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Active lignin stabilization in lignocellulosic biomass fractionation: mechanisms and advancements

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Lignin is one of the most abundant biopolymers on Earth, holding significant potential for the production of bio-based chemicals, fuels, and materials. However, its complex and heterogeneous structure poses challenges for efficient valorization. Active lignin stabilization fractionation offers a way to overcome these challenges, focusing on the selective depolymerization and stabilization and/or even functionalization of lignin during biomass processing. Unlike conventional fractionation methods, this active lignin stabilization fractionation attempts to prevent condensation of the lignin, yielding high-value aromatic compounds for further applications. This review highlights green advances in the field, including the use of deep eutectic solvents and ionic liquids, alongside innovative stabilization techniques, carbocation scavengers, and reductive catalytic fractionation. By integrating these approaches into sustainable biorefineries, this work provides a roadmap for advancing lignin valorization and contributing to the broader goals of green chemistry.

Green foundation

1. The review discusses advances in lignin valorization through stabilization fractionation. Innovations such as stabilization techniques, carbocation scavengers and reductive catalytic fractionation enhance lignin reactivity and yield high-value bio-based chemicals.
2. This field addresses the underutilization of lignin, a major biomass component, by transforming it into valuable materials and chemicals, reducing reliance on fossil fuels. It promotes sustainable biorefineries and aligns with global goals for green energy and circular economy.
3. Future advancements will focus on cost-effective catalysts, tailored green solvents, and fully integrated biorefineries. The review provides insights into stabilizing lignin and preventing condensation, paving the way for scalable and eco-friendly lignin valorization techniques.

Introduction

Lignin is a highly branched, cross-linked biopolymer composed of phenylpropanoid units and, together with cellulose and hemicellulose, forms the fundamental structural framework of plant cell walls.[1] Lignin is derived from a wide variety of biomass sources (such as wood, grass, agricultural products, and more), and the amount varies across plant species, usually consisting of 15–35 wt% of dry biomass. As the second most abundant biopolymer in plants after cellulose, lignin functions as both a glue and a structural framework, binding tightly to polysaccharides (cellulose and hemicellulose) and imparting mechanical strength, rigidity, and compressive resistance to plant tissues. In addition, lignin prevents water permeation and enhances resistance to pathogens and pests.

In nature, lignin is composed of three primary phenylpropanoid structural units formed through enzymatically mediated dehydrogenative radical coupling reactions.[1,2] These structural units originate from three monolignols: coniferyl alcohol, sinapyl alcohol, and *p*-coumaryl alcohol, which respectively give rise to the guaiacyl (G), syringyl (S), and *p*-hydroxyphenyl (H) units, as illustrated in Fig. 1. The distinction among these phenylpropane precursors lies in the degree of methoxyl substitution on their aromatic rings. The distribution of the three lignin structural units differs among plant species: softwoods are dominated by G units, hardwoods contain both G and S units, while grasses possess all three types (H, G, and S). These three phenylpropanoid units are interconnected *via* ether linkages (C–O, such as β-O-4 and α-O-4) and carbon–carbon bonds (β–β, β-1, β-5, *etc.*), forming lignin's highly irregular and cross-linked macromolecular structure. Among these, the β-O-4 ether linkage is the most abundant interunit bond in native lignin, typically accounting for 45–60% of interunit linkages in soft-

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woods, 50–70% in hardwoods, and up to 70–75% in S-rich tissues or specific plant organs.

The chemical structure of lignin is complex, containing a variety of functional groups, such as hydroxyl groups, ether bonds, ketone and aldehyde groups, and aromatic rings.[3] These functional groups give lignin unique chemical reactivity and functional properties, making it show a wide range of application potential in biomass utilization and sustainable development.[4] The presence of phenolic hydroxyl groups offers lignin good antioxidant and chemical reactivity, and can undergo cross-linking reactions with other compounds. This characteristic makes lignin a promising raw material for the preparation of bio-based plastics, adhesives, and composite materials. The presence of ether bonds enhances the structural stability of lignin, while also affecting its binding properties with cellulose and hemicellulose, thereby improving the mechanical properties of composite materials. In the energy field, lignin is regarded as an important source of biomass energy.[5] It can not only be converted into biofuels through thermochemical processes such as pyrolysis and catalytic depolymerization but can also be used as a raw material for biomass power generation. The use of this renewable energy source helps to reduce dependence on fossil fuels, reduce greenhouse gas emissions, and promote the process of sustainable development. In addition, the application of lignin in the agricultural field cannot be ignored.[6] As a soil conditioner, lignin can improve the structure of the soil, and increase its water retention capacity and nutrient supply, thereby promoting plant growth. At the same time, lignin derivatives can also be used as plant growth promoters, which help improve the stress resistance and yield of crops. In terms of environmental protection, lignin, as a renewable resource, has excellent biodegradability and is suitable for the development of environmentally friendly packaging materials and adsorbents. These materials can not only reduce plastic pollution, but also effectively remove heavy metals and organic pollutants in water bodies, providing new ideas for environmental protection.

Isolation is a crucial step in lignin valorization. Because lignin is tightly bound to hemicellulose and cellulose within the biomass matrix, effective isolation typically requires specialized biomass fractionation methods. Several biomass fractionation methods exist, both conventional and novel. The separated lignin remains highly underutilized; although most kraft lignin dissolved in black liquor is combusted primarily for energy and for the regeneration of pulping chemicals, isolated lignin itself is generally used only as a low-value solid fuel.[8] Its complex and heterogeneous chemical structure, along with the variability introduced by different separation methods used in biorefineries, significantly constrains its valorization. This challenge is further compounded by condensation reactions that may occur during fractionation. In addition, lignin exhibits a broad molar mass distribution, which strongly influences its structure and reactivity, thereby affecting its potential applications. The combined effects of structural complexity and high molar mass dispersity ultimately diminish its overall application value. In order to valorize lignin, a reduction in heterogeneity is critical.[9] Economically sustainable methods for fractionating lignin into homogenous fractions are needed to fully utilize its potential. Fractionation has thus emerged as a viable solution for lignin valorization and has attracted interest within the scientific community. Reactive fractionation further attempts to modify the lignin, in order to prevent condensation reactions and obtain lignin or lignin fractions well suited for further use.

Review of methodologies

Fractionation of biomass towards the valorization of lignin has got the attention of researchers in recent years, which can be seen in the recent number of publications. The graph in Fig. 2 is based on search results of peer-reviewed journal articles obtained using Boolean operator for key words "lignin valorization" and "biomass fractionation". Based upon the number of publications by year, an increase in importance and attention to this field can be seen. Search on "Scifinder" showed a significant increase in articles over the past decade, with the highest peak in 2025. This review article aims to explore

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biomass fractionation towards high-value lignin, with its opportunities and challenges.

Fractionation methods from biomass

The recalcitrant structure of lignocellulosic biomass hinders the direct utilization of its three major components. Biomass fractionation is therefore essential for separating cellulose, hemicellulose, and lignin so that each fraction can be valorized individually. Currently, methods for separating lignin from biomass can be broadly divided into two categories: conventional pulping approaches and lignin-first (or lignin-preferred) strategies.

Conventional approaches

The conventional methods, also known as pulping processes, are widely used in the pulp and papermaking industry. Conventional methods for biomass fractionation include kraft, soda, and sulfite pulping processes (Table 1). Lignin is considered a by-product in these processes that traditionally are utilized for obtaining delignified pulp as the main product. These methods tend to give lignin with low purity and high heterogeneity, resulting in difficulty in valorization.

Kraft pulping

The kraft pulping process is the dominant conventional way to chemically produce pulp.[10] White liquor, composed mainly of sodium hydroxide and sodium sulfide, is used for the delignification. The kraft pulping process uses strong alkali conditions under high temperature and pressure and hydrosulfide ions for the depolymerization and modification of the lignin structure.[11] The pulping conditions will vary depending on the species being processed. When lignin and other components have been broken down, they form a liquid called black liquor. After processing, the pulp and black liquor are separated, and some of the black liquor can be acidified to generate the kraft lignin due to precipitation. Technical lignin-generated technologies such as LignoBoost and LignoForce are based on this acidification strategy: LignoBoost improves filtration by implementing a redispersion and secondary acidification step, whereas LignoForce introduces an oxidation step prior to acidification to reduce reduced-sulfur compounds and enhance filterability.[12,13] The recovered kraft lignin will vary depending on the feed used in the process. If, for example, both soft and hardwoods were used in the process, the black liquor streams tend to be combined and will therefore contain both softwood and hardwood kraft lignin.

Kraft pulping is the most commonly used pulping process in the global pulp and paper industry.[14] Since its development in the early 20th century, the Kraft process has gradually become the mainstream process for pulp production due to its strong adaptability, ability to process a variety of wood and non-wood raw materials, and high fiber recovery rate. Currently, the Kraft process accounts for the largest portion of global pulp production, which means that a large amount of kraft lignin is produced every year, making it in sufficient supply and low cost, suitable for further development and utilization.

Kraft lignin possessed a highly condensed aromatic structure enriched in C–C linkages, a relatively high molecular weight, and characteristic sulfur-containing functionalities formed during the Kraft pulping process. These features confer greater thermal stability compared with most other technical lignins. It mainly makes kraft lignin particularly suitable as a precursor for carbon materials, thermosetting resins, and other high-performance applications that benefit from a highly aromatic and thermally robust feedstock. Consequently, Kraft lignin has been widely investigated for producing functional materials and chemical products such as phenolic

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resins, adhesives, dispersants, polymer composites, activated carbon, and other carbon-rich materials, as well as for generating chemicals by pyrolysis or catalytic depolymerization, such as vanillin, phenols, benzene, and so on.[15]

While kraft lignin boasts several advantages, such as its abundancy, low cost and being rich in functional groups, several significant downsides exist. It tends to have impurities such as sulfur compounds, high heterogeneity making it difficult to control its properties for consistent applications, and wide molecular mass distribution. This can make valorization of kraft lignin difficult.[11]

Soda pulping

Soda pulping is another conventional alkaline method to remove and recover lignin from lignocellulosic biomass.[16] It is a chemical process, using alkaline environments with the use of sodium hydroxide to break down biomass, such as agricultural residues. The process consists of depolymerization of lignin through the cleavage of ether bonds, solubilizing the lignin in the cooking liquor. Unlike kraft cooking, no sulfur compounds are used.

As soda lignin is generally produced from non-wood plants, they tend to exhibit more structural diversity than that of kraft lignin.[17] Soda lignin also has a broad molecular mass distribution, like that of kraft lignin, and impurities are also present. This means that soda lignin is also quite heterogenous, leading to problems in downstream processing.

Sulfite pulping

Sulfite pulping uses sulfurous acid and/or sulfite/bisulfite salts containing calcium, sodium, magnesium or ammonium.[18] Unlike the kraft and soda processes that employ alkaline environments, the sulfite process tends to use an acidic environment but can also be done in neutral conditions. The lignin obtained from this process is called lignosulfonates. The conditions used during the pulping process will affect the lignosulfonates.

The formation of lignosulfonates under acidic conditions happens due to the loss of a hydroxyl group or cleavage of the alpha-ether linkage in the lignin, forming a quinone methide intermediate with phenolic or non-phenolic substrates through hydrolysis. Sulfite ions then react with the intermediate at the alpha position, forming benzyl sulfonic acid units. This sulfonation increases the solubility of the lignosulfonates. A condensation reaction can alternatively occur, preventing sulfonation at the alpha position.

In neutral sulfite pulping, hydrolysis happens with only phenolic intermediates. A sulphonic acid group is added to both the alpha and beta positions. The lignosulfonates can then be removed from the pulp through filtration, remaining in the spent liquor. Ultrafiltration can then be employed to further separate the lignosulfonate from the liquor.

Lignosulfonates are particularly affected by condensation, leading to a broad molecular weight distribution.[19] Like the other conventional methods, it also suffers from heterogenous and highly dispersity lignin.

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Lignin-first approaches

As lignin is susceptible to irreversible degradation, difficulty arises in obtaining useful chemicals.[26] In the lignin first biorefineries, the valorization of lignin is considered a primary target, rather than seen as a by-product. The prevention of degradation of the lignin structure is the main goal. Table 2 is focused on lignin first methods.

The lignin-first method is a newer concept, which focuses on the active stabilization of lignin during biomass fractionation. A major benefit of this method is its compatibility with harsher process conditions. The use of mild fractionation conditions, while decreasing condensation, leads to lower yields of isolated lignin. The lignin first method results in high isolated lignin yields and low condensation, thereby avoiding the issues deriving from using mild conditions. The lignin-first method involves obtaining lignin in a valorisable and stabilized form before or alongside carbohydrate valorization. Due to the rigid structure of cellulose, it is far less prone to degradation and can therefore be valorized at a later stage. The lignin first method combines biomass fractionation with tandem lignin depolymerization stabilization, with the formation of stable low molecular products such as monomers and dimers.

Reductive catalytic fractionation (RCF)

RCF uses a metal catalyst under reductive atmosphere.[27] The extraction and conversion of lignin into monomers in the presence of a catalyst leads to higher yields of aromatic monomers than those typically obtained from depolymerization of technical lignin, as there are less C–C bonds present and more C–O bonds. RFC is a two-step process, where lignin is extracted from the biomass with a solvent, whereafter the C–O ether bonds are selectively cleaved using a hydrogen donor and heterogenous catalyst. This process results in depolymerized

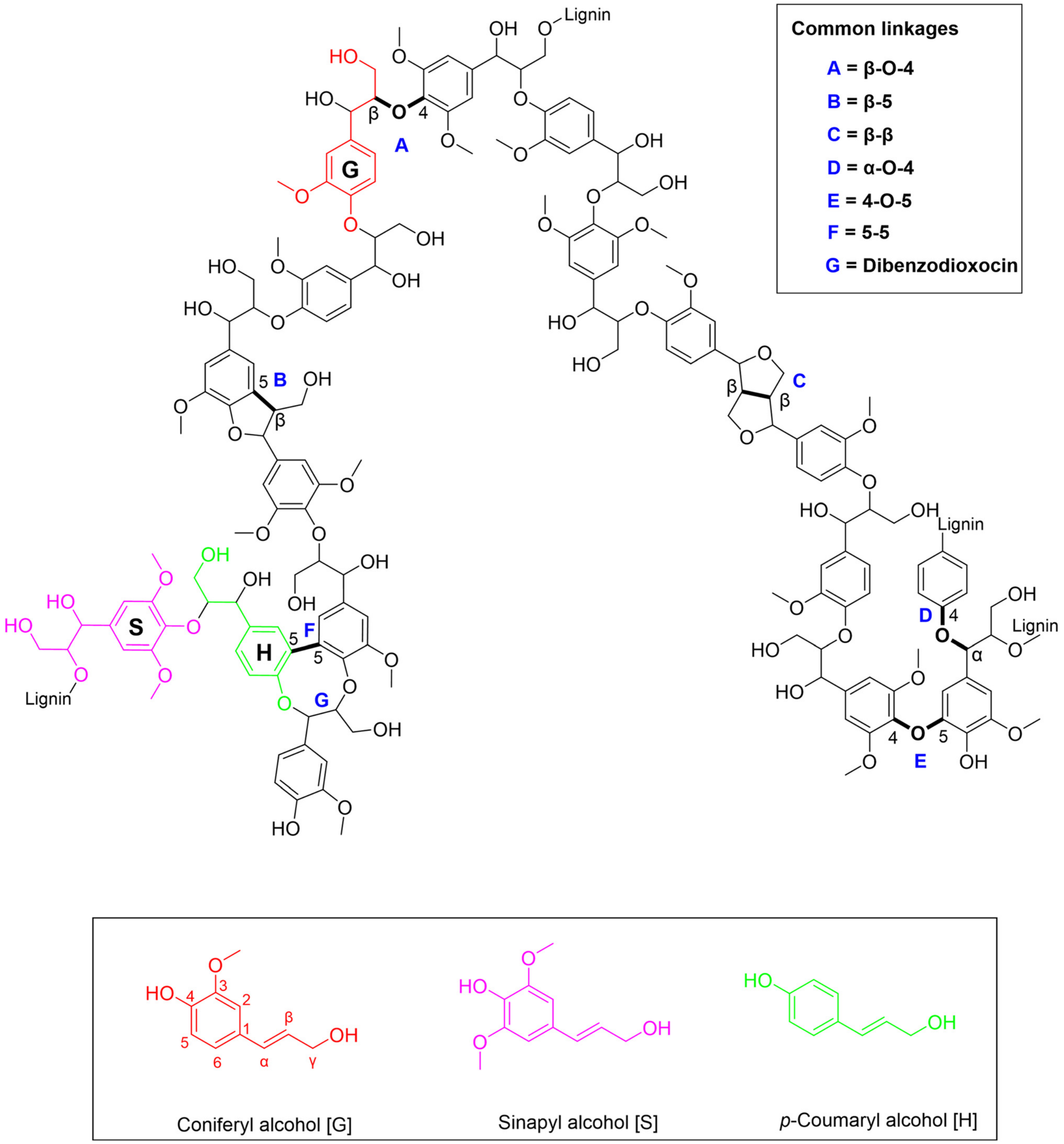

Fig. 1 Illustration of the lignin structure with its common linkages and monolignols (adapted from ref. 7, licensed under CC BY 3.0. Copyright 2024).

lignin oil and solid carbohydrate pulp, which can then be further valorized. Solvents used are usually alcohols or water/organic solvent mixtures, the hydrogen donor pressurized hydrogen gas or originate from the solvent or lignocellulose, and the catalyst a noble metal or nickel.

The main difference between pulping and this method is that catalytic processing of lignin begins while it is still closely associated with the lignocellulosic matrix, before extensive structural modifications occur. Reactive fragments and intermediates that emerge during solvolytic extraction are immediately stabilized into more stable molecules, preventing their participation in condensation reactions. Compared with catalytic hydrogenolysis of technical lignin, which typically yields only 5–15 wt% of aromatic monomers, RCF can deliver substantially higher monomer yields, in the range of 35–55 wt%, greatly improving product selectivity and significantly enhancing the economic potential of lignocellulosic biorefineries.

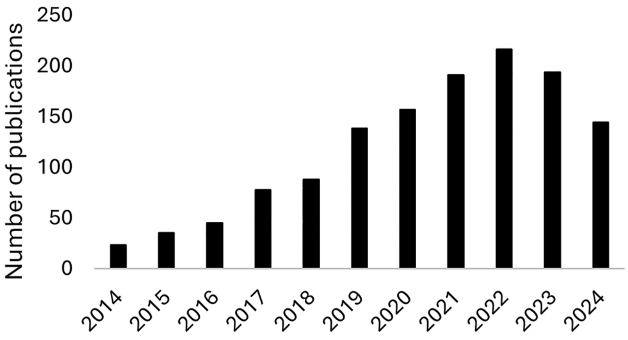

Fig. 2 Number of publications with the search terms "lignin valorization" and "biomass fractionation" per year on Scifinder.

Organosolv

Organosolv method is an important technology in the field of biomass fractionation and is particularly suitable for the selective separation and efficient utilization of lignin, cellulose and hemicellulose.[28] Compared to conventional pulping processes that generate impure lignin, this method has the advantages of being mild, efficient, and highly selective. A wide range of solvents can be used, such as organic alcohols, organic acids, esters, and combined solvents with or without the use of alkaline or acid catalysts. Selective solubilization of lignin is provided by these solvents and causes a slight chemical modifi-

Table 1 Overview of conventional pulping processes

Pulping method	Pulping process	Chemicals	Lignin removal (%, relative to initial lignin content)	Key advantages	Key disadvantages	Ref.
Kraft	Alkaline	Sodium hydroxide, sulfide	90–95%	Abundancy, low cost, rich in functional groups	Impurities, high heterogeneity, wide molecular mass distribution	20 and 21
Soda	Alkaline	Sodium carbonate	85–90%	Less toxic than kraft	Heterogenous, broad molar mass distribution, some impurities	22 and 23
Sulfite	Acidic/neutral	Sulfurous acid or sulfite/bisulfite	Varies up to 75%	High quality pulp	Heterogenous, broad molar mass distribution	24 and 25

Table 2 Overview of lignin first methods

Methods	Processes	Chemicals	Lignin removal (%, relative to initial lignin content)	Key advantages	Key disadvantages	Ref.
RCF	Reductive catalytic process	Organic solvents and metal catalysts	80–90%	Low lignin condensation *via* reductive stabilization, high monomer yields, tunable lignin and carbohydrate fractionation	Requirement for metal catalysts and pressurized hydrogen, high-pressure operation, catalyst separation and stability, increased process complexity	39 and 40
Organosolv	Organic solvent-based	Ethanol, methanol, acetone with an acid catalyst	Up to 80–85%, as low as 30%	High-purity sulfur-free lignin, good fractionation selectivity, relatively low lignin condensation, established solvent recovery	High solvent-to-biomass ratios, energy-intensive solvent recovery, higher overall process cost compared to kraft pulping	41 and 42
ILs	IL-based process	ILs (imidazolium-, ammonium-based salts, *etc.*)	Up to 90%	Selective lignin dissolution and extraction, tunable solvent properties, low volatility and flammability, suppression of lignin condensation, potential for solvent recycling	High solvent cost, energy-intensive synthesis, challenging solvent recovery due to strong lignin–IL interactions and viscosity, potential corrosion and environmental concerns	43 and 44
DES	Mild, low-temperature process	DESs (choline chloride and urea/lactic acid/oxalic acid, *etc.*)	Up to 90%	Biodegradable and low-toxicity solvents, mild processing conditions, lower cost than ionic liquids, effective lignin and hemicellulose extraction, potential for solvent recycling	High viscosity and mass-transfer limitations, long reaction times, solvent recovery challenges, limited standardization and early stage of industrial development	44 and 45

cation through the breaking of aryl ether bonds depending on the conditions. Organosolv fractionation has some downsides, however, having high equipment requirements, as well as using dangerous and costly solvents.

Organic solvents such as methanol and ethanol are widely used for lignocellulosic biomass fractionation.[29] The fractionation is performed at high temperatures and can be done with or without catalysts. Lignins from ethanol and methanol fractionation approaches under mild alcohol/water conditions are preferred if structurally unmodified lignin is desired, as such conditions generally do not introduce significant chemical alterations to the lignin structure. The concentration of alcohol and the severity of the reaction affect how effectively lignin is removed. Lower alcohol concentrations promote the depolymerization of lignin by breaking α and β ether bonds, leading to lignin fragments with a lower molar mass. For instance, a lower ethanol concentration increases the hydronium ion (H_3O^+) concentration, thereby enhancing acid-catalyzed cleavage of α- and β-aryl ether bonds in lignin[30] Additionally, the cleavage of α-aryl ether bonds generates a benzyl carbocation, which can further react with water or ethanol, contributing to the breakdown of lignin.[31] However, condensation reactions may also occur during alcohol fractionation.

Acetic and formic acids are good at fractionation of biomass, as they are good at delignification at high temperatures.[29] These fractionation methods are commonly assisted with the addition of agents such as inorganic acids or oxidizing agents. Use of formic acid tends to be preferred if the primary concern is the removal of lignin. However, acid fractionation can lead to acylation, particularly acetylation when acetic acid is used and formylation when formic acid is present, modifying the lignin structure. Several chemical reactions occur during acid fractionation, such as cleaving of β-O-4 bonds, condensation of lignin, hydrolysis of ester bonds, and esterification of hydroxyl groups. Fractionation with formic or acetic acid at high temperatures leads to cleavage of β-O-4 and C–C bonds, while the formation of new C–O bonds contributes to repolymerization. Under high-severity formic/acetic acid treatments, depolymerization is also supported by the oxidation of the syringyl unit at the Cα position, leading to the formation of carbonyl structures.[32]

Ionic liquids (ILs)

Certain ILs have shown excellent performance in disrupting the crystalline structure of cellulose and facilitating lignin removal during biomass fractionation.[28] ILs assist in the fractionation of lignocellulosic biomass by selectively dissolving lignin and disrupting the interactions between cellulose, hemicellulose, and lignin. The efficiency of this process depends on factors such as the solvation properties of the IL, its viscosity, and the interactions of the IL anion and cation with lignocellulose components. This method is plagued by several problems however, such as the popular liquids being costly and difficult to prepare and recycle.

ILs are salts in liquid form at room temperature.[33] These liquids contain cations, which are organic, and anions, which can be organic or inorganic. Two distinct processes exist, that being the dissolution process, where the entire biomass is solubilized, and the ionosolv process, where only lignin and hemicellulose are solubilized. Delignification depends largely on the type of biomass being processed. Softwood tends to be more resistant to deconstruction than hardwood. Several different ILs exist for biomass processing, with varying degrees of success. Chloride based liquids tend to perform poorly at delignification, while sulfonate and sulfate-containing ILs appear to be the most effective for separating cellulose from lignin and hemicellulose.

IL pretreatments often fragment lignin and lower its molar mass. The anion of the ILs plays a key role in lignin fragmentation, with sulfate-based anions showing the greatest ability to break down lignin, followed by lactate, acetate, chloride, and phosphate. The functional group of the anion influences lignin solubility and depolymerization efficiency. Under certain conditions, IL treatment can facilitate β-O-4 aryl ether bond cleavage, a crucial step in lignin depolymerization. Stronger hydrogen-bonding basic anions (*e.g.*, Cl^-, Br^-, HSO_4^-) enhance cleavage efficiency, though the extent of lignin modification depends on the specific ionic liquid used. After fractionation, precipitation can be performed to collect the extracted lignin. ILs therefore provide a method for lignin removal and recovery, potentially yielding more valuable lignin fractions.

Deep eutectic solvents (DES)

Deep eutectic solvents (DESs) fractionation is promising for lignin fractionation, as they overcome some of the ionic liquid's issues such as high cost, toxicity and low biodegradability.[28] These solvents are synthesized by at least one hydrogen bond donor (HBD) and one hydrogen bond acceptor (HBA). The properties of DES can be altered by changing the hydrogen bond donors and acceptors. DES also shows high solubility of lignin and a low solubility of cellulose.

DESs, like ILs, possess solvent properties that can be adjusted by choosing their components based on molecular structure, chemical nature, ratios, and water content.[34] Most DESs are biodegradable, biocompatible and non-toxic, however their characteristics are depending on the DES constituents. DESs with lactic acid as HBD showed high solubility for lignin and none for cellulose. High lignin solubility was also seen in DES consisting of malic acid and proline.

DES lignin has far higher purity (85–95 wt%) than that of conventional procedures, because DES selectively solubilizes lignin while minimizing the dissolution of carbohydrates and inorganic impurities, enabling more efficient downstream valorization.[35] The lignin is recovered *via* precipitation and purification, with the use of anti-solvents. The impurities left in the DES lignin are typically residues from polysaccharides and DES. The DES lignin tends to have lower molar mass distribution compared to that of native lignin, which is favorable for valorization. The molecular weight is affected by depolymerization and condensation. While the DES depolymerizes the lignin, condensation of said lignin will occur if the treatment conditions are too harsh, such as high temperatures or long treatment time. Choosing the appropriate HBA and HBD for DES is crucial, as they play a significant role in the molecular structures of the resulting lignin.

The abundance of β-O-4 bonds is important for the valorization.[36,37] DES-based lignin fractionation influences the preservation or cleavage of β-O-4 bonds, depending on the solvent composition and process conditions. Tailoring the β-O-4 content in lignin is possible through careful control of DES composition, temperature, reaction time, and solid loading. Lastly, the presence of OH groups is important for the reactivity of lignin. During lignin fractionation with DESs, more of phenolic OH groups are formed as a result of the breaking of β-O-4 bonds and the removal of methyl groups from the methoxy groups in lignin. DES lignin tends to have more phenolic OH groups than native lignin, due to breaking of β-O-4 bonds. Furthermore, condensation can be prevented with the addition of stabilization or capping agents, which rapidly trap the acid-generated benzylic carbocation and block electrophilic aromatic substitution pathways.[38]

Alternative approaches

Enzyme fractionation primarily uses cellulase to hydrolyze the cellulose, with the intent of removing the carbohydrates and thereby extract the lignin.[28] The lignin obtained with this method is called cellulolytic enzyme lignin. The enzymatic treatment helps increase yield, lower use of harmful chemicals, and uses mild conditions. A variety of enzymatic extraction strategies have been developed. One representative example is the hydrothermal pretreatment followed by enzymatic hydrolysis, where hydrothermal treatment disrupts the cell wall architecture and partially solubilizes hemicelluloses, after which cellulase cocktails selectively remove the remaining polysaccharides, yielding lignin with a high degree of native structural preservation.[46] Similar two-step schemes, such as steam-explosion pretreatment followed by enzymatic hydrolysis, dilute acid pretreatment followed by enzymatic polishing, or organosolv pretreatment followed by cellulase/hemicellulase hydrolysis, are also widely employed to obtain structurally representative lignin fractions.[47–49]

In addition to carbohydrate-targeting enzymes, laccase-assisted lignin extraction has emerged as another mild enzymatic strategy. Laccases catalyze the oxidation of phenolic lignin units to generate reactive radicals, and in the presence of mediators, can induce controlled cleavage or modification of lignin-carbohydrate complex (LCC) linkages. This oxidative loosening of the lignin-polysaccharide matrix facilitates subsequent lignin release or improves solvent accessibility, allowing partial lignin extraction under significantly milder conditions than conventional chemical pulping. While laccase-assisted extraction typically yields lower lignin quantities than cellulase-based methods, it offers high selectivity toward lignin-carbohydrate linkages and can enhance lignin purity when combined with mild solvents or buffer systems.

Overall, enzymatically isolated lignins avoid harsh chemical degradation and retain key native linkages. However, challenges such as lower yields, lower purities, lengthy processing times, and the cost of enzyme systems remain limitations that currently restrict large-scale implementation.

Comparison of different approaches

Conventional pulping methods such as kraft, soda and sulfite are used for maximum yield and quality of cellulose.[11] The lignin is exposed to harsh chemical environments during removal, including high acidity, alkalinity, temperature and residence time, leading to β-O-4 cleavage followed by condensation reactions. The result is a highly modified technical lignin, characterized by increased C–C bonding, broad molecular weight distribution, and decreased reactivity. As a result, the lignin is mainly used for energy recovery, rather than chemical upgrading and valorization.

In contrast, lignin first fractionation strategies are designed to preserve the lignin as chemically reactive and structurally defined.[50,51] Methods such as organosolv, DES, and RCF aim to solubilize and stabilize reactive intermediates, thereby suppressing condensation reactions during extraction. The result is lignin with higher β-O-4 content, lower degree of condensation, and more uniform molecular weight distribution than technical lignin, which is essential for further functionalization and valorization.

A fundamental difference is that conventional pulping prioritizes carbohydrate valorization and treats lignin as a side product, while lignin first strategies attempt to maximize overall value of biomass by preserving lignin functionality from the earliest processing stages.[52] This increases the potential to valorize lignin, enabling its use as a renewable source of aromatic chemicals and advanced materials.

Lignin condensation mechanism and prevention strategies

Lignin condensation

Lignin condensation, also called repolymerization, refers to the formation of interunit C–C bonds, which makes the lignin structure less reactive and more complex, as seen in Fig. 3.[53] This complicates the downstream processing of lignin and uses it in further applications such as in the making of chemicals, materials, and fuels. Understanding the structure of condensed lignin is a challenge, mainly due to the involvement of several reactive intermediates and condensation pathways during condensation. Lignin condensation can be characterized into four different categories, benzylic carbocation-induced diarylmethane (DAM) condensation, aldehyde-induced (DAM) condensation, radical-induced coupling reactions, and carbonyl-induced aldol condensation. The most widely known condensation type in lignin is the DAM-type structure Benzylic carbocations are formed when certain bonds in lignin are hydrolyzed, such as β-O-4, α-O-4, γ-O-α, and LCC bonds. These carbocations are important intermediates in several hydrolysis pathways. The carbocations are strong electrophiles, prone to attacking the *meta* position to phenolic hydroxyls, leading to formations of C–C bonds.

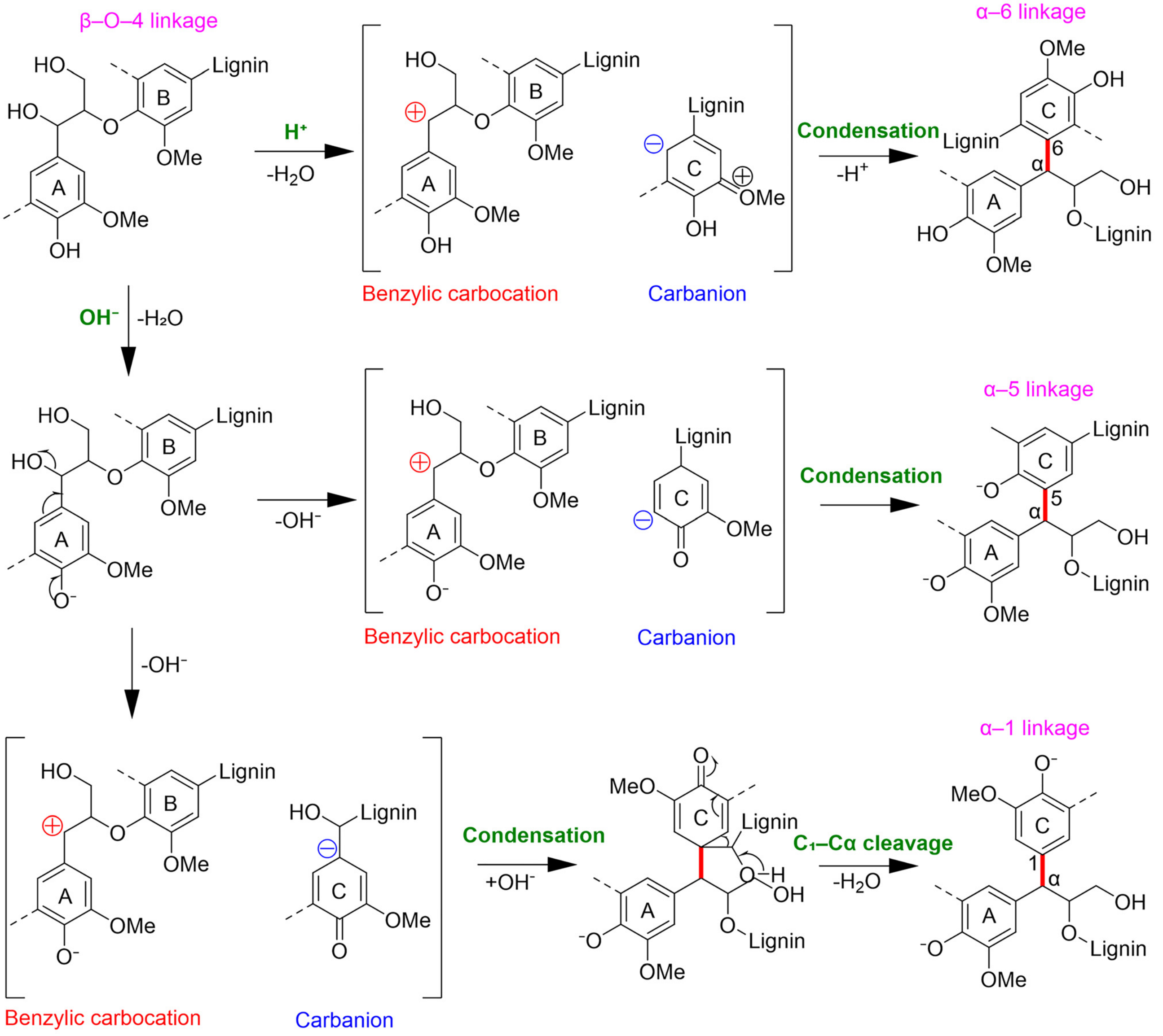

Fig. 3 Condensation pathways of lignin fragments *via* benzylic carbocations formed from β-O-4 linkages under acidic and alkaline conditions. Acid-catalyzed dehydration and base-catalyzed elimination generate carbocation intermediates, which react with electron-rich aromatic sites to form C–C bonds. The resulting condensed structures include α-6, α-5, and α-1 linkages, which contribute to reduced reactivity (adapted from ref. 53 with permission from Elsevier, Copyright 2023).

The β-O-4 linkage is the weakest bond in lignin. It is also where the radical condensation process is initiated, due to radical formation. Nagel and Zhang suggested that under neutral conditions, a quinone methide intermediate is formed, which undergoes homolysis to produce aliphatic and phenoxy radicals.[54] These radicals can then couple with other radicals, thereby forming C–C bonds and contributing to lignin condensation. In contrast, during alkaline or acidic conditions, compounds like vinyl ether and homovanillin tend to be formed rather than radicals.

Aldehydes and ketones can trigger aldol condensation reactions, leading to more complex structures.[55] During acidolysis of lignin, two types of aromatic carbonyl intermediates are formed, a Hibberts ketone set and aldehyde containing compounds. The highly reactive aldehyde can lead to side reactions but can be suppressed by capturing it with ethylene glycol, thereby preventing the condensation. Similarly, during alkaline hydrolysis of lignin, carbonyl-containing lignin fragments are produced *via* an epoxy intermediate pathway.[56] The carbonyl groups can then undergo aldol condensation under alkaline conditions. Furthermore, degradation of carbohydrates into smaller carbonyl-containing fragments could cause DAM-type and aldol condensation.[53]

Industrial delignification methods such as kraft pulping employ harsh processing conditions to extract the lignin.[26] This leads to irreversible degradation, resulting in a condensed residue that is less reactive than the native biopolymer, and is simply incinerated for energy. Effective and selective depolymerization is difficult in all conventional biorefinery lignins such as kraft, sulfite, soda, organosolv, due to the condensed nature of the lignin.

The negative effects of condensation can be seen in its impact on the theoretical monomer yield. This monomer yield is approximately proportional to the square of the fraction of cleavable β-O-4 bonds. Therefore, even small increases in condensation, which lowers β-O-4 linkages, will drastically decrease the attainable monomer yield. This irreversible condensation is the main reason for difficulties in effective and selective lignin to aromatic conversion.

Condensation prevention

Due to the challenges in preventing condensation, millions of tons of low-value lignin are produced annually.[57] Methods to prevent lignin condensation can be broadly categorized into two approaches: one involves trapping and converting reactive intermediates into stable compounds, while the other focuses on stabilizing the β-O-4 linkages directly.

Several fractionation methods have been developed to produce reactive, uncondensed lignin,[26] including ammonia-based fractionation,[58] ionic liquid-assisted fractionation,[59] γ-valerolactone hydrolysis,[60] and mild organosolv techniques.[61] These methods are successful because they utilize milder processing conditions, which help preserve β-O-4 bonds and reduce condensation. However, these approaches often result in lower lignin yields. To increase delignification while maintaining structural integrity, more aggressive methods can be used, though these may compromise the lignin structure, particularly the preservation of β-O-4 linkages. Stabilizing the lignin structure and preventing condensation can be achieved through techniques that either transform reactive intermediates into stable compounds or protect the β-O-4 linkages directly. Use of acidic lithium bromide trihydrate,[62] ionic liquids,[28,63] and γ-valerolactone[60] are examples of strategies that limit the formation of reactive intermediates, thereby enhancing lignin stability during depolymerization.

A promising development beyond these mild approaches is "lignin-first" fractionation, which actively stabilizes lignin during the fractionation process. This allows for harsher operating conditions while maintaining a balance between high lignin yield and structural preservation, effectively minimizing or even eliminating recondensation.

Stabilizers

The extraction of soluble, uncondensed lignin during pretreatment is key to producing lignin monomers, aligning well with existhaing biorefinery processes.[37] However, a major challenge is the formation of C–C bonds during extraction. To address this, protective agents, such as formaldehyde, have been used to block reactive benzylic positions. Adding formaldehyde during pretreatment resulted in near-theoretical yields of lignin monomers after hydrogenolysis, typically 47–78 wt% depending on the biomass, which represent a three- to sevenfold improvement over the 8–15 wt% yields obtained without formaldehyde stabilization.

Formaldehyde prevents C–C bond formation through two mechanisms. First, in an acidic, water-free environment, formaldehyde reacts with 1,3-diols on lignin sidechains to form stable six-membered 1,3-dioxane structures, preventing benzylic carbocation formation. Secondly, formaldehyde undergoes electrophilic aromatic substitution at the *ortho*- and *para*-positions of methoxylated aromatic rings, resulting in hydroxymethylated lignin, which effectively blocks these reactive positions and stabilizes lignin against condensation. Stabilized lignin retains valuable β-O-4 linkages, maintaining its structural integrity and reducing condensation, which facilitates monomer release during depolymerization.[64]

Formaldehyde-stabilized lignin not only prevents condensation but also improves the enzymatic efficiency of lignin removal, as demonstrated in acid-catalyzed IL-based pretreatment of corn.[65,66] However, the unselective hydrogenolysis and alkylation of aromatic rings by formaldehyde can lead to a complex mixture of six to ten major monomers.[67]

To improve selectivity, various protection groups for the 1,3-diol position on lignin have been tested, including aldehyde, ketal, carbonate, and boronate groups, as seen in Fig. 4. While unprotected lignin resulted in a monomer yield of 14 wt%, protection with acetaldehyde and propionaldehyde increased yields to 37 wt% and 42 wt%, respectively, approaching the 46 wt% yield achieved with formaldehyde but with higher selectivity due to the absence of aromatic alkylation. Furthermore, benzaldehyde, furfural and hydroxymethylfurfural were tested, with lower yields. Ketal groups, such as acetone, 2-butanone, 2-methoxypropene, and 2,2-dimethoxypropane provided moderate increases in yield (~20 wt%). Carbonate and boronate groups, like dimethyl carbonate and phenylboronic acid, achieved yields of 16 wt% and 27 wt%, respectively.

Among the protection groups tested, aldehydes demonstrated the best results, as seen in Fig. 4. Acetaldehyde and propionaldehyde particularly excelled in protecting the 1,3-diol positions, significantly suppressing condensation during pretreatment. A study combining acetaldehyde and formaldehyde to protect lignin produced uncondensed, stable lignin fractions that were more easily degradable and convertible into valuable monomers.[68] Under optimized conditions, acetaldehyde led to lignin monomer yields of 33 wt% with high selectivity.

While formaldehyde effectively suppresses condensation, it is a toxic chemical.[69] Other, less harmful methods have been explored, such as acid-catalyzed crude glycerol (ACG) pretreatment.[70] In this system, the acidic environment activated the lignin side chain, enabling glycerol to reacted through etherification at the β-aryl ether position and esterification with hydroxycinnamic acids. These reactions effectively "cap" the reactive intermediates, preventing benzylic carbocation-mediated condensation. As a result, the lignin isolated from ACG pretreatment retained a substantially higher content of β-O-4 linkages (45–60% of interunit linkages) compared with

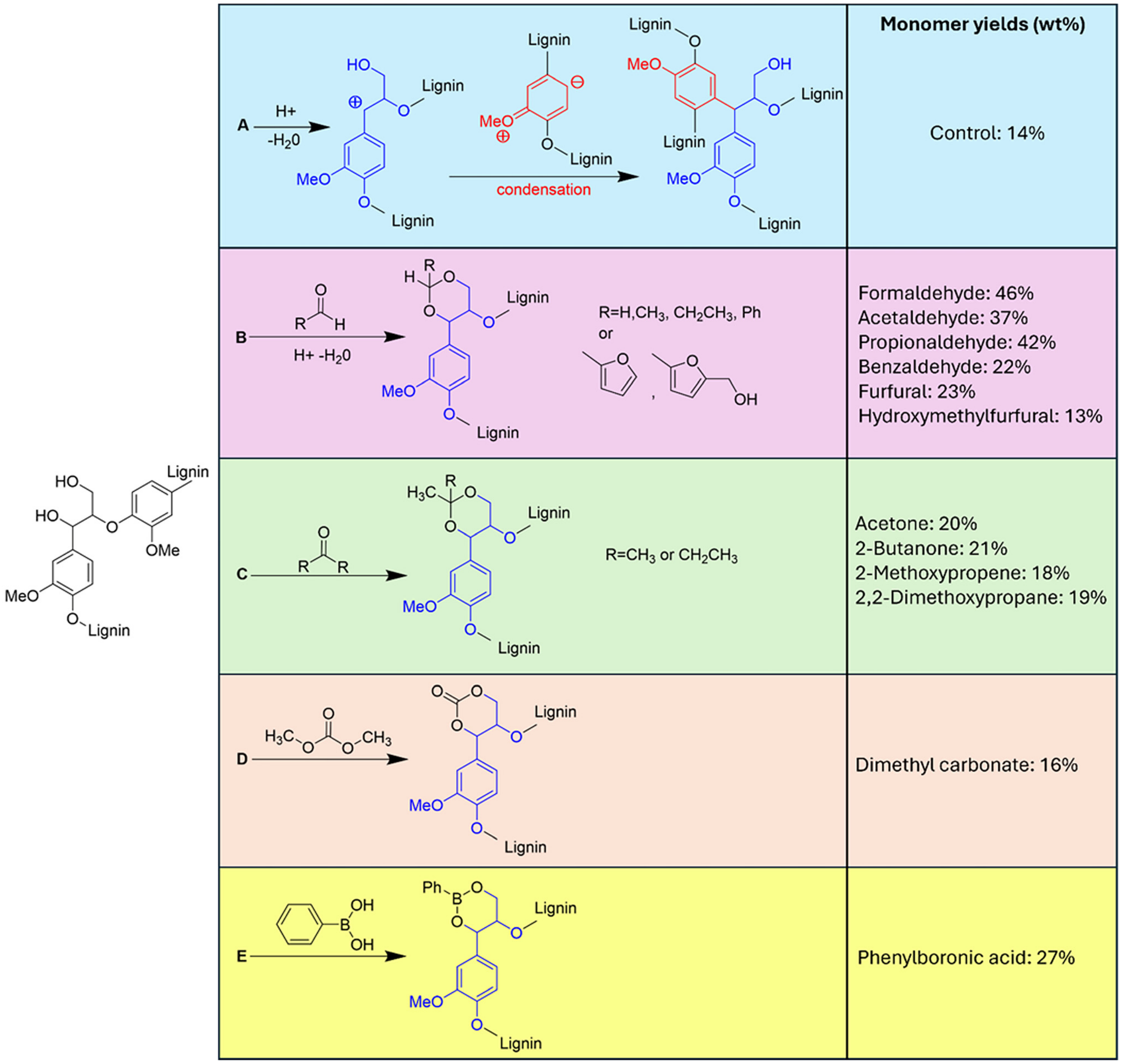

Fig. 4 Stabilizing effect of different protection groups. (A) traditional fractionation without protection group, (B) acetal protection group, (C) ketal protection group, (D) carbonate protection group, (E) boronate protection group (reproduced from ref. 67with permission from Wiley-VCH GmbH. Copyright 2018).

conventional acid pretreatments, despite being obtained under relatively mild temperatures (*e.g.*, 120–140 °C). Moreover, the stabilized lignin exhibits low levels of condensed C–C structures and improved solubility, while the carbohydrate fraction can be efficiently saccharified to fermentable sugars. This demonstrates that ACG pretreatment simultaneously preserves native-like lignin structures and enhances overall biorefinery performance.

Citric acid (CA), combined with sodium hypophosphite as a catalyst, was used to form ester bonds with lignin's hydroxyl groups, preventing the formation of reactive intermediates that could lead to recondensation during acid-catalyzed pretreatments as seen in Fig. 5.[71] The effects of CA on dilute hydrochloric acid pretreatments of corn stalk in hydrated 1,4-dioxane were investigated with sodium hypophosphite as the catalyst at 95 °C for 3.5 h. Both cellulose recovery (62.5–80.9%, relative to initial cellulose content) and lignin removal (72.5–85.0%, relative to initial lignin content) were improved, with the β-O-4 linkage content increasing as the water content rose from 11.4 wt% to 25.9 wt%. Thus, citric acid serves as an effective stabilizing agent, preventing repolymerization of degraded lignin fragments *via* esterification.

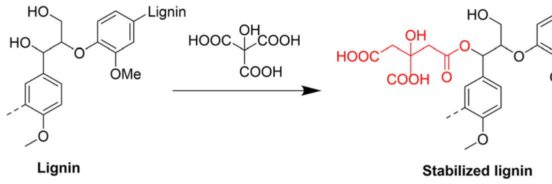

Fig. 5 Proposed pathway for citric acid stabilization.[71]

Pyruvic acid (PA) has been shown to effectively separate hemicellulose, while also inhibiting lignin repolymerization as seen in Fig. 6.[72] Although lignin separation was less controlled, the formation of a six-membered ring structure on the diol structure of lignin's β-O-4 side chain reduced the formation of condensed structures, resulting in lignin fractions enriched in phenolic hydroxyl groups. The PA treatment of eucalyptus was conducted in a high-temperature autoclave, where wood strips were submerged in a 2.0–6.0 wt% PA solution (solid–liquid ratio 1 : 10) and dissociated at 120–160 °C for 20–60 minutes. This method provides a green alternative by enabling both efficient hemicellulose separation and suppression of lignin recondensation.

Another promising approach involves the use of glyoxylic acid (GA) in an acid hydrotrope pretreatment to extract and stabilize lignin.[73] Poplar wood powder was added to *p*-toluenesulfonic acid (*p*-TsOH). The reactions were conducted at temperatures between 70 and 80 °C for durations ranging from 15 to 60 minutes. GA interacts with lignin to stabilize and functionalize it as seen in Fig. 7, with the resulting GA-stabilized lignin (GASL) showing potential for aromatic monomer production. GA targets the electron-rich areas of the lignin aromatic ring, particularly at the *ortho* or *para* positions to methoxyl groups, thereby preventing condensation. Without the addition of GA in the acid hydrotrope system, the monomer yield was just 11.7% (of theoretical lignin monomer yield). However, when GA was included during pretreatment, the hydrogenolysis of GASL significantly increased the monomer yield to 67.7%, close to that of formaldehyde (78%).[37]

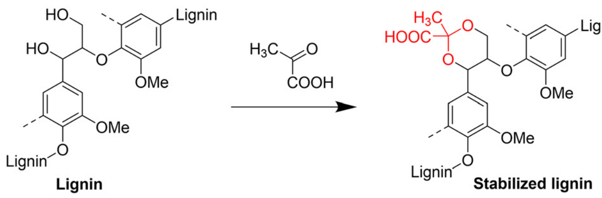

Fig. 6 Proposed pathway for pyruvic acid stabilization.[72]

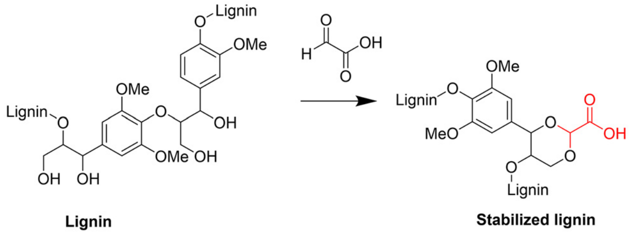

Fig. 7 Proposed pathway for glyoxylic acid stabilization.[73]

Deep eutectic solvents and ionic liquids

Both binary and ternary DES have demonstrated strong solvent power, effectively breaking the bonds between lignin and cellulose.[38] DES consist of hydrogen bond donors (HBDs) and hydrogen bond acceptors (HBAs) and can deliver high-quality cellulose. However, lignin often undergoes unwanted modifications, such as the loss of aryl–ether bonds and the formation of C–C bonds, complicating downstream processing. The tunability of DES offers potential for incorporating stabilization functions to mitigate condensation. Table 3 provides examples of different DES systems and their effects.

During lignin acidolysis of the β-O-4 linkage, both C3 and C2 fragments are formed.[55] While up to 50% of cleavage events in model studies yield C2 fragments, lignin acidolysis predominantly yields C3-ketones. The C2 fragments tend to participate in recondensation reactions rather than appearing as isolated products. Trapping these reactive C2-aldehydes with diols can form cyclic C2-acetals, suppressing recondensation during depolymerization. However, this process typically requires strong acids like triflic acid.

Liu *et al.* sought to avoid the use of corrosive strong acids by developing a tailor-made DES solvent for lignin depolymerization and biomass fractionation.[38] A ternary DES system was created using choline chloride (ChCl) as the HBA and oxalic acid (OA) and diols as HBDs. By tuning the reactivity of a lignin model compound, the system allowed for cleavage/stabilization, or selective derivatization/protection by adjusting the type and ratio of DES components.

The ChCl/OA DES system effectively cleaved the lignin-carbohydrate-complex (LCC) and most of the lignin's β-O-4 linkages.[74] The extracted lignin was of low molar mass and high purity, with low molar mass distribution. Treatment with ChCl/OA resulted in the complete conversion of lignin into guaiacol and aldehyde, though the aldehyde rapidly underwent condensation.[38] In contrast, using a ChCl/ethylene glycol (EG) DES system showed no conversion. To address this, a new ternary DES composition was developed by adding EG, creating a cleavage/stabilization DES (CS-DES). This system successfully trapped the reactive C2-aldehyde and benzylic carbocations, limiting condensation, albeit with lower conversion rates.

Liu *et al.* also developed a derivatization/protection pathway for DES (DP-DES) to hinder β-O-4 bond cleavage.[38] This was achieved by reducing the amount of OA, thereby tuning the acidity of the system. Several diols were tested, including glycerol, 1,3-propanediol, and 1,2-butanediol, with varying product yields. Glycerol yielded the highest isolated product yield (73%), while more hydrophobic diols (1,3-propanediol and 1,2-butanediol) showed lower yields, possibly due to increased viscosity and ion mobility issues. The DES system also performed well with model compounds, giving 71–82%

Table 3 Various DES compositions and their effects

		Conditions						
HBA/HBD	Biomass	T (°C)	t (h)	Lignin removal (%, relative to initial lignin content)	OH content (mmol g^{-1})	β-O-4 content	Molecular weight (g mol^{-1})	Ref.
ChCl/OA	Birch	100	2	50	—	4/100Ar	—	38
ChCl/OA + EG		120	0.33 (20 min)	61	—	23/100Ar	—	
ChCl/OA + various diols (glycerol, 1,3-propanediol, 1,2-butanediol)		80	24	56–67	—	53/100Ar	—	
ChCl/1,4-Butanediol (BDO) + $AlCl_3$	Bamboo	120	1	85	—	32/100Ar	—	79
ChCl/formic acid	Bamboo	110	4	15	—	—	—	75
ChCl/lactic acid				15	—	—	—	
ChCl/maleic acid				63.55	—	—	—	
ChCl/oxalic acid				66.91	—	—	—	
ChCl/oxalic acid & BDO				76.25	—	42.66/100Ar	7271	
ChCl/lactic acid (LA)	Poplar	115	4	61.05	3.18	55.78/100Ar	4067	76
ChCl/thiourea dioxide (TD) and lactic acid (LA)		130	4	69.77	4.63	35.14/100Ar	2696	
ChCl/lactic acid (LA)	Oil palm empty fruit bunch	120	8	61	3.72	—	—	77
ChCl/formic acid (FA)				62	2.66	—	—	
ChCl/citric acid (CA)				20.6	—	—	—	
ChCl/maleic acid (MAE)				10–30	—	—	—	
L-Cysteine monohydrochloride (L-Cys)/lactic acid (LA)	Sugarcane bagasse	90	6	82.6	—	~85% retained	9562	78

β-O-4 content is reported as linkages per 100 aromatic units (Ar/100Ar) unless otherwise stated. Retention values (%) are given relative to native lignin.

isolated yields when using EG. Notably, EG was incorporated into the lignin-derived products *via* covalent bonding at the benzylic position. Higher amounts of OA or elevated temperatures led to β-O-4 bond cleavage.

A ternary DES system combining organic acid and polyol-based DES was later developed for biomass fractionation. A ternary DES system combining organic acid and polyol-based DES was later developed for biomass fractionation.[75] This process reached about 80% lignin removal while preserving the β-O-4 structure and minimizing condensation. The stabilized lignin demonstrated exceptional adhesive properties, outperforming commercial phenolic and urea resins in plywood production. Additionally, the process enhanced enzymatic saccharification, yielding digestible carbohydrates as valuable coproducts. Ternary DES systems have shown better suppression of condensation compared to binary systems, as reflected by their higher retention of β-O-4 linkages (*e.g.*, 45–60% of interunit linkages in ternary DES *vs.* ~20–35% in binary DES) and lower formation of condensed C–C structures, underscoring their superior stabilization performance.[76] A novel ternary DES system comprising choline chloride, lactic acid, and thiourea dioxide efficiently separated lignocellulosic components. The thiourea dioxide provided a reductive microenvironment during delignification, further inhibiting condensation reactions.

Pretreatment of oil palm empty fruit bunch for lignin extraction was conducted using choline chloride combined with lactic acid (CC-LA) and formic acid (CC-FA).[77] This method achieved over 60% lignin removal, with CC-LA yielding lignin of high reactivity due to its phenolic hydroxyl content. The functional groups present in the acids, such as hydroxyl groups and short alkyl chains, enhanced the efficiency of lignin extraction.

A L-cysteine/lactic acid cosolvent system was developed for bagasse fractionation, focusing on protecting the lignin structure.[78] This system efficiently extracted highly uncondensed lignin, preserving over 80% of the β-O-4 linkages relative to native lignin and preventing condensation. Additionally, the method inhibited furfural formation, enabling the recovery of both lignin and cellulose in high purity, with minimal structural degradation of lignin during the process.

In diol-based deep eutectic solvents, hydrogen-bond donors such as ethylene glycol, 1,3-propylene glycol, and 1,4-butanediol act as structural solvent components and nucleophiles, leading to α-alkoxylated β-O-4′ substructures and suppression of lignin condensation during fractionation.[79,80] In these systems, the diol is incorporated through the DES composition rather than added as a tunable alcohol co-solvent.

Ionic liquids (ILs), such as [C_2mim][OAc], enhance enzymatic hydrolysis of biomass.[59] By adjusting the temperature of the IL pretreatment, lignin partitioning into different process streams can be controlled, with higher temperatures promoting greater lignin transfer to the IL stream. During this pretreatment, lignin undergoes depolymerization, and separates into various streams based on molar mass. Larger lignin molecules precipitate, while smaller ones remain in solution. Notably, no new condensed structures form during the process, preventing undesirable lignin condensation reactions.

Carbocation scavengers

In acidic environments, protonation of the Cα-OH group leads to the formation of electrophilic benzylic carbocations.[52] This can result in β-O-4 bond cleavage through water elimination and solvolysis, producing smaller lignin fragments such as phenols or aldehydes. The cleavage occurs *via* dehydration of the protonated α-OH to form a benzylic carbocation, which then undergoes solvolysis or elimination to break the β-O-4 ether bond.[81] Alternatively, these carbocations may undergo nucleophilic attack or form benzylic C–C linkages *via* condensation reactions, leading to unwanted crosslinking, increased heterogeneity, and challenges in lignin depolymerization.[82] To address this, lignin-first strategies have been developed to prevent new C–C bond formation, shown in Fig. 8.[36] Functionalizing benzylic alcohols or reducing and oxidizing them into more stable moieties can block condensation and facilitate depolymerization into lignin-derived monophenols (LMPs).[83] Bisphenols are the precursors in thermoplastics and thermosetting polymers, highlighting their potential as green alternatives.[84]

One approach to counteract harmful inter- and intramolecular condensation is to exploit lignin's natural tendency to condense, directing it toward forming useful products.[36] Phenols such as syringol and phenol are used for arylation, trapping the reactive benzylic carbocation intermediates and preventing crosslinking. Syringol was used to protect a non-phenolic lignin model, veratrylglycerol-β-guaiacyl ether (VG), from acidolysis in concentrated formic acid, producing stable "syringolated" trimers, preventing condensation.[85]

An effective carbocation scavenger must be highly nucleophilic, able to react with carbocations without causing crosslinking.[86] Among various scavengers studied, 2-naphthol has proven effective in competing for carbocations and preventing

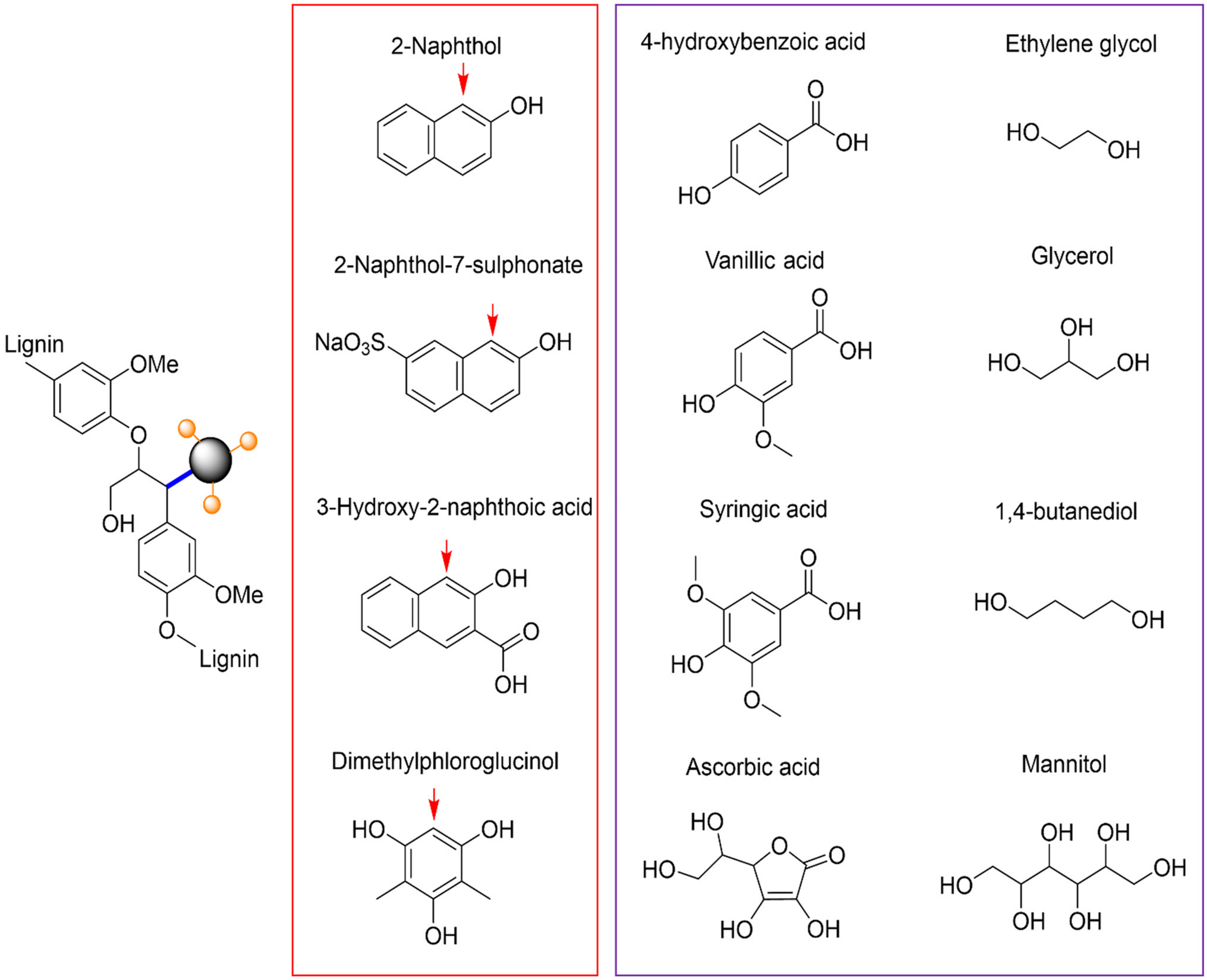

Fig. 8 Left: Illustration depicting a carbocation scavenger that has reacted with a lignin-derived carbocation, resulting in the formation of a new bond (blue) and the integration of functional groups (orange) into the lignin structure. Boxes: Examples of carbocation scavengers utilized in lignocellulose pretreatment. Scavengers with a single nucleophilic position are highlighted in the red box, while those with multiple nucleophilic positions are shown in the purple box. The red arrows indicate the specific nucleophilic site where the reaction takes place (adapted from ref. 95, T. Pielhop, *Chimia*, 2023, 77, 403–416, https://doi.org/10.2533/chimia.2023.403, licensed under CC BY 4.0. Copyright 2023).

repolymerization.[87] Its ability to stabilize carbocations results in a more uniform, low-molar-mass lignin that is easier to extract and offers higher chemical value.[88] The efficiency of 2-naphthol is attributed to its strong nucleophilicity and single substitution, which ensures it reacts only once, preventing it from acting as a crosslinker and thus inhibiting repolymerization.[89] When used in carbocation scavenger-assisted acid pretreatment followed by mild alkaline hydrogen peroxide (AHP) treatment, 2-naphthol successfully prevents lignin condensation while leaving monosaccharide production unaffected.[90,91]

Derivatives of 2-naphthol, such as 2-naphthol-7-sulfonate (NS)[92] and 3-hydroxy-2-naphthoic acid,[93] are also highly effective scavengers due to their strong nucleophilic properties and single reactive site. NS stands out as particularly effective because of its strong acidic and hydrophilic nature, which promotes the formation of hydrophilic groups and reduces the generation of phenolic hydroxyl (PhOH) groups that could lead to non-specific enzyme binding.[92] NS's remarkable performance is largely due to its ability to significantly modify lignin's structure, preventing condensation and facilitating enzymatic hydrolysis. Overall, naphthols, with their single nucleophilic site, outperform monophenols in improving delignification and enzymatic hydrolysis. The studies on scavengers are summarized in Table 4.

Dimethylphloroglucinol, another type of carbocation scavenger, also prevents condensation effectively. Like naphthols, it reacts only once due to its single reactive site, preventing it acting as a crosslinker. Studies have shown dimethylphloroglucinol to be even more effective than 2-naphthol, further enhancing its role in improving lignin treatment.[89,94]

Carbocation scavengers such as phenolic compounds, specifically 4-hydroxybenzoic acid, vanillic acid, and syringic acid, with several free active positions, can also prevent condensation.[96] They have also been utilized to mitigate the inhibitory effects of phenolic compounds during enzymatic hydrolysis, with syringic acid performing the best. Vanillic acid has been used to separate hemicellulose from eucalyptus while preventing lignin condensation, acting as a carbocation scavenger, which reduced lignin yield and increased β-O-4 linkages.[97] They should however be added in excess as to prevent condensation reactions.

Carbon-centered nucleophiles have also been employed to suppress lignin condensation under strongly acidic conditions.[98,99] Funaoka and co-workers introduced a phase-

Table 4 Carbocation scavengers used to prevent condensation

Scavenger	Biomass	Method	Effect	Ref.
2-Naphthol 2-Naphthol-7-sulphonate, mannitol	Pine	Autohydrolysis	Preserved β-O-4 linkages (XPS-inferred), fewer condensed C–C bonds, sulphonate functionalisation (2-naphthol-7-sulphonate), hydroxy functionalisation (mannitol)	92
2-Naphthol-7-sulphonate, mannitol	Poplar	Ethanol/H_2O, acid	Suppressed lignin repolymerization and surface condensation during acid organosolv pretreatment, fewer condensed C–C bonds and increased C–O/C–O–C functionalities (XPS), with sulphonate (2-naphthol-7-sulphonate) or hydroxyl (mannitol) functionalisation.	109
2-Naphthol	Spruce	Steam explosion	Reduced lignin condensation during steam explosion, with retention of phenolic OH groups and incorporation of naphthol-derived aromatic structures, indicating a less condensed and more redox-active lignin.	110
Ascorbic acid	Poplar	Dilute acid	Suppressed lignin repolymerization with reduced formation of condensed linkages (β–β, β-5), slight reduction of β-O-4 linkages mainly in ethanol-extractable lignin, increased ethanol-soluble lignin fraction, and modified hydroxyl group distribution (aliphatic and phenolic OH in residual lignin).	103
2-Naphthol-7-sulfonate Resorcinol, 2-naphthol	Bamboo	Dilute acid	Reduced lignin re-condensation (β–β, β-5), extensive β-O-4 cleavage, increased non-condensed phenolic OH, and altered molecular weight, sulfonate functionalisation (2-naphthol-7-sulfonate) most effective in suppressing re-polymerization	104
4-Hydroxybenzoic acid, vanillic acid, syringic acid	Pine	Dilute acid	Suppressed lignin condensation and secondary depolymerization during acid pretreatment *via* aromatic carbocation scavenging, leading to reduced formation of low-molecular-weight lignin-derived phenolics and a shift toward larger, less inhibitory phenolic structures.	96
Dimethylphloroglucinol, 2-naphthol, amines, alcohols	Spruce	Autohydrolysis	Suppression of lignin re-polymerization *via* carbocation scavenging, yielding lignin with significantly lower molecular weight and dispersity, effective scavengers (2-naphthol, dimethylphloroglucinol) prevent C–C crosslinking, whereas multi-reactive additives promote lignin condensation and increased Mw	89
2-Naphthol, formaldehyde, 1-naphthol	Poplar	Dilute acid	Reduced lignin condensation *via* carbocation scavenging (2-naphthol, formaldehyde), evidenced by lower lignin molecular weight and altered phenolic OH distribution; ineffective suppression with 1-naphthol.	111
2-Naphthol	Beech wood	Autohydrolysis	Reduced lignin re-condensation (carbocation trapping), fewer condensed C–C linkages, reduced unproductive enzyme binding, lignin functionalised with 2-naphthol	112
2-Naphthol, 2-naphthol-7-sulfonate, phenolic acids	Pine	Dilute acid	Suppressed lignin condensation *via* carbocation scavenging, resulting in reduced formation of condensed C–C linkages and decreased generation of low-molecular-weight inhibitory lignin-derived phenolics, scavenger effectiveness dependent on aromatic structure (2-naphthol > phenolic acids)	113

separative reaction system composed of phenol derivatives and concentrated acid, in which lignin and carbohydrates are partitioned into separate phases and modified independently. In this system, phenol derivatives act as carbon-centered nucleophiles, reacting selectively at benzylic (Cα) positions of lignin to form C–C-linked 1,1-diarylpropane (diphenylmethane-type) structures, thereby irreversibly trapping reactive intermediates. As a result, lignin self-condensation is effectively suppressed, yielding light-colored, highly phenolic lignin derivatives that retain much of the native interunit linkage structure. The process was reported to proceed rapidly at room temperature and to be largely independent of wood species, demonstrating the generality of phenol-based carbon-nucleophile protection strategies for lignin stabilization.

Mechanistic evidence for interception of lignin-derived carbocation intermediates has been reported in acid-catalyzed systems, where lignin depolymerization occurs concurrently with nucleophilic stabilization.[100] During formic-acid-mediated delignification of biomass, lignin-like monomers (such as Syringol or phenol) can react with the Cα position of β-O-4 linkages to form phenolized β-O-4 structures.[36,101] This process enabled *in situ* phenolation of lignin while effectively suppressing lignin recondensation. As a result, the formic acid/phenolic monomer system achieved near-complete lignin removal from biomass. The isolated stabilized lignin can subsequently be catalytically depolymerized to produce monomeric monophenols and bisphenols with combined yields exceeding 90 wt% based on lignin.

Building on this mechanistic concept, recent patent literature has extended Cα-functionalization strategies to a broader range of phenolic nucleophiles, including catechol, resorcinol, hydroquinone, pyrogallol, and guaiacol.[102] These disclosures report retention of approximately 30–70% of native β-O-4 linkages, while 90–99% of the α-positions within the retained β-O-4 structures are substituted by the phenolic nucleophiles, supported by detailed NMR characterization of Cα-substituted β-O-4 motifs, demonstrating effective carbocation interception during lignin processing.

Ascorbic acid is another scavenger that has emerged as an eco-friendly additive, enhancing enzymatic hydrolysis in dilute acid pretreatment.[103] Its high-water solubility allows for effective dispersion and stabilization of carbocations, reducing lignin repolymerization. It is considered a cost-effective alternative to traditional carbocation scavengers while minimizing condensation reactions that hinder biomass processing. Resorcinol has also been shown to inhibit repolymerization and increase non-condensed phenolic groups, although it negatively impacts enzymatic hydrolysis.[104] In DES systems, resorcinol however, increased repolymerization.[105] Due to resorcinol having three reactive positions, it can therefore partake in condensation reactions.[89]

A recent study by Wu *et al.* demonstrated *in situ* lignin amination during biomass fractionation by employing an aniline–formic acid system.[106] Aniline acted as the nucleophile, selectively trapping Cα carbocations, directing the reaction toward α-arylation, thereby prohibiting undesired condensation and preserving β-O-4 linkages. This method yielded aminated lignin with high nitrogen content and reactivity, as well as high purity cellulose.

The effectiveness of scavengers is strongly dependent on biomass type, offering substantially greater benefits for softwood pretreatment due to its G-unit–rich, more sterically constrained lignin structure, which makes softwoods inherently more recalcitrant than hardwoods.[107] However, scavengers can still improve biomass saccharification in hardwood pretreatments.[108] Several scavengers can be considered "green", being of renewable sources. 4-Hydroxy-benzoic acid, vanillic acid, and syringic acid can be derived from lignin itself, while ethylene glycol, glycerol, and mannitol can also be sources from renewable sources.[95]

Primary alcohols can react with benzylic carbocations to suppress lignin condensation.[114] Alcohol-based organosolv pretreatments using ethanol and n-butanol have been shown to produce homogeneous lignin fractions retaining a large fraction of β-O-4 aryl ether linkages (~40–60 per 100 C_9 units). In these systems, high alcohol contents (typically ~95 vol%) promote α-alkoxylation of β-O-4 units, stabilizing lignin under acidic conditions, while the alcohol composition is generally maintained constant to demonstrate the effect of alcohol-rich media rather than systematic concentration dependence. Under acidic conditions and microwave heating, methanol can trap enol ether intermediates formed during lignin depolymerization, leading predominantly to the formation of stable dimethyl acetals and thereby suppressing re-condensation reactions.[115]

Furthermore, ethanol- and *n*-butanol-based organosolv fractionation typically yields lignin containing ~40–60 β-O-4′ aryl ether units per 100 aromatic units and number-average molecular weights of ~1–3 kDa, substantially higher β-O-4′ contents than those commonly reported for conventional technical lignins (<20 per 100 aromatic units).[116,117] A mild lignin-first biorefinery using a dioxane/methanol solvent extracted lignin at yields exceeding 50 wt% relative to the initial lignin content, with >99 wt% lignin purity, while preserving β-O-4′ aryl ether linkages corresponding to 19.3% of interunit bonds in the absence of methanol, increasing to 24.1% at 5 vol% methanol and 20.0% at 10 vol% methanol under mild conditions (80 °C).[118]

Reductive catalytic fractionation

Reductive Catalytic Fractionation (RCF) effectively prevents unwanted condensation during lignin depolymerization by employing a nucleophile that captures reactive intermediates without disrupting the depolymerization process.[57] In this method, lignin is broken down in the presence of hydrogen and a metal catalyst during its extraction from biomass. The hydrogen donor and metal catalyst work together, activating hydrogen to cleave ether bonds in lignin, releasing reactive intermediates that preferentially react with hydrogen rather than undergoing condensation.

RCF was first demonstrated by Hibbert in 1948, who used hydrogenolysis with nickel as the catalyst to isolate aromatic monomers from lignin.[119] Since then, traditional noble metals such as platinum (Pt),[120] palladium (Pd),[121] ruthenium (Ru),[122] and rhodium (Rh)[123] have been extensively tested, showing effectiveness in maximizing aromatic monomer production by efficiently cleaving lignin's ether bonds. While these noble metals exhibit excellent catalytic properties, their scarcity and high cost limit their potential for large-scale industrial use.

In recent years, more attention has been given to enriched metals such as nickel (Ni),[124] cobalt (Co),[125] and molybdenum (Mo)[126] as promising alternatives for RCF catalysts. These metals are not only more accessible but also offer substantial catalytic performance.

Selecting the appropriate metal catalyst is critical for achieving high levels of delignification and product yield, as illustrated in Table 5. Typically, catalysts used in RCF include platinum group metals like Ru, Pd, and Ni, supported on materials such as activated carbon or Al_2O_3.[39] Nickel-based catalysts[127] and palladium catalysts[128] are particularly effective at producing 4-propanol guaiacol and 4-propanol syringol as the main products during the RCF of lignocellulosic biomass. In contrast, when using ruthenium[122] or rhodium,[129] the predominant products are 4-propylguaiacol and 4-propylsyringol.

A comparative study by den Bosch *et al.* evaluated the catalytic performance of Ru/C and Pd/C catalysts under identical conditions for the reductive catalytic fractionation of birch wood.[130] The results revealed that while the overall yields of liquid products were similar for both catalysts, the selectivity for specific monomers varied significantly, highlighting the importance of catalyst choice in controlling product distribution.

A molybdenum carbide catalyst on carbon nanotubes facilitated the selective cleavage of lignin-polysaccharide bonds and ester bonds within lignin during catalytic reductive fractionation, while preserving cellulose and hemicellulose.[126] Similarly, MoOx/SBA-15 effectively depolymerizes lignin in lignocellulosic biomass using methanol and hydrogen, yielding monolignols and their ester derivatives.[131] Molybdenum-based catalysts typically produce monolignols with reduced hydrogenation activity, preserving carbohydrate integrity.[132]

A cost-effective, atomically dispersed cobalt catalyst for RCF achieved near-theoretical phenolic monomer yields (48.3 wt% based on lignin), rivaling precious-metal catalysts, with high selectivity (84 mol%) toward 4-propyl-substituted guaiacol and syringol.[133] Similarly, a copper phyllosilicate nanotube catalyst (RCuSNT) enables efficient lignin depolymerization, affording phenolic monomers in yields of 22.5 wt% for softwoods and 38.5 wt% for hardwoods (based on lignin), while largely preserving cellulose and hemicellulose (≈88% retention).[134] The Cu-based catalyst promotes selective C–O bond cleavage with methanol acting as a hydrogen donor, highlighting its potential as a cost-effective alternative for lignin valorization.

Bifunctional catalysts, combining acidic and metallic active sites, are particularly effective in RCF. For instance, a Ru/WZr catalyst uses the acidity of tungstate-zirconia to cleave β-O-4 bonds and ruthenium's hydrogenation ability to stabilize intermediates, yielding 23.6 wt% of lignin-derived phenols while preventing recondensation.[135]

Acidic and alkaline cocatalysts play a critical role in enhancing lignin and hemicellulose removal during RCF, as seen in Table 6. Acidic additives like phosphoric acid (H_3PO_4) improve delignification, boost monomer yields, and help produce cellulose and liquid carbohydrate products with a narrow molar mass distribution.[136] For instance, H_3PO_4 combined with Pd/C or Pt/C catalysts increases the monomer yield from lignin derived from poplar or birch wood.[123] However, alkaline addi-

Table 5 RCF results obtained with different catalysts

Catalysts	Feedstock	Solvent	Monomer yield (% of theoretical lignin monomers)	Conditions			Ref.
				T (°C)	P_{H_2} (bar)	t (h)	
Ni/AC	Poplar sawdust	Methanol	19.9	225	30	3	144
Ru/AC			23				
Pd/AC			28				
Pt/AC			30				
Pd/C	Poplar sawdust	Methanol	32	230	1	3	145
Ni/SiO_2			23.3				
—	Birch sawdust	Methanol : water	7.3	250	20	8	146 and 147
Ru/C			41.4				
Pd/C			34.1				
Pt/C			38.8				
MoO_x/SBA-15	Woody biomass	Methanol	43.4	260	30	4	131
Ru/C	Apple wood	Methanol	38	250	10	3	126
Mo_xC/CNT 600			32				
Mo_xC/CNT 700			42				
Mo_xC/CNT 800			38				
Ru/C	Birch wood	H_20	4.6	200	40	4	123
Pd/C			25.5				
Rh/C			19.7				
Pt/C			33.6				
Pt/C + H_3PO_4		Dioxane/H_2O	46.4				
Rh/C + H_3PO_4			45.5				
$Co_{0.15}$/N–C	Birch sawdust	Methanol	48.3	240	30 at 25 °C 120 at 240 °C	4	133

Table 6 RCF results obtained with different cocatalysts

				Conditions			
Catalysts	Feedstock	Solvent	Monomer yield	T (°C)	P_{H_2} (bar)	t (h)	Ref.
Pd/C	Oakwood sawdust	Methanol	6	180	30	2	137
Pd/C + $Al(OTf)_3$			46				
Pd/C + HCl			14				
Pd/C + H_2SO_4			10				
Pd/C + H_3PO_4			13				
Pd/C + CH_3COOH			15				

tives like NaOH can trigger repolymerization, particularly in softwood lignins, reducing monomer yields and causing cellulose loss due to depolymerization.[136]

Water-stable metal triflates, such as Al(III) triflate, have also been shown to enhance delignification and increase monomer yields. When combined with Pd/C catalysts, these metal triflates can more effectively cleave lignin β-O-4 bonds, leading to a higher yield of monomers such as propanol guaiacol and syringol.[137]

Solvents and hydrogen sources are crucial in determining the efficiency of RCF. Polar solvents, like water or alcohol–water mixtures, are essential for effective delignification, selectively breaking C–O bonds in lignin while preserving the carbohydrate fraction.[128,136] The choice of solvent significantly impacts monomer yield, as different solvent systems influence both the degree of delignification and the types of phenolic monomers and dimers produced, as seen in Table 7. For example, methanol tends to favor the formation of 4-propanol syringol and 4-propanol guaiacol,[122] while other alcohol solvents can produce 4-propenyl-substituted methoxyphenols.[130,138]

Hydrogen sources, whether from gaseous hydrogen or donor solvents like alcohols, also greatly affect RCF product composition. Internal hydrogen sources, such as hemicelluloses or formic acid, can assist in lignin reduction as well.[139,140]

Different types of feedstocks, such as hardwood, softwood, and herbaceous plants, exhibit varying compositions of cellulose, hemicellulose, and lignin, which significantly influence product yields in lignin depolymerization, as seen in Table 8.[132] Hardwood typically contains a higher proportion of β-O-4 linkages, resulting in greater yields of phenolic monomers compared to softwood. Reaction conditions such as time as seen in Table 9 as well as temperature and hydrogen pressure are also of importance. The polarity of solvents is critical for lignin extraction, phenolic monomer yield, and saccharide retention in reductive catalytic fractionation.[141] Polar solvents, particularly alcohol/water mixtures, enhance both lignin extraction and depolymerization, with increased water concentrations generally boosting monomer yields, although this can reduce hemicellulose retention.[124,136] Additionally, methanol has been shown to be more effective than ethanol for delignification.[136] Hydrogen-donor solvents, including various alcohols, also contribute positively to lignin depolymerization.[142] Ultimately, the choice of catalysts, feedstock, solvents, and reaction conditions is essential for maximizing the yields of desired products.[143]

Challenges however remain, including the development of stable, regenerable bifunctional catalysts, the isolation of pure lignin monomers, and finding eco-friendly solvents. Addressing these issues is crucial for optimizing RCF for industrial applications.

Enzymatic stabilization

The depolymerization of lignin in plant cell walls is facilitated by four primary enzymatic activities: lignin peroxidases, manganese peroxidases, versatile peroxidases, and laccases.[150] Among these, laccases play a crucial role due to their ability to

Table 7 RCF results obtained with different solvents

				Conditions			
Catalyst	Feedstock	Solvent	Monomer yield	T (°C)	P_{H_2} (bar)	t (h)	Ref.
Ni/C	Birch sawdust	Methanol	54	200	1	6	142
		Ethanol	48				
		Isopropanol	27				
		Ethylene glycol	50				
		1,4-Dioxane	15				
Pd/C	Birch sawdust	Water	44	200	30	3	128
		Methanol	29				
		Ethylene glycol	28				
		Ethanol	16				
		Isopropanol	11				
Ni/C	Beech sawdust	Methanol	51.4	200	20	5	124
		Methanol : water (6 : 4)	45.7				
		Methanol : water (8 : 2)	39.3				

Table 8 RCF results obtained with different feedstock

Catalysts	Feedstock	Solvent	Monomer yield	Conditions T (°C)	P_{H_2} (bar)	t (h)	Ref.
Ru/C	Wheat straw	Methanol	20	250	40	15	148
	Sugarcane		33.7				
	Bagasse		43.8				
	Switchgrass		41.5				
Ru/C	Birch	Ethylene glycol	21.6	185	0	3	145
	Beech		22.3				
	Eucalyptus		22.1				
	Willow		17.2				
	Cyprus		4.2				
	Pine		7.8				
RCuSNT	Pinus	Methanol	22.5	240	30	4	134
	Larch		18				
	Poplar		38.5				
	Beech		30.8				
	Eucalyptus		27.6				

Table 9 RCF results obtained with different reaction time

Catalyst	Feedstock	Solvent	Monomer yield	Conditions T (°C)	P_{H_2} (bar)	t (h)	Ref.
Pd/C	Birch	Ethanol : water	20	210	1	2	149
			33			15	
	Poplar		15			2	
			17			15	

depolymerize lignin in a milder environment compared to other enzymes, using O_2 instead of H_2O_2, with water as the only by-product.[151] This makes laccases particularly appealing for sustainable lignin degradation.

Combining deep eutectic solvents (DES) with laccase offers a promising alternative to harsher methods. DES can efficiently dissolve lignin, while certain laccases, such as *Trametes versicolor*, have demonstrated good biocompatibility with DES systems, even retaining or enhancing activity in some.[152] However, laccase activity can also be lost in other DES systems.[153] When the right combination of DES and laccase is used, it facilitates selective lignin breakdown, aiding in the production of valuable aromatic compounds and increasing lignin valorization.

Fungi have been shown to break down Kraft lignin more effectively than bacteria, which tend to only modify or partially degrade it.[154] Fungi were the only organisms that significantly mineralized Kraft lignin, while bacteria were only able to partially degrade and modify it. Both laccase and fungi caused some polymerization of lignin, with fungi producing more extensively cross-linked polymers. However, fungi also demonstrated the ability to break down even highly cross-linked lignin, managing a fine balance between polymerization and lignin degradation.

Zhu *et al.* used *Bacillus ligniniphilus* L1, an extremophilic bacterium engineered for enhanced lignin valorization.[155] Through metabolic engineering, the bacterium's pathways were optimized to degrade lignin, reduce its molar mass, and convert it into valuable aromatic compounds like vanillin. This biologically driven process bypasses harsh chemical treatments and energy-intensive conditions, offering a more sustainable way to transform waste lignin into high-value chemicals, addressing challenges in lignin biorefineries such as low yield and efficiency.

Outlook

The active lignin stabilization fractionation from biomass presents a promising avenue for producing high value bioproducts and advancing sustainable biorefining processes. As the demand for renewable materials continues to grow, efficient methods for extracting and modifying lignin are crucial. This review has outlined various fractionation techniques, highlighting both the challenges (such as lignin condensation during extraction) and opportunities for improvement.

The use of protective groups and carbocation scavengers has proven to be effective in inhibiting condensation and improving lignin quality, with stabilizers such as formaldehyde and DES systems showing significant promise. However, despite these advances, there remain challenges in balancing lignin yield with structural integrity, particularly in harsher fractionation methods. Future research should focus on optimizing these methods, including refining the application of DES systems and exploring new scavenger molecules for broader applicability.

Additionally, scalability remains a critical challenge for many of these technologies, and bridging the gap between laboratory-scale successes and industrial implementation will require further investigation into process integration and economic feasibility. Future directions should also explore combined approaches, such as coupling ionic liquids with catalytic systems, to enhance both lignin yield and quality. Furthermore, a deeper understanding of the reaction mechanisms responsible for lignin condensation could enable the design of even more targeted and efficient stabilization strategies.

Ultimately, active lignin stabilization fractionation holds great potential for optimizing the valorization of lignin, contributing to a more sustainable and circular biorefining industry. By continuing to innovate and refine these methods, lignin can become a more valuable feedstock for biotechnological applications, paving the way for the development of novel, renewable chemicals and materials.

Author contributions

A. S.: investigation, software, data curation, and writing – original draft. R. W.: investigation, validation, and writing – original draft. P. E. and H. G.: supervision and writing – review and editing. C. X.: supervision, conceptualization, funding acquisition, and writing – review and editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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