From stabilization strategies to tailor-made lignin macromolecules and oligomers for materials
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Lignocellulose is a renewable and sustainable resource. It includes terrestrial plants and part of nonedible waste streams of current industries. This raw material is an alternative carbon source for fossils. Lignin from lignocellulosic biomass is undervalorized. This aromatic biomacromolecule that is used as a fuel offers many striking properties such as high thermal stability, biodegradability, UV-blocking, antioxidant, and antimicrobial activities. Recent advances in biomass fractionation provide tailoring of lignin properties in-situ. Outlined innovative methods should ease lignin upgrading toward advanced engineered materials at no extra refining steps, minimizing the use of harmful chemicals and maximizing the biomass utilization.

Introduction
Renewable and sustainable materials with equal or better properties than commercial incubates derived from fossils are desired to minimize the environmental impact. Lignocellulosic biomass is abundant in nature (1.8–10^11 t/year) and available as a solid waste stream of current industries. For the processing of such biomass, pretreatment or fractionation facilities are needed (future biorefineries) that will mimic oil refineries supplying a range of products. One of those products will be lignin. Lignin valorization beyond calorific value improves the economy of future biorefineries [1]. There are barriers to making lignin a suitable feedstock for industry. Besides technical and economic obstacles, there are heterogeneity and poor reactivity of lignin, which are rooted in the way it is generated. Lignin could be obtained from pulp and paper, and cellulosic ethanol industries. The current objective of these industries are carbohydrates derived fibers and ethanol, where lignin is a secondary product and treated as such.

It is difficult to apply industrial lignin in materials production. Phase separation is a common drawback due to poor affinity between lignin and the other components. Low concentration of functional groups results in poor reactivity of such lignins. This necessitates the refining of industrial lignin. Introduction of compatibilizer or extra functionalization through chemical modification improves lignin properties [2–6]. Another option is lignin fractionation. It generates fractions with defined structural features, physicochemical properties, and lower heterogeneity of the size of molecules [7–9].

The difficulties of technical lignin valorization partially stemmed from lignin structure. During conventional biomass fractionation processes, the native structure of lignin changes irreversibly [10]. To overcome this, new stabilization strategies, also known as lignin-first, were proposed (Figure 1) [10–12]. Reductive catalytic fractionation (RCF) is one of them. RCF is a complex process based on heterogeneous catalysis, and it involves three main steps: solvolysis, depolymerization, and reductive stabilization [12–14]. Development of the method demonstrates that the availability of the β-O-4’ motif is key for the reaction outcome (Figure 2, A). The β-O-4’ bond is the main linkage between monomers in lignin (45–84%). That, in turn, moved the focus on the preservation of native lignin structure. The idea was to provide high-quality starting material suitable for lignin depolymerization. Such lignins with preserved or stabilized structures hold the potential for overcoming challenges in direct lignin application for materials [15,16].

Tailoring lignin properties during biomass fractionation is advantageous. Elimination of extra steps simplifies the process and leads to a higher atom economy—high reactivity of the native lignin that cause condensation works to the benefit of tailoring of its properties. Highly reactive and usually toxic chemicals needed for post modification of lignin could be avoided.

Two main types of functional groups are participating in lignin modification or added to the macromolecule: (I)
Schematic overview of lignin transformation during biomass fractionation: conventional (1); active stabilization of β-O-4' bonds (2); active stabilization of depolymerized lignin fragments (3).

Figure 2

(A) β-O-4' bonding motif in guaiacyl lignin; (B) common reactive centers for chemical modifications or grafting polymerization methods; (C) main strategies for the preparation of hybrid materials.
hydroxy groups, that could be subdivided into aliphatic (Alk-OH) and aromatic (Ar-OH) in accordance to the difference in acidity or reactivity; (II) aromatic groups, such as guaiacyl position 5 or 6 (Figure 2, B) [17–23].

During the pretreatment or fractionation process of biomass, lignin can undergo several transformations. It starts with the water elimination from the benzylic position (Figure 3, A to B) [10]. When conditions are harsh enough, lignin undergoes a fragmentation reaction such that cleavage of each Ar-O-Alk bond will lead to phenol OH groups increase. Formed carbocations and lignin fragments are rather reactive. Their presence leads to condensation reaction—new C–C bond formation with lignin fragment (Figure 3, C). Condensation and dehydration reactions lower Alk-OH group content [24].

Active stabilization methods could be grouped by the moment when stabilization takes place. The main possibilities of active lignin stabilizations are depicted in Figure 3 [10,25]. Briefly, lignin with minor modifications is isolatable before significant cleavage or condensation if mild conditions are applied. The addition of a stabilizing or trapping agent is another option. The presence of aldehyde in the reaction media prevents carbocation formation (Figure 3, D). Aldehyde reacting with the aliphatic (Alk-OH) groups stabilizes lignin forming cyclic acetal. When carbocation formed it is still possible

Figure 3

Lignin reaction coordinates during biomass fractionation and resulting chemically stabilized products from lignin.
to intercept such species with nucleophiles like phenols or alcohols (Figure 3, E and F). Unstabilized carboxations will lead to a cleavage reaction, and up to quantitative cleavage is reachable, resulting in a mixture of monomers, dimers, and other oligomers. Formed fragments could still be controlled in the same manner (Figure 3, G, H, and I).

This review presents the latest advances in lignin extraction and functionalization and their potential for improving the production of lignin-based materials. Also, selected examples of isolated lignin modification and active stabilization will be compared.

Native structure preservation
Processes producing native-like lignin on a bigger scale for downstream applications are attractive. Promising combinations of mild conditions, new solvent systems, and physical protection are studied. Part of the bonds within lignin macromolecule or between lignin and carbohydrates need to be cleaved to release lignin. Cleavage reaction of the β-O-4' bond results in residues like G and H (Figure 3) at the one end of the lignin macromolecule, whereas at the other end, there will be an aromatic hydroxy group. Yet, it is possible to preserve native-like structure and minimize grafting reactions at reasonable lignin yields.

To state few, ionic liquids [26], deep eutectic solvents (p-TsOH/ChCl or LA/ChCl) [27–29], and so-called “hydrotropes” [30,31] are capable for such fractionation. Fractionation was performed at a very mild condition due to good lignin solubility—the process was conducted below the boiling point of water in a very short time, from 30 to 60 min. Good lignin yield adjoins fair to high β-O-4’ linkage retention. Side reactions are cleavage with the formation of Hibbert ketones (Figure 3, H, etc.), and esterification of α and γ positions of the β-O-4’ motifs. When a deep eutectic solvent contains alcohol as a component its incorporation back into the lignin bond will take place (Figure 3, E, G or H).

Active stabilization
Active stabilization based on the reaction of lignin with aldehydes (Figure 3, D) takes place before carboxation formation, thus reaching a very good level of structure preservation. Deprotection at mild conditions results in overall good β-O-4’ motifs retention [32].

Control of aliphatic hydroxyl groups
Alcohol organosolv pulping is one of the most used fractionation or pretreatment methods for biomass. Such solvents as MeOH, EtOH, BuOH, ethylene glycol, etc. are environmentally preferable in comparison with other alternatives. Most of the alcohols applied could be sourced through enzymatic digestion of the carbohydrate part of the biomass. It is possible to control lignin modification by varying the amount of alcohol, type of the acid catalyst, and diluting solvent. For example, high alcohol fractionation catalyzed by Brønsted acid will predominantly lead to stabilization of lignin structure. Alcohol molecule incorporates into α position of the β-O-4’, unit preserving it from cleavage (Figure 3, E).

Active stabilization
Alcohol-based lignin stabilization has progressed very rapidly. Initially, high β-O-4’ bond retention was reached at the expense of lignin yield [33]. Optimization of the solvent system increases the yield of lignin [34–36]. Changing the processing strategy to a flow-through fractionation further increases yields of lignin and β-O-4’ bond retention. Physical protection of extracted lignin by removal from the reaction zone minimize condensation reactions of lignin in the setup. Continuous separation of lignin provides extra options to tune the process. It allows for lignin fractionation by molecular weight and functional group distribution [35]. Yet, flow-through setups suffer from high solvent demand and low lignin titers in the feed. By cycling the solvent, it was possible to mitigate these disadvantages. Ethanol protected lignin was obtained using a flow-through setup and cycling of the solvent [37]. Besides commonly used MeOH or EtOH, other alcohols were also tested. Rice and grain husk butanol fractionation lead to up to 60% β-O-4’ bond retention, with moderate lignin extraction efficiency [38,39]. Lignin extraction depends on its solubility in a given solvent. A delay in the time of lignin extraction is observed for alcohol-based fractionation. Lignin needs a proper level of modification to became soluble [40,41], thus suggesting that by tuning the Hildebrand solubility parameter of the solvent, it is possible to control the degree of modification of lignin. A higher degree of alcohol incorporation was needed to extract lignin with butanol in comparison with an ethanol-based fractionation [40]. In general, protection with mono alcohols will lower the number of Alk-OH groups. Alcohols with a long alkyl chain on incorporation will increase lignin hydrophobicity, making lignin compatible with hydrophobic materials.

Application of diols (ethylene, propylene glycols, butanediols, etc.) in the active stabilization fractionation maintains Alk-OH content. For example, good retention of the modified β-O-4’ motif was achieved by 1,3-butaneol or 1,4-butanediol-based fractionation (Figure 3, E) [42]. Fractionation of biomass with polyethylene glycol (PEG) provides, seemingly, greener access to pegylated lignin (see below) [43,44].

For increasing the number of available aliphatic hydroxy groups, a common triol such as glycerol can be applied. Glycerol is a low-cost solvent generated from the biodiesel industry. Good delignification, short reaction time, partial α-etherification, and γ-esterification was
Extra aliphatic hydroxy groups could be introduced through aldehyde active stabilization if formaldehyde is used as a stabilization agent (Figure 3, D). Then alkylation of aromatic ring by formaldehyde take place, introducing one extra aliphatic hydroxyl group to each guaiacyl unit. Yet, reaction was never optimized, considered unwanted [32].

Post isolation
All groups present in lignin after isolation are “inter-convertible” and can be used to increase the amount of aliphatic hydroxy groups. For example, available guaiacyl groups are convertible into Alk-OH [6]. The reactivity of lignin in the production of PU adhesives was enhanced by hydroxymethylation. Hydroxymethylation leads to two times increase in total aliphatic hydroxyl group content [46]. Material obtained from modified lignin has better thermal stability and tensile strength. Oxialkylaton with glycerol carbonate could convert Ar–OH groups to Alk-OH and increase the number of aliphatic hydroxyl groups [47]. Diols, such as ethylene glycol or PEG, could also be introduced [44,48]. The pegylation of kraft lignin improves its emulsifying and dispersant activities. However, to produce such PEG-modified lignin, it is needed to tosylate PEG to boost its reactivity, making the process less benign.

Control of aromatic hydroxyl groups
Lignin contains aromatic hydroxyl groups. Therefore, it could be a sustainable alternative to phenols in phenol-formaldehyde resins or to bisphenol A in epoxy resins formulations. Both applications depend on the availability of aromatic hydroxy groups.

Active stabilization
It was demonstrated before that phenol pulping such as Battelle-Geneva’s process, leads to phenol incorporation into the lignin structure. However, the exact structural transformations were not demonstrated. By applying a water-phenol system under acidic conditions, good delignification and phenol OH groups increase was demonstrated [49]. Phenolated lignin as an additive to phenol was used to prepare phenolic foam, where mechanical and thermal insulation properties were the same as pure phenol-based material.

Post isolation
In contrast, direct phenolate of lignin needs harsh conditions (120–180 °C, an acid catalyst, usually concentrated H2SO4). Different hydroxy and dihydroxybenzenes could be introduced [6,50–53]. Up to 50% increase of Ar–OH in comparison with the starting material was demonstrated. Arylation takes place at the expense of Alk-OH groups. The same could be reached using benzylic alcohols, such as salicyl alcohol, for alkylation; then guaiacyl groups at 5 or 6 position become the reactive centers [52,53]. The combination of these two approaches leads to a five times increase in Ar–OH groups availability per gram of lignin.

It is possible to increase the amount of aromatic hydroxy groups without the introduction of new aromatic building blocks. Part of Ar–OH groups in lignin are methylated. Selective demethylation (ionic liquids, with aniline as a methyl acceptor) of kraft lignin transformed guaiacyl residues into catechol groups [54]. Selective demethylation of lignin could be also achieved enzymatically [55] or by HBr. Lignin demethylation increases lignin reactivity in reactions producing PU material [56].

If the cleavage has occurred
The majority of lignin stabilization strategies target the stabilization of the molecules after β-O-4’ bond cleavage reaction. High-value monomers are separated from the rest of the lignin-derived products. Oligomers unavoidably formed under such conditions. Yet, their valorization was not well studied. Interestingly, after β-O-4’ bond cleavage reactions, the same types of groups are stabilized on oligomers and on monomers [57]. Thus, mixtures of monomers, dimers, and higher oligomers are rather homogeneous on the functional group types present (Figure 3, G, H, and I).

Active stabilization
Under RCF conditions, each successfully cleaved β-O-4’ bond will yield Ar–OH and Alk-OH groups. Lignin-derived dimers and mixtures obtained through RCF of biomass were used to produce precursors for epoxy resins and epoxy thermoset polymers [58]. Like RCF, the mixture from the hydrogenation of aldehyde stabilized lignin was separated into monomers and oligomers. These oligomers outperform unfractonated technical lignin in solubility—wider range, color—lighter, and PU materials formulations [59].

Stabilization with diols opens access to other types of functional groups. One aldehyde or ketone group, masked as acetal or ketal, and one Ar–OH group will be generated from β-O-4’ bond cleavage reaction [41]. It is possible to control between reactions leading to preferably acetal or ketal (Figure 3, G and I) residues by varying acid catalyst and solvent system properties.

Other lignin modification
Lignin modification is not limited to the discussed methods. However, the list of active stabilization methods is limited. For example, all oxidation methods that provide lignin with preserved β-O-4’ bonds are created for isolated lignin. Lignin oxidation is a powerful
transformation to access highly functionalized macromolecules. Oxidation of α and γ position of the β-O-4′ motif was achieved, yielding corresponding α-ketones, γ-aldehydes, or γ-carboxylic acids [34,38,60–63].

Conclusion and outlook

Active lignin stabilization provides access to a new dimension of lignin-based materials. Control of lignin structure—molecular weight, branching, functional complexity—during fractionation process allows access to one-step product compatible with other materials [64] that also ease lignin intrinsic properties transfer (e.g. biodegradability, UV-blocking, antimicrobial activity) to newly synthesized polymer or composite material [65].

Introduction of functional groups beyond typical for lignin—aromatic rings, aromatic and aliphatic hydroxy groups—significantly expand the application area of lignin that would help in the design of smart materials. It contributes to design of materials reprocessibility and recyclability [18]. Vitrimers could be one of such possibilities. Known examples of dynamic bonds and their introduction are in the line with lignin possibilities and demonstrated modifications [66].

It is difficult to compare active stabilizations between each other. More researchers should follow a unified research practice [67]. There are many active stabilization methods for monomers. Co-forming oligomers desired better analysis and valorization. All described methods provide mixtures of lignin-derived products. Polymer chemistry is not used to such feeds. Therefore, this study demonstrates a whole end-to-end biorefinery process in which up to 78% of wood is converted into set of useful chemicals. The efficiency of RCF process was revealed by a life-cycle assessment and techno-economic analysis.

Declarations of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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The guidelines describe standards and best practices, as well as minimum requirements for biomass fractionation. Ground principles of good laboratory practices in the area are formulated.