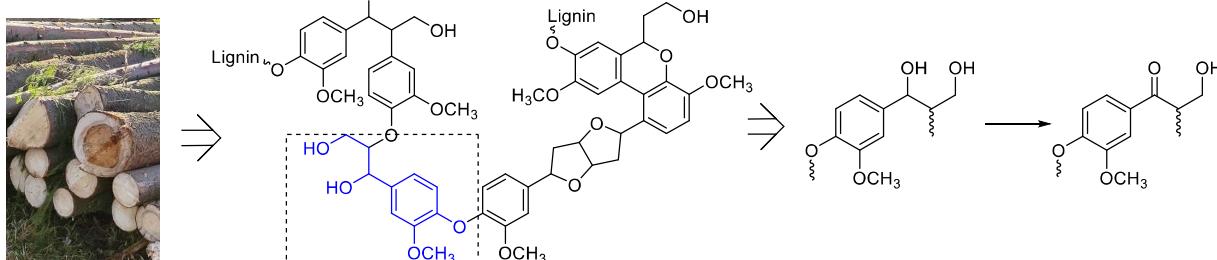
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Introduction

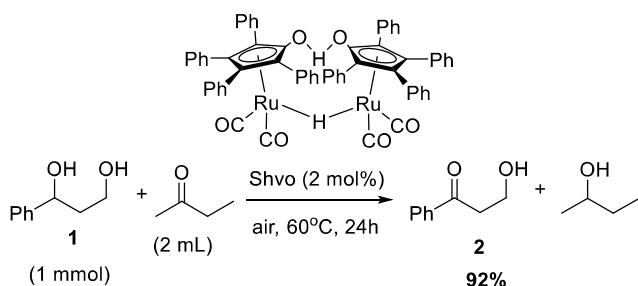
Lignin - the nature's aromatic polymer is one of the potential sustainable feedstocks for fuels and material manufacturing processes. Chemical modification of lignin functional group is the way for improving lignin stability and imparting desirable properties for further synthesis of novel materials and lignin-based biologically active compounds.

In this project, we have investigated the selective modification of monomeric lignin model compounds by ruthenium catalyzed hydrogen borrowing reaction methodology. The preliminary results obtained suggest feasibility of the method also for oxidation of native spruce milled wood lignin.

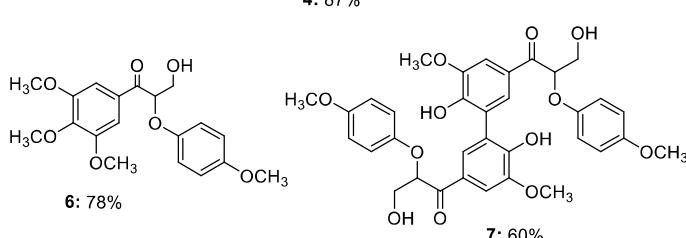
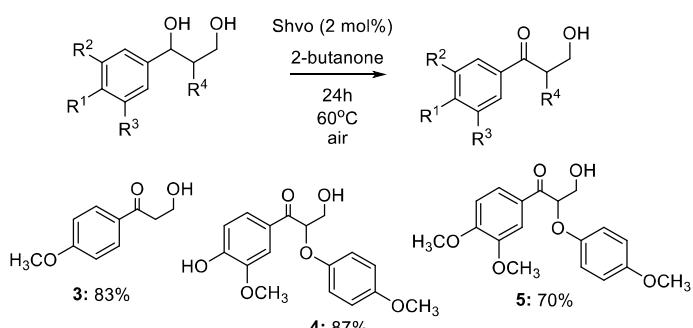


Experimental part

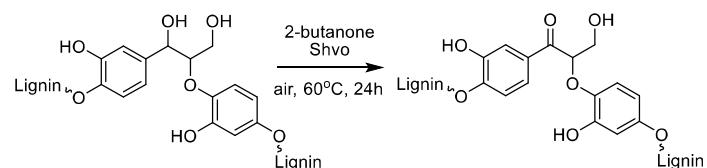
- Shvo-catalyzed transfer hydrogenation screening using the 3-phenyl-1,3-propanediol model compound



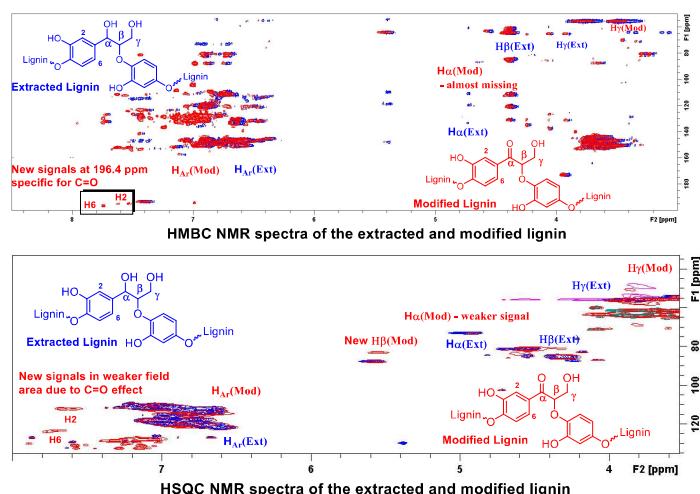
- Application of Shvo-catalyzed transfer hydrogenation reaction to lignin model monomers



- Application of Shvo-catalyzed transfer hydrogenation reaction to lignin extracted from milled spruce sapwood



- Extracted and modified lignin analysis using 2D NMR spectroscopy to confirm the efficiency of the reaction



Conclusion

We have developed a feasible methodology for selective functionalization of diol fragments in lignin model compounds, using a ruthenium-catalyzed hydrogen borrowing procedure. After screening of the model compounds, this methodology was applied to native lignin, resulting in selective modification of the benzylic hydroxyl groups.

Main funding: Suomen Luonnonvarain Tutkimussäätiö – Finnish Natural Resource Research Foundation 2020-22.

Related publications: Badazhkova, V.; Savela, R.; Leino, R. *Dalton Transactions* 2022; DOI: 10.1039/D2DT00267A.

A formulation synthesis toward bio-based packaging material: in situ polymerization of lignin in fibre suspension at controlled conditions

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INTRODUCTION

Plastics are widely used for packaging and other applications in our daily life, which have brought up many societal benefits.¹ Yet, most of the plastic products have an extremely short lifetime and have ended up as for single-use.²

Lignocellulosic biomass have been identified to be a more promising source for bioplastics over past years.^{3,4} Furthermore, most cases where lignin is used in packaging materials requires binary mixtures and cross-linkers to satisfy the application requirements, e.g. in barrier and mechanical strength.⁵ Herein, we provide a route to a formulation for the bio-based packaging materials, which is synthesized with polymerized lignin from *in-situ* polymerization in fibre suspensions at controlled conditions, as shown in **Figure 1**.

MATERIALS AND METHODS

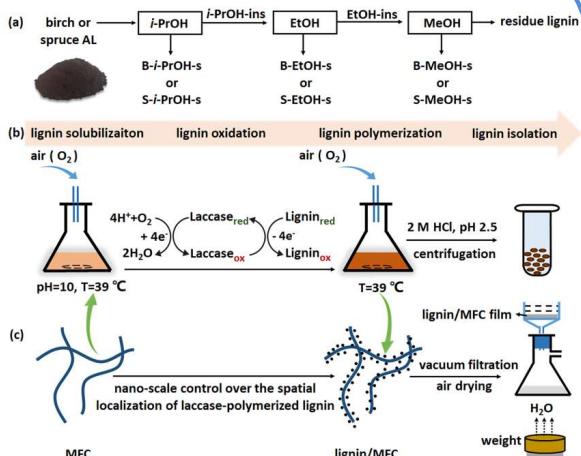


Figure 1. Representative schemes for the (a) preparation of well-defined AL fractions by sequential solvent extraction, (b) laccase-catalyzed polymerization of lignin fractions in an alkaline aqueous solution, and (c) *in situ* alignment of laccase-polymerized lignin on the surface of MFC as well as the fabrication of the lignin/MFC film.

RESULTS

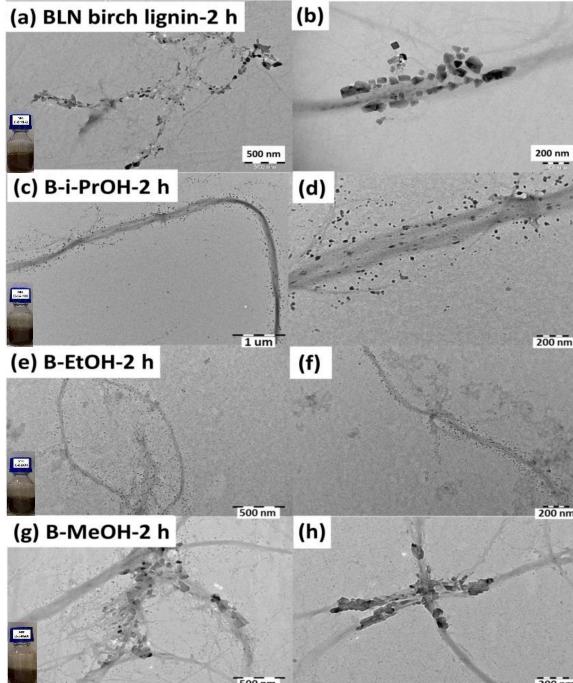


Figure 2. TEM images of spatial confinement of the laccase-polymerized lignin (15%) on micro-fibrillated cellulose (MFC) fibers



Figure 3. Photograph of the translucent lignin/MFC nanocomposite films (a) directly on top of the background and (b) rolling of the 15-B-i-PrOH film to demonstrate good mechanical robustness.

Table 1. Mechanical and barrier properties of cellulose/lignin films

	MFC	15-B- <i>i</i> -PrOH	15-B-EtOH	15-B-MeOH
Young's modulus (GPa)	3.03±0.1	3.41±0.3	3.16±0.5	3.72±0.4
tensile strength at break (MPa)	81.66±4.2	76.83±3.9	63.66±2.2	92.45±8.5
strain at break (%)	7.3±1.3	6.5±1.6	6.2±1.0	6.4±2.6
WVTR (g/m ² /day)	212.2±3	178.8±4	202.2±3	210.3±10
Water contact angle (°)	43.9±5.5	50.4±2.1	55.8±2.2	46.9±1.7
Surface free energy (mJ/m ²)	54.7	49.5	45.7	53.2

ACKNOWLEDGMENTS

Business Finland Project (43674/31/2020) is acknowledged for the research funding to the current work. CH-Bioforce Oy (Espoo, Finland) is thanked for providing birch and spruce ALs. MetGen Oy (Kaarina, Finland) is thanked for supplying the industrial bacterial-derived alkaliophilic laccase MetZyme. This work is also part of activities within the Johan Gadolin Process Chemistry Centre (PCC) at ÅAU.



Nanosphere of laccase-polymerized lignin as carrier for AgNPs in constructing antimicrobial hydrogel via DLP 3D printing^[1]



Luyao Wang,¹ Qingbo Wang,¹ Anna Slita,² Oskar Backman,¹ Zahra Gounani,³ Emil Rosqvist,⁴ Jouko Peltonen,⁴ Stefan Willför,¹ Chunlin Xu,¹ Jessica M. Rosenholm² and Xiaoju Wang^{*1,2}



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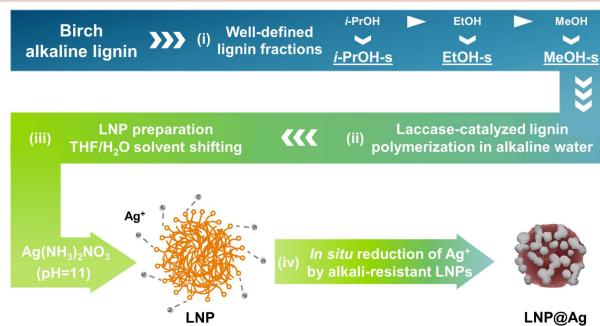
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Motivation & Challenges

The exceptional characteristics of spherical lignin nanoparticles (LNPs), such as durable dispersity in water, surface functionality (-OH, -OCH₃), and large specific surface area, have attracted a heightened interest in integrating this nano-sized polyphenol into biomaterials.

However, the insufficient resistance of LNPs to high pHs and certain organic solvents has prevented their surface functionalization in a dispersion state and applications where maintaining nanosphere morphology intact under harsh conditions is demanded.

i. Laccase-catalyzed lignin polymerization



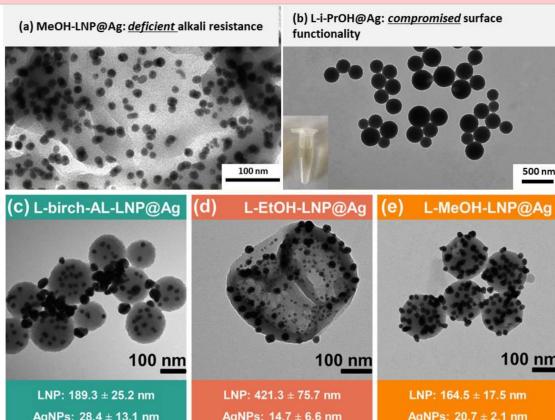
Enzymatic lignin valorization strategy (bacterial-derived alkaliphilic laccase; 39 °C; pH 10 aqueous medium)

- Environmentally more acceptable than chemical and thermal methods
- Require less energy input; Operate most often under mild conditions in the absence of toxic solvents

LNPs fabricated from laccase-polymerized lignin exhibit enhanced alkali resistance

- Oxidative radical-radical coupling raised lignin condensation with the formation of robust interunit carbon-carbon linkages
- More than 80% LNPs could be retained as uniformly nanosized lignin under pH 11

ii. Fractionation-dependent lignin polymerization kinetics



Molar mass of lignin fractions: i-PrOH-s < EtOH-s < MeOH-s < birch AL

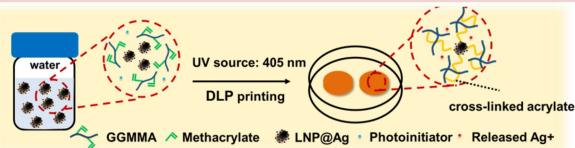
Molar mass increase of polymerized lignin: L-i-PrOH-s (6.6-fold) > L-EtOH-s (2.9-fold) > L-birch AL (2.8-fold) > L-MeOH-s (2.2-fold)

Lignin sequential solvent fractionation plays a balancing role:
Laccase-catalyzed lignin polymerization → consume phenolic-OH and –OCH₃ → sufficient alkali-resistance
In situ Ag⁺ reduction → require phenolic-OH and –OCH₃ on LNPs surface

Objectives

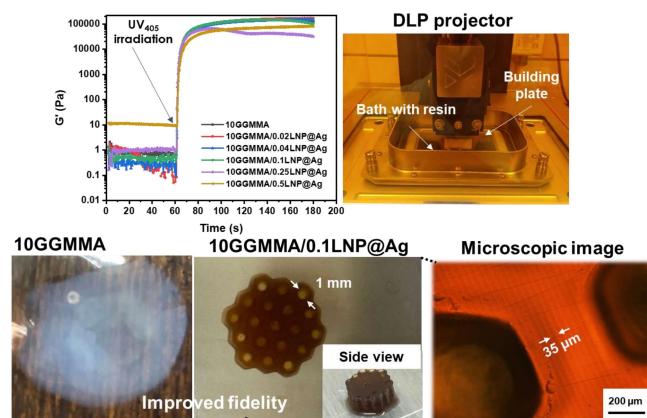
- Develop a simple and green method to tailor the structural and chemical features of lignin to provide **LNPs with dispersion stability and functionality under harsh conditions**
- Fabricate functional and robust biopolymer-based nanosphere for *in situ* reducing silver ions (Ag⁺) from silver ammonia solution (pH 11)
- Construct antimicrobial hydrogel with sustainable resin via lithography-based 3D printing technology

iii. Construct antimicrobial hydrogel via 3D printing



Formulation of photocurable resin

- Main polymeric matrix: methacrylated O-acetyl-galactoglucomannan (GGMMA) → photocrosslinkable biopolymer
- 90 wt% water; 10 wt% GGMMA and 0.1 wt% LNP@Ag loading; 0.25 wt% photoinitiator (lithium phenyl-2,4,6-trimethylbenzoylphosphinate)



Performance of natural-polymer-based resin/hydrogel

- Fast-photocurable property
- AgNPs has a strong UV absorption at 400-500 nm, which encompasses the UV₄₀₅ light source → AgNPs in GGMMA resin served to mitigate excess light penetration into the honeycombs, performing as a "photo-absorber" → Improve printing fidelity
- Strong antibacterial activities against both *E. coli* and *S. aureus*

Conclusions

- The alkali-resistance of LNPs as demanded for *in situ* reduction of silver nanoparticles (AgNPs) from silver ammonia solution (pH 11) was achieved by upgrading the technical lignin via a combination of lignin solvent fractionation with laccase-catalyzed polymerization.
- Importantly, this work provides a new frontier in lithography-based DLP printing research focusing on natural-polymer-based resin with good structural stability and printing fidelity.

Reference: [1] L. Wang, et al. (2022). Green Chemistry, 24(5), 2129-2145.

CH-Bioforce Oy (Espoo, Finland) and MetGen Oy (Kaarina, Finland) are acknowledged for providing lignin and laccase, respectively.

Modification of lignin to enhance its compatibilization with PLA

By Lulu Zhu, Natural Materials Technology, Åbo Akademi University

Introduction



- polylactic acid (PLA)
- polycaprolactone (PCL)
- poly(hydroxybutyrate)(PHB)
- poly(3-hydroxybutyrate-cohydroxyvalerate)(PHBV)
- poly (hydroxylalkanoates)(PHA)
- cellulose
- Starch
-

Biodegradable thermoplastic polymers

But large demand for these biobased polymers can affect current food related feedstocks!!

Large quantities of lignin are produced from the biorefineries and pulp and paper industries as byproduct and do not interfere with the food related feedstock. Utilization of lignin into thermoplastic polymers is cost effective and promising biodegradable alternative for the petroleum based thermoplastic polymers.

Lignin

- Polyphenolicity: it is easy to derive and participate in cross-linking reactivity
- Strong UV absorption and free radical quenching ability
- Biocompatibility and antibacterial activity
- Biodegradable

Lignin - thermoplastic material

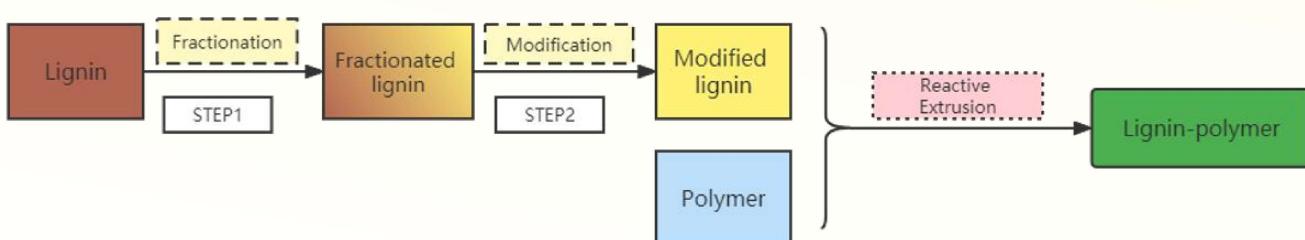
- Antioxidant
- UV protection
- Weathering resistance
- Anti-aging
- Antibacterial
- Biodegradable

The addition of lignin can improve the mechanical properties of thermoplastic materials
It can improve tensile strength, impact strength and elongation at break

However

- Lignin has heterogeneity and its structure is uncertain
- Lignin is poorly dispersed in polymers
- The high Tg of lignin has high thermal stability, but the thermal processability decreases

- Fractionation
- Compatibilization
- Modification



Flow chart of research ideas for the development of lignin-polymer composites



A New Methodology to Elucidate Lignin Structure-Properties-Performance Correlation

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INTRODUCTION

Unveiling the interrelation between lignin structure, its properties and performance in specific applications is of primary importance for lignin engineering for high-value products. Herein, we suggest a new efficient methodology to quantitatively evaluate the roles of lignin specific functionalities in selected applications. The method consists in changing only one structural variable at a time, while keeping all others constant prior to performance evaluation.

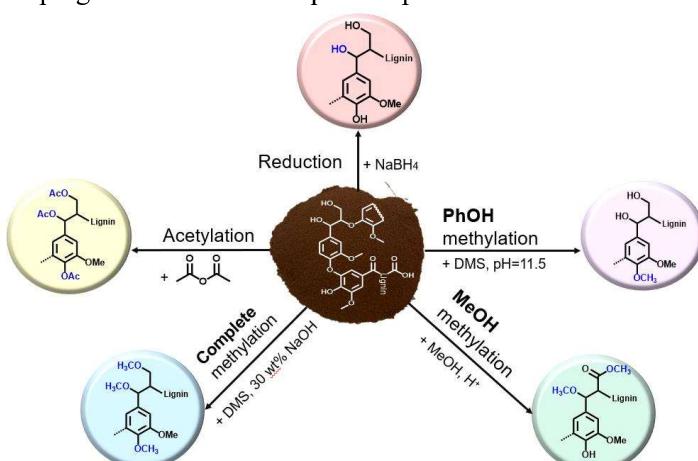


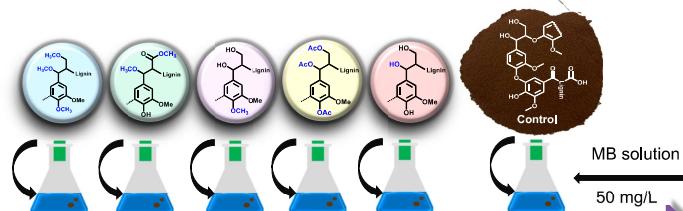
Fig. 1. Reactions used for selective masking of specific lignin functionalities

EXPERIMENTAL

Indulin AT was chosen as a lignin substrate as the main type of commercially available lignin standard (softwood Kraft). The modifications reactions were carried out by earlier developed protocols [1,2,3] (Fig. 1) and analyzed by a comprehensive NMR methodology [2].

Methylene Blue (MB) Adsorption

The aim of the experiment is to elucidate structure – performance correlation. The test was performed by the earlier reported protocol [4] at MB concentration of 50 mg/L.



Differential Scanning Calorimetry (DSC)

DSC was employed to measure the glass transition temperature (Tg).

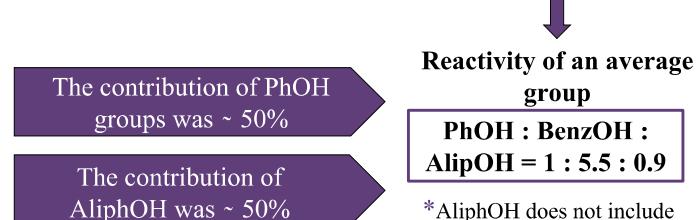
RESULTS AND DISCUSSION

Lignin performance as a sorbent

- The contribution of OH groups in lignin sorption capacity was crucial.
- The role of the other functionalities (including COOH and CO) was negligible.

Table 1. Amount of main lignin functionalities in Indulin AT (per 100Ar) [5]

PhOH	AlipOH	Sec.OH	β -O-4	Total OH	COOH	CO
66	49	18	7	115	17	15



* AliphOH does not include BenzOH

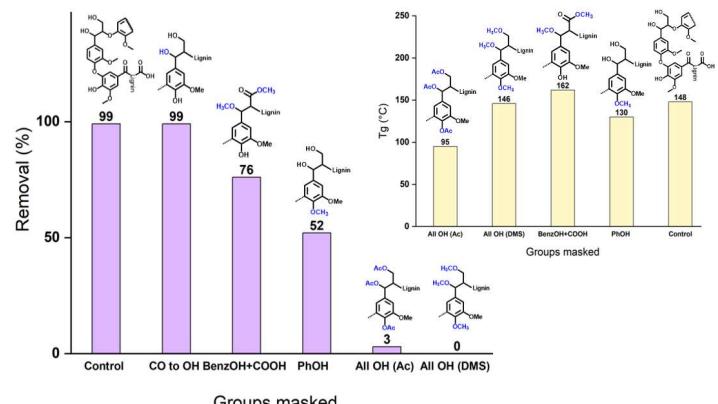


Fig. 2. The effect of lignin functional groups on Tg and sorption performance

Conclusions

- The correlation between specific lignin functionalities based on its Tg and sorption were used as demonstrators.
- OH groups play the key role in lignin sorption performance.
- PhOH and AlipOH contribute equally.
- From the AlipOH groups, the benzylic OH showed the highest activity.

Acknowledgement

Support from the Academy of Finland (grant 341596), Carl Tryggers Stiftelse (CTS 20:1701) and Formas (2020-02321) is greatly acknowledged.

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From biomass and lignin fractionation to controlled fabrication of lignin nanoparticles (LNPs)

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Introduction

Lignin, as the most abundant aromatic biopolymer in nature, has attracted great attention due to the complexity and richness of its functional groups for value-added applications. The yield of production of lignin and the reactivity of prepared lignin are very important to guarantee the study and development of lignin-based chemicals and materials. Various fractionation techniques have been developed to obtain high yield and relatively high-purity lignin as well as carbohydrates (hemicelluloses and celluloses) and to reduce the condensed and degraded nature of conventional biorefinery lignin^[1]. Herein, novel and efficient biomass fractionation and lignin fractionation towards lignin valorization are summarized and discussed (Figure 1).

In addition, the development of lignin micro- and nanoparticles (LNPs) not only cleverly avoided the heterogeneity of lignin, but also endowed it with a variety of properties of nanomaterials which greatly expands the application of lignin in many fields^[2]. Enlightened by the unique solubility of industrial lignin and the forming conditions of LNPs, we here report a simple but rapid and reversible approach for the fabrication of LNPs via switching pH values (Figure 2,3,4).

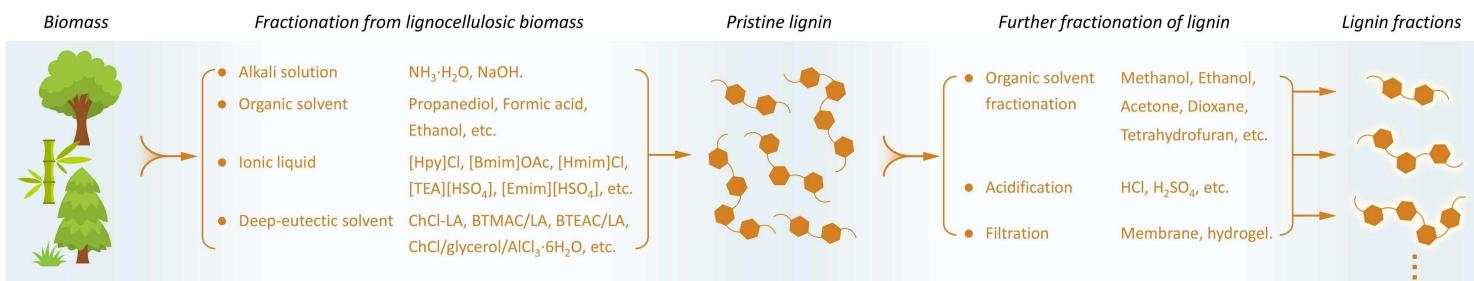


Figure 1. Schematic illustration of the approaches of fractionation of lignin.

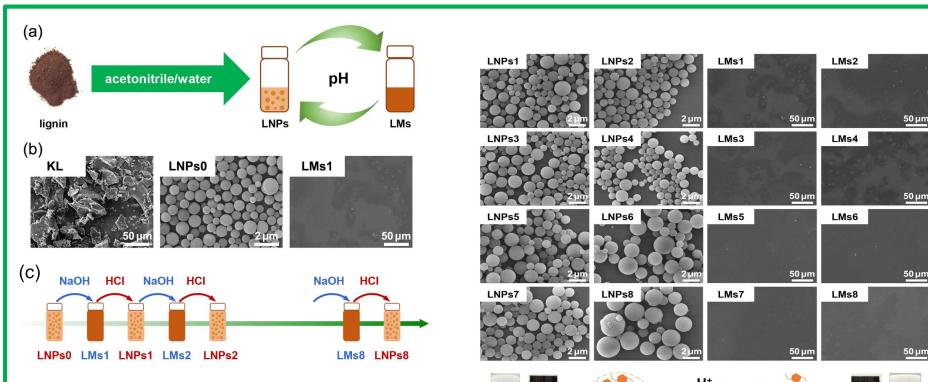


Figure 2. (a) Schematic illustration of the preparation of lignin nanoparticles (LNPs) and lignin molecules (LMs) in acetonitrile/water binary solvent. (b) SEM images of KL, LNPs0, and LMs1. (c) Schematic of the alternation of forming and dissolving of LNPs.

LNPs: lignin nanoparticles **LMs:** lignin molecular solution

Figure 3. SEM images of regenerated LNPs (left, after adding HCl) and dissolved LMs (right, after adding NaOH).

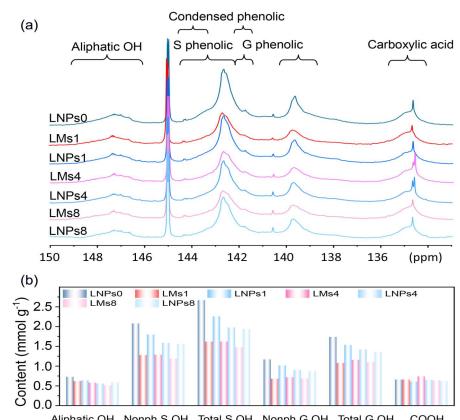


Figure 4. (a) Quantitative ³¹P NMR spectra. (b) Content of hydroxy (-OH) and carboxyl groups (-COOH) of LNPs and LMs.

Results and conclusions

Efficient lignin fractionation could play a critical role in lignin valorization, which can lead to higher profits for pulp and paper industries and second-generation biorefineries as well as a better understanding of lignin chemistry. Most importantly, fractionation improves lignin valorization but should not result in greater waste such as solvent recovery.

One simple, rapid, and reversible approach for the fabrication of lignin nanoparticles (LNPs) was developed. In the acid and neutral acetonitrile/water system, the LNPs with regular spherical shape showed good properties of dissolution and regeneration, respectively. This procedure can be rapidly repeated many times simply by alternately adding acid and alkaline solutions without destroying the molecular structures of lignin.

References

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Acknowledgements

The Key Laboratory of Horticultural Plant Genetic and Improvement of Jiangxi Province, Key Technology Research and Development Program of Tianjin (19YFZCSN00950), Tianjin Enterprise Technology Commissioner Project (19JCTPJCS2800), National Natural Science Foundation of China (32171717, 32071720, 21706193), the Young Elite Scientists Sponsorship Program (YESS20200389, TJSQNTJ-2017-19), the China Postdoctoral Science Foundation (2021M692402), and China Scholarship Council (202008120139) are acknowledged.

Characterization of organosolv lignin using GC-MS, solution NMR in combination of PCA as a tool for data visualization

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1. Introduction

Lignin is a highly cross-link network polymer with a native aromatic-enriched structure that benefit them as a renewable and sustainable source of chemicals^[1].

Due to the inherent complexity of lignin and its alteration during extraction process, it is challenging to maximize the usage of lignin without clarifying its structural information. Among other techniques, GC-MS and NMR are well-known methods to provide a well-established picture about lignin.

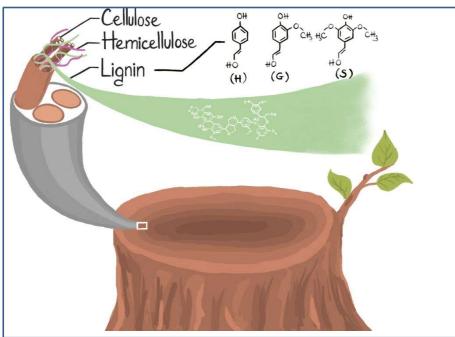


Figure 1. Lignocellulosic biomass and its components including cellulose, hemicellulose and lignin. P-hydroxyphenyl (H); guaiacyl (G) and syringyl (S) are three fundamental monolignols building up lignin.

2. 2D-HSQC

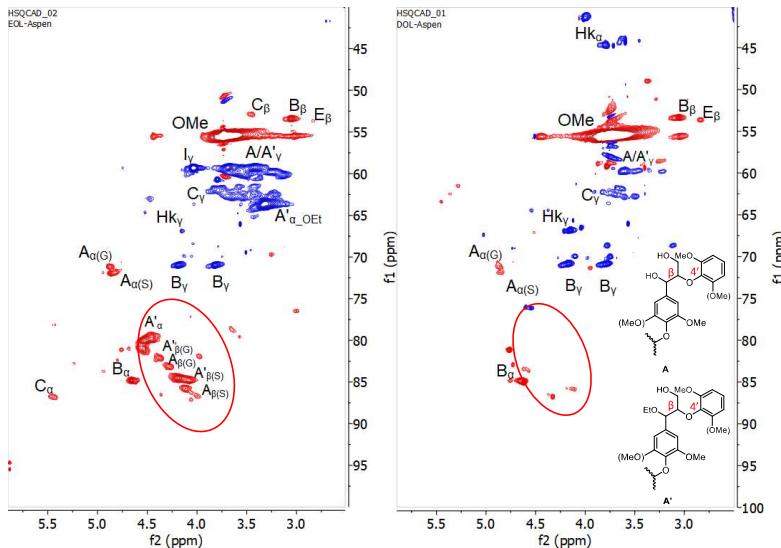


Figure 2. HSQC of ethanol organosolv (left) and dioxane organosolv (right) lignin from aspen in oxygenated-aliphatic side chain region ($^3\text{C}/\delta\text{H}$ 100–40/6.0–2.5 ppm). Red cross peaks are CH_3 and CH_2 ; blue cross peaks are CH_2 ^[2]

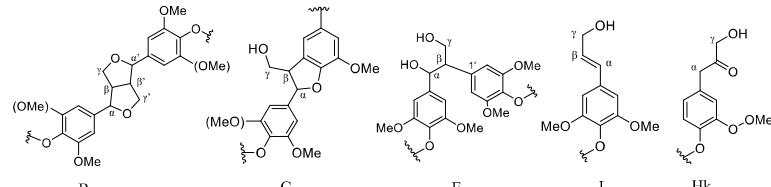


Figure 3. (A) β -O-4' alkyl-aryl ethers; (A') β -O-4' alkyl-aryl ethers with ethoxylated α -OH; (B) resins; (C) phenylcoumarans; (E) β -1' linkage; (I) cinnamyl alcohol-end groups; (Hk) Hibbert's ketone (end-group).

3. ^{31}P NMR & principal component analysis (PCA)

^{31}P -NMR data provides information about total hydroxyl contents from aliphatic side chain, carboxylic acid, and phenolic groups of isolated lignin.

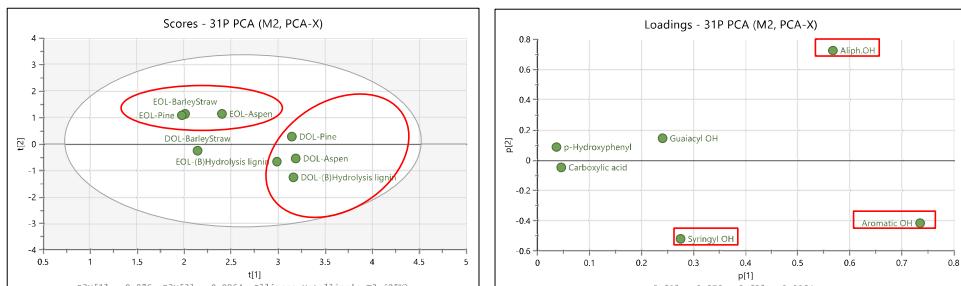


Figure 4. 8 observations (lignin from different originates extracted by ethanol/dioxane) together with 6 variables (-OH groups) are projected by PCA using SIMCA16. Score plot (left) and loading plot (right) visualizing ^{31}P NMR data of organosolv lignin.

4. GC-MS

Thioacidolysis is well-known as a chemical degradation method to determine the amount of *uncondensed monolignols* that connected via β -O-4' linkage in lignin.

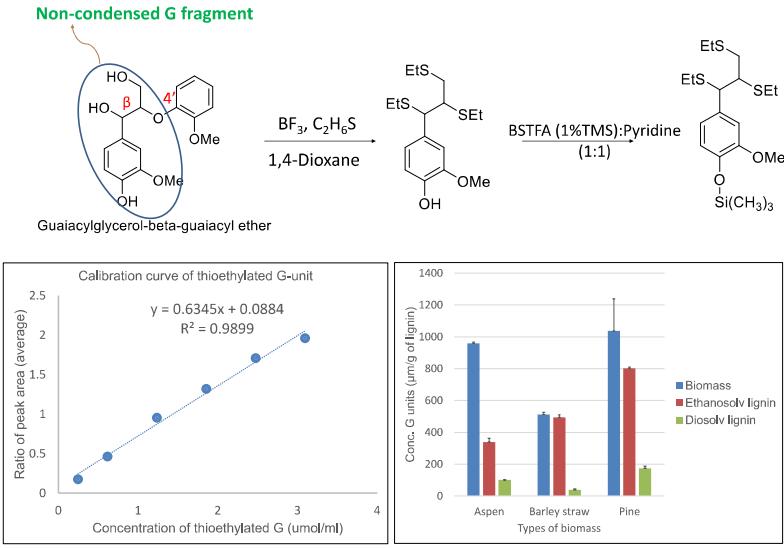


Figure 5. Calibration curve was built from model compound (three replicates for each point, $R^2 = 0.989$, max RSD%<5%) (left) for quantitatively estimation of non-condensed G units; and the bar chart (right, two replicates for each sample) for comparison of uncondensed G units from the biomass and its organosolv lignin extracted by ethanol (red), dioxane (green), respectively.

5. Conclusions

- 2D-HSQC is a powerful tool to reveal interlinkages of isolated lignin.
- ^{31}P NMR shows the variation in hydroxyl contents of lignin.
- β -O-4' linkages are broken down more vigorously under dioxane extraction condition.
- Content of uncondensed guaiacyl unit (G) in lignin significantly varies compared to its biomass source.

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Catalytic Oxidation of Lignin to Valuable Chemicals

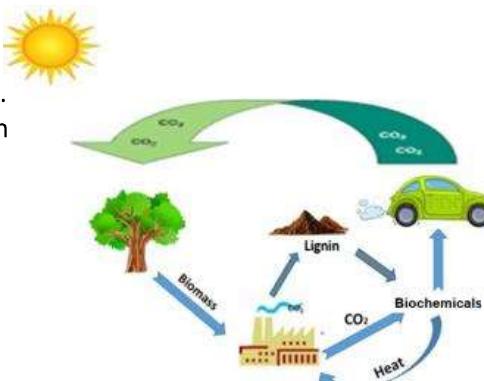
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Background

Lignin is the sustainable aromatic resource with large volume in nature. It contains amounts of carbon-carbon and aryl ether bonds with high bond energy, which makes it difficult to be converted [1]. It is a by-product from the paper and pulp industry. In the investigation of oxidative depolymerization, heterogeneous and homogenous catalysis have shown great potentials [2].

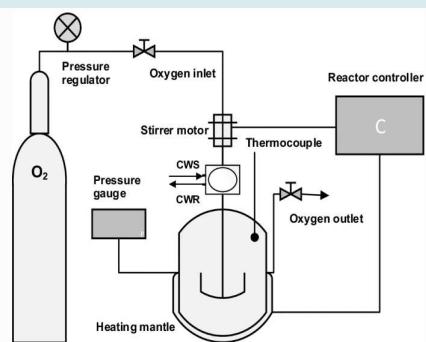


CuMn/δ-Al2O3 catalysts

Recently, promising results were achieved where lignin was converted into valuable chemicals via catalytic oxidative depolymerization process. The results were obtained on a laboratory scale. Using CuMn/δ-Al₂O₃ catalyst showed great potentials, but further development and tuning of the experimental conditions are needed to improve yields of monomers. A detailed understanding of the catalyst and its properties is needed to improve the performance of the catalyst.

Experimental setup

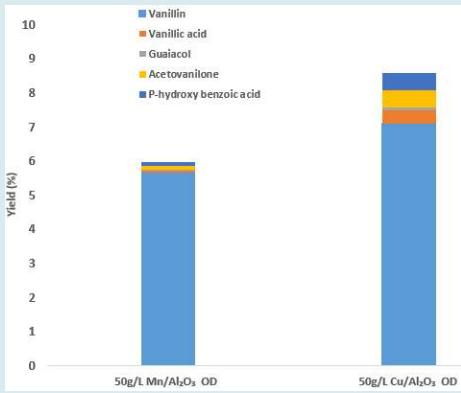
Batch flow setup system



Schematic diagram of continuous flow system [3].

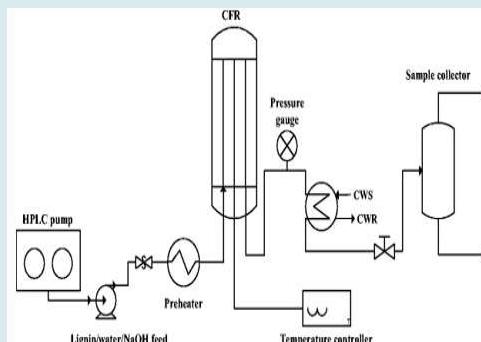
Results

Ultra Performance Liquid Chromatography results showing monomers yields.



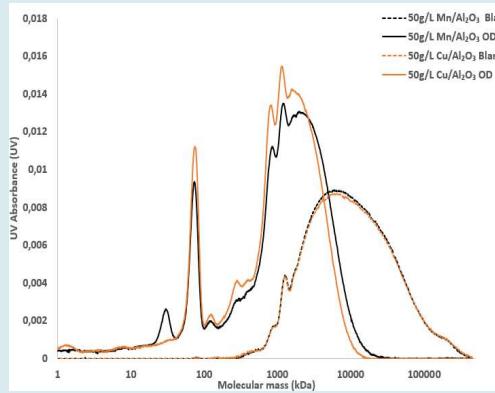
The UPLC results from the batch system shows monomer yields after catalytic oxidative depolymerization of lignin using 5 wt% Mn/δ-Al₂O₃ and 5 wt% Cu/δ-Al₂O₃ catalysts. From both catalysts, Cu/δ-Al₂O₃ showed better monomers production with 50 g/L of lignin.

Continuous flow setup system



Schematic diagram of continuous flow system [4].

Size Exclusion Chromatography results showing degree of depolymerization.



The SEC results from the batch system shows the molecular weight distribution of both the blanks and products obtained from the catalytic oxidative depolymerization of lignin at 200 °C using 5 wt% Mn/δ-Al₂O₃ and 5 wt% Cu/δ-Al₂O₃ catalysts. Depolymerised product show the molecular weight shifts to lower values.

Conclusion

- The Cu/δ-Al₂O₃ catalyst has shown good results in the conversion of lignin to valuable chemicals like vanillin.
- Both batch and continuous flow systems have shown potentials in the heterogeneous and homogenous catalyst systems.
- Both UPLC and SEC results have shown promising yields and depolymerization in the catalytic conversion of lignin to valuable chemicals.

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Utilization of Lignin Carbohydrate Complexes in 3D Printing: Structure and Surface-Active Correlation

INTRODUCTION

Doctoral student:

Marie Alopaeus

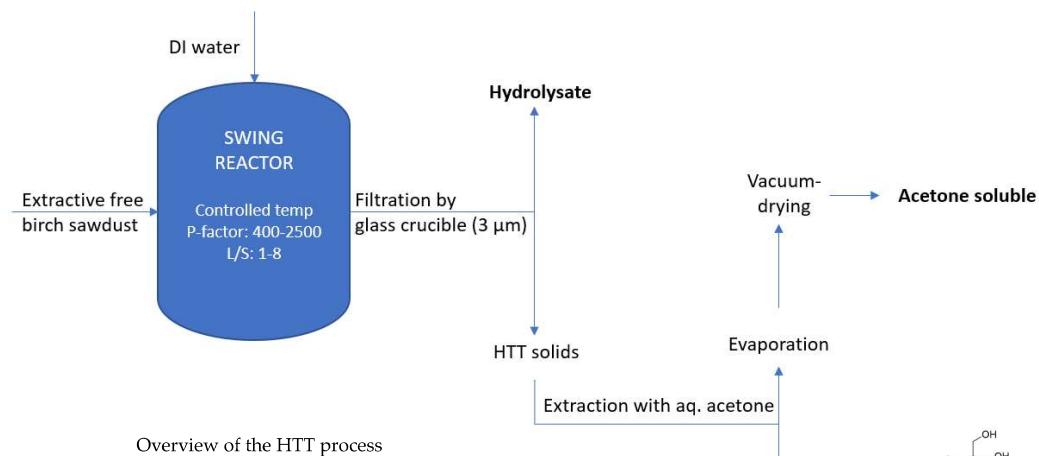
Main supervisors:

Prof. Chunlin Xu

Docent Patrik Eklund

Hydrothermal treatment (HTT) of wood material is a biorefinery process that generates lignin as a by-product, that can be used for low-value applications. Recently Balakshin *et al.* have presented an HTT process where all streams can be utilized for producing lignin as potential high-value products. Furthermore, under specific HTT conditions, lignin-carbohydrate complexes (LCCs) were generated with higher yields than reported earlier. LCCs are a promising material for producing high-value materials as it possesses properties of both lignin and carbohydrates. Due to these properties, LCC's is a promising feedstock for 3D printing.

BACKGROUND



OBJECTIVES

Comprehensive analysis of LCCs, lignin and hemicellulose

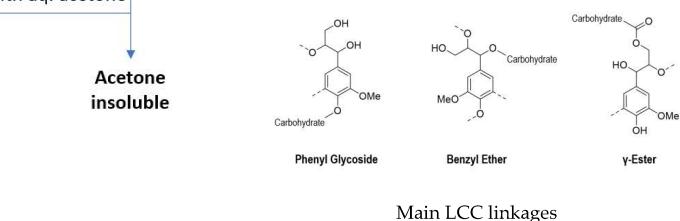
Structures will be investigated with different NMR methods, i.e., ^{13}C , ^1H and ^{31}P and HSQC NMR. By different wet chemistry techniques, hemicellulose components, carbohydrate linkage sites (by methylation), degree of acetylation (by HPLC) and molecular weight distribution (by SEC-MALLS) can be studied and determined. The monomeric and oligomeric carbohydrate content as well as their degradation products can be analyzed by HPLC.

Development of new ink formulations

Samples containing extracted fibers will be defibrillated to form a hydrogel of lignin nanocellulose (LNC). The rheology of the formulation will be determined by a Rokit Invivo direct ink writing (DIW) bioprinter. The 3D scaffolds with varied properties will be prepared. The printability and ink fidelity of the formulation would be studied with a DIW bioprinter.

Thermoplastics

LCC-PLA blends will be made by a solvent blending approach. Different ratios of LCC and PLA will be extruded into filaments and parameters such as melting point, shear viscosity and storage modulus will be investigated. The obtained values will be given to an AI model. Selected filaments will be further used for fused deposition modelling (FDM) printing to make 3D scaffold prototypes. DSC analysis and three-point-bending tests will be performed to evaluate the printing temperature, mechanical properties and printability of the filaments. By comparing the parameters with the LCC structure, the structure-performance correlation could be established. With the aid of the AI, key parameters and correlations (e.g., LCC:PLA ratio) can be predicted.



EXPECTED RESULTS

- Provide significant information on the use of bio-based materials in making thermoplastics and in 3D printing
- Characterization and alteration of LCC properties to meet the need for rheological properties and functionalities needed for ink formulations for 3D printing
- To be able to use LCC-based materials in advanced applications with superior performance

Scaling up nanofiltration of kraft black liquor for lignin recovery

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Introduction

Lignin, and specifically low molecular weight lignin, is an underutilized resource from the pulp and paper industry with the potential of being a significant raw material for renewable fuels and chemicals. Lignin can be separated from the kraft black liquor by membrane processes. Two steps are required to get the low molecular weight lignin: ultrafiltration (UF) and nanofiltration (NF) (Figure 1). The aims of this study are:

- Select a membrane for pilot scale studies based on flux and lignin retention parameters at laboratory scale
- Test the selected membrane at pilot scale at two different conditions and assess the scalability of the NF step based on the data obtained

Results

- Lignin retention was higher at laboratory scale than at pilot scale, but a slight decrease was expected due to the change of membrane module configuration.
- Similar lignin retentions were obtained for both pilot scale studies, with condition A giving a slightly higher lignin retention than B (Table 1).

Table 1: Volume reduction achieved (VR) and lignin retention at the VR achieved for both laboratory and pilot scale concentration studies.

		VR reached	Lignin retention
Laboratory scale	A	35%	SelRO MPF-36: 92.2% NF090801: 94.5%
	B	30%	SelRO MPF-36: 83.5% NF090801: 91.7%
Pilot scale	A	80%	NF090801: 81.8%
	B	80%	NF090801: 81.5%

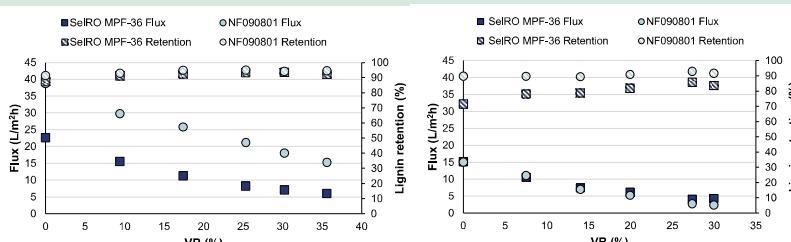


Figure 2A: Flux and lignin retention vs VR for lab scale concentration study at condition A.

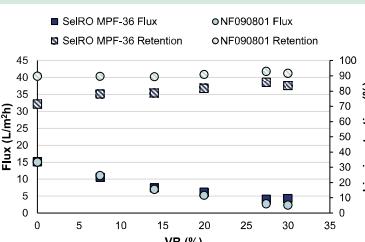
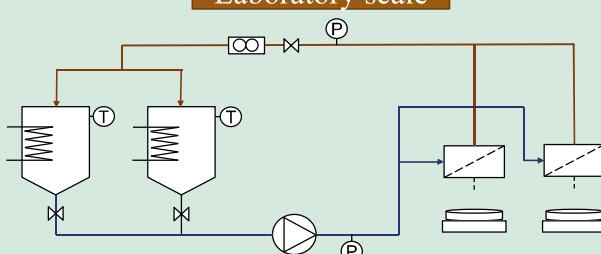


Figure 2B: Flux and lignin retention vs VR for lab scale concentration study at condition B.

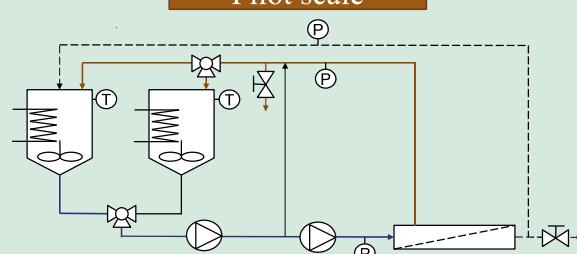
Methods

Laboratory scale



Conditions	Membranes tested
A: 50°C, 35 bar	Flat sheets: - SelRO MPF-36 (Koch Membrane Systems)
B: 70°C, 15 bar	- NF090801 (SolSep BV)

Pilot scale



Conditions	Membrane tested
A: 50°C, 25 bar	Spiral wound module: NF090801 (SolSep BV)
B: 70°C, 15 bar	

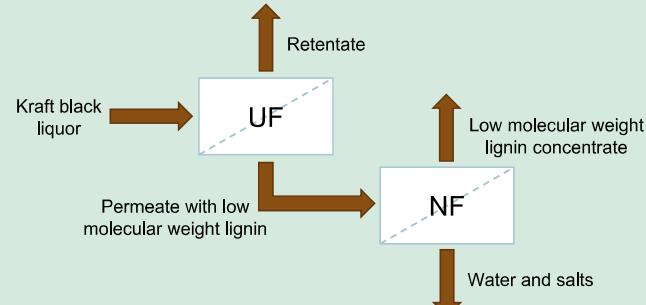


Figure 1: Two-step membrane processes for the separation of low molecular weight lignin.

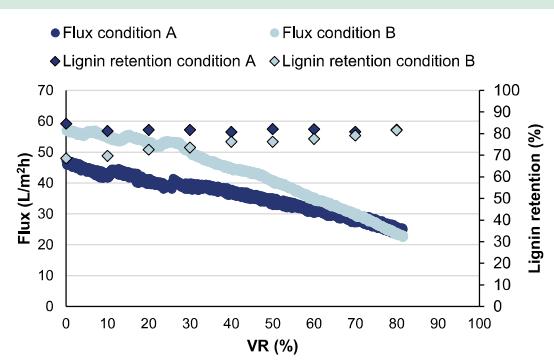


Figure 3: Flux and lignin retention vs VR for NF090801 spiral wound module in pilot scale concentration studies at conditions A and B.

Conclusions

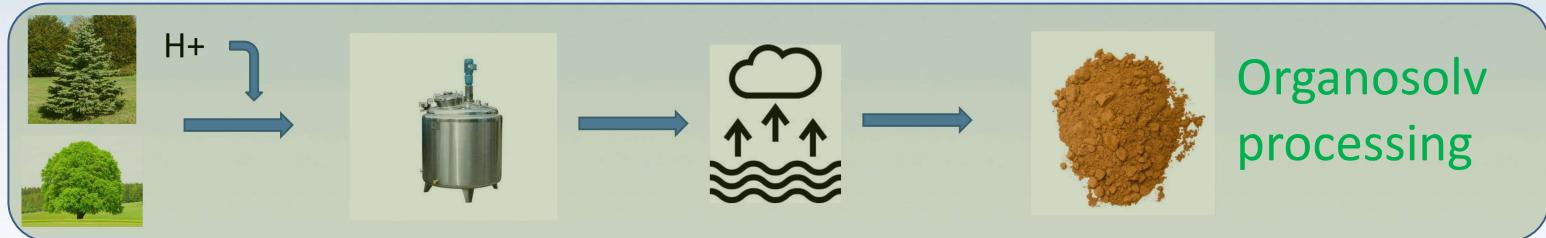
- Based on laboratory scale results, the NF090801 membrane was selected for the on-site pilot scale experiments in spiral wound module configuration.
- The pilot scale experiments demonstrated that it is possible to scale up the NF step, and that combined with a previous UF step, high lignin yields from kraft black liquor can be achieved.
- The pressure and temperature conditions need to be further optimized for operation at pilot scale.

Solvent fractionation of acid catalysed organosolv beech and spruce lignins

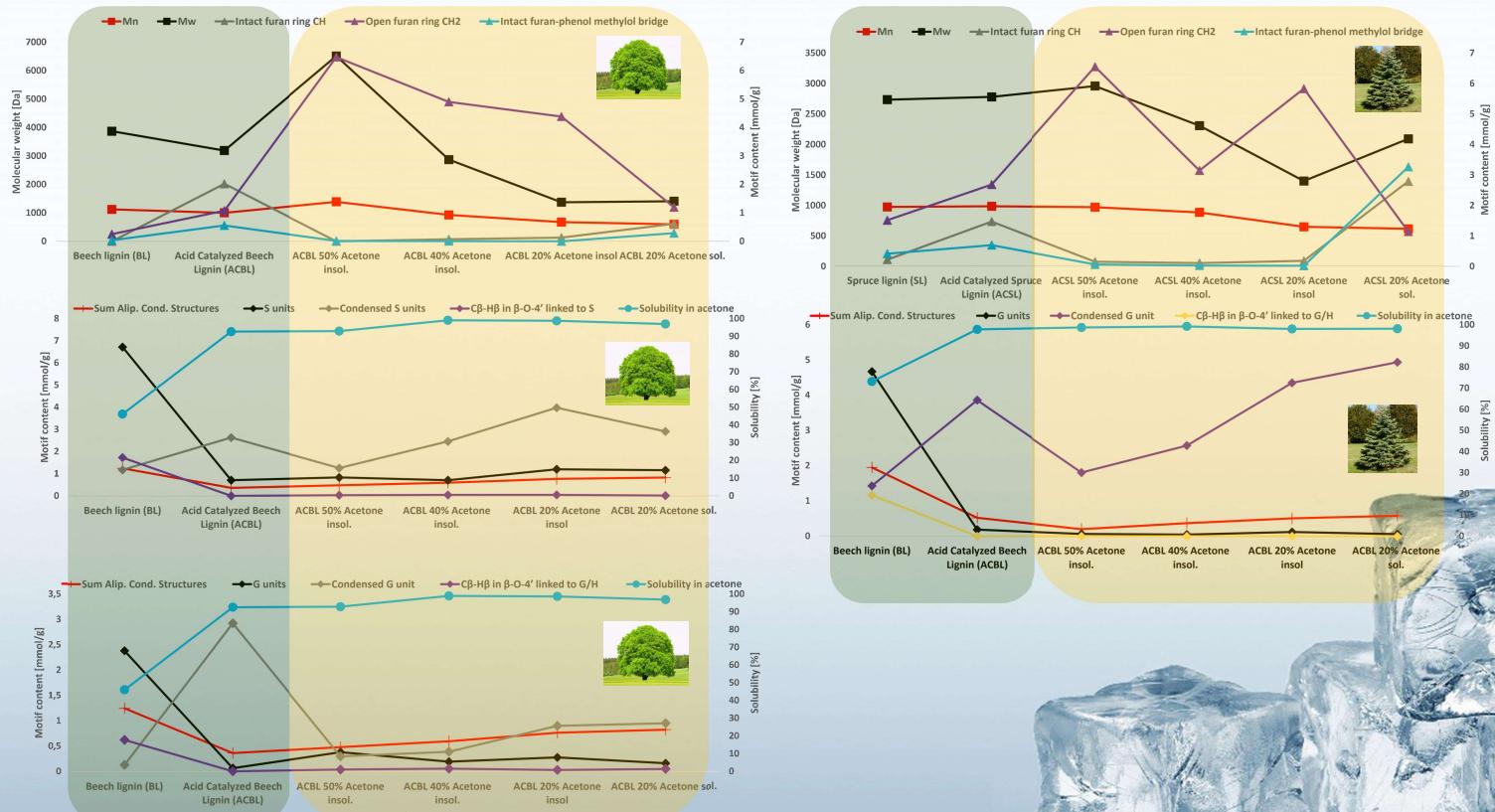
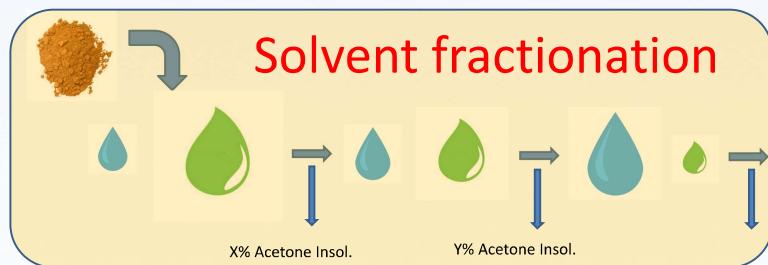
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Introduction

The present work sets out to investigate the possibility of conducting solvent-based lignin fractionation (80-20vol.% acetone) subsequent organosolv processing of both soft- and hardwood (spruce and beech, respectively) material. This in order to evaluate the possibility of producing lignin fractions with more uniform properties for eased downstream applications. Precipitates at any respective acetone% where collected and dried for further analysis (HSQC, GPC and solubility trials).



Organosolv processing



- Primary condensed structures are enriched upon a lower proportion of acetone in water
- A lower proportion of acetone in water dissolved lower molecular weight fractions of the lignin
- Cleavage of aryl-ether linkages ensures close to complete solubility in acetone.
- Application of acid converts the traditional lignin monomers into their condensed versions.
- Application of acid introduces sugar dehydration products into the lignins.
- Lignin precipitation due to anti-solvent

Lignin encapsulated pine essential oils for enhancing the antibacterial activity of CNFs packaging films in active food packaging

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INTRODUCTION

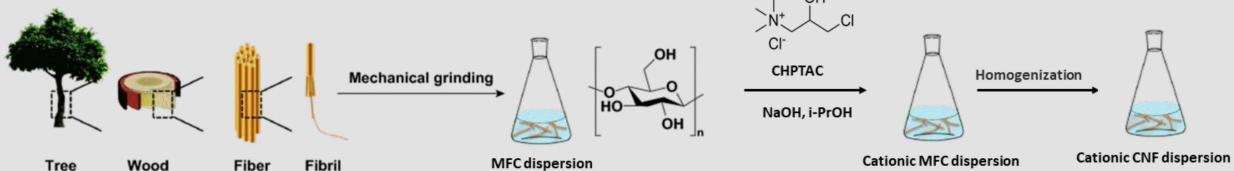
Packaging is used to preserve food quality and provide hygiene safety for the consumer^[1]. It helps in the handling, transportation, and storage by protecting food products from physical (crushing, abrasions, and shocks), chemical (ultraviolet radiations), and biological (microorganism) damage^[2]. In active packaging, deliberately added materials (absorbers or emitters) interact with the inner environment of the package to enhance the shelf life of the food. Capsules are widely used in packaging technology to deliver bioactive agents. One way to control the release rate of bioactive components is to surround or coat them with biocompatible materials^[3].

Cellulose nanofibers (CNFs) can be used to produce films or added as reinforcement elements into other materials due to their large surface area and high aspect ratio. And lignin is made up of cross-linked phenylpropane units, giving the lignin hydrophobicity, specific antioxidant, antibacterial, and UV-shielding properties^[4]. Meanwhile, pine essential oils also have antibacterial and antioxidant activity and would cooperate with lignin^[5].

In this study, lignin acts as a carrier to encapsulate pine essential oils in it, and the CNFs are used as a surfactant to stabilize the emulsion. The release of pine essential oils is controlled by lignin and CNFs to prolong the preservation time of food.

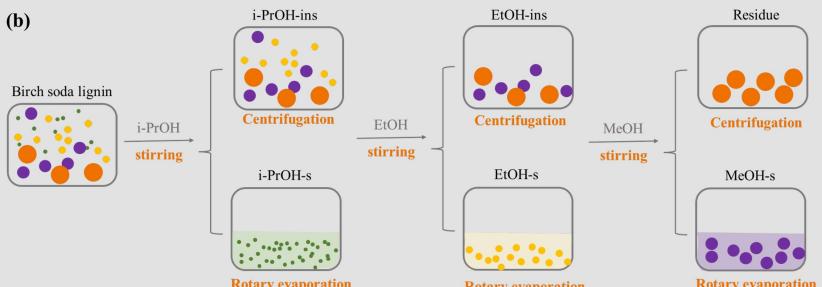
METHODS

(a)



Production of water-soluble cationized nanocellulose using 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTAC).

(b)

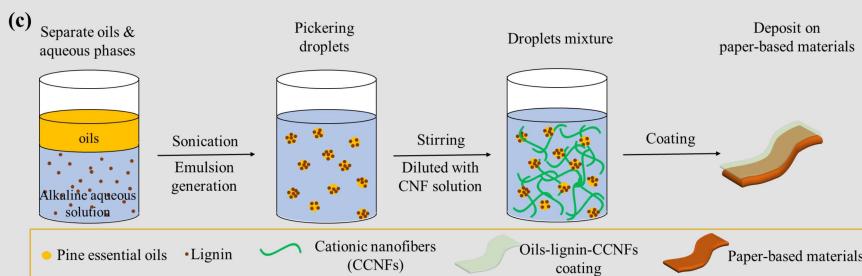


By aiming at isolating lignin fraction with decreased heterogeneity, different fractions of an industrial hardwood soda lignin are prepared through sequential solvent fractionation (i-PrOH, EtOH, and MeOH).

CHARACTERIZATION

1. Chemical characterization (SEM, TEM, FTIR spectra)
2. Structural and compositional characterization (HSQC, Quantitative ¹³C NMR, GC-MS)
3. Mechanical properties, water vapor permeability, water contact angle, oxygen permeability
4. Antibacterial properties (E.coli, Salmonella, S.aureus and listeria)
5. Biodegradability and recyclability

(c)



Preparation of antibacterial, antioxidant and UV resistance pickering emulsion stabilized by CCNFs.

OBJECTIVES

1. To graft the quaternary ammonium salt onto CCNFs.
2. To identify the lignin extracted with different solvents which has the highest activity and is most beneficial to stabilizing the capsule system.
3. To encapsulate pine essential oils with lignin and form a stable pickering emulsion with CCNFs.
4. To control the release rate of pine essential oils effectively by lignin, whereby the shelf life of a food product is prolonged.

Coatings of Lignin Spheres for Packaging/Textiles

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Introduction

- The utilization of colloidal lignin particles (CLPs) and certain epoxy compounds, such as glycerol diglycidyl ether (GDE), in the creation of multiresistant surface coatings, has previously been reported (Henn et al., 2021).
- This coating has been shown to work on textiles and plastic-like films (such as biomaterials films). The coating adheres to such materials and protects them from stains, sunlight, water, and microbial degradation.
- This research aims to modify the CLP surface coating for use in bio-based packaging and textiles. The coating would enable wider use of biomaterials by increasing the properties of the substrates, reducing the need for fossil-based, non-degradable materials in packaging and the toxic chemicals used in textile dyeing.

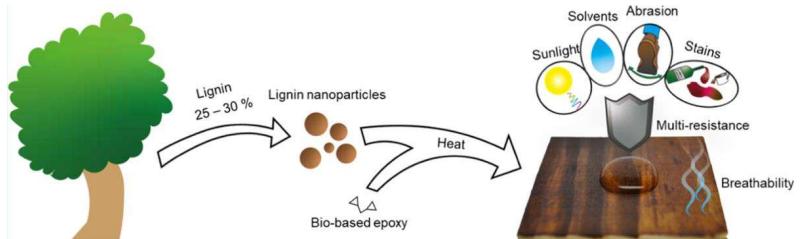


Fig 1. Colloidal Lignin Particles and Epoxies for Bio-Based, Durable, and Multiresistant Nanostructured Coatings

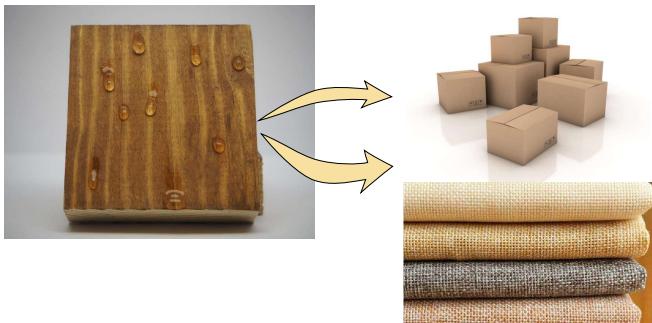


Fig 2. Water repellency of coated wood with colloidal lignin particles

Challenges

Although the multiresistant lignin nanoparticle coating, developed at Aalto University, could be used to reduce the chemical waste of the textile dyeing and improve bio-based substrate for packaging, still there are some challenges that need to be addressed such as flexibility of coating, the brownish color of coating on packaging film, controllable initiation of curing.

Hypothesizes

Packaging: The coating, despite being water-based, becomes more hydrophobic as it cures. The coating is thought to improve the hydrophobicity of hydrophilic packing biomaterials, as well as their gas barrier, mechanical, and water resistance, and light resistance.

Textile: The coating has shown significant water repellency on textiles, owing to the addition of hydrophobic agents, and might thus be utilized not only as a dye but also as a functionalizing agent.

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Chemical structure and selected applications of lignins

Enzymatic treatment of lignin in an industrial setting

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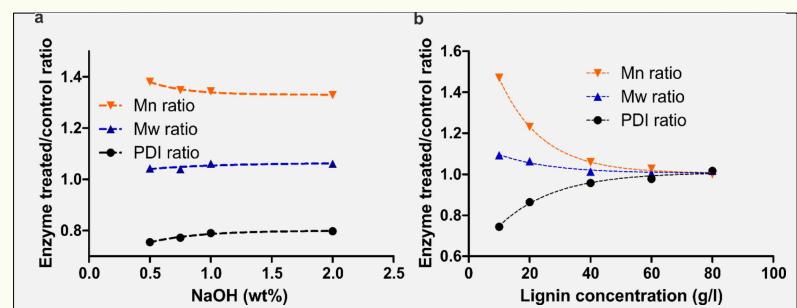
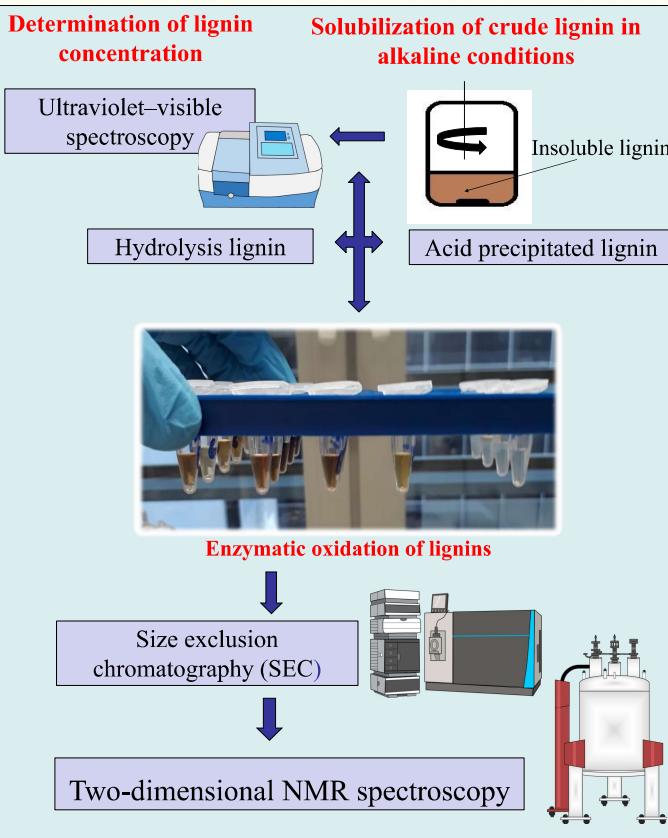
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Abstract

Lignocellulosic biomass (LCB) is an auspicious source of renewable chemicals in future. To develop renewable chemicals from LCB novel pre-treatment methods can be used to separate the three major components, which are cellulose, hemicellulose and lignin. Treatment methods, where the polysaccharides are hydrolysed, resulting in the production of Hydrolysis Lignin (HL) is utilized in the present research. The main result of the present work was to investigate possibilities to use enzymatic oxidation in valorization of HL at industrial scale. The three laccases *AmLac*, *ScLac* and *SvLac* used showed activity in industrial conditions i.e., 50 g/l in 1% NaOH solution. In addition to the activity, the treated lignin was analyzed via NMR.

Methods



a) Enzymatic treatment results in different NaOH solutions, displayed as a ratio of the change. b) Different lignin concentrations in 1% NaOH solution at pH 10

	Monomeric ratio %			S/G Ratio	Inter-unit linkages %		
	G	S	H		β -O-4	β -5	β - β
ScLac treated	22	75	3	3	71	3	26
Control sample	20	77	3	4	52	5	43

Results of the HSQC analysis, the main subunits of lignin as well as the linkages are shown as a % ratio of their integration signals.

Conclusion

We have shown that NaOH solution conditions are favorable for normal bacterial laccases, where high lignin solubilization and alkaline conditions both inhibit enzymatic activity. Enzymatic oxidation at high lignin dosage was possible but leads to polymerization, which results in higher molecular weight fractions.

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