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New opportunities in the valorization of technical lignins

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Abstract

Sugar-based biorefineries have faced significant economic challenges. Biorefinery lignins are often classified as low-value products (fuel or low-cost chemical feedstock) mainly due to low lignin purities in the crude material. However, recent research has shown that biorefinery lignins have a great chance of being successfully used as high-value products, which in turn should result in an economy renaissance of the whole biorefinery idea. This review summarizes recent developments from our groups, along with the state-of-the-art in the valorization of technical lignins, with the focus on biorefinery lignins.

A beneficial synergistic effect of lignin and cellulose mixtures used in different applications (wood adhesives, carbon fiber and nanofibers, thermoplastics) has been demonstrated. A similar phenomenon causes crude biorefinery lignins, which contain a significant amount of residual crystalline cellulose, to perform superior to high-purity lignins in certain applications. Where previously specific applications required high-purity and/or functionalized lignins with narrow molecular weight distributions, simple green processes for upgrading crude biorefinery lignin are suggested here as an alternative. These approaches can be easily combined with lignin micro/nanoparticles (LMNP) production. The processes should also be cost-efficient compared to traditional lignin modifications.

Biorefinery processes allow much greater flexibility in optimizing the lignin characteristics desirable for specific applications than traditional pulping processes. Such lignin engineering, at the same time, requires an efficient strategy capable of handling large datasets to find correlations between process variables, lignin structures and properties and finally their performance in different applications.

Keywords: Lignin; biorefinery; crystalline cellulose; lignin valorization; nanoparticles, phenol-formaldehyde resins, lignin market

1. Introduction

Plant biomass is a potential source of renewable energy, but by far not the only one: other alternatives, such as solar energy, wind energy, water energy, each possibly coupled with green hydrogen fuel, methanol or ammonia production as energy carriers might be more successful. However, plant biomass is the main source of renewable chemicals. Lignin, one of its main components accounting for 15 – 30% of its total mass, is the most abundant aromatic-aliphatic polymer and therefore has very good potential to be the major renewable source of chemicals in future. The need for lignin valorization has become well understood in the scientific community, which has given rise to a large number of studies being issued over the last years.^[1-5]

It should be mentioned that the term “biorefinery” is not well defined yet. The wider concept (as common in Europe) considers both biofuel processes and the current the pulp and paper industries as biorefineries. Biofuel processes are also often denoted as “sugar-based biorefineries”, because the carbohydrate constituents are further processed into the biofuel components. A more narrow conception (as used in North America) does not include pulp&paper in the biorefinery scope. Considering the crucial role of lignin (and other biomass components) as future chemicals, we have to support the former concept which considers pulping as a biorefinery case. In this review, however, we address significant differences between valorization of technical lignins from pulp and biofuel production, and will use “biorefinery” to specify to sugar-based biorefinery processes (biofuel processes) while denoting lignins from pulping with their intrinsic names, such as Kraft lignin, soda lignin or lignosulfonates.

1.1. Effect of lignin on biorefinery economy

Presently, conventional pulp mills are the major suppliers of technical lignins. Most of the commercially available types of technical lignins generated during wood pulping are lignosulfonates (LS) and Kraft lignins (KL).

LS, generated by sulphite pulping processes, are currently the only lignin-based commercial products of significant volume; their current market is about 1 million t/year^[6]. However, it should be noted that LS is a rather special lignin type representing highly sulfonated lignins; therefore, their structure and most of their properties are rather different from those of other technical lignin types.

Commercialization of KL in a reasonably large scale is just starting, providing the transition from merely burning lignin-containing streams to satisfy process energy demands to a

non-energetic, chemical utilization. With new lignin recovery processes which have been commissioned in the last years, such as LignoBoost™ and LignoForce™, the potential market is expected to expand to about 3.5-14 million t/year [7]. Soda lignins, from an alternative commercial pulping process, are available in very low quantities only (5–10 Kt/year; [8]) and cannot compete commercially with the other two lignin types that dominate the market.

As only 5-20% [7] of Kraft lignin available in black liquor could be used for lignin isolation without compromising energy autarchy of the mill, the commercialization of Kraft lignins results in an additional 5-10% revenue from Kraft lignin. About the same revenue can be gained from increasing pulping capacity due to mill debottlenecking at the recovery boiler site.

If sugar/bioethanol biorefinery concepts are realized in the near future, the corresponding biorefinery lignins are expected to become the major source of technical lignins. Their volume is predicted to be about 225 Mt/year in North America alone [9]. Thus, although Kraft lignins are much closer to the market, the potential volume of biorefinery lignins is one to two orders of magnitude higher (

Table 1).

Table 1 Comparison of pulping and biorefinery lignins.

Lignin source	Potential production, Mt/y	Purity	Feedstock range	Process flexibility	Cost	Application value	Additional revenue, %
Pulping	5-20	med.-high	narrow	narrow	med.-high	med.-high	5-20**
Biorefinery	>200	low	wide	wide	low	low-high*	~50-100

*according to the current research

** for Kraft lignins

Recently, further developments in the biorefinery field have faced significant economic challenges. The only focus of the current biorefinery approach is carbohydrate-based biofuels (bioethanol, butanol) or their monomeric sugar precursors. The process residues called “biorefinery lignins” (BRLs) - in fact, they are cello-lignins as the biorefinery residues contain large amounts of cellulose - are often regarded as low-value products at the fuel or low-cost chemical feedstock value [4,7,9,10]. However, lignin can and should contribute dramatically to the biorefinery economy as a high-value product. In contrast to Kraft pulp mills, there is no limitation to use up all lignin produced in a sugar-based biorefinery mill for potential non-energetic purposes.

As the corresponding process and lignin market has not yet been established, only very approximative estimations for additional revenue of a biorefinery mill through lignin are possible at present. In lignocellulosic ethanol production, the amount of lignin was estimated to be about 1 kg (calculated per “pure” lignin without residual cellulose, which can amount to 30-50% of the crude biorefinery lignin) per 1 liter ethanol produced^[9] (or 0.5 kg per 1 kg of sugars). The current ethanol price is about \$0.37/L^[11]. If lignin is fully utilized in high-value applications of sufficient market size, it can replace petrochemicals in the range of \$1.0 – 2.5/kg (see below), i.e. the revenue from lignin (to be shared between lignin producers and customers) will be a few times higher than the revenue from ethanol.

Thus, the use of lignins as high-value products should result in a renaissance of the whole biorefinery idea, with this lignin utilization **being a game-changer rather than just a value-added asset**. However, targeted lignin engineering is required to obtain a high-value product with specific characteristics. This is in stark contrast to current biorefinery approaches that are optimized towards (monomeric) sugar production and leads to a seemingly paradox conclusion: *to render sugar/biofuel biorefineries economically more successful, the main focus should be on lignin optimization and utilization.*

2. Recent achievements in valorization of technical lignins

The Department of Energy (DOE)^[9] defines 3 major areas of lignin valorization:

1. Heating fuel and energy through combustion (short term)
2. Application of lignin as macromolecule (middle term)
3. Lignin as source of aromatic monomers and oligomers (long term)

The first area is beyond the scope of this review as it deals with low-value products only; we will address the other two areas of lignin valorization herein. Noteworthy, most of the academic research is on lignin decomposition^[12–17], whereas the main industrial interests and developments are in applications of polymeric lignin^[18–20].

Lignin-derived aromatic monomers

Nowadays, monomeric chemicals produced from lignin are vanillin, phenols and other aromatic monomers^[7,9,13,15,16,21]. One of the main research topics is the use of technical lignins for BTX (a mixture of benzene, toluene, and xylene) production. Although such an application is attractive considering the enormous market size of BTX, its implementation seems rather problematic in our opinion, not only from a technical, but also from an economic standpoint.

Lignin transformation to BTX is generally a two-step process that includes depolymerization into oxygenated aromatic monomers followed by a hydrodeoxygenation (HDO) and demethoxylation ^[13,14]. Most of such state-of-the-art reductive depolymerization and upgrading strategies employ high temperatures (>200-300°C) and pressures (>5 MPa H₂) in combination with transition metal catalysis, such as Ni-Mo or Co-Mo/Al₂O₃ catalysts ^[15,16]. Despite substantial research, a decent yield for these processes is still a distant goal. The realistic output achieved by now is about 5%, mainly due to the great structural heterogeneity of the resulting low-molecular-weight species and their diverse reactivities which restricts the yield of a single product. Moreover, the HDO catalysis often causes catalyst sintering and deactivation through hydrothermal instability and coke formation ^[4,22]. The low yields of individual products as well as the reduced catalyst recovery are the major challenges in promoting economically feasible utilization of lignin after its depolymerization / decomposition. The endothermic nature of lignin degradation and related upgrading processes does not allow energy production, which additionally restricts possible profits from this process.

The economy of other degradation processes might look more promising if sufficient yields of high-value monomers are achieved and/or the residual reaction products (e.g., lignin oligomers) can be used as a mixture without isolation of individual components. Vanillin production from lignin followed by utilization of oligomeric fractions for polyurethane synthesis is a good example of such an approach ^[21].

The rationale behind lignin degradation is the use of monomeric products as platform chemicals for synthesis of certain polymers (e.g., thermoplastics and thermosets). However, in our opinion, it sounds more attractive to engineer appropriate lignin products (including economically feasible derivatization and post-processing) for a direct use of polymeric lignin^[18] rather than its degradation to monomers/oligomers which are then further used to re-build specific polymers with desired characteristics. Decomposition of specific types of lignins sounds reasonable if they are not suitable for polymeric applications as is. However, most of current lignin decomposition methods require rather high lignin reactivity (in the side chains and the aromatic nuclei), specifically a low degree of condensation, low molecular weight, high amount of β-O-4 (or other Alk-O-Ar) linkages and a low amount of carbohydrate “impurities” ^[17,23]. These requirements are challenging to be met for most of common technical lignins, which are already rather degraded and condensed. To overcome these obstacles, i.e. to preserve ether linkages and avoid lignin condensation, more sophisticated biorefinery processes have been suggested, which, however, would be of significantly higher production costs ^[23]. Alternatively, plant lignins can be genetically modified ^[24] for more efficient depolymerization, but this is not a routine task either and will also introduce additional

costs. To overcome these problems, it would be ideal to design a decomposition process which is able to cope with the available characteristics of these technical lignin characteristics, such as very degraded side chains (with a low amount of reactive centers), a high phenolic content and a high degree of condensation, i.e. by effecting cleavage of C-C bonds rather than cleavage of ether linkages, as in a recently published method [25].

Thus, lignin valorization through depolymerization looks rather challenging so far, both from a technical and an economical point of view. In addition, one should keep in mind that lignin degradation products are usually obtained as very complex mixtures due to the very high structural and chemical heterogeneity already in the starting lignins. Therefore, applications of polymeric lignin seem to be more realistic ways of lignin valorization which are currently closer to market launch [9,18,19]. Hence, the focus of our review is in this direction.

Efforts in polymeric lignin valorization have been continually made through the last decades including various applications, such as phenol-formaldehyde (PF) and epoxy resins, polyurethanes (PUs), lignin-based carbon fibers (CFs), lignin-thermoplastic blends and composites and others. These applications have been comprehensively reviewed [9,18,19]. Therefore, we will not discuss details of these more conventional applications, but instead focus on new promising aspects of lignin valorization including lignin-cellulose synergism, production of lignin (nano-, micro-, colloidal) particles (LMNPs, CLPs) as well as new achievements in the valorization of biorefinery lignins, which can be critical for bringing lignin valorization, and hence the whole biorefinery in general, onto a new level.

2.1. Lignin-cellulose synergism

Although this review is dedicated to lignin, it cannot set cellulose aside: it has been demonstrated that the presence of crystalline cellulose significantly improves lignin application performance, which sounds very attractive for lignin valorization, especially for biorefinery lignins as discussed below. Therefore, fundamentals of the phenomenon of this lignin-cellulose synergism is briefly discussed.

2.1.1. Positive effect of lignin on nanocellulose properties

Recent studies have shown that lignin has significant influence on the cellulose nanofiber morphology, surface polarity and colloidal stability, controlling the different properties of the materials, such as hydrogels, filaments, dried films and composites. An increasing amount of residual lignin in partially bleached pulp was claimed to enhanced the fibrillation process[26]. Hence, for some pulp types, a reduction in the energy consumption in the fibrillation process has been noted[27,28]. Rheological investigations on a series of ligno-cellulose nanofibers (LCNF) with

varying contents of residual lignin showed that a higher lignin content to increase agglomeration and flocculation of CNFs, resulting in hydrogels with more viscoelastic character and better dewatering properties^[29]. In addition, residual lignin improved the thermal stability^[30] and decreased enzymatic digestibility due to the limited enzyme accessibility, coming from binding between proteins and lignin^[31,32].

Different contents of lignin in LCNFs affected the properties of the dried films compared to lignin-free films. The presence of lignin significantly reduced the filtration time, because of the more hydrophobic nature and greater stiffness of the lignin-containing fibrils, which results in more open pores in the wet filter cake^[26]. The films obtained after cold pressing showed a more uneven surface and inferior mechanical properties due to the interference of lignin with hydrogen bonding between cellulose nanofibers. Interestingly, when hot pressed (100 °C, 2 h) after the filtration, the films became smoother because lignin acted as cementing material or binder between the cellulose fibrils. In this case, the presence of lignin did not influence the mechanical properties^[26]. In general, the films (after cold or hot pressing) were more hydrophilic, with a water contact angle higher than that of lignin-free films^[26,33]. Moreover, LCNF nanopapers showed lower water absorbency and significantly reduced oxygen permeability^[26].

Y. Liu^[34] reported that addition of small amounts of industrial lignin (Kraft or lignosulfonates) to carboxylated cellulose nanofibers resulted in lignin-CNF films with outstanding tensile strength and strain-to-failure properties in comparison with the composite polymer-CNF films (**Figure 1**). The excellent mechanical property was explained by the better colloidal stability and dispersibility of CNFs in lignin-containing suspensions, with the lignin component inhibiting aggregation of cellulose fibrils during drying.

LCNFs were reported to be better miscible with non-polar solvents because of their more hydrophobic nature. This leads to better dispersion and film forming capability in coatings as well as better mixing with hydrophobic polymers, such as polycaprolactone^[35], polystyrene^[36] or poly(lactic acid)^[37]. The use of LCNFs further resulted in the composite films with improved reinforcement compared to the ones made of the bleached CNF counterpart. Efforts to obtain filaments from mechanically produced LCNFs have failed due to their anionic surface charge and short fibril length that hinder binding^[38]. By contrast, composite approaches employing polyvinyl alcohol (PVA)^[39] to produce films as well as using carboxymethyl cellulose (CMC)^[38] to allow LCNF spinning into filaments have been successful.

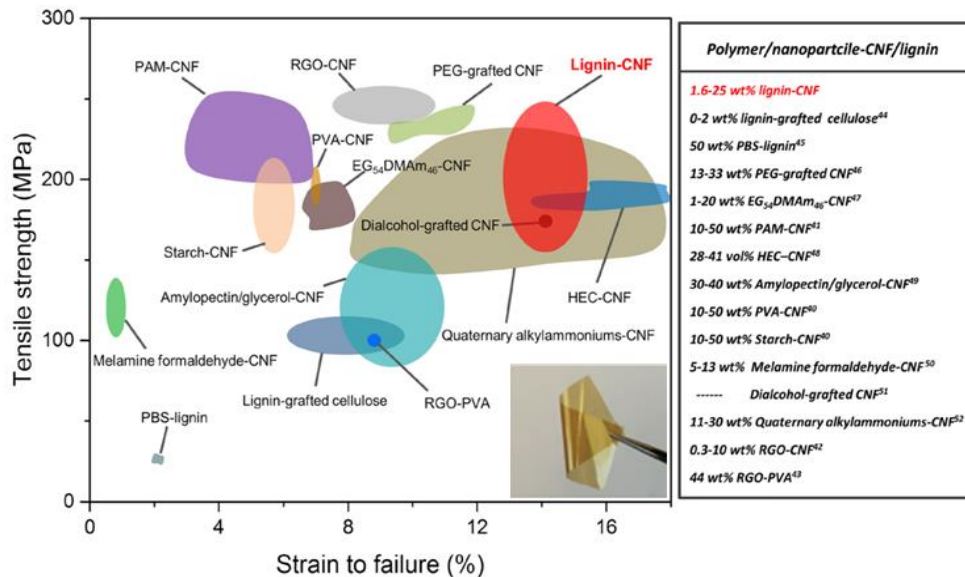


Figure 1. Comparison of mechanical properties of CNF and LCNF nanocomposites polymer/nanoparticle contents below 50 wt %. PVA, **PBS, EG-DMAm**, and HEC refer to poly(vinyl alcohol), poly(butylene succinate), ethylene glycol methyl ether methacrylate / *N,N*-dimethylacrylamide copolymer, and hydroxyethyl cellulose, respectively [34].

2.1.2. Positive effect of cellulose nanocrystals (CNCs) on lignin performance.

2.1.2.1. Carbon fiber and nanofiber

In recent years, increased attention has been devoted to the development of carbon fibers (CFs) carbon nanofibers [40,41], carbon nanotubes and other forms of carbon from biopolymers, such as lignin and cellulose. Wet-spinning is largely used for the production of conventional CFs from polyacrylonitrile (PAN).^[42] However, lignin alone cannot be wet-spun. Some studies reported efforts to blend lignin with acrylonitrile^[43] or PAN^[44]. Notably, addition of cellulose to lignin makes it possible to obtain fibers by wet-spinning of completely renewable precursors. In 2012, Lehman et al. patented the production of lignin-cellulose precursor fibers by wet-spinning as well as dry-jet wet-spinning from solution of cellulose-lignin blends in ionic liquids (ILs)^[45]. The long polymeric chain of cellulose introduces viscoelastic properties to the lignin matrix upon co-dissolution and compensates the limitations of lignin in wet-spinning.

Ma et al.^[46] reported that spinnability, viscoelastic properties and fiber strength depend on the overall consistency of the spinning dope and the lignin-cellulose ratio. The addition of lignin, such as KL or organosolv lignin (OSL), to cellulose in IL solutions gradually decreased the visco-elasticity of the system. At lignin shares of 50% the visco-elastic properties suitable for spinning

could only be maintained by an increase of the total polymer concentration to 20 wt%, from a standard concentration of 13 wt%.

Crystallinity, orientation and tenacity of the regenerated cellulose-lignin fiber improved with higher cellulose content. On the one hand, lignin-cellulose composite fibers produced higher yields than the pure-cellulose fiber after carbonization. On the other hand, the addition of cellulose significantly decreased the stabilization time of lignin from 24 h to 2 h. Therefore, by the combination of cellulose and lignin, the limitations of the individual components to obtain carbon fibers can be mitigated [47,48]. It was also reported that the cellulose-lignin (30%-70%) composite fibers obtained by dry-jet-wet spinning, produced carbon fibers with better mechanical properties (780 MPa tensile strength and 68G Young modulus) than in the case of fibers produced by melt-spinning of softwood-based lignin alone [49,50].

The positive effect of CNC addition (up to 15%) was observed in electrospinning lignin - PVA aqueous suspensions (at 75:25 and 80:20 ratios)^[51-53] so that defect-free nanofibers were successfully produced. While large phase-separated domains with characteristic sizes in the order of 500–1000 nm are observed for CNC-free systems (**Figure 2a**), the characteristic domain size is reduced or phase separation completely suppressed if CNCs are added (**Figure 2b,c**). It was hypothesized that the molecular mobility of the lignin–PVA matrix was decreased with the addition of CNCs, and therefore, phase separation was reduced. Noteworthy, the addition of CNCs affected only the surfaces of lignin-rich electrospun fibers, whereas no surface effects were observed when CNCs were added into PVA fibers, suggesting that CNCs are more closely associated with lignin [51]. The thermal stability of the lignin-PVA system was observed to increase with CNC addition owing to a strong interaction of the lignin–PVA matrix with the dispersed CNCs, mainly via hydrogen bonding, as deduced from FTIR experiments. Moreover, the addition of CNCs as the reinforcing solid phase significantly improved thermomechanical properties of fiber mats and spin-casted films, as analyzed by dynamic mechanical analysis (DMA) and nanoindentation (

Figure 3). It was furthermore reported that addition of CNCs resulted in the stabilization of the matrix against water absorption. These results provide evidence of the molecular interactions as well as efficient stress transfer between the lignin-PVA matrix and the dispersed CNCs.

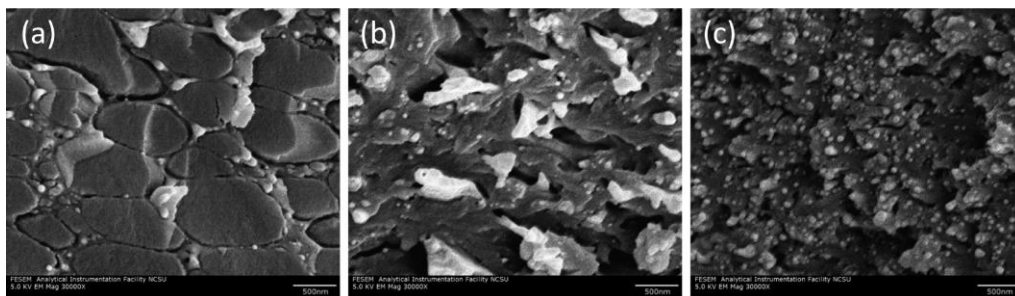


Figure 2 Scanning electron microscopy of the cross-section of solid thin films produced from lignin–PVA–CNC systems prepared by evaporation-casting, lignin/PVA:CNC (%) of 75/25:0 (a), 75/25:5% (b), and 75/25:15% (c).^[52]

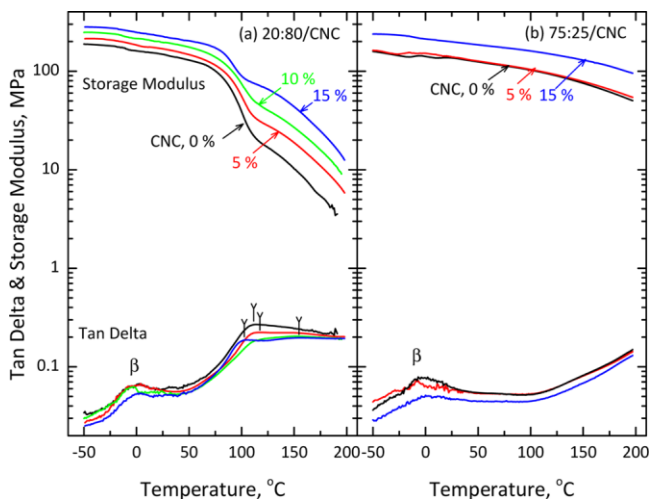


Figure 3 Dynamic mechanical analysis: storage tensile modulus (E') and loss angle tangent ($\tan \delta$), as a function of temperature for lignin/PVA:CNC electrospun fiber mats: 20:80/% CNC (a) and 75:25/%CNC (b). ^[53]

2.1.2.2. Wood adhesives

CNC has been used to reinforce phenolic resins, such as phenol-formaldehyde (PF) and lignin-phenol-formaldehyde (LPF) resins, in the form of both liquid suspensions and powders^[54]. The addition of CNCs to the LPF improved the wet bending strength, namely modulus of elasticity (MOE) and modulus of rupture (MOR), of the oriented strand board (OSB) products. The addition of CNC into PF resin also boosted the bonding strength of 3-ply plywood after 48 hours soaking and after boil-dry-boil treatment. Adding CNC into LPF through post-blending increased the wet shear strength of the respective plywood. The modified resin improved the wet shear strength of plywood panels, with the highest values at the addition of 0.25% CNC. Further increase in CNC content, however, decreased the strength due to CNC aggregate formation ^[55].

The addition of CNC also significantly improved molded composites with PF powder resins with regard to bonding strength development, flexural strength (MOR and MOE), reduced thickness swelling and water absorption in OSB panel produced with methylene diphenyldiisocyanate (pMDI)-based adhesives. Furthermore, replacing wood flour-based glue fillers with CNC in the amount of about 1:0.05 in various formaldehyde-based adhesives (urea formaldehyde (UF), melamine-urea formaldehyde (MUF), and PF) led to a significant improvement of the cure speed in pressing of wood panels – resulting in press cycle-time reduction and increased production rate -, improved wet and dry strength, reduced glue consumption

reduction, as well as better viscosity stability, uniformity and cleanability^[56]. Although no lignin has been used in these resin formulations, similar improvements can be expected for lignin-based resins according to the tendencies described previously^[54].

2.1.2.3. Thermoplastics

The production of thermoplastic materials with added functionality represents another economically beneficial way of lignin utilization. Possibilities of manufacturing 100% bio-based thermoplastics by lignin addition to bioplastics, such as polylactic acid (PLA) and polyhydroxybutyrate (PHB) have been investigated. In PLA blends, lignin is capable of decreasing PLA photodegradation of the blends exposed to ultraviolet and visible (UV-vis) light, improving the mechanical properties compared to the pure PLA^[57]. The introduction of lignin also improves the thermal stability and flame retardancy of PLA composites^[58]. However, the incorporation level for lignin is often limited to less than 30%^[59]. Once this limit is exceeded, the blend loses its mechanical performance becoming brittle and fragile, which was shown in a few studies that confirmed the reduction of the tensile strength and thermal stability in PLA-lignin blends^[60–62]. This issue can be resolved by multicomponent blends including cellulose as the tertiary component. The synergistic effect of the addition of both cellulose and lignin to the thermoplastics has been studied by several researchers. Generally, the combination of lignin and cellulose generated mutually beneficial effects, with cellulose reinforcing mechanical strength of the blends and lignin improving cellulose dispersion in a mixture^[63], also positively affecting other physical properties of the composite, such as thermal stability and hydrophobicity^[64].

Yang et al. prepared and characterized melt extruded PLA nanocomposite films by dispersing CNCs and lignin nanoparticles (LNPs) (see below) in two different concentrations (1 and 3 wt%) in neat PLA and glycidyl methacrylate grafted PLA (g-PLA)^[63]. Thermal results, as well as the different obtained morphologies for CNC- and LNP-reinforced PLA nanocomposites, confirmed that good dispersion of the nanostructures was achieved due to the masterbatch/grafting combination. The authors established a synergistic improvement of CNC and lignin with regard to optical, thermal, mechanical and antioxidant properties of the composites. More specifically, a synergistic effect of LNP and CNC on transparency and the capability to block UV light was reported. The combination of CNC and LNP caused more effective nucleation and crystal growth, with increased crystallinity values for ternary systems with respect to binary nanocomposites. The synergistic effect resulted in the best mechanical performance (tensile strength and elastic modulus) of a ternary system containing 1 wt% LNP and 3 wt% CNC^[63]. Based on these results it was of interest to understand the performance of powder lignins – instead of LNPs – and crystalline

celluloses – instead of CNC – aiming at a maximal replacement of petroleum-based thermoplastics, such as polyethylene (PE), polypropylene (PP), polystyrene (PS), with biopolymer(s) without deteriorating product characteristics and economics.

A few studies attempted to valorize lignocellulosic biowaste through fabrication of bioplastics. Agustin-Salazar et al. studied the influence of holocellulose (HC) and acid-insoluble lignin (AIL) isolated from pecan nutshell on the physical properties of PLA-based biocomposites (total fillers amount 30 wt%) [65]. The HC fraction improved the mechanical properties of the material resulting in a higher modulus compared to the plain matrix. Moreover, it enhanced the viscoelastic response of the blend by restricting the melt's molecular mobility. At the same time, the AIL improved the ductility and elongation at break in the composite. Angelini et al. reinforced a poly(3-hydroxybutyrate) (PHB) matrix and studied the influence of HC and AIL isolated from lignocellulosic waste on the characteristics of PHB [66]. Analysis of the rheological properties of the blends showed a remarkable improvement of viscoelastic properties of the melts. The addition of AIL resulted in higher moduli and complex viscosity values of the blend melt, caused by the formation of a co-continuous filler network within the PHB matrix that reduced chain mobility, thus hampering PHB crystallization. In contrast, HC was shown to promote melt crystallization during rapid cooling.

2.1.2.4. Thermosets

Lignin's phenolic structure as well as the phenolic and aliphatic hydroxyl groups are the basis of its use in the manufacture of various thermosetting materials, including polyurethane (PU), phenolic and epoxy resins [67,68]. In this case lignin can be used either as a raw material or as a reinforcing filler. In the PU system, the chemical reaction occurs between lignin hydroxyl groups and isocyanate. It can be used to generate various materials, including elastomers and plastics as well as soft, semirigid and rigid foams. The modifying approach that implies direct polyol replacement with lignin leads to a material with high modulus, but low toughness, as was shown by Cheradame [69]. The addition of polyols helps to improve the material's performance by adjusting characteristics, such as the Young's modulus, hardness, breaking and tensile strength, and elongation at break [69–72]. The compressive and thermal properties can also be controlled by the addition of tertiary components to the lignin-based PU materials. Commonly chain extenders that improve the accessibility of lignin hydroxyl groups and therefore positively affect the degree of crosslinking are used to tailor the material characteristics. Moreover, similarly to thermoplastics, the presence of cellulose may help to improve the final properties of lignin-based thermosets. Li and Ragauskas demonstrated that the addition of cellulose nanowhiskers (CNW) to ethanol

organosolv lignin-based polyurethane foams significantly improved the mechanical and thermal properties of the material^[73]. Due to the CNWs' rigidity and the crosslinking introduced by the CNWs, the reinforced foams demonstrated increased density, which was directly correlated to the amount of CNWs added. A maximum amount of 5 wt% resulted in the highest material density. This helped to improve the material's strength (160% increase), modulus (212% increase), as well as T_g and T_d values. CNCs were also used to reinforce a lignin-based PU elastomer film. The presence of CNC increased the tensile strength and modulus of the film, which was attributed to the PU-CNC interactions in the hard domains which helped to avoid the unwanted stiffening of the soft domains. Notably, the elongation at break of the CNC-modified films decreased, probably related to the fact that CNCs do not arrange astatically under high strength. Thermal characteristics of the films were not significantly affected by the presence of CNC, although a slight increase in thermal stability of the reinforced material was observed^[74].

2.2. Lignin micro- and nano- particles (LMNP), colloidal lignin particles (CLP)

Valorization of industrial lignins towards particles or colloidal nanoparticles has been the subject of many efforts, as summarized in a recent review^[75]. Nano- and submicron sizing and the particles' special shapes enhance some typical lignin properties, such as antioxidant and UV-protection, antimicrobial and thermal stability, or provide the material with new properties beneficial for mechanical reinforcement, good miscibility with different chemicals, emulsion stabilization etc. New properties can also be obtained from multiple components integrated in the form of particles^[76]. As the result, micro- and nano-sized lignin particles possess valuable properties in different applications, such as in particulate coatings, to stabilize Pickering emulsions, to reinforce phenolic foams^[77], to carry silver nanoparticles in drug delivery^[78] and others^[75,79].

Sub-micron lignin particles can be produced by a variety of methods, well summarized in recent reviews^[75,80]. Different sizes and shapes are obtained by different approaches and under various different conditions, such as solvent or pH shifting, crosslinking/polymerization, mechanical treatment, ice-segregation, template-based synthesis, electrospinning, CO_2 / antisolvent precipitation, and aerosol processing^[80]. Lignin particles were also obtained by aqueous dialysis of lignin dissolved in tetrahydrofuran (THF) ^[81]. The particle size can be controlled by varying the concentration of the lignin solution before dialysis. An enzymatic treatment together with catalytic crosslinking was used to synthesize internally reinforced lignin particles (ca. 200 nm) ^[82]. Moreover, the particles were decolorized with H_2O_2 in alkaline condition under ultrasonication.

With regard to commercial applicability and scale-up, lignin particles are preferably produced in the form of a dry powder. Efforts of Österberg et al. ^[83] were directed at the feasibility

of a nanoprecipitation process to produce CLP into flake-like dry form by solvent evaporation. They suggested a potentially industrially scalable, closed-cycle process^[84] consisting of 5 steps (

Figure 4a): 1) dissolution of lignin in THF-ethanol (EtOH), 2) injection of the solution into water, resulting in the formation of CLP in a water-THF-EtOH system, 3) recovery of organic solvents via rotary evaporator and cycling back to dissolve lignin, 4) water removal from CLP by ultrafiltration and return of the water into the nanoprecipitation step, 5) dry spraying of the wet CLP through a stream of air at 180 °C. The produced dry particles were re-dispersable to form CLPs with an average size of 200 nm.

In another scenario, Ago et al. produced dry lignin particles that were fractionated according to size with high yield in a single-step aerosol flow reactor^[85]. As shown in

Figure 4b, the lignin precursor solution was first nebulized to small droplets, forming an aerosol with the carrier gas while flowing through the hot-zone of the heating tube. Then, the dry particles were collected by an impactor and fractionated according to size (

Figure 4c,d). The lignin particles displayed perfectly spherical shape (

Figure 4e) with high structural integrity that was not dismantled even after high shear treatment in oil or water. In addition, due to their high oil-water interface activity, oil-in-water (O/W) Pickering emulsions with high stability were obtained (

Figure 4d).

Importantly, LMNP can be produced with a scalable process at reasonable costs of 900 - 1,200 USD/t, ^[75,79] depending on raw materials used and processing conditions. Major cost drivers for LMNP manufacturing include lignin, utilities, and depreciation.

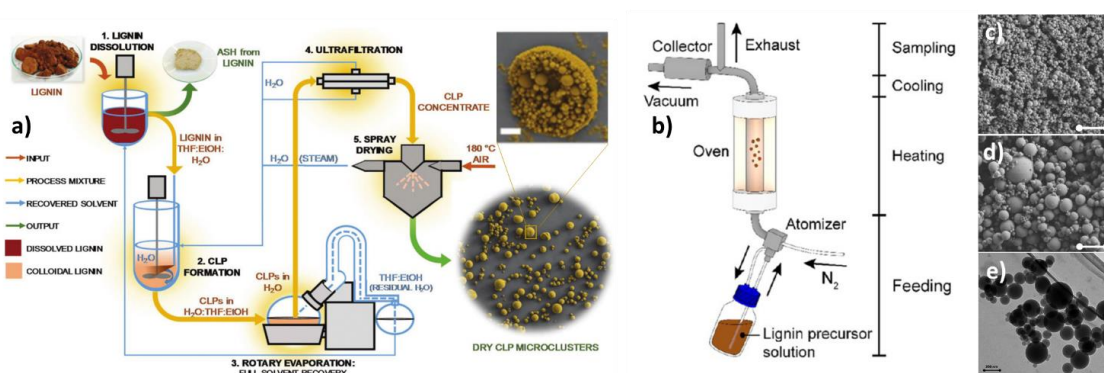


Figure 4 Process schemes for the production of lignin particles by a) solvent shifting and evaporation, b) aerosol-flow process. c) and d) SEM micrographs of solid lignin spheres with different size obtained at different fractions, e) TEM micrograph of intact spherical lignin particles.

Based on techno-economic analysis, de Assis et al. [79] suggested emulsion stabilizers, UV protection products, chelating agents and polymer nanofillers as promising LMNP applications. Although these products are of quite high values, their market size is relatively small as compared to potential lignin production ability (see below). Therefore, these products may not have a significant impact on lignin commercialization as only a minor part (< ca 100 Kt/year) of potentially produced bulk amounts of lignin can be utilized in these applications. The possibility of LMNP in replacing petrochemicals in applications of larger size, specifically various thermoplastics, phenol-formaldehyde resins and polyurethanes, is of great interest for a wider commercialization of technical lignins. The value of these products is apparently marginal with the evaluated LMNP price^[79]. Consequently, it is important to find ways to reduce the production costs of LMNPs. The cost analysis suggests to target on:

- the technical feasibility of the production of LMNP at higher concentration of lignin in the feed solution;
- using lower-cost feedstocks, such as crude biorefinery lignins (see below);
- the use of low-cost solvents suitable for lignin dissolution with low heat of evaporation, such as aqueous acetone and ethanol mixtures
- reduction of solvent losses and improvement of solvent recovery.

LMNP/CLP production is apparently a strong alternative to various processes to chemically modify technical lignins for various applications^[86], such as thermoplastics, PU, PF resins, coating and others. Therefore, it is of great interest to compare LMNPs with chemically modified lignins in these applications in terms of costs and performance to decide on the best approach. It must also be considered that chemical lignin modifications often apply hazardous chemicals in contrast to green LMNP/CLP production^[86].

In summary, CNC and LMNP in various composite applications have been used so far predominantly as reinforcement elements in rather small concentrations of a few percent to improve the performance of the products. However, such an improvement is often not even required for existing products, already maximal replacement of currently used petrochemicals with green and renewable products at comparable performance level is sufficient. Economic benefits will obviously be desirable in addition. In this case, replacement of a larger amount of petrochemicals can be achieved with inexpensive “conventional” lignin powder at the expense of a probable decrease of the mechanical and other properties, which can be restored with addition of catalytic amounts of – albeit more expensive - LMNPs and CNCs/CNFs.

2.3. Current advances in valorization of biorefinery lignins for high-value applications

Biorefinery lignins – lignins from sugar-based, biofuel-targeting biorefineries – are usually considered as low value products of approximately fuel value, which is primarily due to their low lignin purities^[4,7,9,10]. Their upgrade, apparently a must for higher-value products, is assumed to be technically challenging and/or costly. In addition, lignins from hardwood (HW), the main biorefinery feedstock, are often considered as less reactive and therefore less valuable for many applications as compared to softwood (SW) lignins., This vision has been challenged recently with new attractive features of biorefinery lignins.

The research and development work has been mainly conducted with a specific type of biorefinery lignins, so called Omno Polymers™, which are a product of the Plantrose technology, which consists of a 2-stage process involving subsequent subcritical and supercritical water hydrolysis (SSWH) of various types of plant biomass.

2.3.1. Crude, cellulose-containing biorefinery lignins as high-value products

SSWH lignins were tested in direct replacement of PF resins and adhesives^[87-90] using the Automatic Bond Evaluation System (ABES) test. Surprisingly, the crude lignins containing 20-45% residual cellulose (**Table 2**) exhibited superior performance in lignin – plywood PF blends (30% substitution), superior to the corresponding high-purity lignins without cellulose accompaniment (

Figure 5a), with a sample with about equal amounts of lignin and cellulose (SHR-50 in Table 2) performing best. Similar results were obtained with lignin-PF resin blends for oriented strand boards (OSB). The ratio of lignin to cellulose is not the only influencing factor; cellulose characteristics (**Table 3**) have also a strong effect on the bond performance^[87]. Pilot trials on plywood and OSB panel production showed that about 35% of resin could be replaced with SSWH lignin without any increase in the hot press time, which is the usual bottleneck in production^[87,88]. Selected SSWH lignins showed significantly higher bond performance than other technical lignins that originated from various pulping processes (Kraft, soda, organosolv) and different biomass (SW, HW, non-wood) (**Figure 5b**). The performance of cellulose-free lignin (SHL-50), extracted out of SSWH, was similar to that of the reference lignins. These data underline the key role of the cellulose part in the SSWH lignins.

Table 2 Main characteristic of SSWH lignins.

Characteristics	SHR-50*	SHL-50*	SHR-80*	SHL-80*	SHR-SW*
Carbohydrates (%)	44.2	0.3	19.5	1.1	32.2
RC** (mmol/g)	0.65	1.20	0.95	1.19	1.22

Lignin Mw (Da)	4386	4255	4865
Lignin Đ	4.07	3.58	3.19

* SHR: supercritical hydrolysis residue (hardwood), the number corresponds to the lignin content; SHR-SW: supercritical hydrolysis residue produced from softwood (pine);

SHL: supercritical hydrolysis lignin extracted from the corresponding SHR

** number of “reactive centers” (non-substituted 5- or 3-position in phenolic units), determined by ³¹P NMR

Table 3 Molecular parameters of the cellulose fraction in SSWH lignin samples.

Sample	DC (%)	Cellulose II (%)	M _w (kDa)	M _n (kDa)	M _z (kDa)	Đ	C=O (μmol/g)
SHR-50	82.1	78	28.7	20.2	43.8	1.4	97.3
SHR-80	83.3	100	96.5	51.5	253.7	1.9	219.1

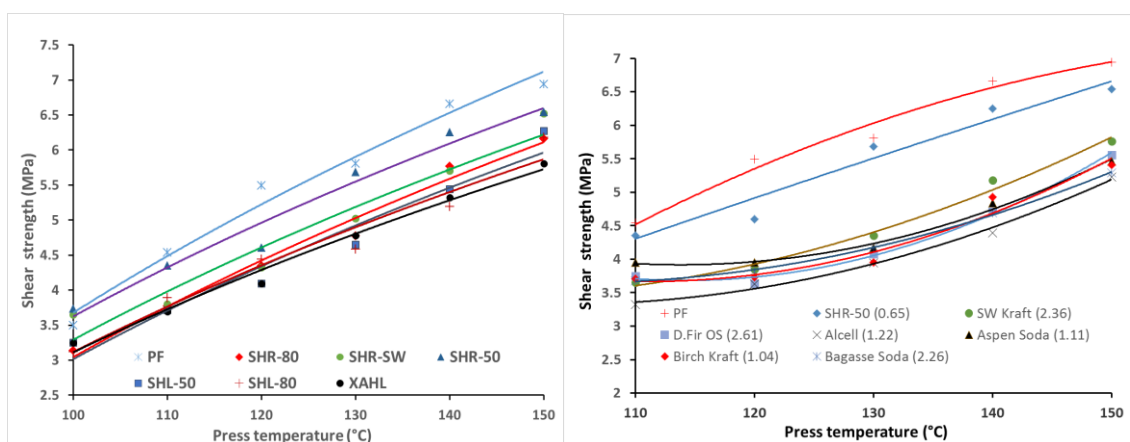


Figure 5 ABES bonding strength (at 90 s press time) of plywood PF blended with lignins (70:30 w/w); Left: different SSWH lignins; right: SSWH lignin (SHR-50) versus different technical lignins. The numbers in parentheses indicated the amounts of the “reactive centers” (RC in mmol/g), see **Table 2**.

Recent reports indicate that such lignin-cellulose synergisms can be observed also with other types of biorefinery lignins. For example, Dehne et al. ^[91] demonstrated that crude biorefinery lignins, after steam-refining and enzymatic hydrolysis of non-debarked poplar, performed better in lignin-PF formulations with 20% lignin share than the corresponding purified (alkali extracted) lignin. However, the effect was not as strong as that observed with SSWH lignins above. Interestingly, the addition of 30% of microcrystalline cellulose (Avicell) to high purity Kraft lignin

did not affect the performance emphasizing once again the importance of specific cellulose characteristics and indicating that just addition of any crystalline cellulose is not necessarily productive.

The same type of hydrolysis lignin showed better performance in thermoplastic polypropylene (PP) blends compared to various Kraft, soda and organosolv pulping lignins of high purities at 50% PP replacement, although still being below the values of the neat PP control^[91]. Interestingly, after derivatization of the lignins by acetylation, the performance of this biorefinery lignin became the worst among the lignins tested.

To explain the superior performance of crude biorefinery lignins, it was suggested that the crystalline cellulose in crude biorefinery lignins might have a similarly positive influence on lignin performance as CNC discussed above^[86,88]. Although the effect of the residual crystalline cellulose in crude biorefinery lignins on lignin performance is not as pronounced than that of pure CNC, the production costs of crude biorefinery lignins are dramatically lower than those of pure CNC, which is in the range of \$5-7/kg ^[92]. The Plantrose™ process also produces highly crystalline cellulose streams containing minor amounts of lignin ^[89] for which the the above-discussed lignin-CNC/CNF synergism could also be valid. The understanding of the mechanism of this lignin-cellulose synergism and the optimum cellulose characteristics (MW, degree of crystallinity, crystal dimension, cellulose I/II ratio) are of primary importance for a purposeful engineering of optimal biorefinery lignins for specific applications.

2.3.2. Customized and functionalized lignins crude biorefinery lignins

If high-value applications require high purity, cellulose-free, fractionated or derivatized lignins, crude biorefinery lignins can be further upgraded by various simple and potentially cost-efficient processes.

2.3.2.1. Solvent fractionation

Lignin extraction yields are highly dependent of the composition of the aqueous solvent mixtures used for extraction ^[88,93]. In particular aqueous ethanol (EtOH, 60-70% w/w) can extract about 60% of crude SSWH lignin at room temperature and 90% aqueous acetone more than 80%. Fractionated lignins can be produced using step-wise or/and gradient extraction (**Figure 6**) with solvents containing various proportions of EtOH or/and acetone, to obtain desired molecular weight and T_g in the fractions Thus, considering the relatively low cost of EtOH and its low toxicity as

compared to other organic solvents suggested for lignin fractionation earlier ^[94], this extraction process should be both greener and more cost efficient for high-value lignin products.

A similar approach to fractionation of Kraft and organosolv lignins based on mixtures of different green organic solvents was developed recently by VTT^[95]. A great practical benefit of this approach is a significant decrease in the volume of solvent needed for fractionation. This was achieved by first dissolving lignin in an aqueous organic solvent (e.g. acetone) with maximal dissolution power and then precipitating specific lignin fractions by progressive dilution with water. Problems related to rather sticky precipitates might occur for some lignin types, and additional efforts are required to overcome such problems during process scale-up. General process aspects and issues of lignin fractionation were comprehensively reviewed very recently ^[96].

2.3.2.2. Functionalizing extraction.

Certain lignin modifications, for instance alkylation and acylation, are able to upgrade lignin towards important applications, such as thermoplastic blends, carbon fibers, surfactants, and sorbents^[18,19,97–100]. Acetylation of softwood Kraft lignin, made it possible to dry-spin its concentrated solutions in acetone (75 wt%) ^[100]. Usually, a degree of substitution (DS) of 100% is targeted, meaning that all available hydroxyl groups are functionalized. However, such complete lignin modifications typically require expensive or/toxic chemicals and therefore they may not be easily viable on an industrial scale. In contrast, a simpler process that simultaneously functionalizes and extracts lignin from biorefinery residues (functionalizing extraction) has been proposed recently. Although only partial derivatization occurs, it can be sufficient for achieving the targeted lignin performance. Extraction of lignin from SSWH residues with an aqueous ethanol (or other alcohols, such as methanol, propanol) under mild conditions in the presence of catalytic amounts of a strong acid (H₂SO₄) results in partial alkylation of lignin during the extraction process. Similarly, the use of acetic acid (or other organic acids) for extraction results in partial lignin acetylation (acylation). Degree of substitutions of up to 23% ethyl or acetyl groups have been achieved ^[88,101]. Moreover, the yields of the functionalized lignins are higher than that in a similar extraction without derivatization. Other characteristics of lignin, such as molecular weight, glass transition temperature (T_g), and molecular structure, can be tuned by the process variables. The combination of lignin modification and extraction in a very simple approach that uses inexpensive chemicals and allows for a process of significantly lower costs compared to other known processes for functionalized lignins.

2.3.2.3. Combination of biorefinery lignin purification, fractionation, and reactive extraction with LMNP/CLP production.

The solutions from purification, fractionation or reactive extraction of crude biorefinery lignins usually contain only the lignin part without any significant amounts of carbohydrates or process chemicals. These solution can therefore be directly used for production of LMNPs or CLPs. This can, for instance, be achieved by means of an aerosol-flow reactor as recently proposed by Rojas et al. and Österberg et al., respectively (

Figure 4). Similar opportunities are strongly limited for lignin-containing pulping spent liquors, which contain significant amounts of carbohydrates, their degradation products and inorganic pulping chemicals, so that the lignins have to be isolated from the spent liquors first. Overall, the easy use of low-cost biorefinery lignins for LMNP/CLP production should dramatically reduce the production cost and make these products available for medium-to-large market size applications [79,102].

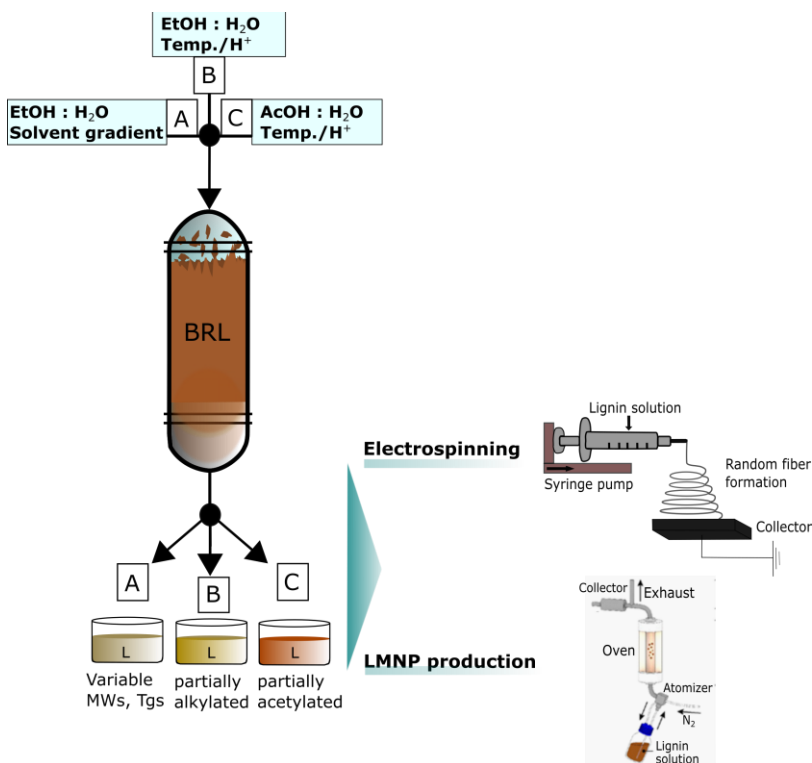


Figure 6 One-pot purification, fractionation and functionalization of crude biorefinery lignins (BRL) and direct use of these solutions for LMNP production or nanofiber production by electrospinning.

Further cost reduction can be achieved by choosing appropriate solvents. The maximal lignin concentration to produce LMNP from *N,N*-dimethyl formamide (DMF) solution was 2%, resulting in estimated manufacturing cost of 1750 US\$ t⁻¹ [79]. However, the use of acetone as the solvent allows increasing the lignin concentration to 5%^[102] giving a ca. 60% decrease in the LMNP manufacturing costs (747 US\$ t⁻¹). [79]

2.3.4. On the role of “pseudo-lignin” in biorefineries

Terms such as “humins”, “polyfurans” or “pseudo-lignin” refer to black, often charry and intractable byproducts of thermal biorefinery processes. Their occurrence decreases the yields of the desired products, such as furfural or hydroxymethylfurfural, and many efforts are dedicated to minimization or suppression of their formation. Their structure has been postulated to consist of polymeric, linear or crosslinked furans, while recent results have shown that the major part of the humins consists of ladder-type, mixed aromatic-quinoid furanobenzoquinones. Generally, these compounds are not derived from lignin but from carbohydrates, but because of their structure they are covered by the traditional Klason lignin analytical procedure. This also explains their “pseudo-lignin” denomination.

The phenomenon of humin formation has been known in industry since the 1930s [103]. “Pseudo-lignin” is usually considered as an undesirable side product of biorefinery due to its negative effect on subsequent enzymatic hydrolysis steps, which the “pseudo-lignin” has in common with its “true-lignin” counterpart [104]. In contrast to that, there is no evidence of a negative effect of *pseudo*-lignin in other lignin-typical application. In fact, softwood organosolv lignins obtained under very severe conditions and therefore containing large amounts of *pseudo*-lignins, showed significantly better performance than common organosolv lignins not contaminated with *pseudo*-lignins.^[105] Incorporation of the pseudo-lignins’ benzoquinoid-furanoid structures into the lignin structures may generate additional cross-linking positions - similarly to incorporation of formaldehyde into lignin structure in lignin-phenol-formaldehyde formulations - and thus increase lignin reactivity in certain applications, such as thermosets.

2.4. Integrated biorefinery approaches - summary

Biorefinery lignins can be used in various high-value applications, much above their fuel value. Among their peculiarities is the significant content of crystalline cellulose and the cost-effective upgradability. Moreover, biorefinery lignins are very suitable feedstocks to implement

new tendencies in lignin valorization, such as lignin-cellulose synergism and LMNP/CLP production (and applications), resulting in significant process and cost superiority to traditional lignin types from the pulping industry. These positive features stimulate reconsideration of the value and utilization of biorefinery lignins in different applications. So far, only rather scarce data is available, but future will certainly see a surge of academic studies, commercial developments and finally market applications.

Overall, the new integrated biorefinery approach summarized in **Figure 7** suggests application of all process streams for quite high-value products in contrast to the traditional current biorefinery focused largely on the biofuel or monomeric sugar part. In that approach, high-value biorefinery lignins are extracted from pretreated solids (e.g. SSWH or hydrothermally treated), and then possibly fractionated, derivatized or converted into LMNPs. The extracted solids still can be used for monomeric sugar production by enzymatic hydrolysis or alternatively for other high-value applications ^[46,53,56,63,65,86], in particular when a synergism between lignin and cellulose can be expected.

The decision on optimum integrated biorefinery approaches and specific conditions must be made based on sound process-structure-performance correlations for all involved biorefinery streams and considerations of economic aspects.

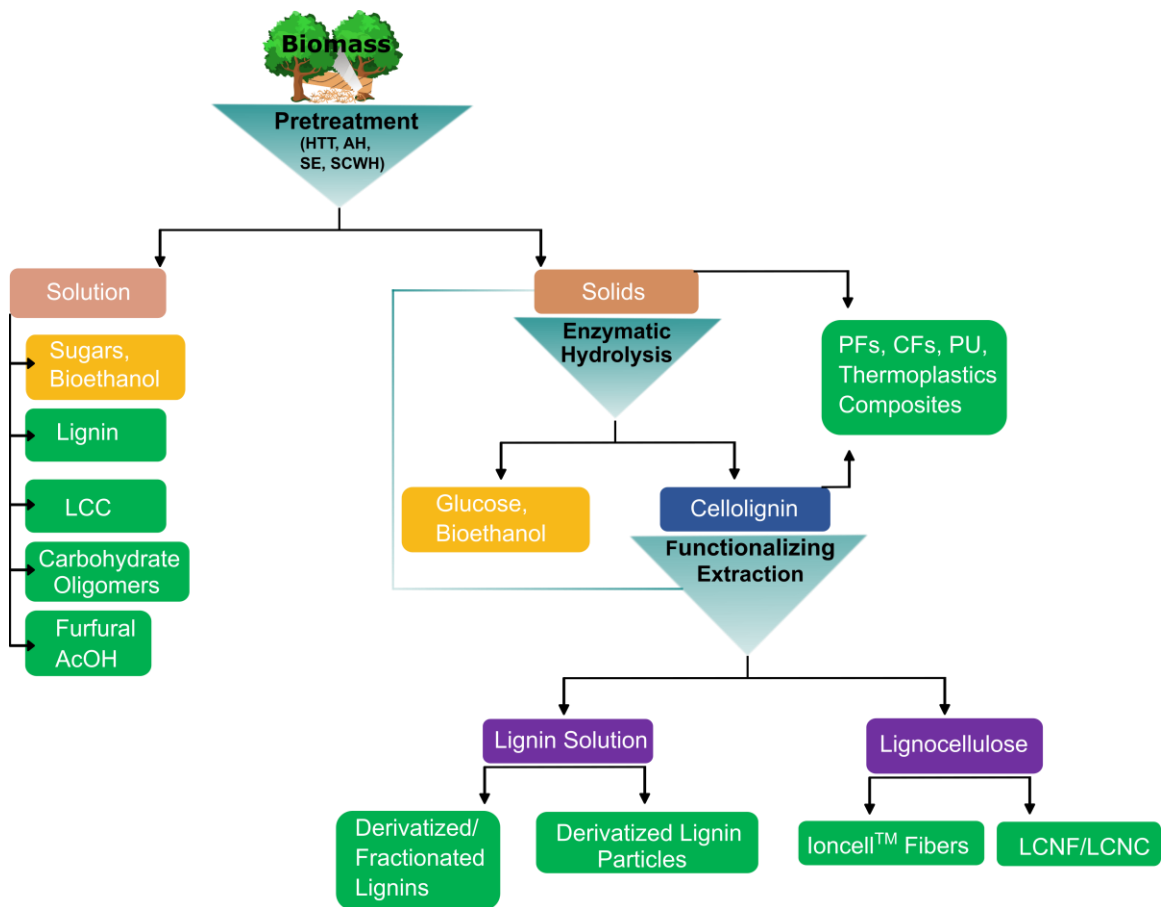


Figure 7. Integrated biorefinery approach targeting high-value products from lignin and polysaccharides (in green) while the traditional main products - monomeric sugars and bioethanol – become by-products (in yellow). Abbreviations: HTT – hydrothermal treatment; AH – acid hydrolysis; SE – steam explosion, SCWH – supercritical water hydrolysis.

2.5. Potential lignin market and some techno-economic aspects of lignin valorization

Economic strategies for valorization of different lignin types for different applications are illustrated in a plot showing estimated lignin production costs and production volume *vs* the volume of potential applications and the potential revenue (**Figure 8**). Most values of lignin costs and volumes are approximated as the market is not yet established. **Figure 8** therefore provides general tendencies rather than accurate numbers.

Apparently, it is reasonable to consider not only the mere material costs, but also the additional costs required to recover lignin *versus* the costs of incineration according to current biorefinery scenarios. Often, the “cost” of crude biorefinery lignins is considered to be equal to the lignin fuel value (ca \$50-200/t)^[10]. However, the expenses required to get lignin combusted, e.g., capital costs for the furnace and other equipment as well as operational costs for washing, drying,

neutralization etc., should be included as well. Thus, if one wants to use the lignin instead of incinerating it, the “costs” of the starting material, crude biorefinery lignin, should be significantly below the fuel value. Sometimes it can be even negative, i.e. when the expenses to get lignin burnt are higher than its energy value. The Russian wood hydrolysis industry is an example for that [106].

BRLs have a big cost advantage over other lignin types especially when crude BRLs can be used without further processing (see 2.3.1). If crude BRLs are to be upgraded (see 2.3.2), the low costs of the starting material render different opportunities economically feasible - in contrast to pulping lignins, especially organosolv ones - and also lower the final product costs as compared to those other lignins (see 2.3.2.3)^[79,102]. The outstanding economical potential of such lignins in thermoplastics applications is obvious from the plot in **Figure 8**. Note the use of product revenue instead of product value/price and potential requirement for specific application instead of product market size; these values account for the product yields from lignin (e.g. 5-20% for BTX and phenol derivatives) and provide more realistic pictures for different lignin scenarios as compared to previous estimates.^[7,107] The values in **Figure 8** are rather approximate due to rather limited lignin market and most applications still being in the development stage.

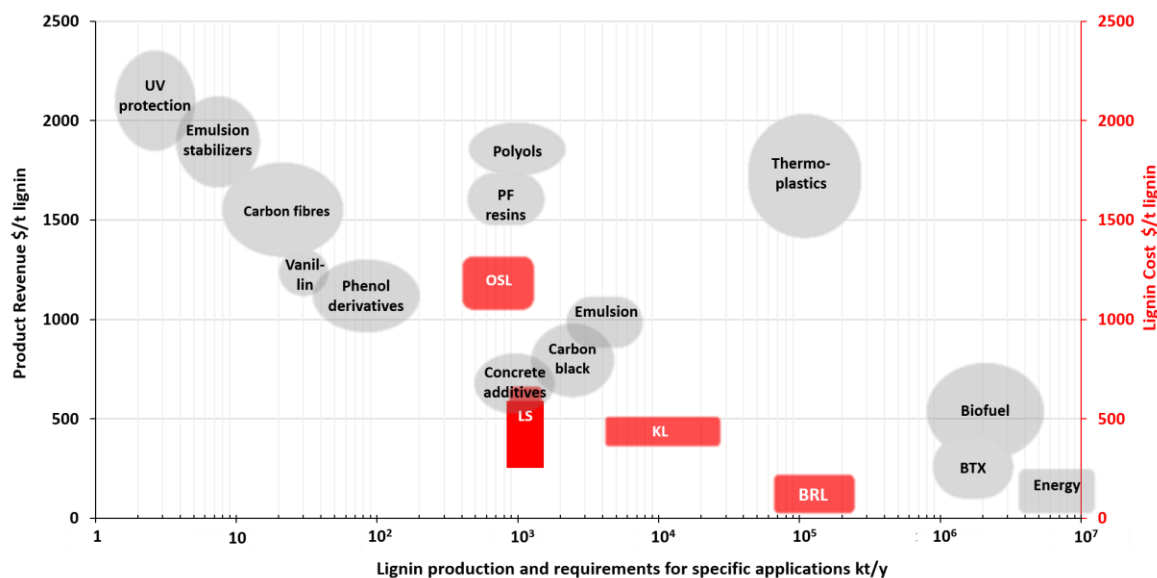


Figure 8. Evaluation of lignin market potentials based on publicly available information ^[1,7,9,79,107]. Abbreviations: OSL – organosolv lignins, LS – liginosulfonates, KL – Kraft lignins, BRL – (crude) biorefinery lignins.

High-value/small market size applications (top left corner of the diagram in **Figure 8**) would be interesting for specific customers and producers of lignin specialties, such as biomedical applications, but not for bulk commodity lignin producers, such as typical Kraft and sulfite mills. Similarly, the use of lignin in very high-volume/low-price sectors (fuel, BTX) is beneficial for lignin customers who get green, sustainable and cheap substrates, but not for commodity lignin producers because the lignin revenue will remain too low. Thus, the “sweet spot” for Kraft lignin producers would be in the high-value application areas of PF, polyols, or thermoplastics; CFs could be also of potential interests provided that the technology and the market develop significantly, as currently expected. All these applications would also be of interest for producers of BRLs, which expectedly operate at much higher production volume ^[4,9] and at lower costs. Thermoplastics applications are of special interest due to their high market size and good value. OSLs have the highest production costs and therefore should be used in the areas where their performance is much better than that of other lignin types and the price difference is acceptable for the customer. This will apparently define the potential market size of this lignin type, which is not clear yet.

Questionable economic rationales for the use of lignin for aromatic monomers production can be illustrated on the example of BTX. The current market price for BTX is in the range of \$1000 – 1200/t with a market size of about 300 Mt/year ^[1]. However, with an ideal yield of 20% - the current yield is about 5% - the revenue from the lignin used in BTX production would be about double as compared to the fuel value ^[9], i.e. ca \$200/t lignin at the current prices. If the residual 80% of the reaction byproducts (“lights”) can be used for generation of syngas, which still has to be technically proven, the revenue can increase to about four times of the fuel value ^[9], i.e., approx.. \$400/t lignin. Thus, in addition to the numerous technical challenges in the process, the potential BTX production costs (CAPEX and OPEX) would bring down the profit for the lignin producer to a rather low (if any) value. A similar situation should be expected for production of other individual phenols, with their value being in the range of \$800-1500 /t.

In contrast, the profitability of vanillin production from lignin would be much better. Although the reaction yield of vanillin from lignin is still low (8-12% w/w), the price of vanillin is about an order of magnitude higher than that of BTX ^[9]. In addition, the remaining oligomeric degradation products might be used as feedstock for PU production^[21], rendering revenue and profitability of this approach rather promising. In fact, this approach would provide even higher revenue (90% x (1500 to 2000 \$) = 1400 to 1800 \$/t lignin) from the byproducts than from the target vanillin (10% x 12000 \$=1200 \$/t lignin). The main limitation should be the low market size for vanillin; it is about 2-10 kt/year only ^[21] which would require only 20-100 kt of lignin. Apparently, most of this volume is already occupied by LS as precursor.

Another important issue defining the potential market size for lignin is the replacement ratio, i.e. the percentage of a current product that can be replaced by lignin without any losses in final performance. Very high replacement levels or even 100% lignin-based products are often targeted in scientific research. They are usually achieved through complex and expensive lignin modifications, but are less suitable for scale-up and commercialization. However, a scenario considering lower replacement levels at lower production costs can be more cost-efficient for the industry, especially as the potential market size is significantly higher than the lignin production level, at least in the near future (**Figure 8**). For example, replacement of ca. 10% thermoplastics with lignin would consume about 20 million tons of lignin annually, which is way above the current lignin production. This can be achieved with a low-cost lignin (e.g. BRL), while high replacement ratios would require derivatized lignins^[98–100] of significantly higher cost.

Noteworthy, there are two scenarios for the use of lignin in PF resins: direct replacement of industrial PF resin *versus* phenol-only replacement during LPF formulation, the latter being the most common research target. However, as phenol makes up only ca. 40% of PF by mass and the price of PF is somewhat higher than that of phenol (approx. \$1600/t vs \$1200/t, respectively^[7]), the economic benefit from 20% PF replacement is higher than from 50% phenol replacement. In addition, crude BRL can completely replace a set of 4 fillers using for plywood glue formulation^[87] providing also technological and logistic benefits. In general, although the creation of 100% lignin-based products is a very noble and attractive goal, it is also rather unrealistic at present. Partial replacement of the current petrochemicals with lignin should be a logical intermediate target.

3. Lignin engineering

Lignins, in contrast to other biorefinery products, such as ethanol, butanol, monomeric sugars and others, do not have a well-defined structure. Moreover, there is a large variety of products called “lignin”, but these lignins are different in chemical composition, molecular structure and hence physical properties. Not surprisingly, the behavior of these lignins in various applications is different. This is illustrated in **Figure 9**. About 30 different organosolv lignins were produced from the same feedstock (pine) under different pulping conditions^[108] and tested in lignin-PF (LPF) adhesive formulations. The results showed large differences in the adhesive performance of the lignins, indicating that the biorefinery process conditions do affect the lignin performance. Moreover, the plot illustrates that only one lignin (red color) showed adhesive performance similar to an industrial PF resin used for comparison; four lignins (yellow color) showed slightly lower, but acceptable performance while the rest (blue color) failed. This test series exemplarily

demonstrated that a random selection of lignins for high-value applications is very unlikely to be successful. A directed development of the lignin-based product and the underlying lignin material with best characteristics for a specific application, so-called lignin engineering, is critical. Unfortunately, such targeted lignin optimization approaches are still rare today. In most situations, lignins are obtained as by-products from biorefineries optimized for sugar/bioethanol production - without consideration of desirable lignin properties and specific lignin usages. In such a setting, the possibility of success of lignin valorization in high-value products is obviously rather low. The alternative approach of lignin engineering requires a thorough understanding of the correlations between the process conditions, structures and properties of the resulting lignins and their required behavior in specific applications.

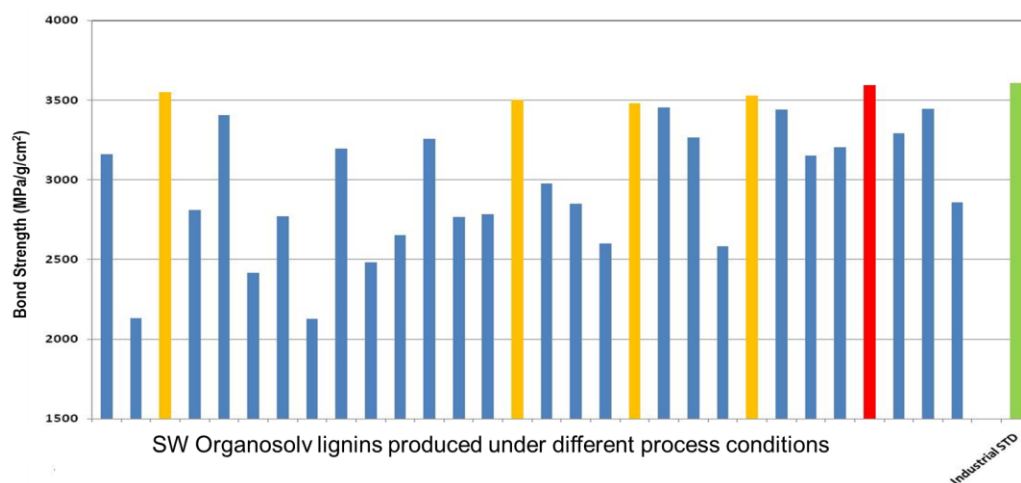


Figure 9. Adhesive performance of lignin-PF resins produced from 30 pine organosolv lignin samples produced under different pulping conditions^[108]. Different bar colors define different performance compared to the industrial standard (green): red – fitting the current standard; yellow – acceptable, close to standard; blue – unacceptable.

The final lignin product can be engineered by tuning the following variables (**Figure 10**):

- Feedstock type (softwood, hardwood, non-wood biomasses and agricultural waste)
- Type of process (different pulping and biorefinery methods)
- Process conditions (e.g., reaction time, temperature, pH, liquid-to-solid ratio)
- Lignin isolation methods
- Post-processing (e.g., fractionation, chemical modification, LMNP/CLC production).

It should be noted that the main current pulping processes are limited with regard to variations in feedstock and process conditions, which are set according to the target properties of the chemical pulps. Here, lignin engineering is rather restricted and can only be done through post-processing of pulping lignins. In contrast, variations in biorefinery conditions are well possible, they affect only the yield of the target products (sugars/ethanol, biofuels) but not (or not significantly) their properties. Thus, sugar-based biorefineries offers much more opportunities and much greater flexibility for lignin engineering than the pulp and paper industry. However, this biorefinery flexibility also results in challenges related to the selection of the best lignin candidate from a huge variety of types.

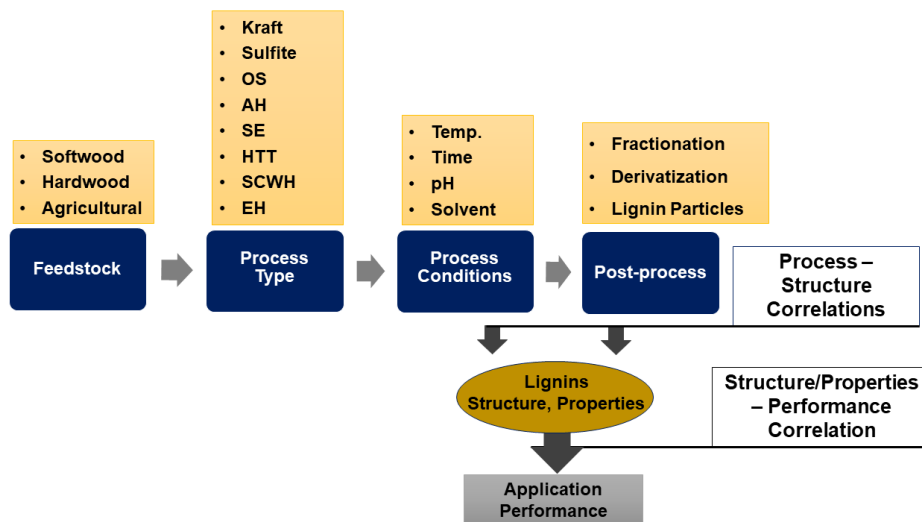


Figure 10. Main variables in lignin engineering. Abbreviations: OS – organosolv pulping; AH – acid hydrolysis; SE – steam explosion; HTT – hydrothermal treatment; SCWH – supercritical water hydrolysis; EH – enzymatic hydrolysis.

Many current concepts argue that inconsistencies or variations in pulping and biorefinery lignins as a chemical feedstocks can be mitigated by lignin derivatization^[4,18,75,97], with the new functionalities having a much stronger effect on lignin properties than the original functionalities. Consequently, lignin optimization via alterations in feedstock and process conditions is not important from this point of view. However, a variation in the structure of the original lignins should eventually result in corresponding differences in the amount of newly introduced functionalities. Also differences in the molecular weight of the original lignins would likely remain

after derivatization. Thus, even derivatized lignins can be well different as feedstocks for the chemical industry.

Much current research targets the maximal degree of substitution (DS) in lignin derivatization. However, this approach may not be optimal from industrial and economic viewpoints. The optimization of the DS in terms of cost-performance rather than targeting maximal DS should be considered in lignin engineering.

Lignin engineering through structure – properties – performance relationships implies large number of samples to be efficiently evaluated. Any product development must be based on a thorough characterization of the starting materials and their changes upon further processing. Consequently, the analytical approach for lignin evaluation should be reliable, informative – providing sufficient amounts of relevant structural information, productive - requiring minimum labor and other resources, and fast enough – being able to handle sufficiently large sample amounts in the allotted time. This requires optimization and validation of the current analytical protocols as well as development of new analytical methods, in particular towards higher throughput.

3.1. Aspects of lignin structural analysis pertinent to lignin engineering: fingerprinting and structure quantitation by NMR

Lots of different methods exist in lignin analysis, including wet chemistry and spectroscopic/spectrometric techniques, each providing specific information and having certain pros and cons ^[109–111]. The wealth of analytical tools to characterize lignins cannot be covered here. Suffice it to say that it is of primary importance to select the right specific tool from the methodology toolbox, depending on the research object and research task. In lignin engineering, reactivities and product parameters need to be linked to structural changes in the starting lignins, and these structural alterations are not necessarily large. Sum parameters are of little use here, but in-depth and detailed structural information and quantification of structural elements and functionalities is needed. This can be achieved by a complimentary set of wet-chemical methods, such as functional group analysis and degradation techniques, and/or by nuclear magnetic resonance (NMR) spectroscopy techniques. The latter vary in time requirements, information content, and quantifiability, for instance ¹H and ³¹P NMR are express methods while high-resolution, quantitative ¹³C and 2D NMR methods are time-consuming but quite comprehensive.

2D NMR methods are considered as the most powerful analytical approach in lignin analysis in general, and are on the way to becoming a gold standard also in lignin engineering. The combination of the two spectral dimensions, mostly the combination of ¹H and ¹³C, provide a great advantage: the signals which are highly overlapping and superimposed in both the ¹H and ¹³C

domain can be well separated even for the very complex lignin macromolecules. Contained carbohydrate components can be analytically covered at the same time. The technique is very successful in comprehensive analysis of various native lignins in which lignin structure can be described by a manageable amount of structural units and inter-unit links (**Figure**). 2D NMR was also decisive in identification and quantification of new substructures of technical lignins which are much more complex than native lignins as pronounced structural changes during processing add to the already high structural heterogeneity in native state^[17,31,112,113]. 2D NMR spectra (HSQC) of technical lignins acquired on an advanced NMR spectrometer provide a few hundred signals which are perfectly suited for lignin fingerprinting (**Figure 9**) and thus to detect differences between engineered lignins or to monitor biorefinery lignins along a processing line. Most of the NMR signals in 2D lignin spectra are of rather low intensity as the chemical structures of biorefinery lignins, and technical lignins in general, are extremely diverse. Identification and exact quantification of all these structural moieties on a molecular level would not only be a tremendous, almost unachievable task, but also have no practical rationale. Today, an advanced quantification of known moieties in technical lignins can report below 50% (often below 20%) of structural units only, leaving the majority of the structure uncharacterized^[1,17,114] (**Figure**). This is different from the structurally much less diverse native lignins, for which the structural assignment rate can be much higher and in some cases complete.

Due to the heterogeneity of technical lignins, characterization aims at the functional level quantifying specific lignin functionalities rather than attempting to detect each individual lignin substructure. For this purpose, 2D NMR is less suited, but quantitative ¹³C NMR is able to comprehensively characterize different lignin functionalities and therefore to obtain a general quantitative picture of the structure of the whole lignin macromolecule (**Table 4**). A combination of quantitative ¹³C and 2D NMR methods is the most powerful approach in characterization of very complex and heterogeneous biorefinery and technical lignins of diverse types.

Summarizing numerous analytical works on the characterization of technical lignins, we can clearly state that all biorefinery and pulping processes result in significant lignin degradation. It is always accompanied with a decrease in aliphatic OH (primary and especially secondary ones), oxygenated aliphatic moieties in general and β -O-4 units specifically and an increase in phenolic OH, COOH, saturated aliphatic moieties, degree of condensation (DC) and demethylation when compared to native lignins (**Table 4**). However, there are also significant structural differences between various technical lignins depending on the biomass source, process utilized and its severity as well as specific ways of lignin isolation from process streams and potential fractionation.

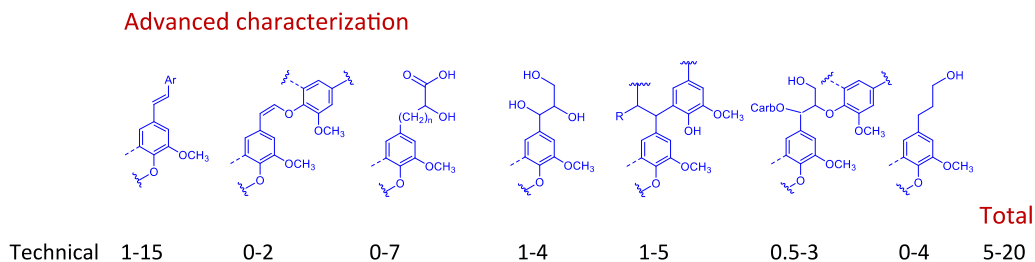
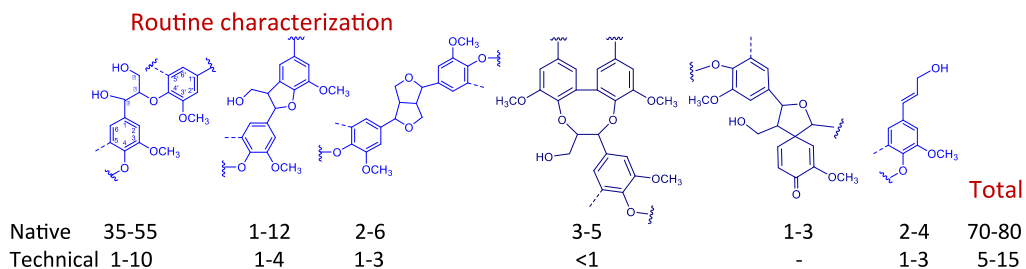


Figure 11 Example of a determination of lignin structures in native and technical lignins with a semiquantitative HSQC NMR method. Numbers indicate XXXXXX

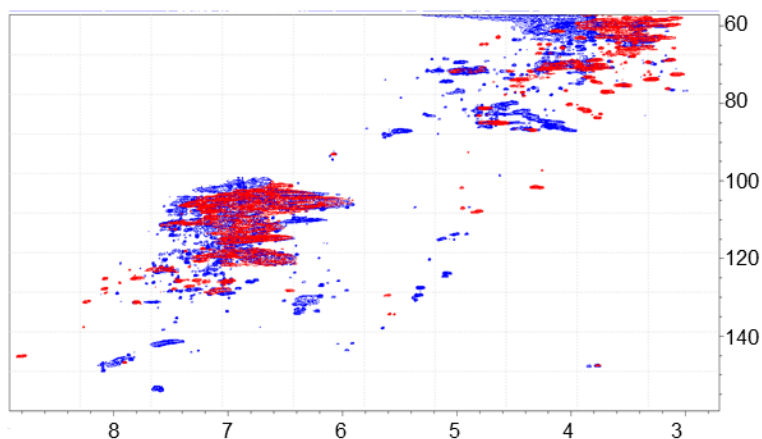


Figure 9 Fingerprinting of Alcell (blue) and aspen Kraft (red) lignins using a HSQC NMR technique, recorded on a Bruker 950 MHz NMR spectrometer equipped with a CryoProbe™ probehead.

3.2 Small-scale performance evaluation methodology as bottleneck in lignin engineering

Although further development is clearly necessary, already now structural lignin analysis is quite reliable and informative. The evaluation of lignin performance in various applications is the real bottleneck in lignin engineering. Current approaches are often time-consuming, require much work and large lignin quantities, and are therefore low productivity. The development of small-scale and fast screening methods for performance evaluation of lignins in various

applications is paramount in lignin engineering and for expanding binary structure-property correlations into ternary structure-property-performance correlations which characterize quality and suitability of lignins for specific applications.

Table 4 Amounts of various lignin moieties (per 100Ar).

Moieties/range	Alcell	Indulin	AKL	SEPL	Sucrolin	SBL	AMWL	PMWL
Total CO	29	15	21	23	30	19	16	20
Non-conj. CO	15	7	11	11	17	7	3	3
Conj. CO	14	8	10	12	13	11	13	17
Total COOR	21	17	28	22	38	37	13	6
Non-conj. COOR	17	15	25	18	27	27	8	4
Conj. COOR	4	2	3	4	11	10	5	2
Total OH	103	115	107	124	92	96	156	140
Aliph. OH	33	49	31	61	43	37	134	107
OHpr	19	31	17	33	19	17	72	67
OHsec	14	18	14	28	24	20	62	40
Phenolic OH	70	66	76	63	49	59	22	33
S:G-ratio	1.18	NA	1.31	1.63	0.53	0.51	2.11	NA
OMe	103	81	120	126	81	92	164	97
ArH	202	234	199	201	207	213	221	253
DC, %	44	66	44	37	58	53	11	43
β -5	3	4	2	2	1	1	2	10
β - β^{**}	3	4	5	4	2	1	8	4
β -O-4	7	7	1	17	4	2	52	42
Oxygen. Aliph.	82	93	93	128	64	52	237	214
Saturated Aliph.	149	109	145	116	161	140	56	32
Side chain length	281	233	269*	289	293	248	322	272
Alkyl ethers	50	44	54*	68	21	15	103	107
Carbohydrates	<1	~1	4	<1	<1	~1	<1	~1
M _{Ar}	178	173	201	194	203	195	218	180

*corrected for sugar content; **The number of C₉-units involved in resinol structures; as the structure is symmetric, the number of resinol structures is ½ of the C₉-units involved.

The automatic bond evaluation system (ABES) test is a rare exception from the general lack of suitable test methods and is a very good example of a high-throughput approach (**Figure**) that is very efficient at evaluating lignin performance in adhesives applications. In this method, adhesives are tested between small pieces of different materials, the bonds being formed under well controlled conditions (temperature, humidity, press time, curing, etc.) and tested mechanically, e.g. in shear mode, immediately or after different curing or storage times. The method enables evaluation of adhesive bond strength development and strength maxima as a function of temperature and time for different adhesive formulations. It has been developed into an ASTM standard test method D 7998-15 (ASTM 2015).

Naturally, ABES tests have been used to screen different lignin types in resin and adhesive applications, for instance in substituting plywood PF and OSB PF resins, see

Figure 5. The results of the ABES tests usually correlate well with pilot-scale and industrial trials of manufacturing and testing plywood and OSB panels.

The lignin community would be in high need for developments of similar small-scale high-throughput screening methods for such important potential lignin applications as thermoplastics, polyurethanes (PU), carbon fibers (CF), activated carbons, and others.

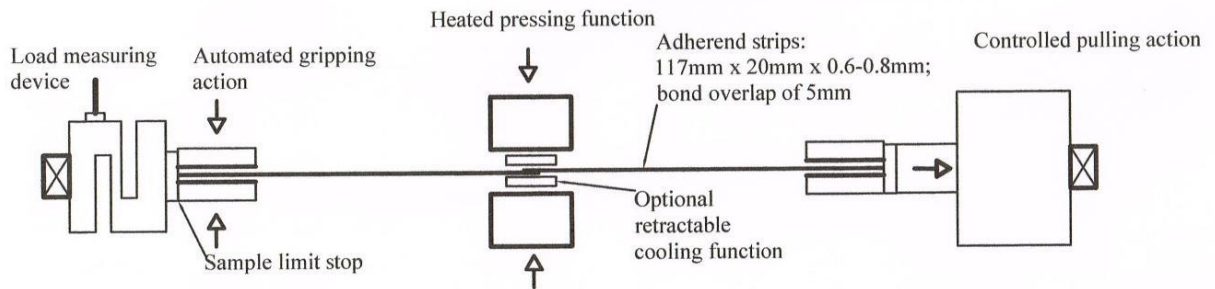


Figure 13 Image: a typical test sample mounted in an ABES test system. Schematic: bonding and testing concept according to the ABES setup.

3.3 Problems in establishing structure-property performance correlations for lignin applications

The fact that fast and easy analytical methods (see 3.1.) are scarce and the lack of suitable fast performance test methods (see 3.2.) sometimes lead to claims of alleged correlations between structure and properties of lignins with their application performance, which are more based on “educated guesses” rather than on unambiguous experimental data, which might result in erroneous conclusions. The application of lignin in PF adhesive formulations provides an illustrative example in this regard.

Based on the mechanism of phenol-formaldehyde resin formation, it has become widely accepted that lignin reactivity and adhesive performance in lignin-PF blends must correlate with the amount of lignin “reactive centers”, specifically with the number of free 3- and 5-positions in the lignin’s phenolic moieties ^[1,7,115]. Also, the best performance of lignin in these applications was claimed to be associated with its minimal ^[7] or an optimum molecular weight ^[115]. Recent results,

however, showed no such correlation between the lignin structure (**Table 3**), in particular the amount of reactive centers or the molecular weight, and the bond performance, neither for cellulose-containing SSWH lignins (

Figure 5a) nor for different technical lignins of high purity (

Figure 5b). As an important practical outcome, hardwood lignins, with their intrinsically lower number of free 3- and 5-positions, seem to have no application disadvantages as compared to softwood and non-wood lignins (

Figure 5b), as the current reactivity correlation dogma apparently no longer holds.

While PCA analysis shows a correlation of the number of reactive centers and lignin molecular weight with the shear strength of plywood produced with LPF resins ^[115], there is no correlation between the structural lignin parameters and the resulting bond quality of plywood as determined by so-called “% wood failures”, the main parameter used in the industry. Recently, a few other publications supported the absence of correlation between the amount of lignin reactive centers or lignin molecular mass and the bond performance of the resulting LPF. Lourençon et al. did not find a statistically significant difference in the performance of different fractions of *Eucalyptus grandis* Kraft lignin with different chemical structure incorporated into LPF formulations (50% phenol replacement with lignin) ^[116]. LPFs from the hardwood (eucalyptus) lignins performed similarly to a softwood Kraft lignin based LPF. Solt et al. showed that various fractions of softwood Kraft lignin with different molecular mass incorporated into LPF (50% phenol replacement with lignin) did not result in differences in adhesive performance either ^[117]. In addition, the HSQC spectrum of LPF shows a very interesting phenomenon, not mentioned in the paper ^[116]: no covalent linkages between lignin and PF polymer can be observed in the spectrum. All diphenylmethane moieties reported in fact belong to phenol crosslinking, but do not include phenolic lignin units, since characteristic signals of guaiacyl diarylmethane moieties (at about 29/3.8 ppm) are missing.

These results imply that the number of “reactive centers”, according to the conventional definition, may not necessarily correlate with the adhesive bond strength. Two hypotheses can now be considered:

1. Crosslinking between lignin and PF polymer occurs, but may not be the decisive factor for adhesion strength. Lignin, in contrast to monomeric phenols and formaldehyde, is already a polymer and therefore intensive crosslinking is not needed; just a single covalent bond would be enough to crosslink two polymeric molecules in lignin-PF blends.
2. Crosslinking between lignin and PF does not occur; the lignin acts then “only” an efficient filler or/and an extender. In this case, the main factor is the compatibility of lignin with PF (and other adhesives) ^[18].

Experimental data indicate that the amount of the reactive centers is not the only important factor and other characteristics, such as steric factors, flexibility of the lignin macromolecule, lignin compatibility, play perhaps a more important role in lignin-PF blend performance. For a better description of the structure-property-performance relationships more sophisticated models should be developed.

Another example of an attempt to elucidate the structure – performance correlation of lignin products was lignin-based carbon materials. The production of nanofibers via electrospinning solely based on lignin, i.e. without any spinning additive, has been demonstrated recently^[41]. The authors used an industrial hardwood Kraft lignin isolated according to the LignoBoost™ technology and refined by a sequential solvent fractionation procedure to extract a high molar mass fraction with low polydispersity and little inorganic and organic impurities. The authors highlighted the need of a systematic approach towards lignin valorization due to the high lignin heterogeneity. They provided a model workflow (**Figure 10**) which considers the importance of the characteristics of the initial lignin precursor for the properties of the resulting carbon fibers^[41]. However, it is extremely difficult - if possible at all - to draw conclusions about structure-property relationships from a single lignin sample. A potential solution to the problem is to compare different lignins with varying properties to eliminate some influencing variables. This way a library of lignin precursors can be established which can be used as reference for future studies, provided the lignin analytics employed are comparable and accurate. In their most recent study, Schlee et al. have started following this strategy by comparing two well-characterized Kraft lignins (softwood and hardwood ones) with variable characteristics. The lignins that were compared regarding their suitability as precursors for the manufacture of activated carbon nanofibers used as supercapacitor electrodes span a wide range of characteristics (molar mass, side-chain linkages, functional groups). A valid correlation of few lignin properties with the carbon structure, porosity and the final performance of the supercapacitors was determined. . In the future, this type of study needs to be refined to progressively compare more similar lignin samples to be able to sharpen the correlation.

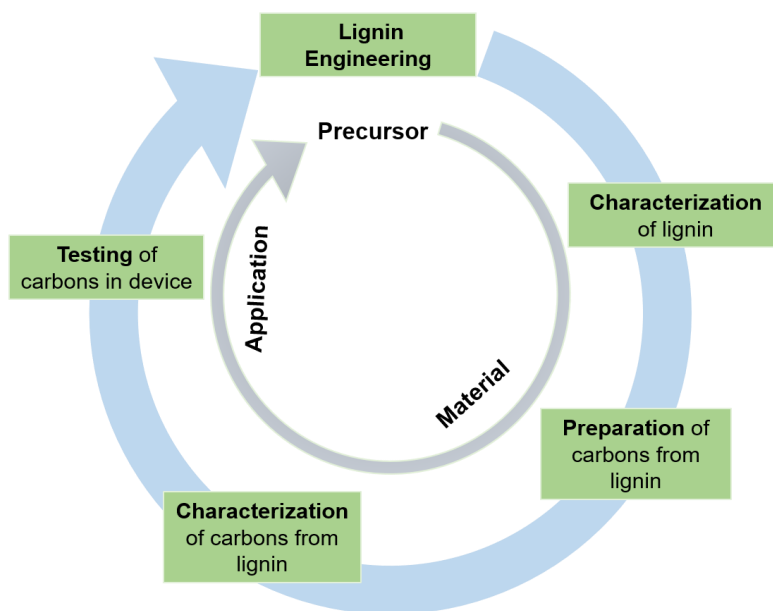


Figure 10. Workflow for engineering of lignin carbon materials modified based on [41].

3.4. Strategies to address lignin structure – property – performance correlations

Currently, the most common approach towards lignin structure-property-performance relationships is comparing the performance of a few lignins of different type, i.e. from different biomass (softwood, hardwood, non-wood) and different processes (Kraft, soda, sulphite, organosolv, various biorefineries), in a specific application. However, these lignins have a large number of different characteristics (various chemical subunits, molecular weight, physical characteristics etc.), and it gets extremely difficult (if possible at all) to attribute the difference in their performance to specific lignin characteristics. To address structure – performance correlations, two potential approaches can be used:

1. Selective (analytical) lignin modification to change only one variable (ideally) at the time keeping all others constant;^[111,118]
2. The use of large number of different lignins followed by comprehensive modeling.

The first approach has been successfully used to understand lignin reactivity in different pulping processes^[119,120]. It also provided useful information on structure-properties correlation regarding the effect of lignin methylation on Tg and miscibility of the modified lignins with PE and PP^[121–123]. However, no effect on lignin performance has been reported yet.

The second approach has been applied during extensive research on organosolv lignins^[124,125] and theoretical models (MatLab) to find correlations between process conditions and resulting lignin structural characteristics have been investigated. However, no simple correlation between

lignin structure and its properties (T_g , M_w , melting flow) and performance (in LPF resins) has been found yet, which calls for more sophisticated modeling. Application of digitalization, artificial intelligence (AI) and machine learning (ML) is expected to be very useful in this regards.

Once structure-performance correlations have been identified, an important step will be to define the sensitivity of the performance to changes in certain lignin properties, such as hydroxyl group content, molecular weight, or polydispersity. This is important because lignins are inherently variable from batch to batch due their natural origin and varying sources. To determine the most sensitive variable(s) would be very important for industrial process control.

Lignin engineering is important, but not sufficient on its own, for the final product optimization. In the one-to-one replacement of petrochemical precursors with lignins it should not be forgotten that lignin is chemically and structurally inherently different from the currently used petrochemicals. This clearly indicates the need for adjustment and optimization of the existing process, and not only the lignin. Thus, the best final product will be obtained through engineering of lignin and the optimization of the production process.

Closing remarks

Current biorefinery concepts should be elaborated and optimized for integrated utilization of all products in high-value applications rather than focusing on bioethanol, biofuels or sugars only, as is still common at present. Engineering of lignin for high-value applications will be a game changer within these efforts. Biorefinery lignins will become the main target in such optimized biorefineries, while sugars/bioethanol are still utilized and valued, although now actually being by-products.

Biorefinery lignins can be used, if applied correctly, in various high-value applications, way beyond their fuel value. This can be achieved direct use of biorefinery lignins – lignins comprising given amounts of crystalline cellulose - and/or after sustainable and cost-effective upgrading. These promising opportunities favor a rethinking of the value utilization of biorefinery lignins.

Lignin engineering for high-value applications requires serious analytical efforts and method development including lignin structural analysis and, especially, high-throughput methods for evaluation of lignin performance in specific applications. New and comprehensive lignin structure-performance relationships are urgently needed and at the same time the current ones should be revised and further developed.

Attempts to find a “best-for-everything” lignin or a “killer application” for all lignin types are unreasonable. Each lignin type should find its own place, and each application will rest on suitable lignins particularly useful for that particular purpose.

List of abbreviations – Phil, could you please take care of it?

ABES	Automatic Bond Evaluation System
AH	Acid hydrolysis
AI	Artificial intelligence
AIL	Acid insoluble lignin
BRLs	Biorefinery lignins
BTX	Benzene, toluene, and xylene
CFs	Carbon fibers
CLPs	Colloidal lignin particles
CMC	Carboxymethyl cellulose
CNC	Cellulose nanocrystals
CNF	Cellulose nanofibers
CNW	Cellulose nanowhiskers
DC	Degree of condensation
DMA	Dynamic mechanical analysis
DMF	Dimethyl formamide
DOE	Department of Energy
DS	Degree of substitution
EH	Enzymatic hydrolysis
EtOH	Ethanol
GMA	Glycidyl methacrylate
HC	Holocellulose
HDO	Hydrodeoxygenation
HTT	Hydrothermal treatment
HW	Hardwood
ILs	Ionic liquids
KL	Kraft lignin
LCNF	Ligno-cellulose nanofibers
LMNP	Lignin micro-nano-particles
LNP	Lignin nanoparticles
LPF	Lignin-phenol-formaldehyde
LS	Lignosulfonates
ML	Machine learning
MOE	Modulus of elasticity
MOR	Modulus of rupture
MUF	Melamine-urea formaldehyde
O/W	Oil-in-water
OSB	Oriented strand board
OSL	Organosolv lignin
PAN	Polyacrylonitrile
PE	Polyethylene
PF	Phenol-formaldehyde
PHB	Polyhydroxybutyrate, Poly(3-hydroxybutyrate)
PLA	Poly(lactic acid)

pMDI	Methylene diphenyl
PP	Polypropylene
PS	Polystyrene
PU _s	Polyurethanes
PVA	Polyvinyl alcohol
RF	Radio frequency
SCWH	Supercritical water hydrolysis
SE	Steam explosion
SHL _s	Supercritical hydrolysis lignins
SHR _s	Supercritical hydrolysis residues
SSWH	Subcritical and supercritical water hydrolysis
SW	Softwood
THF	Tetrahydrofuran
UF	Urea formaldehyde
UV-vis	Ultraviolet and visible

References

- [1] A. Berlin, M. Balakshin, *Bioenergy Res. Adv. Appl.* **2014**, 315–336.
- [2] L. Cao, I. K. M. Yu, Y. Liu, X. Ruan, D. C. W. Tsang, A. J. Hunt, Y. S. Ok, H. Song, S. Zhang, *Bioresour. Technol.* **2018**, *269*, 465–475.
- [3] S. Gillet, M. Aguedo, L. Petitjean, A. R. C. Morais, A. M. da Costa Lopes, R. M. Łukasik, P. T. Anastas, *Green Chem.* **2017**, *19*, 4200–4233.
- [4] A. J. Ragauskas, G. T. Beckham, M. J. Bidy, R. Chandra, F. Chen, M. F. Davis, B. H. Davison, R. A. Dixon, P. Gilna, M. Keller, P. Langan, A. K. Naskar, J. N. Saddler, T. J. Tschaplinski, G. A. Tuskan, C. E. Wyman, *Science (80-.)*. **2014**, *344*, 1246843.
- [5] C. O. Tuck, E. Pérez, I. T. Horváth, R. A. Sheldon, M. Poliakoff, *Science (80-.)*. **2012**, *337*, 695–699.
- [6] J. Miller, M. Faleiros, in *RISI Lat. Am. Pulp Pap. Outlook Conf.*, **2016**.
- [7] L. Dessbesell, M. Paleologou, M. Leitch, R. Pulkki, C. (Charles) Xu, *Renew. Sustain. Energy Rev.* **2020**, *123*, 109768.
- [8] T. D. H. Bugg, R. Rahmanpour, *Curr. Opin. Chem. Biol.* **2015**, *29*, 10–17.
- [9] J. E. Holladay, J. F. White, J. J. Bozell, D. Johnson, in *Top Value Added Chem. from Biomass*, **2007**, pp. 1–79.
- [10] S. V. Obydenkova, P. D. Kouris, E. J. M. Hensen, D. M. J. Smeulders, Y. van der Meer, M. D. Boot, *Bioresour. Technol.* **2019**, *291*, 121805.
- [11] 2020 Insider Inc., Finanzen.net GmbH, “Markets Insider,” can be found under <https://markets.businessinsider.com/commodities/ethanol-price>, **n.d.**
- [12] R. Rinaldi, R. Jastrzebski, M. T. Clough, J. Ralph, M. Kennema, P. C. A. Bruijninx, B. M. Weckhuysen, *Angew. Chemie - Int. Ed.* **2016**, *55*, 8164–8215.
- [13] A. L. Jongerius, P. C. A. Bruijninx, B. M. Weckhuysen, *Green Chem.* **2013**, *15*, 3049–3056.
- [14] M. P. Pandey, C. S. Kim, *Chem. Eng. Technol.* **2011**, *34*, 29–41.
- [15] M. V. Galkin, J. S. M. Samec, *ChemSusChem* **2016**, *9*, 1544–1558.
- [16] J. Zakzeski, P. C. A. Bruijninx, A. L. Jongerius, B. M. Weckhuysen, *Chem. Rev.* **2010**, *110*, 3552–3599.

- [17] W. Schutyser, T. Renders, S. Van Den Bosch, S.-F. Koelewijn, G. T. Beckham, B. F. Sels, *Chem. Soc. Rev.* **2018**, *47*, 852–908.
- [18] W. G. Glasser, *Front. Chem.* **2019**, *7*, 1–17.
- [19] J. H. Lora, W. G. Glasser, *J. Polym. Environ.* **2002**, *10*, 39–48.
- [20] A. Duval, M. Lawoko, *React. Funct. Polym.* **2014**, *85*, 78–96.
- [21] P. C. Rodrigues Pinto, E. A. Borges da Silva, A. E. Rodrigues, in *Biomass Convers. Interface Biotechnol. Chem. Mater. Sci.*, **2012**, pp. 381–420.
- [22] S. Elumalai, B. Arumugam, P. Kundu, S. Kumar, in *Biomass, Biofuels, Biochem.*, Elsevier B.V., **2020**, pp. 459–483.
- [23] L. Shuai, M. T. Amiri, Y. M. Questell-Santiago, F. Héroguel, Y. Li, H. Kim, R. Meilan, C. Chapple, J. Ralph, J. S. Luterbacher, *Science (80-)*. **2016**, *354*, 329–333.
- [24] Y. Li, L. Shuai, H. Kim, A. H. Motagamwala, J. K. Mobley, F. Yue, Y. Tobimatsu, D. Havkin-Frenkel, F. Chen, R. A. Dixon, J. S. Luterbacher, J. A. Dumesic, J. Ralph, *Sci. Adv.* **2018**, *4*, 1–10.
- [25] L. Dong, L. Lin, X. Han, X. Si, X. Liu, Y. Guo, F. Lu, S. Rudić, S. F. Parker, S. Yang, Y. Wang, *Chem* **2019**, *5*, 1521–1536.
- [26] E. Rojo, M. S. Peresin, W. W. Sampson, I. C. Hoeger, J. Vartiainen, J. Laine, O. J. Rojas, *Green Chem.* **2015**, *17*, 1853–1866.
- [27] K. L. Spence, R. A. Venditti, O. J. Rojas, Y. Habibi, J. J. Pawlak, *Cellulose* **2011**, *18*, 1097–1111.
- [28] M. Delgado-Aguilar, I. González, Q. Tarrés, M. Àngels Pèlach, M. Alcalà, P. Mutjé, *Ind. Crops Prod.* **2016**, *86*, 295–300.
- [29] H. Q. Lê, K. Dimic-Misic, L.-S. Johansson, T. Maloney, H. Sixta, *Cellulose* **2018**, *25*, 179–194.
- [30] S. S. Nair, N. Yan, *Cellulose* **2015**, *22*, 3137–3150.
- [31] A. Berlin, M. Balakshin, N. Gilkes, J. Kadla, V. Maximenko, S. Kubo, J. Saddler, *J. Biotechnol.* **2006**, *125*, 198–209.
- [32] L. O. Morales, M. Iakovlev, R. Martin-Sampedro, J. L. Rahikainen, J. Laine, A. van Heiningen, O. J. Rojas, *Bioresour. Technol.* **2014**, *161*, 55–62.
- [33] H. Bian, Y. Gao, R. Wang, Z. Liu, W. Wu, H. Dai, *Cellulose* **2018**, *25*, 1309–1318.
- [34] Y. Liu, *ACS Sustain. Chem. Eng.* **2018**, *6*, 5524–5532.
- [35] S. Herzele, S. Veigel, F. Liebner, T. Zimmermann, W. Gindl-Altmatter, *Ind. Crops Prod.* **2016**, *93*, 302–308.
- [36] D. Ballner, S. Herzele, J. Keckes, M. Edler, T. Griesser, B. Saake, F. Liebner, A. Potthast, C. Paulik, W. Gindl-Altmatter, *ACS Appl. Mater. Interfaces* **2016**, *8*, 13520–13525.
- [37] A. Winter, L. Andorfer, S. Herzele, T. Zimmermann, B. Saake, M. Edler, T. Griesser, J. Konnerth, W. Gindl-Altmatter, *J. Mater. Sci.* **2017**, *52*, 60–72.
- [38] H. Orelma, A. Tanaka, H. Rautkoski, I. Nurminen, J. Kouko, A. Koponen, *Cellulose* **2017**, *24*, 3869–3882.
- [39] T. Horseman, M. Tajvidi, C. I. K. Diop, D. J. Gardner, *Cellulose* **2017**, *24*, 2455–2468.
- [40] P. Schlee, S. Herou, R. Jervis, P. R. Shearing, D. J. L. Brett, D. Baker, O. Hosseinaei, P. Tomani, M. M. Murshed, Y. Li, M. J. Mostazo-López, D. Cazorla-Amorós, A. B. Jorge Sobrido, M.-M. Titirici, *Chem. Sci.* **2019**, *10*, 2980–2988.
- [41] P. Schlee, O. Hosseinaei, D. Baker, A. Landmér, P. Tomani, M. J. Mostazo-López, D. Cazorla-Amorós, S. Herou, M. M. Titirici, *Carbon* **2019**, *145*, 470–480.
- [42] E. Frank, L. M. Steudle, D. Ingildeev, J. M. Spörl, M. R. Buchmeiser, *Angew. Chemie - Int. Ed.* **2014**, *53*, 5262–5298.
- [43] S. P. Maradur, C. H. Kim, S. Y. Kim, B.-H. Kim, W. C. Kim, K. S. Yang, *Synth. Met.* **2012**, *162*, 453–459.
- [44] X. Dong, C. Lu, P. Zhou, S. Zhang, L. Wang, D. Li, *RSC Adv.* **2015**, *5*, 42259–42265.
- [45] A. Lehmann, H. Ebeling, H.-P. Fink, *WO Pat. 2012/156441 A1* **2012**.

- [46] Y. Ma, S. Asaadi, L.-S. Johansson, P. Ahvenainen, M. Reza, M. Alekhina, L. Rautkari, A. Michud, L. Hauru, M. Hummel, H. Sixta, *ChemSusChem* **2015**, *8*, 4030–4039.
- [47] N. Byrne, M. Setty, S. Blight, R. Tadros, Y. Ma, H. Sixta, M. Hummel, *Macromol. Chem. Phys.* **2016**, *217*, 2517–2524.
- [48] N. Byrne, R. De Silva, Y. Ma, H. Sixta, M. Hummel, *Cellulose* **2018**, *25*, 723–733.
- [49] C. Olsson, B. Hagström, E. Sjöholm, A. Reimann, in *Carbon Fibres from Lignin-Cellulose Precursor- ISWFPC*, **2015**.
- [50] C. Olsson, E. Sjöholm, A. Reimann, *Holzforschung* **2017**, *71*, 275–283.
- [51] M. Ago, J. E. Jakes, L. S. Johansson, S. Park, O. J. Rojas, *ACS Appl. Mater. Interfaces* **2012**, *4*, 6849–6856.
- [52] M. Ago, K. Okajima, J. E. Jakes, S. Park, O. J. Rojas, *Biomacromolecules* **2012**, *13*, 918–926.
- [53] M. Ago, J. E. Jakes, O. J. Rojas, *ACS Appl. Mater. Interfaces* **2013**, *5*, 11768–11776.
- [54] Y. Zhang, L. Kouisni, X.-M. Wang, M. Paleologou, M. W. Feng, G. Brunette, *Cellulose Nanocrystals - Thermoset Resin Systems, Applications Thereof and Articles Made Therefrom*, **2014**, WO 2014/124541 A1.
- [55] Z. Liu, Y. Zhang, X. Wang, D. Rodrigue, *Mater. Sci. Appl.* **2015**, *6*, 567–575.
- [56] M. W. Feng, X.-M. Wang, Y. Zhang, S. Raymond, R. Berry, *Nanocrystalline Cellulose Derived Formaldehyde-Based Adhesive, Uses Thereof And Process For Preparing Same*, **2016**, US2016/0271610 A1.
- [57] I. Spiridon, K. Leluk, A. M. Resmerita, R. N. Darie, *Compos. Part B Eng.* **2015**, *69*, 342–349.
- [58] R. Zhang, X. Xiao, Q. Tai, H. Huang, J. Yang, Y. Hu, *J. Appl. Polym. Sci.* **2013**, *127*, 4967–4973.
- [59] S. Yang, T.-Q. Yuan, Q. Shi, R.-C. Sun, in *Green Chem. Chem. Eng.*, **2019**, pp. 405–426.
- [60] M. A. S. Anwer, H. E. Naguib, A. Celzard, V. Fierro, *Compos. Part B Eng.* **2015**, *82*, 92–99.
- [61] O. Gordobil, I. Egüés, R. Llano-Ponte, J. Labidi, *Polym. Degrad. Stab.* **2014**, *108*, 330–338.
- [62] I. Spiridon, C. E. Tanase, *Int. J. Biol. Macromol.* **2018**, *114*, 855–863.
- [63] W. Yang, E. Fortunati, F. Dominici, G. Giovanale, A. Mazzaglia, G. M. Balestra, J. M. Kenny, D. Puglia, *Eur. Polym. J.* **2016**, *79*, 1–12.
- [64] R. Liu, Y. Peng, J. Cao, Y. Chen, *Compos. Sci. Technol.* **2014**, *103*, 1–7.
- [65] S. Agustin-Salazar, P. Cerruti, L. Á. Medina-Juárez, G. Scarinzi, M. Malinconico, H. Soto-Valdez, N. Gamez-Meza, *Int. J. Biol. Macromol.* **2018**, *115*, 727–736.
- [66] S. Angelini, P. Cerruti, B. Immirzi, G. Scarinzi, M. Malinconico, *Eur. Polym. J.* **2016**, *76*, 63–76.
- [67] M. Alinejad, C. Henry, S. Nikafshar, A. Gondaliya, S. Bagheri, N. Chen, S. K. Singh, D. B. Hodge, M. Nejad, *Polymers (Basel)*. **2019**, *11*, 1202.
- [68] J. Huang, S. Fu, L. Gan, in *Lignin Chem. Appl.*, **2019**, pp. 163–180.
- [69] H. Cheradame, M. Detoisien, A. Gandini, F. Pla, G. Roux, *Br. Polym. J.* **1989**, *21*, 269–275.
- [70] S. S. Kelley, T. C. Ward, T. G. Rials, W. G. Glasser, *J. Appl. Polym. Sci.* **1989**, *37*, 2961–2971.
- [71] V. P. Saraf, W. G. Glasser, G. L. Wilkes, J. E. McGrath, *J. Appl. Polym. Sci.* **1985**, *30*, 2207–2224.
- [72] H. Yoshida, R. Mörck, K. P. Kringstad, H. Hatakeyama, *J. Appl. Polym. Sci.* **1990**, *40*, 1819–1832.
- [73] Y. Li, A. J. Ragauskas, *RSC Adv.* **2012**, *2*, 3347–3351.
- [74] B.-L. Xue, J.-L. Wen, M.-Q. Zhu, R.-C. Sun, *RSC Adv.* **2014**, *4*, 36089–36096.
- [75] M. Österberg, M. H. Sipponen, B. D. Mattos, O. J. Rojas, *Green Chem.* **2020**, *22*, 2712–

- 2733.
- [76] W. J. Stark, P. R. Stoessel, W. Wohlleben, A. Hafner, *Chem. Soc. Rev.* **2015**, *44*, 5793–5805.
- [77] B. Del Saz-Orozco, M. Oliet, M. V. Alonso, E. Rojo, F. Rodríguez, *Compos. Sci. Technol.* **2012**, *72*, 667–674.
- [78] A. P. Richter, J. S. Brown, B. Bharti, A. Wang, S. Gangwal, K. Houck, E. A. Cohen Hubal, V. N. Paunov, S. D. Stoyanov, O. D. Velev, *Nat. Nanotechnol.* **2015**, *10*, 817–823.
- [79] C. Abbati de Assis, L. G. Greca, M. Ago, M. Y. Balakshin, H. Jameel, R. Gonzalez, O. J. Rojas, *ACS Sustain. Chem. Eng.* **2018**, *6*, 11853–11868.
- [80] S. Beisl, A. Miltner, A. Friedl, *Int. J. Mol. Sci.* **2017**, *18*, 1244.
- [81] M. Lievonen, J. J. Valle-Delgado, M.-L. Mattinen, E.-L. Hult, K. Lintinen, M. A. Kostiaainen, A. Paananen, G. R. Szilvay, H. Setälä, M. Österberg, *Green Chem.* **2016**, *18*, 1416–1422.
- [82] M.-L. Mattinen, J. J. Valle-Delgado, T. Leskinen, T. Anttila, G. Riviere, M. Sipponen, A. Paananen, K. Lintinen, M. Kostiaainen, M. Österberg, *Enzyme Microb. Technol.* **2018**, *111*, 48–56.
- [83] T. Leskinen, M. Smyth, Y. Xiao, K. Lintinen, M.-L. Mattinen, M. A. Kostiaainen, P. Oinas, M. Österberg, *Nord. Pulp Pap. Res. J.* **2017**, *32*, 586–596.
- [84] K. Lintinen, Y. Xiao, R. Bangalore Ashok, T. Leskinen, E. Sakarinen, M. Sipponen, M. Farooq, P. Oinas, M. Österberg, M. Kostiaainen, *Green Chem.* **2018**, *20*, 843–850.
- [85] M. Ago, S. Huan, M. Borghei, J. Raula, E. I. Kauppinen, O. J. Rojas, *ACS Appl. Mater. Interfaces* **2016**, *8*, 23302–23310.
- [86] M. Balakshin, E. A. Capanema, Z. Huang, I. Sulaeva, O. J. Rojas, M. Feng, T. Rosenau, A. Potthast, *NWBC 2018 - Proc. 8th Nord. Wood Biorefinery Conf. Helsinki* **2018**, 151–156.
- [87] E. A. Capanema, M. Y. Balakshin, *Adhesive Compositions Comprising Type-II Cellulose*, **2016**, WO 2016/049569 A1.
- [88] M. Balakshin, E. A. Capanema, in *14th Eur. Work. Lignocellul. Pulp*, Grenoble, France, **2016**.
- [89] E. A. Capanema, M. Y. Balakshin, P. D. Fritzgibbon, M. Kosa, T. M. McLarty, C. S. Sanderson, *Cellulose-Containing Compositions and Methods of Making the Same*, **2016**, WO 2016/049567 A1.
- [90] E. A. Capanema, M. Y. Balakshin, *Methods for Preparing and Collecting Polyaromatic Compounds, and Products Comprising Polyaromatic Compounds*, **2016**, WO 2016/049564 A1.
- [91] L. Dehne, C. Vila Babarro, B. Saake, K. U. Schwarz, *Ind. Crops Prod.* **2016**, *86*, 320–328.
- [92] C. Abbati de Assis, C. Houtman, R. Phillips, E. M. (Ted) Bilek, O. J. Rojas, L. Pal, M. S. Peresin, H. Jameel, R. Gonzalez, *Biofuels, Bioprod. Biorefining* **2017**, *11*, 682–700.
- [93] E. A. Capanema, M. Balakshin, in *18th ISWFPC - Int. Symp. Wood, Fiber, Pulping Chem.*, Vienna, Austria, **2015**.
- [94] R. Mörck, H. Yoshida, K. P. Kringstad, *Holzforschung* **1986**, *40*, 51–60.
- [95] J. Domínguez-Robles, T. Tamminen, T. Liitiä, M. S. Peresin, A. Rodríguez, A.-S. Jääskeläinen, *Int. J. Biol. Macromol.* **2018**, *106*, 979–987.
- [96] H. Sadeghifar, T. Wells, R. K. Le, F. Sadeghifar, J. S. Yuan, A. J. Ragauskas, *ACS Sustain. Chem. Eng.* **2017**, *5*, 580–587.
- [97] S. Laurichesse, L. Avérous, *Prog. Polym. Sci.* **2014**, *39*, 1266–1290.
- [98] D. A. Baker, T. G. Rials, *J. Appl. Polym. Sci.* **2013**, *130*, 713–728.
- [99] Y. Li, S. Sarkanen, *Macromolecules* **2005**, *38*, 2296–2306.
- [100] M. Zhang, A. A. Ogale, *Carbon* **2014**, *69*, 626–629.
- [101] M. Y. Balakshin, E. A. Capanema, M. Colakyan, F. Lipiecki, *Upgrading Lignin From Lignin - Containing Residues Through Reactive Extraction*, **2019**, US 10,240,006 B2.

- [102] T. V. Lourençon, L. G. Greca, D. Tarasov, M. Borrega, T. Tamminen, O. J. Rojas, M. Y. Balakshin, *ACS Sustain. Chem. Eng.* **2020**, *8*, 1230–1239.
- [103] T. Khol'kin, *The Technology of the Wood' Hydrolysis Industries*, Lesnaya Promyshlennost (In Russian), Moscow, **1989**.
- [104] F. Hu, S. Jung, A. Ragauskas, *Bioresour. Technol.* **2012**, *117*, 7–12.
- [105] A. Berlin, M. Y. Balakshin, *Extraction Process of Levulinic Acid from Lignocellulosic Biomass*, **2013**, US 2013/0252292 A1.
- [106] M. L. Rabinovich, *Cellul. Chem. Technol.* **2010**, *44*, 173–186.
- [107] R. J. A. Gosselink, Lignin as a Renewable Aromatic Resource for the Chemical Industry, **2011**.
- [108] M. Y. Balakshin, A. Berlin, in *Bio-Based Chem. East Strateg. Sci. Bus. Breakthr. Technol.*, Boston, MA, USA, **2010**.
- [109] C.-L. Chen, in *Wood Struct. Compos.*, **1991**, pp. 183–261.
- [110] S. Y. Lin, C. W. Dence, *Methods in Lignin Chemistry*, Springer-Verlag, Berlin Heidelberg, **1992**.
- [111] G. F. Zakis, *Functional Analysis of Lignins and Their Derivatives*, **1994**.
- [112] J. Ralph, L. L. Landucci, in *Lignin and Lignans* (Eds.: C. Heitner, D. Dimmel, J.A. Schmidt), **2010**, pp. 137–243.
- [113] M. Y. Balakshin, E. A. Capanema, C.-L. Chen, H. S. Gracz, *J. Agric. Food Chem.* **2003**, *51*, 6116–6127.
- [114] E. A. Capanema, M. Y. Balakshin, H.-M. Chang, H. Jameel, in *Proc. Int. Conf. Pulping, Papermak. Biotechnol.*, **2008**, pp. 647–651.
- [115] R. J. A. Gosselink, J. E. G. van Dam, E. de Jong, E. L. Scott, J. P. M. Sanders, J. Li, G. Gellerstedt, *Holzforschung* **2010**, *64*, 193–200.
- [116] T. V. Lourençon, S. Alakurtti, T. Virtanen, A.-S. Jääskeläinen, T. Liitiä, M. Hughes, W. L. E. Magalhães, G. I. B. Muniz, T. Tamminen, *Holzforschung* **2020**, *74*, 175–183.
- [117] P. Solt, A.-S. Jääskeläinen, P. Lingenfelter, J. Konnerth, H. W. G. van Herwijnen, *For. Prod. J.* **2019**, *68*, 365–371.
- [118] M. Y. Balakshin, E. A. Capanema, in *Inc. 13th ISWFPC (International Symp. Wood, Fibre Pulping Chem. Vol. II.*, Auckland, **2005**, pp. 353–360.
- [119] J. Gierer, I. Norén, *Holzforschung* **1980**, *34*, 197–200.
- [120] M. Y. Balakshin, I. Deineko, in *Int. Symp. WOOD PULPING Chem. PROCEEDINGS, ISWPC Proc. 1997 9th Int. Symp. Wood Pulping Chem.*, Japan, **1997**.
- [121] H. Sadeghifar, C. Cui, D. S. Argyropoulos, *Ind. Eng. Chem. Res.* **2012**, *51*, 16713–16720.
- [122] S. Kubo, J. F. Kadla, *Macromolecules* **2004**, *37*, 6904–6911.
- [123] Y. Li, S. Sarkanen, *Macromolecules* **2002**, *35*, 9707–9715.
- [124] A. Berlin, M. Y. Balakshin, R. Ma, V. Maximenko Gutman, D. Ortiz, *Organosolv Process*, **2011**, WO 2011097720 A1.
- [125] M. Y. Balakshin, A. Berlin, H. T. Dellicolli, C. A. N. J. Grunert, V. M. Gutman, D. Ortiz, E. K. Pye, *Processes For Recovery of Derivatives of Native Lignin*, **2013**, US8378020B1.