

Increasing the value of a biorefinery based on hot-water extraction: Lignin products

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ABSTRACT: In conventional pulping technologies, lignin is used mainly as a low-cost source of energy. Small quantities of industrially produced lignin are used for the production of chemicals and materials. Biorefinery technologies are emerging that have an ultimate goal of replacing fossil sources for the production of fuels and other products. To achieve this goal effectively, biorefinery technologies must take advantage of lignin as the most abundant natural aromatic polymer and use it to add higher-value products to product portfolios. Lignin has the potential to be used in making a broad range of high-quality products, including carbon fibers, thermoplastics, and oxygenated aromatic compounds. Existing processes focus primarily on the quality of cellulose and result in a severely modified and contaminated lignin of relatively low value. Lignin produced in more flexible biorefinery operations is more uniform and less contaminated than currently available industrial lignins, opening the door for broader applications of lignin and lignin products. The results of isolation and characterization of lignin dissolved during hot-water extraction and some potential applications of this lignin are discussed.

Application: A biorefinery based on hot-water extraction may produce a range of high-value products from lignin isolated from extracts of hardwoods.

Conventional pulping technologies based on lignocellulosic materials are focused on the production of cellulose. Lignin, extractives, and most of the hemicelluloses are primarily used as an energy source, recovered in small amounts for use, or are waste products. For example, kraft delignification results in a black liquor solution, which is burnt in a recovery boiler during the regeneration of pulping chemicals. Due to a high heating value of 23.26–25.58 kJ/g [1], lignin represents the main source of energy in this process. Meister, however, described the incineration technology as having “little thermodynamic or economic sense. With two-fifths of the plants’ absorbed energy being used to make the one-quarter of its dry mass that is lignin, lignin represents a large investment of biochemical effort by the plant. Reducing this macromolecule to CO₂ destroys much of that investment” [2]. Consistent with that concept is a growing demand for the development of alternative technologies using all lignocellulosic constituents to produce fuels, materials, and chemicals, while replacing increasingly limited and costly fossil fuels [3,4]. In accordance with the biomass refining philosophy, those new technologies are envisioned as following sequential treatments that create separate streams of relatively clean lignocellulosic components. After purification, carbohydrate-rich streams may undergo chemical or biological conversion to produce fuels, materials, and chemicals [4–6]. Streams rich in lignin and extractives have high potential for the production of high-value,

low-volume products to enhance the profitability of this type of biorefinery [7]. Lignin converted to higher-value products may play an important role in enabling success of biorefineries; in the production of 60 billion gallons of ethanol or other bioderived fuel, the resultant amount of lignin would be projected to be about 0.225 billion tons. Furthermore, the U.S. Department of Energy (DOE) has set a goal to replace 30% of the transportation fuel supply with biofuels by 2030 [8]. That is a significant amount of nature’s most available aromatic polymer. The structure and properties of lignin produced in such operations will be closer to native lignin than current industrial lignins, which contain sulfur and are more condensed than native lignin. One serious drawback of industrial lignins today is their variability. Lignin from the production of biofuels, biochemicals, and biomaterials could be more uniform due to the application of the mild processes, which are sought in biorefinery operations to preserve the original value of the constituents. Studies to evaluate use of lignin for the production of a wide range of products, including thermoplastics, adhesives, and chemicals (e.g., oxygenated aromatic compounds) have been conducted and the commercial development for some of these products has been accomplished [8–13]. New studies on biorefinery-produced lignin are necessary to broaden its application and increase its use and value, thus paving the way to change an old saying that “you can make anything you want from lignin except for money.”

PRETREATMENT OF LIGNOCELLULOSICS

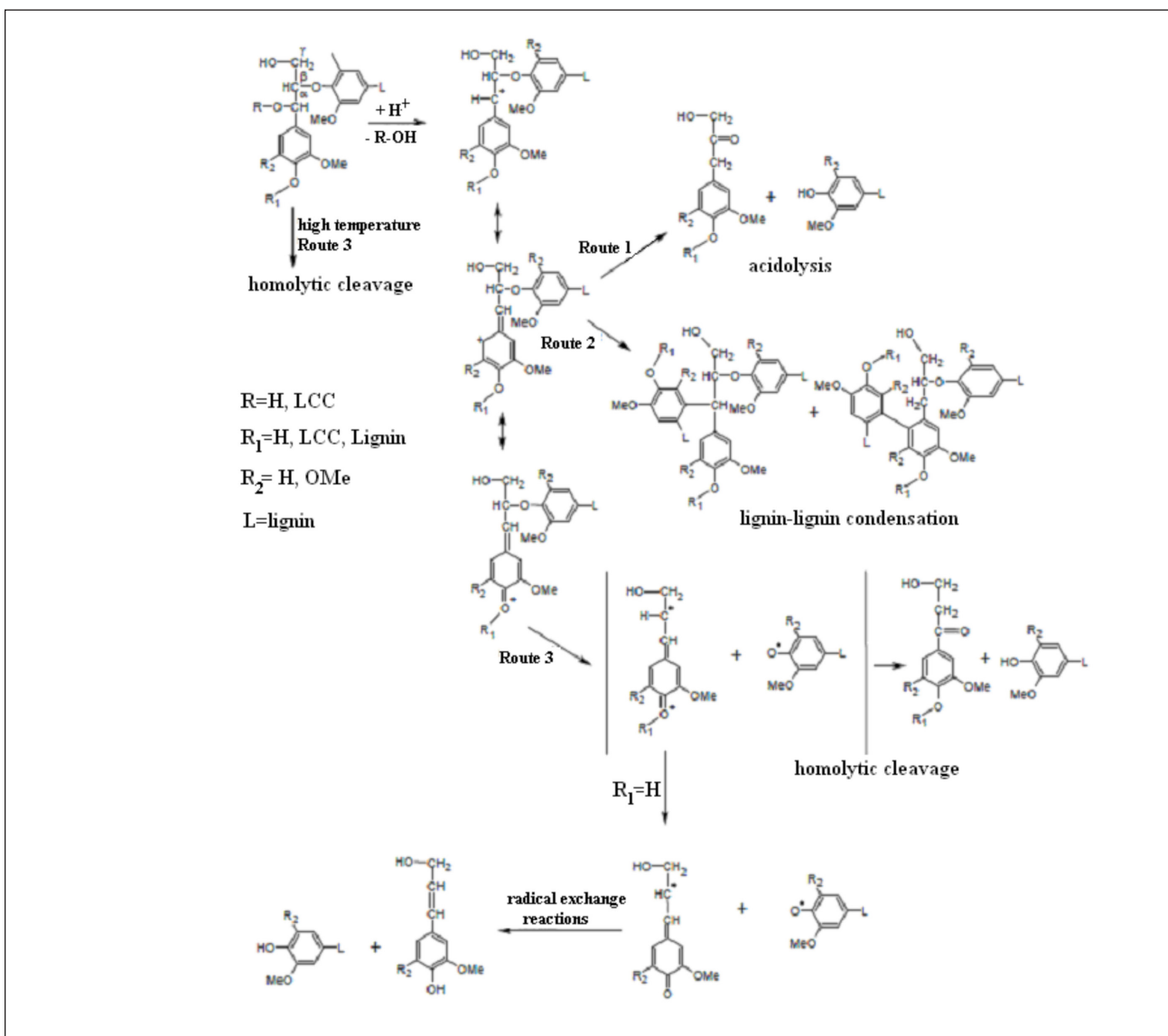
Extensive research has been performed in the evaluation of pretreatments, which are seen as the first step of sequential refining of lignocellulosics. Pretreatment is generally intended to remove hemicelluloses and lignin, reduce cellulose crystallinity, and increase porosity to facilitate the ability to process the cellulose-enriched residue – for example, acid/enzymatic hydrolysis followed by fermentation [4,5,14–17]. Different methods have been suggested, including physical, chemical, and biological pretreatments. This report will focus on lignins recovered during hot-water extraction (HWE) pretreatment of hardwoods/sugar maple (*Acer saccharum*).

Hydrothermal pretreatment and effect on lignin

Pretreatment based on hydrothermal treatment, i.e., use of

water and heat only, has been recommended frequently to create a cleaner, more environmentally benign process with a low corrosion risk for equipment and lower quantities of hydrolyzate neutralization residues. A water prehydrolysis stage has also been studied and used in some commercial pulping operations prior to kraft pulping with the goal of hemicellulose removal from the final pulp [18–21].

Water treatment of wood at high temperatures has been investigated for the effect on lignin by studying water extracts, extracted wood, and lignin isolated from wood and extracted wood [22–35]. The amount of lignin extracted from wood during autohydrolysis at temperatures lower than 230°C is species dependent and may be as high as 25% of the amount of lignin originally present; it also depends on the temperature and time of treatment [22,27]. Recent studies have postulated that, during hydrothermal treatment, lignin melts,



1. Proposed lignin reactions during hot-water extraction (HWE)/autohydrolysis; $\text{R}_2 = \text{H}$, guaiacyl (G) unit; $\text{R}_2 = \text{OMe}$, syringyl (S) unit (adapted from [40,41]).

migrates through the cell wall, coalesces to form spherical droplets, and deposits on the cells upon cooling [36,37]. The lignin droplets formed this way have been considered as an obstacle of the following enzymatic saccharification of the biomass [38]. While the main cause of the reduced enzymatic digestibility of biomass in the presence of the pretreatment liquor remains unknown, hot washing of the pretreated biomass at temperatures higher than the lignin glass-transition temperature (T_g) increases the efficiency of hydrolysis. For example, the yield of glucose for a given enzyme dose was doubled after hot washing of the pretreated poplar compared to unwashed control [38].

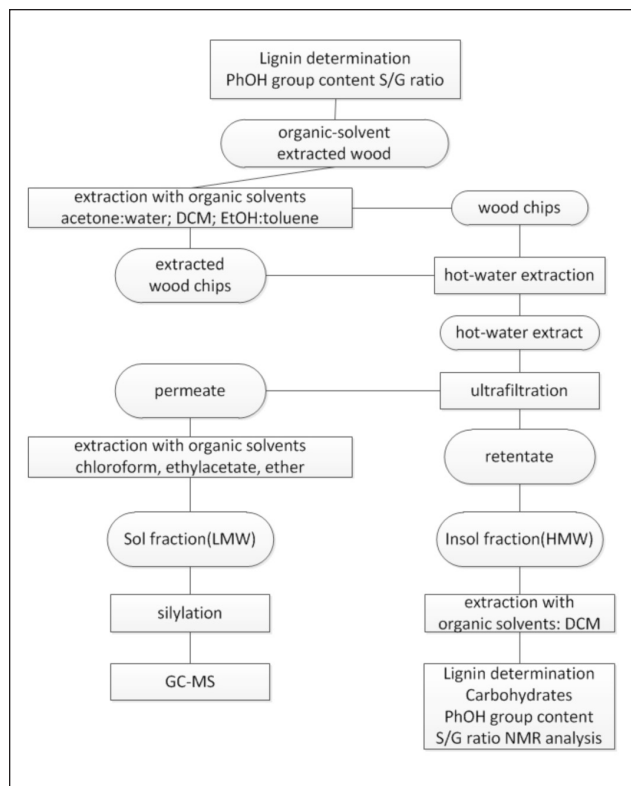
The lignin reaction pathway during HWE is expected to follow homolytic/acidolytic cleavage (depolymerization) and $C_2(C_\beta)-C_\alpha$ crosslinking (polymerization), illustrated in **Fig. 1** [28,29,31,39–41].

The relative importance of these reaction routes depends on the conditions of autohydrolysis and the chemical properties of treated lignocellulosic biomass. Milled wood lignin (MWL), the most broadly accepted lignin preparative representing protolignin [42], was subjected to conditions prevailing during autohydrolysis to evaluate modifications that lignin may endure in wood during autohydrolysis [43]. Milled wood lignin containing fewer components of high-molecular weight than MWL of the original *Eucalyptus globulus* wood has been isolated from the corresponding water-extracted wood (water treatment at 170 °C) [29]. The decrease in molecular weight of lignin is consistent with the cleavage of the β -O-4 bonds reported in that study. In respect to the differences in reactivity of syringyl-guaiacyl (SG) hardwood and guaiacyl (G) softwood lignins, Guo and Lai [44] proposed that the β -aryl ether units present in aspen lignin are more readily acid-hydrolysable than the β -aryl ether units present in spruce lignin. In accordance with the steady decrease observed in the content of methoxyl groups in lignin isolated from extracted aspen wood with increasing time of autohydrolysis at 195°C, the autohydrolysis reactions also included lignin demethylation [24].

The stability of lignin-carbohydrate bonds (LC bonds) in mild acid conditions is an important consideration for the effect of water treatment performed at elevated temperature (up to 230°C) on wood. Model experiments have suggested that even though some LC bonds undergo cleavage in acid [45,46], the degradation rate varies depending on the type of structure. For example, while studying the stability of benzyl-ether LC bonds, Košíková et al. [45] concluded that etherified benzyl models were more stable than nonetherified counterparts. In studies of the stability of lignin and LC bonds during water treatment of wood at temperatures up to 230°C, the cleavage of the LC benzyl-ether bonds was confirmed [28], but the extent of that process is unknown.

Hot-water extraction

HWE has been recently suggested as a promising first phase in sequential disassembling of wood, especially suitable for hard-



2. Experiments performed to study modification of noncarbohydrate wood constituents during hot-water extraction (HWE) with model species sugar maple [*Acer saccharum*].

wood species [4]. Hardwoods are characterized by a high content of O-acetyl-4-O-methylglucuronoxylan, which is readily soluble in mild acid conditions as acidity of the process gradually increases to a final pH of ~3.5. This increase is initially due to deacetylation of xylan chains, which is followed by the release of other acidic compounds, such as aromatic acids [33]. The process performed for 2 h at 160°C results in solubilization of ~10% of the total amount of lignin in sugar maple [47].

Figure 2 presents the experimental procedure performed to clarify the nature of changes taking place on noncarbohydrate hardwood constituents during HWE in our laboratory. The model species used in these experiments was *A. saccharum* [32–35]. Dissolved lignin appeared in the hot-water extract in two distinct fractions of lignin/ligninlike material: an insoluble fraction (insol fraction), which readily precipitates from the hot-water extract (fraction higher molecular weight, HMW) and a soluble fraction (sol fraction), which may be extracted from the permeate produced after the removal of the precipitate with organic solvents, such as chloroform or ether (fraction of lower molecular weight, LMW).

Ultrafiltration performed using a membrane of 1000 Da nominal molecular-weight cutoff under N_2 yielded an insol fraction of ~1.8% of the total amount of wood used in HWE as retentate. The lignin content of the insol fraction was 87% (Klason + acid-soluble lignin). The insol fraction was purified by mild acid hydrolysis (pH 2, 2 h, 60°C, N_2) and the lignin

content increased to ~93%. The acid-labile LC bonds, such as benzyl-ether bonds, might have been broken during this treatment. Carbohydrate analysis demonstrated that xylose was the predominant sugar in the acid-purified insol fraction (more than 75% of the remaining carbohydrates were xylose-based). The syringyl-to-guaiacyl (S:G) ratio [42,48] of ~2.6 was measured for the purified insol fraction; i.e., the extracted lignin was more than twice as high as the S:G ratio characteristic for lignin in sugar maple [48]. That result is consistent with demonstrated high solubility of S-units during hydrothermal treatment [27]. High content of S-units in lignin dissolved during HWE of hardwoods may also imply fiber origin of extracted lignin because S-predominant lignin is mostly present in fibers [49,50]. The relatively high content of the phenol (PhOH) groups compared to MWL was lower than that registered for kraft and organosolv lignin [9] (**Table I**). That was in accordance with a higher S:G ratio of the lignin in insol fraction because the precursor of S-units in lignin, sinapyl alcohol, favors the β -O-4 bonding in lignin and, hence, decreases the PhOH content [49]. That was also associated with LMW lignin, lower than that of kraft lignin and organosolv lignin, as was confirmed in SEC experiments. As Table I shows, the purified insol fraction was of higher polydispersity than kraft and organosolv lignin [9].

During HWE, the PhOH content of lignin remaining in sugar maple increased from 0.35 mmol/g lignin to 1.83 mmol/g lignin. This considerable increase in the content of PhOH groups of lignin remaining in extracted wood was a strong indication of the cleavage of β -O-4 bonds during HWE/autohydrolysis (Fig. 1) [28–32,34,35,47].

The sol fraction is a fraction of LMW organic compounds recovered by the extraction of permeates obtained during laboratory ultrafiltration of the hot-water extract of sugar maple with organic solvents (chloroform or ether) (Fig. 2). The total amount of material extracted in this way was ~1.5% of o.d. wood used in HWE. The sol fraction was analyzed by gas chromatography-mass spectrometry (GC-MS). A wide range of identified phenolic compounds corroborates hot-water solubility of phenolic extractives (corresponding to leaching of phenols from leaves or bark [51]) or extraction of phenolic products of lignin cleavage (e.g., vanillin, guaiacol, syringol, *p*-hydroxy benzaldehyde, syringaldehyde, *p*-hydroxybenzoic acid, vanillic acid, syringic acid, coniferaldehyde, sinapaldehyde, dihydroconiferyl alcohol, dihydroferulic acid, medioresinol, and syringaresinol [23,32,33]. Identified dissolved aromatic acids contribute to the autohydrolysis processes during HWE by providing additional sources of the H⁺ ions: *p*-hydroxybenzoic acid, pK_a = 4.3; ferulic acid, pK_a = 4.27; vanillic acid, pK_a = 4.08; syringic acid, pK_a = 3.86 [52]. Evidence for the occurrence of homolytic cleavage of the β -aryl ether bonds was found based on the presence of syringaldehyde, sinapaldehyde, syringic acid, and syringaresinol. Those compounds were proposed to be formed via homolytic cleavage of an initially formed quinone methide (Fig. 1, route 3) or they may have resulted

Lignin	PhOH mmol/g	S/G	MW	PD
SKL	3.8	-	2,800	2.0
HKL	4.3	1.2	2,400	1.8
Organosolv	4.3	1.3	2,200	1.7
Insol	3.0	2.6	1,600	3.1

I. Properties of softwood kraft lignin (SKL), hardwood kraft lignin (HKL), organosolv lignin [9], and the purified insol fraction.

from oxidation reactions (syringic acid) [28,41]. Coniferyl alcohol, which may also be expected as a result of homolytic cleavage of the phenolic β -aryl ether structure (Fig. 1), was not identified in the sol fraction.

Depending on the conditions of HWE, the total amount of insol and sol fractions of hot-water extract may amount to more than 3.3% of o.d. wood used in HWE or 15% of the total material dissolved during HWE (160°C, 2 h). At the proposed biorefinery capacity of 1000 dry tons of wood per day [4], the annual production of those two fractions would be more than 10000 tons. That is a significant amount of valuable material with high potential to increase the economic returns of the HWE of lignocellulosic hardwoods, enhancing the desirability of hardwood biorefineries.

In contrast to kraft lignin, the most readily available source of lignin today, the lignin released during HWE has the significant advantage of being sulfur free. Because of its considerable sulfur content, the use of kraft lignin is limited, despite an annual production of more than 25 x 10⁶ tons in the United States alone [53]. Even though as a fuel source kraft lignin is inefficient, producing less than one-quarter as much energy as an equivalent mass of middle distillate fuels, most kraft lignin is used for energy production and is burned in the kraft recovery process. Less than 2% of lignin is used for other purposes [9,10]. Nearly three-quarters of commercial lignin products today are used as dispersants, emulsifiers, binders, and sequestrants; smaller applications include adhesives and fillers [8]. A wide range of products can be proposed on the basis of the aromatics/lignin separated from hot-water extracts of hardwoods as the insol and sol fractions. Some potential products consistent with the use of lignin as a macromolecule, and with the use of aromatic monomers that likely are production targets for the insol and sol fractions, are discussed in the following sections. From an overall thermodynamic point of view, it is more desirable to avoid lignin depolymerization to the greatest extent possible to enhance the uses and add value to the polymer that nature has already assembled. Doing so will affect some of the potential products [8].

Insol fraction

Adhesives

The insol-fraction lignin can be evaluated for the production of adhesives [2,8,11] in which the recovered lignin will be used in combination with furfural as another designed prod-

uct of the HWE-based biorefinery (furfural is a dehydration product of xylose and arabinose produced under acid conditions and high temperature during HWE). Use of this adhesive derived from the water-based treatment of wood would be consistent with an increasing interest in the development of biorenewable adhesives to substitute for synthetic thermosetting resins. Particularly, there is increasing interest in replacing phenol-formaldehyde-based resins with more environmentally friendly alternatives, as formaldehyde is identified as a carcinogen and may be suspended for use in consumer and packaging goods and building products in the future [8]. Electrophiles other than protons have been shown to react with phenolic lignin model compounds at the positions meta to the PhOH, i.e., the 2- and 6-positions of the phenylpropanoid unit, in acidic media [54]. In a study of autohydrolysis of aspen wood, Chua and Wayman [25] observed an extensive condensation of lignin and attributed this effect to the reaction between lignin aromatic rings with high electron density at C6 and furfural and hydroxymethyl furfural (HMF, a dehydration product of hexoses), which are electrophilic due to the aldehyde group and C = C double bonds. Accordingly, the insol fraction containing both lignin and carbohydrates appears to be an excellent candidate to produce resin under acid conditions (as previously commented, xylose is the dominant carbohydrate in the insol fraction of sugar maple and xylose converts to furfural in acid conditions). That type of thermosetting resin would be a renewable green alternative for environmentally unfavorable phenol-formaldehyde resins.

Lignin-based polymer blends

Even though lignins of different origin vary in chemical configuration and physicochemical properties, which can cause pronounced differences in mechanical behavior and thermal mobility, one important area of lignin application study has been the production of thermoplastics [9]. To improve the processability and mechanical properties of lignin fibers, lignin may be blended with various synthetic or biorenewable polymers which, when carefully chosen, decrease T_g and increase the plastic response to mechanical deformation. Thermoplastics have been made by blending different technical lignins, such as kraft and organosolv lignins, with different synthetic polymers, among which polyethylene oxide (PEO) showed the most promising results [9]. Incorporation of small amounts of PEO (5%–10%) sufficiently disrupted the lignin complex structure and produced superior mechanical properties, comparable to polystyrene. Blends were prepared by mechanical mixing followed by thermal extrusion. The lignin recovered after HWE is expected to be of higher thermal mobility and better processability than organosolv lignin because it is characterized by lower condensation level (associated with a higher S:G ratio) and a lower hydrogen bonding potential due to the PhOH groups [9,32,34,35]. One important difference between organosolv lignin and lignin produced during HWE is that organosolv has ethanol incor-

porated in side chains, primarily as an ethoxylated benzylic position, to the extent of 0.1–0.2/C₉ [55]. Lignin ethoxylation leads to a reduced T_g and better thermoplasticity of lignin. This effect is similar to alkylation, which results in lignin that, even though quite brittle, can be effectively plasticized by blending with suitable aliphatic polyesters [9,53].

Lignin-based carbon fibers

From the 1950s onward, the demand for carbon fibers as a reinforcing material in composite products has grown and today, carbon-fiber composite products are used routinely in sports equipment, marine products, and construction and in the aircraft and the automotive industries. Carbon fibers are produced in a two-step thermal process. The first step is a stabilization stage in which the precursor fibers produced in melt spinning are thermostabilized at 200°C–300°C under tension. The second step is thermal treatment of fibers at 1000°C–2000°C in inert atmosphere conditions that maintain the fibrous structure. Even though expensive, polyacrylonitrile (PAN) (US\$17–US\$26/kg) is the most important precursor material for the production of carbon fibers and almost 80% of commercially available carbon fibers are derived from PAN. It has been estimated that the cost of carbon fibers can be significantly reduced if lignin and lignin and/or lignin synthetic polymer blends (US\$6.5–US\$11/kg) are used for the production instead of PAN [56]. Carbon fiber production has been identified by the Pacific Northwest National Laboratory (DOE) and by the LigniMatch, GMV Center for Environment and Sustainability at Chalmers and Göteborg University, as one of the most interesting routes for use of biorefinery lignin [8,56]. Carbon fibers of satisfactory mechanical properties have been made from blends composed primarily of kraft lignin and organosolv lignin with overall yields of up to 45%.

Because mechanical properties of carbon fibers are highly size dependent and increase with decreasing diameter, the production of lignin-based carbon fibers of lower diameter (<10 μ m) than achieved at present is an important goal [9,57,58]. For lignin recovered as a biorefinery product, the insol fraction is expected to be of similar processability and final carbon fiber properties to organosolv lignin. Furthermore, it is expected to be more appropriate for use in carbon fibers than kraft lignin because its chemical structure is more similar to native lignin and it has more tunable properties. For lignin extracted during HWE, properties may be adjusted by a change of P-factor of HWE (i.e., temperature and time) [59], thus changing the parameters of membrane separation (e.g., pore size and pH) and/or conditions of the acid hydrolysis purification step. Those modifications are expected to provide for better processability, including lower polydispersity, less contamination, and lower condensation level compared to conventional technical lignins such as kraft lignin and lignosulfonates. The major challenge for making carbon fibers from lignin is the implementation of the laboratory-scale carbon fiber methodology in full-scale industrial processes while maintaining high-quality products.

Activated carbon

Activated carbon (AC) is a strong adsorbent due to large surface area (500–2000 m²/g) and pore volumes. It has a wide range of applications, including cleaning environmentally hazardous emissions from air and water. While the production of potable water is currently the largest end use of AC, the need for AC is expected to grow as environmental demands become stricter. Coal and lignocellulosic materials are commonly used for the production of AC. From lignin, AC may be produced in a two-step process starting with carbonization of the starting lignin material followed by the activation of the resulting char. Physical activation is commonly performed using carbon dioxide or steam. Chemical activation may proceed simultaneously with carbonization. Lignin has been found to be an effective raw material for the formation of micropores. During chemical activation of lignin, a surface area larger than that of commercial activated carbons has been produced recently; a surface area of 2000 m²/g was achieved with K₂CO₃ at 800°C and of 2753 m²/g (micropore volume of 1.37 cm³/g) with KOH activation at 850°C after carbonization [60,61]. The adsorption capacity of those ACs was comparable to commercial activated carbons [61]. Because good results have been obtained with hydrolysis lignin [61], it is projected but not yet proven that lignin from the similar HWE hydrothermal treatment recovered as the insol fraction will react similarly and provide a good source of AC.

Production of oxygenated aromatic compounds

Oxidation in alkaline medium is an established process for the depolymerization of lignins to high-value chemicals, among which vanillin and syringaldehyde are of prime interest. Vanillin, with an approximate selling price of US\$11–US\$20/kg (versus US\$1200–US\$4000/kg when extracted from *Vanilla sp.* pods), finds application in the chemical and pharmaceutical industries for the production of herbicides; anti-foaming agents; and drugs such as papaverine, L-dopa, and an antimicrobial agent, trimethoprim [62]. Syringaldehyde, with a selling price of less than US\$20/kg, has chemical structure and properties similar to vanillin and is used in similar applications. Its prospective uses include the production of hair and fiber dye and drugs for obesity and breast cancer [63]. The extent of lignin oxidation may be improved by the introduction of catalysts. Thus, lignin dissolved during HWE can be examined for oxidation in alkaline mediums in the presence of Fe³⁺ and Cu²⁺ catalysts in the form of CuO, Fe₂O₃, and mixtures of CuO and Fe₂O₃ [64].

Recently developed metal organic frameworks (MOFs) (Cu/Fe/benzenetricarboxylate) have demonstrated yields of up to 80% of original lignin used [64,65]. Lignin can also be oxidatively depolymerized with polyoxometalates (POMs) under acid conditions. Oxidation in the presence of POMs can be performed anaerobically when POMs perform the oxidizing function, in which case reduced POMs are reoxidized in a separate step with oxygen. Alternatively, in aerobic conditions POMs perform a catalytic function [66]. While the con-

version of lignin to oxygenated lignin building blocks may be performed using different oxidative depolymerization procedures that are convenient alternatives for the more complicated conventional petrochemical routes, separation techniques for those monomers may still constitute a related challenge and work on both the production and separation steps is needed [8].

Sol fraction

The permeate obtained in ultrafiltration of hot-water extract was extracted in our laboratory with chloroform and the sol fraction was recovered after chloroform evaporation (Fig. 2). This method of laboratory isolation of sol fraction is unacceptable in industrial conditions (a large amount of chlorinated organic solvent, which is reasonably anticipated to be a human carcinogen, is used), and a feasible way of separation in the industrial conditions is under study. Different approaches could be considered to recover the sol fraction, including the use of hydrophobic membranes and a combination of extraction with an appropriate nonpolar solvent (hexane) and adsorption onto a neutral acrylic ester sorbent [12,67,68].

Recently, a new category of switchable solvents has been introduced. Those solvents change from being hydrophobic, with very low miscibility with water when in air, to being hydrophilic and completely miscible in water under an atmosphere of CO₂ [69]. The GC-MS analysis of the sol fraction recovered after HWE of sugar maple revealed that it consists of phenolic compounds, mainly S and G derivatives of benzaldehydes and benzoic acids, although small amounts of the corresponding cinnamaldehydes and cinnamic acids were also found [33]. Rich in phenolic compounds, the sol fraction exhibited a relatively high free radical scavenging ability and antioxidant activities [70,71]. The antioxidizing potential of the sol fraction of sugar maple, comparable to that of ascorbic acid (vitamin C), suggests a need to assess its antitumor properties, which are currently under study. The sol fraction of HWE may be recovered in a two-step process consisting of polymerization followed by membrane separation. Polyphenol oxidases/laccases are able to oxidize phenols with a redox potential value lower than that of laccases (0.5–0.8 V vs. NHE) [72]. The laccase treatment of phenolic compounds present in the HWE would result in the production of phenoxy radicals, which would subsequently participate in coupling reactions forming aromatic oligomers/polymers.

Polymerization of phenols to poly(phenylene oxide)s has been demonstrated using, for example, syringic acid and 2,6-dimethylphenol in the presence of laccases of different origin [73,74]. In the presence of hydrogen peroxide (H₂O₂) which acts as an electron acceptor, lignin peroxidase (LiP) can also catalyze the oxidative polymerization of phenols [74,75]. Treatment of willow hydrolysate with laccase, LiP, and laccase and LiP combined led to the removal of monoaromatic phenolic compounds, which increased fermentability of the hydrolysate. That detoxification effect of enzymes corroborated a mechanism of oxidative polymerization [76].

After polymerization of the phenolic compounds present in the sol fraction, the resulting polymer would have no carbohydrate contamination and may be used in the production of lignin-based products, similar to those suggested for the insol fraction.

CONCLUSION

In the development of new biorefinery technologies, lignin should be considered carefully as a significant potential source of valuable chemicals and materials. Its use for the production of chemicals and materials is expected to increase in the future. Mild conditions applied in biorefinery operations should enable the production of lignin with properties that are different from lignins recovered from conventional pulping technologies and that can be adjusted to suit production of high-value products. **TJ**

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Biorefineries will produce a significant amount of lignin that will be used for the production of chemicals and materials. It will be more economically beneficial than lignin used for the production of energy. We clarified the structure and composition of lignin dissolved during hot-water extraction and suggested some potential uses of this lignin.

Separation of lignin from hot-water extract occurred in two steps that resulted in HMW and LMW lignin from the extracts. We found that the amounts of HMW lignin that can be separated by ultrafiltration and LMW lignin that can be separated from the resulting permeate by liquid-liquid extraction are the same.

Pulp and paper mills considering the introduction of biorefinery operations in their production processes should analyze lignin as a source of chemicals and materials, which can be more economically effective than using lignin for the production of energy. Next, we will focus on use of HMW lignin for the production



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of adhesives and thermoplastics and use of LMW lignin as an antioxidant.

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