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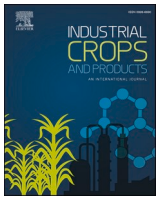

A critical review on lignin structure, chemistry, and modification towards utilisation in additive manufacturing of lignin-based composites

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ABSTRACT

The complex but highly abundant and renewable biopolymer lignin has gained recent attention as a promising candidate towards utilisation of naturally occurring substances for advanced material applications. This review provides a comprehensive overview of lignin in terms of structure, chemistry, and modifications towards utilisation in additive manufacturing, especially for the manufacturing of lignin-based composites. The heterogeneous and complex nature of lignin presents challenges for its integration and functionalisation in various additive manufacturing processes, but its diverse properties entail promising opportunities in the development of environmentally friendly and renewable components for high-value applications. Hence, this review discusses various routes of lignin isolation and modifications that enable the obtainment of different lignins with target-specific properties that improve its processability and enhances its compatibility with various polymer matrices. Additionally, this article presents recent developments in lignin-based composite formulations in different additive manufacturing technologies, such as material extrusion, direct ink writing, digital light processing, stereolithography, and selective laser sintering. The great advancements made within this field of science in recent years highlight the importance of lignin processing to unlock its full potential in additive manufacturing, paving the way for the development of high-value and sustainable composite materials with tuneable application-specific properties. Finally, material- and additive manufacturing technology related challenges and future directions regarding the use of lignin in additive manufacturing of composites are discussed, emphasising the importance of source and processing methods to overcome current challenges in this emerging field of research.

1. Introduction

The continuous utilisation of non-biodegradable fossil-derived plastics has led to environmental pollution and serious health threats due to constant inhaling and ingesting of microplastics, which in turn has led to an increasing interest towards the replacement of these raw materials with naturally occurring renewable and abundant substitutes towards a more sustainable, safer, and greener future (Ji et al., 2020; Jiang et al., 2023). In this regard, lignocellulosic biomass consisting of cellulose, hemicellulose, lignin, and small amounts of proteins and other extractives, has gained a profusion of interest towards the utilisation of naturally occurring substances for value-added applications (Ji et al., 2020). In recent years, lignin has attracted increasing attention due to its abundance as the second most abundant natural biopolymer on earth, but also from recent developments in utilising lignin in different forms and modifications as a valuable and renewable polymer with emphasis on sustainability (Ebers et al., 2021).

Amongst the potential applications that pure or modified lignin entails, additive manufacturing (AM), also known as three-dimensional (3D) printing, has recently emerged as a promising tool to process lignin into valuable products (Ebers et al., 2021). The AM process uses a 3D digital model to fabricate different materials layer by layer into the designed and desired physical objects (Wan et al., 2023). Compared to conventional manufacturing processes, AM offers the flexibility of manufacturing objects of complex geometries with high accuracy and efficiency, while reducing waste and costs. In simple terms, AM enables the fabrication of structures that cannot be done by other methods. Due to the often toxic, volatile, and non-degradable nature of

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petroleum-based materials, the need for development of green and sustainable materials from renewable sources is constantly increasing.

This review provides an overview of the structure and chemistry of lignin from formation in nature to applications in additive manufacturing. The complexity of lignin and great variety in structure based on raw material source and extraction method complicates its utilisation. Thus, the most common lignin extraction methods and a variety of modification approaches are presented and compared in this work. Additionally, recent studies on research conducted on the utilisation of lignin in AM for the manufacturing of bio-based composites are reviewed. Lastly, the concluding section of this paper discusses the current trends, challenges, and future perspectives regarding the utilisation of lignin as a value-added material in the field of additive manufacturing of composites.

The graphs in Fig. 1 below show the number of publications (journals & reviews) with certain keywords according to CAS SciFinder. SciFinder is a widely recognised scholarly database, which can be used to gain a comprehensive understanding of the landscape of a certain topic of interest. It can be concluded that a significant interest towards additive manufacturing and 3D printing has gradually increased since 2010. Likewise, the interest in lignin research is constantly growing, indicating a wider realisation of its potential. As indicated in the graphs, the use of lignin in additive manufacturing is low. However, in recent years a greater interest towards both lignin modification and manufacturing of lignin-based composites can be seen, which may resolve some of the challenges encountered regarding the suitability and compatibility of lignin as a bio-based candidate in the field of additive manufacturing.

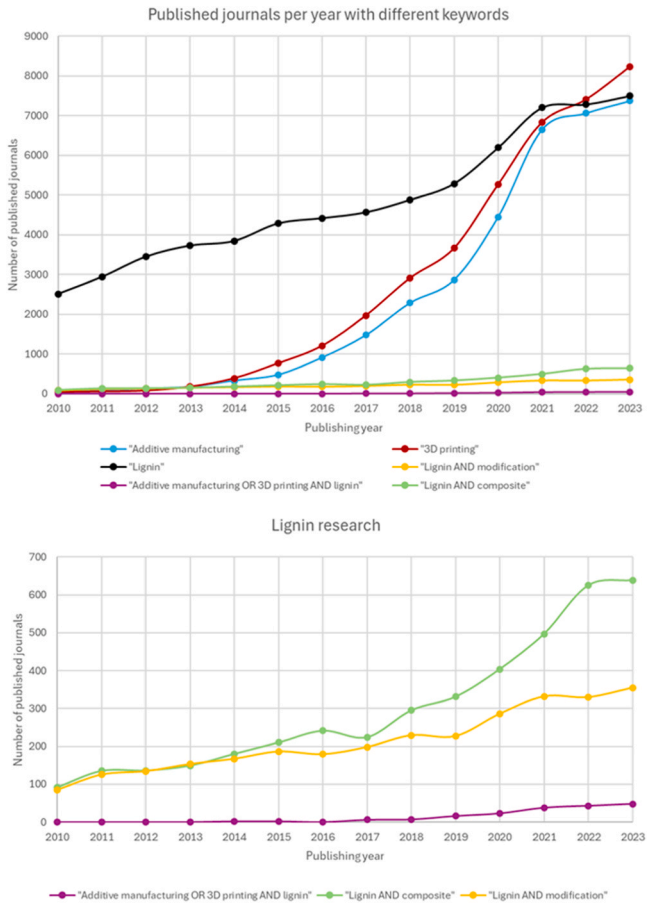


Fig. 1. The numbers of publications according to CAS SciFinder with different keywords.

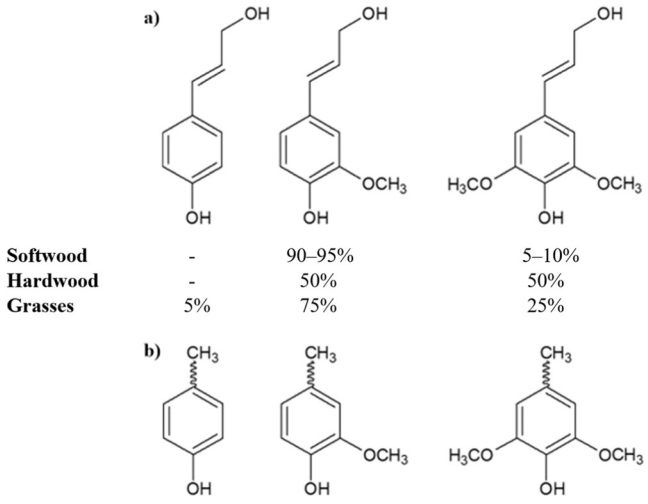
2. Lignin structure and chemistry

Lignin is one of the most important renewable natural resources today and is used as an environmentally accepted and sustainable alternative to fossil-derived polymers and chemicals for different value-added applications (Agustiany et al., 2022). It accounts for 10–40 % of the dry mass of lignocellulosic biomass and is typically considered as waste in refinery industries (Chen et al., 2023). This three-dimensional and highly cross-linked biopolymer consists of three main types of monolignol monomers, which are p-coumaryl, coniferyl, and sinapyl alcohols (Fig. 2a) (Azadi et al., 2013; Morena and Tzanov, 2022; Ullah et al., 2022; Upton and Kasko, 2016). Through polymerisation of these hydroxycinnamyl alcohols, p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units are derived (Fig. 2b) (Vanholme et al., 2019). The main monolignols are derived from phenylalanine and differ both in content depending on the plant species source, and in the degree of methoxylation (Morena and Tzanov, 2022). In softwoods the most common monomer type is coniferyl alcohol, while in hardwoods there are equal amounts of both coniferyl and sinapyl alcohol (Erfani Jazi et al., 2019; Upton and Kasko, 2016). Grasses additionally contain *p*-coumaryl alcohol, and thus contains all three of the main monomers. Due to these differences in monomer content, the types of bonds formed through polymerisation varies greatly.

2.1. Lignin formation

The complicated formation of lignin is a process involving biochemical, physiological, and spontaneous non-biological chemical activities (Achyuthan et al., 2010). Monolignols are biosynthesised and transported to lignifying sites where they undergo enzymatic radicalisation and non-enzymatic coupling. The biosynthesis step involves two different pathways, which are the shikimate and the phenylpropanoid pathways (Achyuthan et al., 2010; Rippert et al., 2009). In the shikimate pathway, erythrose 4-phosphate undergoes enzymatic reactions to form phenylalanine and tyrosine, two vital components for the phenylpropanoid pathway (Fig. 3).

In the review article “The shikimate pathway” by Hermann K.M. & Weaver L.M., a comprehensive description of the shikimate pathway is presented (Herrmann and Weaver, 1999). A sequence of seven metabolic steps is described about the conversion of phosphoenolpyruvate



Softwood	-	90–95%	5–10%
Hardwood	-	50%	50%
Grasses	5%	75%	25%

Fig. 2. a) The three main types of monolignol monomers and their content in lignocellulosic biomass. From left to right: p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. b) Corresponding polymerised building block units derived from the hydroxycinnamyl alcohols. From left to right: p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) (Azadi et al., 2013; Vanholme et al., 2019).

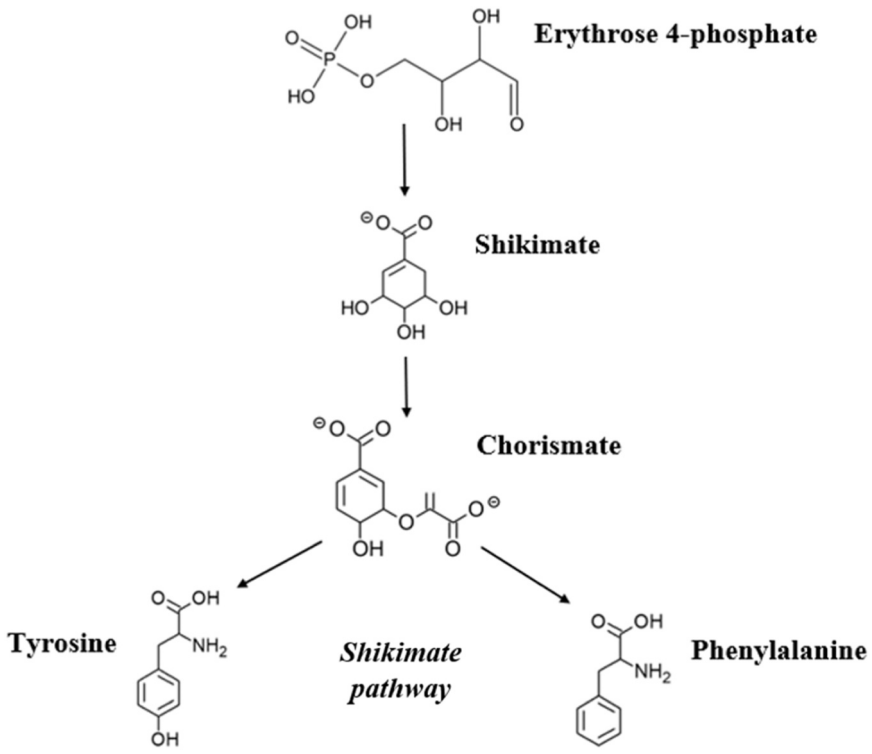


Fig. 3. The shikimate pathway. Erythrose 4-phosphate, a product of carbohydrate metabolism, turns into Shikimate in four enzymatic steps. With the aid of three different enzymes, shikimate turns into chorismate, which through reactions yields the two precursors of hydroxycinnamyl alcohols: tyrosine and phenylalanine (Achyuthan et al., 2010).

and erythrose 4-phosphate to chorismate, the precursor of aromatic amino acids and secondary metabolites.

Polymerisation of monolignols is the final step of lignin biosynthesis, which takes place in the cell walls (Tobimatsu and Schuetz, 2019). The phenylpropanoid pathway begins by deamination of phenylalanine or tyrosine, which initiates through hydroxylation reactions of the aromatic ring (del Río et al., 2020). The hydroxylation reaction is then followed by phenolic *O*-methylation and the reduction of side-chain carboxylic groups to form aldehydes and finally alcohols, with the aid of different enzymes. The enzymes participating in the biosynthesis of monolignols are listed in Table 1.

Once synthesised, monolignols are secreted from the cell walls and activated by oxidation systems, such as peroxidase (H_2O_2) and laccase (O_2), and becomes oxidised monolignol radicals (del Río et al., 2020; Tobimatsu and Schuetz, 2019). These oxidised radicals then react with radicals on the free-phenolic ends of lignin polymers through cross-coupling reactions, forming lignin polymers. Through the polymerisation reaction different bonds are formed. The differences stem from the great diversity of monomers, permutations in the radical coupling step and variations during re-aromatisation (Erfani Jazi et al., 2019). The most common bonds found in lignin are β-*O*-4', β-5', β-β', 4-*O*-5', 5-5', and β-1' (del Río et al., 2020; Erfani Jazi et al., 2019; Jiang et al., 2023). A simplified overview of the phenylpropanoid pathway and biosynthesis of the main monolignols as reported by Achyuthan et al. (2010) is illustrated in Fig. 4.

Table 1
Participating enzymes in the biosynthesis of monolignols (Achyuthan et al., 2010; del Río et al., 2020).

Abbreviation	Enzyme
PAL	Phenylalanine ammonia lyase
TAL	Tyrosine ammonia lyase
C4H	Cinnamate 4-hydroxylase
4CL	4-coumarate:coenzyme A ligase
F5H	Ferulate 5-hydroxylase
C3H	*p*-coumarate 3-hydroxylase
HCT	*p*-hydroxycinnamoyl-CoA:quinate / shikimate hydroxycinnamoyltransferase
CSE	Caffeoyl shikimate esterase
CCoAOMT	Caffeoyl-CoA *O*-methyltransferase
CCR	Caffeoyl-CoA reductase
COMT	Caffeic acid *O*-methyltransferase
CAD	Coniferyl alcohol dehydrogenase
SAD	Sinapyl alcohol dehydrogenase

Once the monolignols are synthesised through the phenylpropanoid pathway, they are transported to lignifying sites where they undergo oxidative radicalisation in a reaction mediated by peroxidases and/or laccases (Achyuthan et al., 2010; del Río et al., 2020; Vanholme et al., 2010). The numbering system and the radicalisation position occurrence tendency is shown in Fig. 5 (Gellerstedt and Henriksson, 2008). The oxidised monolignol radicals polymerises through cross-coupling reactions with radicals on the free-phenolic ends of the growing lignin polymer (del Río et al., 2020; Tobimatsu and Schuetz, 2019; Vanholme et al., 2010). The monolignol radicals favour coupling at their β position, forming β-β', β-*O*-4', and β-5' dimers (Achyuthan et al., 2010; Vanholme et al., 2010). To further polymerise and increase the length and size of the lignin polymer, the dimers need to be oxidised again to a phenolic radical to couple with other monomer radicals. Through this so-called endwise coupling, the polymer grows with the addition of one unit at a time. Through coupling of lignin oligomers, 5-5' bonds occur. This is rare in S/G-lignins, but fairly common in G-lignins with approximately 4–5 % of the linkages being 5-5' bonds. Some of the most common linkages formed during polymerisation is shown in Fig. 6, with their abundance in softwood and hardwood expressed in percentage (Achyuthan et al., 2010; Sadeghifar and Ragauskas, 2020; Vanholme et al., 2010).

For a more detailed and broader understanding of the formation of lignin, the review article "Supramolecular self-assembled chaos: polyphenolic lignin's barrier to cost-effective lignocellulosic biofuels" by

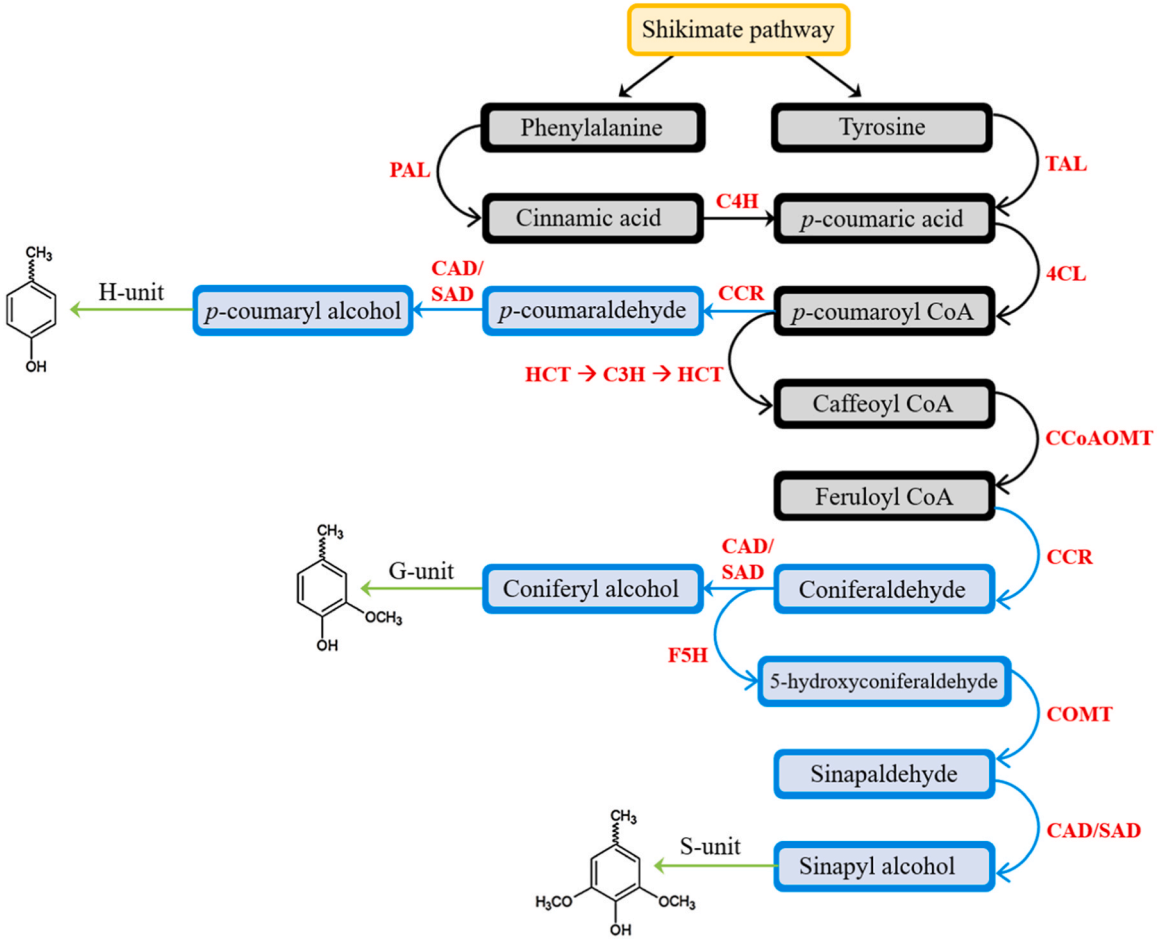


Fig. 4. Enzymes (red) and substrates/products (rectangles) involved in the phenylpropanoid pathway (black) and biosynthesis of the main monolignols (blue). Next to the main monolignol alcohols are their corresponding polymerised building block units (Achyuthan et al., 2010).

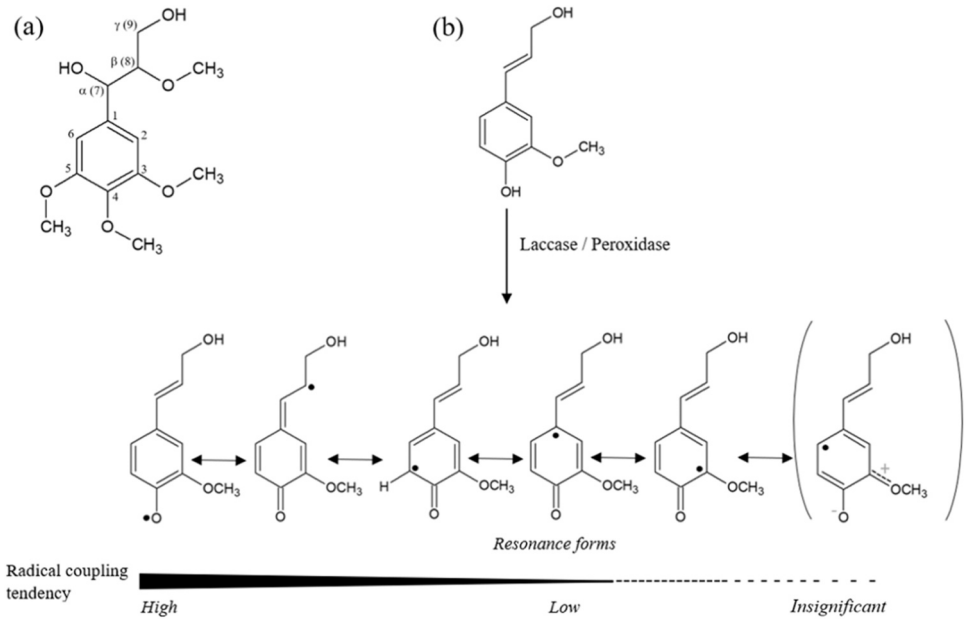
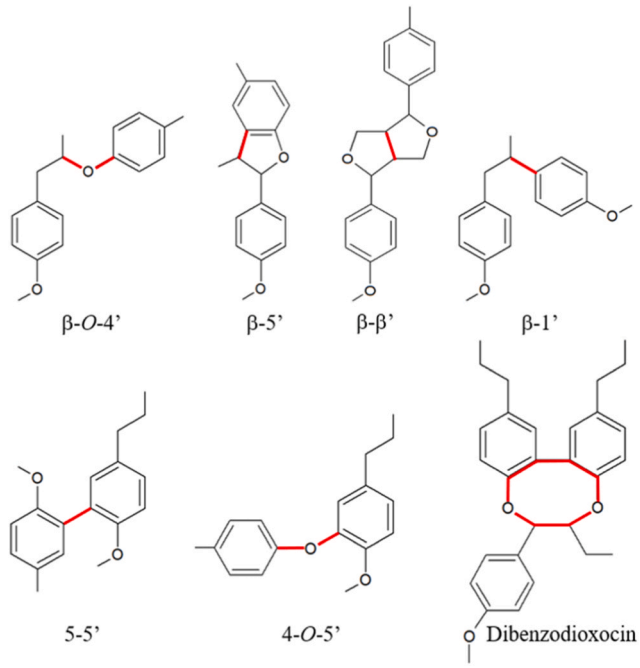


Fig. 5. (a) Monolignols numbering system. (b) Enzymatic formation of monolignol radicals. The radical coupling tendency is indicated by the intensity of the line (Gellerstedt and Henriksson, 2008).



Linkage	Softwood	Hardwood
β-*O*-4'	45–50%	60–62%
β-5'	9–12%	3–11%
β-β'	2–4%	3–12%
β-1'	7–10%	1–7%
5-5'	18–25%	3–9%
4-*O*-5'	4–8%	7–9%
Dibenzodioxocin	-	-

Fig. 6. Common linkage types in lignin, their denotation, and abundance in softwoods and hardwoods (Gellerstedt and Henriksson, 2008; Sadeghifar and Ragauskas, 2020).

Achyuthan et al. (2010), explains the formation of lignin step-by-step, including multiple different researchers suggested formation routes. Another useful literature explaining the formation of lignin is presented in the book "Monomers, polymers, and composites from renewable resources" in chapter 9 by Gellerstedt and Henriksson (2008).

2.2. Lignin structure

Peter Klason (1848–1937) was the first to clarify the lignin chemistry through his work, and suggested that lignin is made from coniferyl alcohol (Liao et al., 2020). Later, the structure of softwood lignin (spruce) was established by Freudenberg (1965), Alder (1977), and Brunow et al. (1998), and the structure of hardwood (beech) lignin by Nimz (1974). Although the conventional definition of lignin is that it is composed of the three main monolignols, many other phenolic compounds have been found to perform as genuine lignin monomers in different plant species, increasing the complexity of this polymer (del Río et al., 2020). It is now recognised that additional phenolic compounds originating from the phenylpropanoid pathway, so-called monolignol ester conjugates, participates in radical coupling reactions and incorporation into the lignin polymer. These conjugates may occur from incomplete conversions, truncations, or extensions of the "traditional" pathway. Apart from monomers derived from the phenylpropanoid pathway, del Río et al. (2020) reported phenolic compounds originating from outside the phenylpropanoid pathway. These compounds would instead arise from flavonoid, hydroxystilbene, or hydroxycinnamamide biosynthetic pathways, and participate in coupling and incorporation into the lignin polymer. Some of these compounds are presented in Fig. 7.

Due to the broad variety of "additional" monolignols participating in coupling and polymerisation, apart from the three main monolignols, it is challenging to define the true structure of lignin (del Río et al., 2020). Simultaneously, it evidently demonstrates that the polymerisation of lignin is flexible and that any phenolic compound transported to the cell wall can potentially be oxidised and incorporated into the lignin structure.

2.3. Technical lignins

To utilise lignin in value-added applications, it must be isolated from biomass (Laurichesse and Avérous, 2014; Yu and Kim, 2020). The extract obtained through various methods of lignin isolation is called technical lignin. Since the extraction of technical lignin modifies its structure, it must be considered how the process affects the structure to effectively utilise the acquired technical lignin for different purposes. The isolation processes can be classified based on the method of extraction into two groups (Azadi et al., 2013). The first group of methods involves processes in which soluble lignin is degraded into fractions and extracted by separating the solids from the liquor. Such processes are kraft, soda, sulphite, and organosolv pulping processes. The other group of methods are processes in which polysaccharides are selectively hydrolysed, leaving a solid residue of lignin and some products of condensed carbohydrates. Some of the commonly utilised processes for the extraction of technical lignins from biomass are shown in Fig. 8.

Some of the most important technical lignins are kraft lignin, lignosulphonate, organosolv lignin, and soda lignin (Acosta et al., 2016). The kraft process involves cleavage of the bonds of wood components using sodium hydroxide and sodium sulphide under strong alkaline conditions (Acosta et al., 2016; Laurichesse and Avérous, 2014). From the so-called black liquor, lignin is obtained by acidified precipitation (Lange et al., 2013). Kraft lignin has many properties that differ from native lignin and other technical lignins, such as a great number of phenolic groups and condensed chemical structures (Acosta et al., 2016; Laurichesse and Avérous, 2014). Due to the degradative nature of this process, the number average molecular weight (M_n) of kraft lignin is fairly low and narrow, approximately between 1000 and 3000 Da (Lange et al., 2013; Laurichesse and Avérous, 2014).

Lignosulphonate is extracted from wood by sulphite chemical pulping (Acosta et al., 2016; Laurichesse and Avérous, 2014). In the process, an aqueous solution of sulphur dioxide (SO_2) and a base of sodium, ammonium, magnesium, or calcium is utilised to cook the wood biomass. In the case of hardwood and softwood, lignosulphonates are extracted by stripping and recovery of sulphur from the waste pulping liquor (Lange et al., 2013). Due to the presence of sulphur in the

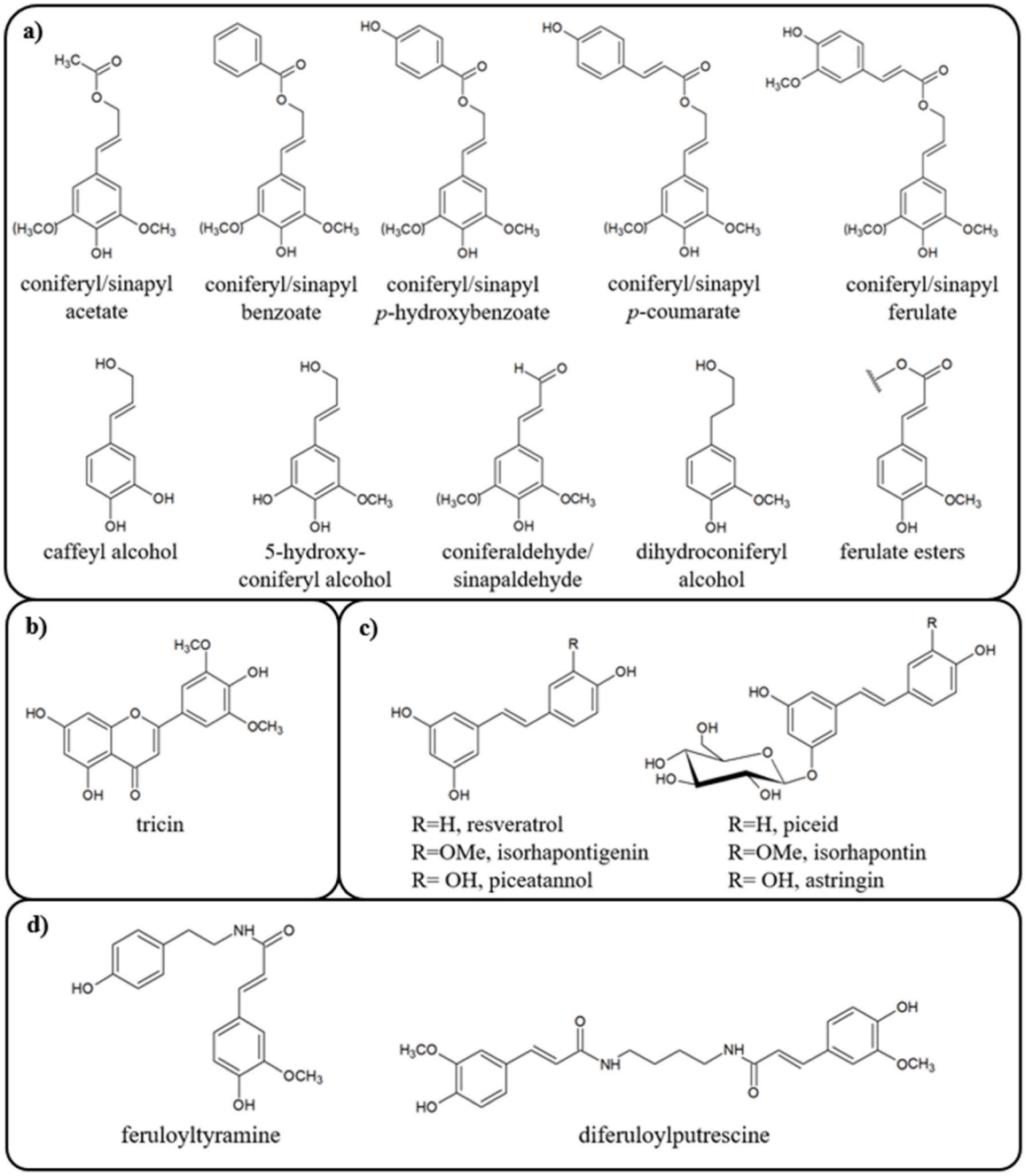


Fig. 7. a) Monolignol ester conjugates originating from the phenylpropanoid pathway. b) Phenolic compounds derived from tricin. c) Hydroxystilbenes resveratrol, isorhapontigenin, and piceatannol on the left, and their respective *O*-glucosides piceid, irorhapontin, and astringin on the right. d) Feruloyltyramine and deferuloylputrescine derived from hydroxycinnamamides biosynthetic pathway (del Río et al., 2020).

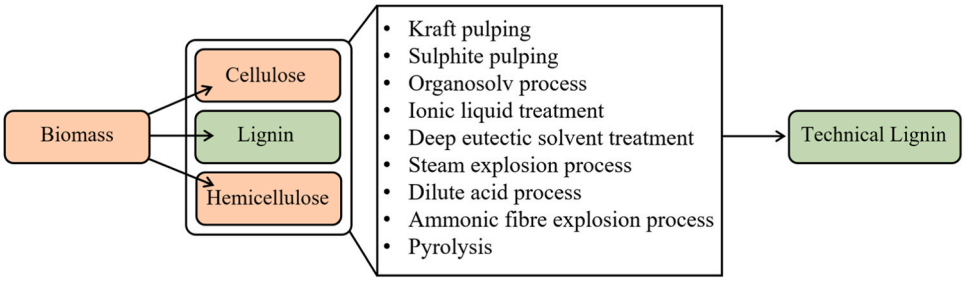


Fig. 8. Extraction of technical lignins (Azadi et al., 2013).

extraction of both kraft lignin and lignosulphonates, these technical lignins are sulphur-containing lignins (Acosta et al., 2016; Laurichesse and Avérous, 2014). For lignosulphonates, they occur as sulphonate groups on aliphatic side chains. Compared to kraft lignin, lignosulphonates have a broader number-average molecular weight, ranging from 1000 to 140,000 Da (Lange et al., 2013).

Sulphur-free lignins are obtained from solvent pulping (organosolv lignin) and alkaline pulping (soda lignin) (Acosta et al., 2016; Laurichesse and Avérous, 2014). Organosolv lignin is obtained by cleavage of different bonds through solubilisation, such as aryl glycerol-β-aryl ether and α-aryl ether, by using organic acids, aqueous solutions, or a mixture of them as solvents (Acosta et al., 2016). Through this solubilisation process, a quite pure and less modified technical lignin is obtained, resembling the chemical structure of native lignin (Acosta et al., 2016; Laurichesse and Avérous, 2014). The number-average molecular weight of organosolv lignin is often small (< 1000 Da) (Lange et al., 2013).

The soda lignin extraction process is similar to the kraft process in that the lignocellulosic material is treated with highly alkaline solutions, but without hydrogen sulphide anions (Acosta et al., 2016). The native lignin network is hydrolytically cleaved, followed by acid precipitation, heating, and filtration to extract the technical lignin. The absence of hydrogen sulphide anions results in a sulphur-free and fairly chemically unmodified lignin (Lange et al., 2013; Laurichesse and Avérous, 2014). The similarity of lignin extraction between the kraft and soda processes is also reflected on the properties of these technical lignins (Acosta et al., 2016). A simple process-scheme for these extraction processes is shown in Fig. 9.

These processes are industrial extraction processes, while numerous alternative extraction methods have been and are constantly developed (Liao et al., 2020). A comprehensive review of these processes by Liao et al. (2020) describes both these industrial and alternative approaches well, along with sources and composition of lignocellulosic biomass, and the structure, chemistry, biosynthesis, characterisation, modification, properties, and applications of lignin.

2.4. Chemical modification of lignin

Although the complex structure of lignin results in low reactivity, its high carbon content and aromaticity make it a promising alternative for biobased applications (Agustiany et al., 2022). Thus, modification of lignin is essential to enhance the chemical reactivity or compatibility between different materials (Agustiany et al., 2022; Liao et al., 2020). Typical modification routes involve fragmentation or depolymerisation of the lignin structure, creation of new chemically active sites, hydroxyl group modification or functionalisation, and graft co-polymerisation (Agustiany et al., 2022; Figueiredo et al., 2018; Laurichesse and Avérous, 2014). These modification methods are briefly explained below.

2.4.1. Lignin depolymerisation

Through depolymerisation or fragmentation of lignin, its molecules can be converted into small compounds for specific applications (Figueiredo et al., 2018). Some of the thermochemical lignin-depolymerisation methods are pyrolysis, hydrogenolysis, oxidation, and hydrolysis.

Pyrolysis. With pyrolysis, lignin can be turned into liquid bio-oil, solid char, or gasses through thermal treatment (Figueiredo et al., 2018). The principle of the method is to heat organic substances in the absence of oxygen to break down the structure into smaller fractions, while the lack of oxygen inhibits unwanted combustion to carbon dioxide (Figueiredo et al., 2018; Pandey and Kim, 2011). The complexity of lignin pyrolysis is affected by the type of feedstock, reaction temperature, heating rate, additives, and more (Ferdous et al., 2002; Figueiredo et al., 2018; Pandey and Kim, 2011). As the type of lignin varies greatly depending on the source and fractionation method, its composition and functional groups affects the conversion and product yields of pyrolysis (Ferdous et al., 2002). Pyrolysis of lignin can be divided into three stages, initiating with a dehydration stage followed by an active, and then a passive pyrolysis stage (Leng et al., 2022). During the dehydration stage, which occurs below 200 °C, additional reactions such as demethoxylation, demethylation, and decarboxylation, occur around 150 °C between terminal functional groups and the branches, producing different gases. The active stage occurs between 200 and 450 °C in which the most abundant bonds β-*O*-4' are broken. This is considered the initiation stage of depolymerisation, forming many lignin monomers, such as cinnamyl alcohol, p-coumaryl, guaiacol, etc. Further reactions with increasing temperatures give rise to secondary reactions of the newly formed lignin monomers. In this passive stage of pyrolysis, functional group removal, side-chain scission and rearrangement, and polymerisation can occur.

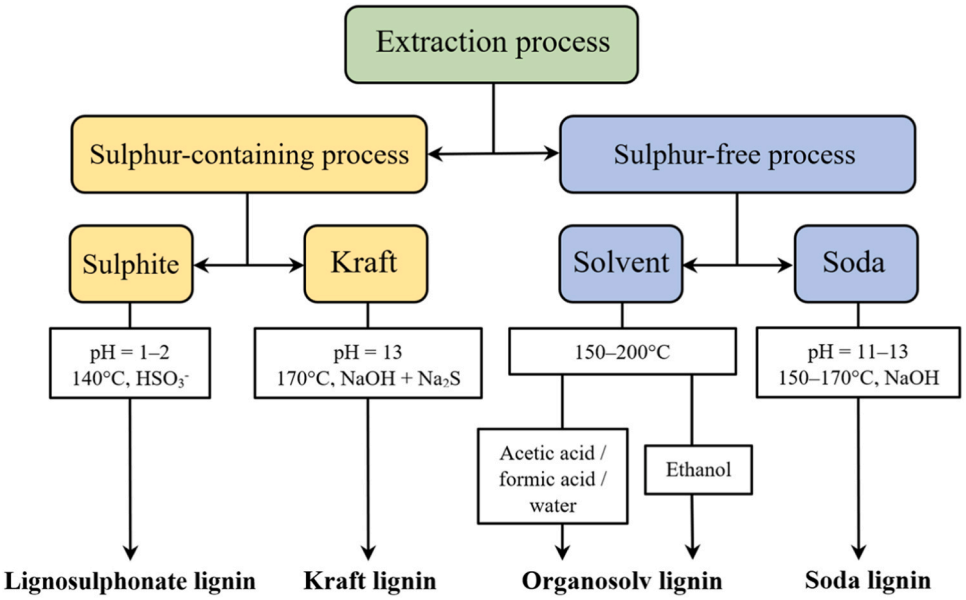


Fig. 9. Separation of lignin from biomass through the sulphite, kraft, solvent, and soda pulping processes with typical conditions and chemicals used to obtain corresponding technical lignins (Laurichesse and Avérous, 2014).

Hydrogenolysis. The hydrogenolysis process is similar to pyrolysis, with the exception that hydrogen is present in the reaction (Pandey and Kim, 2011). Hydrogenolysis is applied to break down C-O-C bonds in lignin by using an active hydrogen-donating solvent or by treating it in gaseous hydrogen, acquiring different monomeric phenols as products (Figueiredo et al., 2018; Pandey and Kim, 2011). Hydrogenation yields more monophenols and forms less char than pyrolysis (Pandey and Kim, 2011). The product yield can be further increased with suitable solvents and catalysts, simultaneously increasing the speed of the reaction.

Oxidation. For lignin depolymerisation through oxidation, the most used oxidants are nitrobenzene, oxygen, hydrogen peroxide, and metallic oxides (Figueiredo et al., 2018; Laurichesse and Avérous, 2014; Pandey and Kim, 2011). Through oxidation, aromatic aldehydes and their corresponding carboxylic acids can be obtained. Vanillin and vanillic acid, as well as syringaldehyde and syringic acid can be obtained from alkaline oxidation of softwood and hardwood lignin, respectively (Figueiredo et al., 2018). The main modification approaches of lignin by oxidation involves cleavage of inter-unit linkages, oxidation and ring cleavage of aromatic rings, and oxidative modifications of propanyl sidechains (Ma et al., 2018). The rate of oxidation is influenced by the amount of phenolic groups present, the concentration of oxygen, and pH (either acidic or alkaline oxidation) (Figueiredo et al., 2018). The choice of oxidants, oxidation conditions, and addition of selected catalysts targets specific bonds of the lignin structure through which selected fractions can be obtained (Ma et al., 2018).

Hydrolysis. Depolymerisation of lignin by hydrolysis is done with water near supercritical conditions (22 MPa, 374 °C) (Figueiredo et al., 2018; Joffres et al., 2013; Pandey and Kim, 2011). Near or at sub- or supercritical conditions, water can act as an excellent medium for efficient, fast, and homogeneous reactions due to its properties at these conditions, such as low viscosity and the capability to solubilise organic substances (Joffres et al., 2013; Toor et al., 2011). Through hydrolysis of lignin, different phenols, guaiacol, catechol, and methoxy phenols are produced. Additionally, the methoxy groups can be further depolymerised, but the benzene ring remains stable throughout the process. One drawback of lignin hydrolysis depolymerisation is the possible re-polymerisation of monomers (Pandey and Kim, 2011). However, the addition of phenol can prevent this reaction. Saisu et al. (2003) depolymerised organosolv lignin by hydrolysis both with and without the addition of phenols. The phenol-free reaction yielded more insoluble lignin, while the phenol-containing reaction decreased the yield of insoluble lignin, suggesting a decrease in re-polymerisation. Other routes to avoid re-polymerisation include the addition of catalysts, the use of an alkaline supercritical medium, or the use of a mixture of water and other solvents (Joffres et al., 2013).

2.4.2. *New chemically active sites*

Lignin consists of a variety of functional groups, including hydroxyls, carbonyls, carboxyls, and methoxyls (Figueiredo et al., 2018; Laurichesse and Avérous, 2014; Verdini et al., 2022). By modifying these groups, their activity and reactivity can be enhanced by either increasing the hydroxyl groups reactivity or by modifying the nature of these active sites. Through these changes, new efficient and more reactive macromolecules can be obtained. These modification routes can increase both the solubility of lignin in organic solvents and its chemical reactivity and reduce the brittleness of the polymer. Consequently, the ease of processing lignin improves (Laurichesse and Avérous, 2014). Typical methods for these modifications include hydroxyalkylation, amination, nitration, sulphomethylation, and sulphonation (Figueiredo et al., 2018; Verdini et al., 2022). These modifications of the lignin backbone are illustrated in Fig. 10.

Hydroxyalkylation. Hydroxyalkylation is one of the methods used to

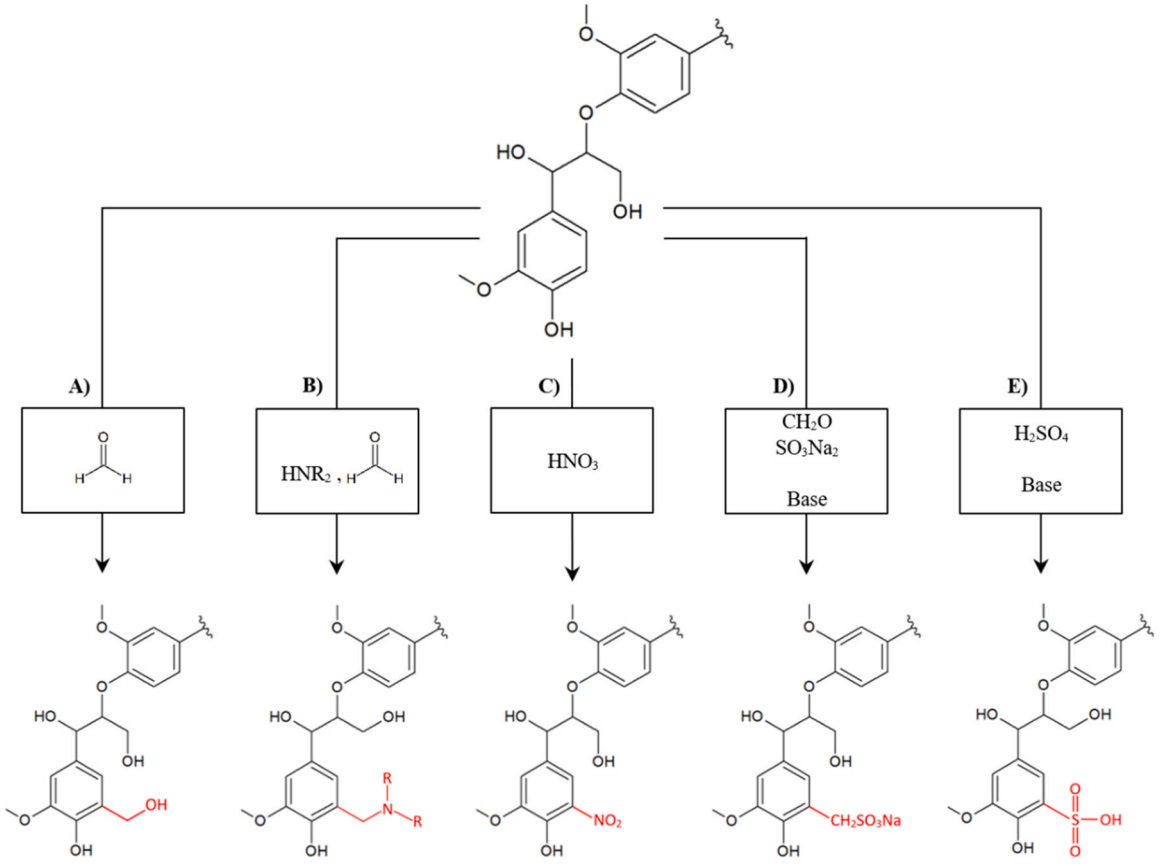


Fig. 10. Illustration of modifications to synthesise new chemically active sites. A) Hydroxyalkylation, B) amination, C) nitration, D) sulphomethylation, and E) sulphonation (Bertella and Luterbacher, 2020; Figueiredo et al., 2018).

introduce new chemically reactive sites in lignin (Li et al., 2020). This approach focuses on the conversion of phenolic hydroxyl groups to aliphatic hydroxyl groups through etherification. Another approach is to incorporate hydroxyl groups at the end of lignin polyether chains. Hydroxyalkylation is performed in aqueous alkali solutions with formaldehyde or alkaline oxide. Ethylene, propylene, and butylene oxides are typically utilised for this process. The conversion of phenolic hydroxyl groups to aliphatic hydroxyl groups not only increases the reactivity of these groups, but can also through chain extension reduce electronic and steric constraints (Ahvazi et al., 2011; Li et al., 2020).

Amination. Incorporating amine functional groups into the lignin structure is done by amination (Figueiredo et al., 2018; Laurichesse and Avérous, 2014; Suota et al., 2021). The most common amination approach is the Mannich reaction, which can be carried out under acidic, alkaline, or neutral conditions. Typically, the reaction is done under alkaline conditions by charging formaldehyde and different types of amines (Figueiredo et al., 2018; Laurichesse and Avérous, 2014). Amination of lignin increases its molar mass and lowers its glass transition temperature (T_g) (Suota et al., 2021). Additionally, the solubility, surface tension, and reactivity of the aminated product increases.

Nitration. The most commonly used nitrating agents for lignin nitration are nitric acid in concentrated acetic anhydride, acetic acid, or sulphuric acid, and the process is performed in non-aqueous solvents (Figueiredo et al., 2018; Laurichesse and Avérous, 2014; Meister, 2002). Through nitration, a lignin product, nitrolignin (NL), with a molecular weight ranging from 600 to 2000 Da, and a nitrogen content of approximately 6–7 % can be obtained (Figueiredo et al., 2018; Laurichesse and Avérous, 2014). Nitrolignin has been utilised in different graft interpenetrating polymer networks together with polyurethane. The resulting polymer networks showed increased toughness and strength and maintained retractability (Figueiredo et al., 2018; Huang and Zhang, 2002; Laurichesse and Avérous, 2014).

Sulphomethylation and sulphonation. Sulphomethylation and sulphonation are processes through which sulphonate ($CH_2SO_3^-$) and sulphate (SO_3^-) groups can be added to lignin respectively (Meister, 2002). Sulphomethylation is performed in neutral or basic pH conditions with equal moles of alkali metal sulphite salt, methanol, and dissolved phenolic lignin units (Figueiredo et al., 2018). The reaction can be modified based on desired substitution degree by changing conditions and ratio of regents. The sulphonation reaction is done by using sulphuric acid or sodium sulphite.

2.4.3. *Hydroxyl group modification/functionalisation*

Located at the C-γ and the C-α positions on the side chain are phenolic and aliphatic hydroxyl groups present in lignin (Bertella and Luterbacher, 2020; Figueiredo et al., 2018; Laurichesse and Avérous, 2014). In addition, guaiacol and syringol units of the aromatic rings are highly reactive (Bertella and Luterbacher, 2020). The presence of these functional sites in the structure allows controlled chemical modifications of the polymer. Below, some of the main methods for the functionalisation of the hydroxyl side groups are explained, including alkylation, ester- and etherification, phenolation, and urethanisation (Figueiredo et al., 2018). These modifications of the lignin backbone are illustrated in Fig. 11.

Alkylation. The oxygen atoms of the hydroxyl, carbonyl, and carboxyl groups are sites where lignin alkylation can take place (Figueiredo et al., 2018; Meister, 2002). For the alkylation reaction there are three common approaches using different substances, which are diazoalkanes, alcohol in the presence of a catalyst, and alkylsulphates together with sodium hydroxide. One well-known alkylation/dealkylation reaction is demethylation where demethylated lignin are byproducts in the production of DMSO (Figueiredo et al., 2018;

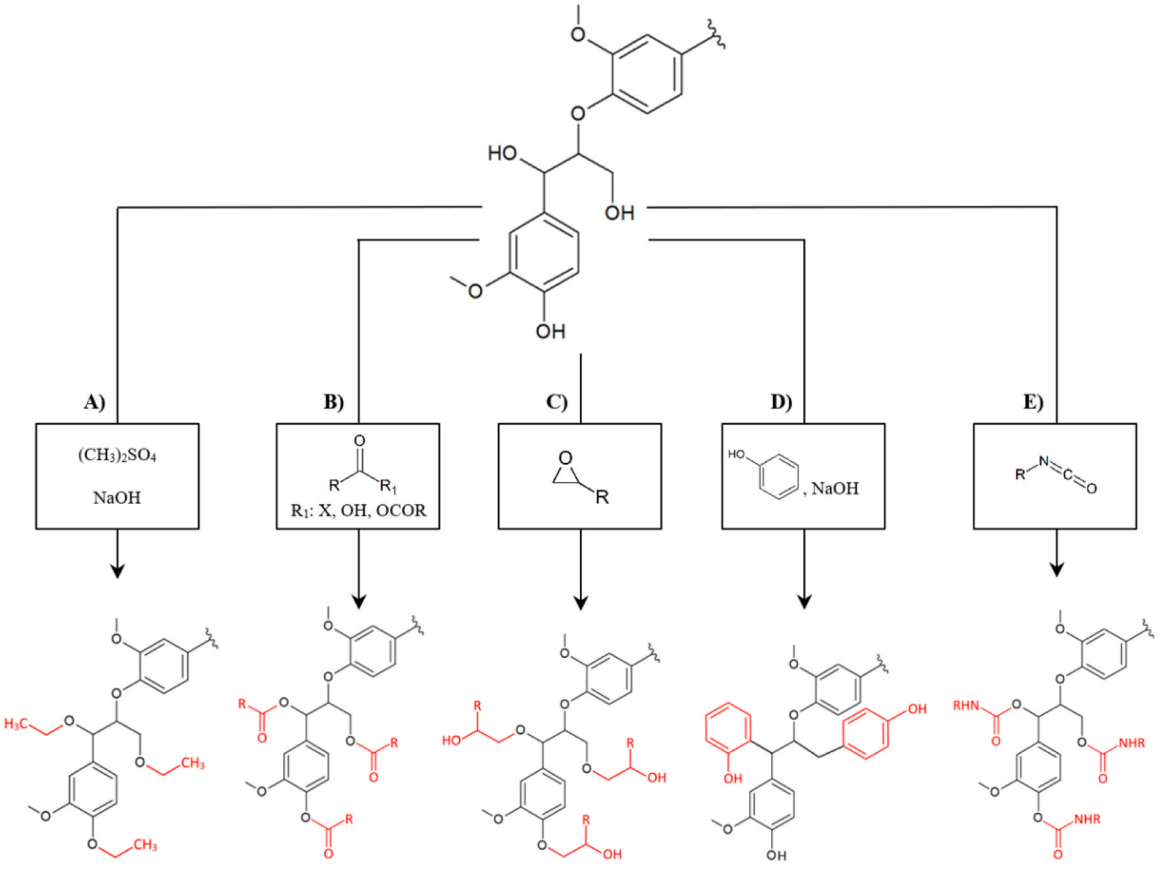


Fig. 11. Illustration of modification/functionalisation of hydroxyl groups. A) Alkylation, B) esterification, C) etherification, D) phenolation, and E) urethanisation (Bertella and Luterbacher, 2020; Figueiredo et al., 2018).

Laurichesse and Avérous, 2014). The demethylated lignin combined with polyethylenimine has been used in the production of formaldehyde-free wood adhesives.

Esterification. The process of lignin esterification can be achieved through three different procedures, which are ring opening reactions, condensation polymerisation, and dehydration polymerisation, using, for example, cyclic esters, carboxylic acid chloride, and dicarboxylic acids, respectively (Figueiredo et al., 2018). Esterification is one of the most convenient lignin modification approaches, which is commonly used to enhance the solubility of lignin for assessment and analysis on molar mass and structure (Wang et al., 2016). A general property change, which occurs in lignin through esterification, is that the value of T_g decreases, while several other properties are affected by the source and isolation method of the lignin, as well as the chain length of the substitutes. The general esterification reaction is based on the conversion of alcohols to ester through nucleophilic substitution (Kazzaz et al., 2019). The carbon on the reagent's ester group gets attacked by a lone pair electron of the aromatic hydroxyl group, replacing hydroxy groups on the aromatic ring with carbonyl groups.

Etherification. Lignin-based polyethers can be produced by polymerisation, cross-linking, or solvolysis (Figueiredo et al., 2018). Polymerisation approaches include the use of alkylene oxides, or polymerisation with epichlorohydrin. Diglycidyl ethers can be used for the cross-linking reaction, while ethylene glycol can be used for solvolysis. The most common etherification method is the so-called oxypropylation reaction (Figueiredo et al., 2018; Kazzaz et al., 2019; Laurichesse and Avérous, 2014). This reaction is performed by mixing lignin with NaOH or KOH, and suitable reagents, such as propylene carbonate or propylene oxide (Kazzaz et al., 2019). After reacting in certain conditions, the mixture is acidified to precipitate the oxypropylated lignin.

Phenolation. The process of increasing the phenol groups content in lignin is called phenolation or phenolysis and is typically performed by mixing phenols and lignin in the presence of organic solvents (Effendi et al., 2008; Figueiredo et al., 2018). For lignosulphonate, phenolation is the most common method of modification, resulting in an increased content of phenolic hydroxyl groups and increased reactivity as phenolic substitute (Figueiredo et al., 2018; Laurichesse and Avérous, 2014). The increase of phenolic hydroxyl groups results in an increase of reactive sites in the lignin molecular structure (W. Li et al., 2023). During the reaction, phenol condensation on the side chains of lignin and ether bond cracking occurs, resulting in a decrease in molar mass.

Urethanisation. Urethanisation is another method aimed at modifying the hydroxyl groups present in lignin through reactions with isocyanate groups, forming a urethane link (Bajwa et al., 2019; Figueiredo et al., 2018; Laurichesse and Avérous, 2014). Due to the versatility and quantity of hydroxyl groups present in lignin, it can function as a bio-based polyol as an alternative to fossil-based products in the production of lignin-based polyurethane (Laurichesse and Avérous, 2014). There are two approaches to produce lignin-based polyurethane, of which the first is done in one step and the second in two steps (Bajwa et al., 2019; Figueiredo et al., 2018; Laurichesse and Avérous, 2014). The one-step approach involves addition of diisocyanate and/or diol as a co-monomer, while the two-step approach initially involves the production of a pre-polymer with the aid of isocyanate and polyol, followed by polymerisation of the pre-polymer with lignin.

2.4.4. Graft co-polymerisation

Lignin graft co-polymers are produced by polymer chains attaching to the hydroxyl groups on the lignin structure (Duval and Lawoko, 2014; Figueiredo et al., 2018). The resulting polymer is a star-like branched polymer with a lignin core. There are two different ways the graft co-polymerisation can occur, which are typically referred to as the "grafting from" and "grafting onto" techniques. These two approaches are shown in Fig. 12.

"Grafting from" polymerisation. In the "grafting from" technique, lignin act as a macro-initiator onto which monomers attaches through reactions with lignin hydroxyls (Duval and Lawoko, 2014; Figueiredo et al., 2018). Chains of monomers are then built up through polymerisation to form polymer chains, either through ring-opening polymerisation (ROP) or radical polymerisation.

The most common ROP method produces oxypropylated lignin as OH groups of lignin react with propylene oxide (Duval and Lawoko, 2014; Figueiredo et al., 2018). With increasing chain length, the viscosity and T_g of the newly formed polymer decreases. Additionally, both ε-caprolactone and lactide has been used to produce lignin graft

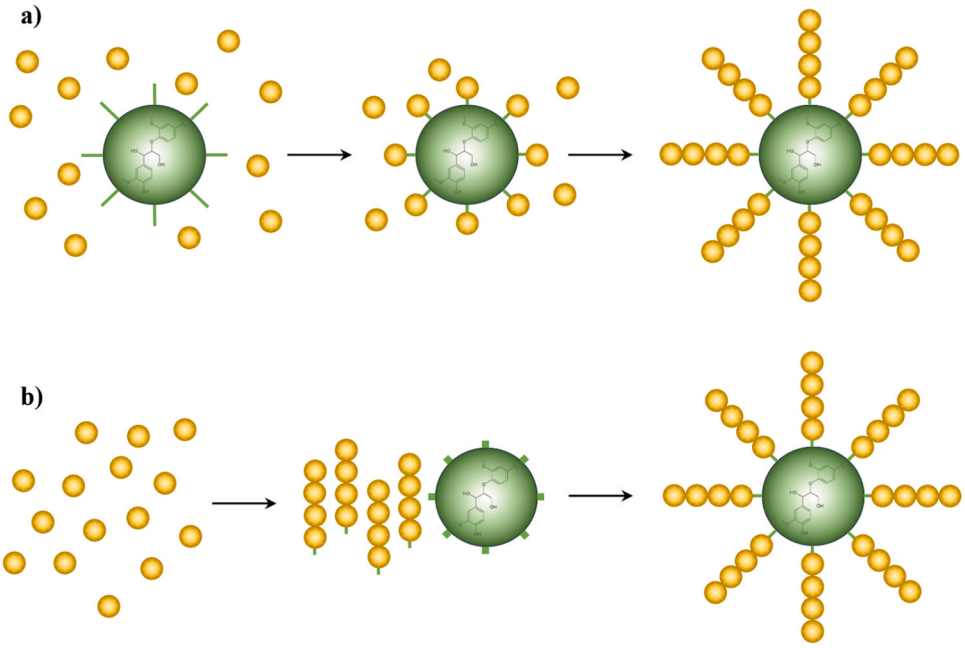


Fig. 12. The two graft co-polymerisation methods. a) The "grafting from" approach in which lignin act as a macro-initiator onto which monomers attaches either through ROP or radical polymerisation. b) The "grafting onto" approach where chains of monomers are initially synthesised and then grafted onto the lignin structure by functionalising their end-groups (Duval and Lawoko, 2014; Figueiredo et al., 2018).

polymers by ROP.

Radical polymerisation requires radicalisation to produce free radicals in the lignin structure, which initiates polymerisation of vinylic monomers onto lignin. (Duval and Lawoko, 2014; Figueiredo et al., 2018). The radicalisation mainly occurs by irradiation or by using a chemical initiator, such as peroxide. By radical polymerisation, many different graft co-polymers have been synthesised, but the technique is not as precise as ROP since the reaction is harder to control, homopolymerisation of vinyl monomers and coupling reactions between the radicals can occur, and the position of the radical cannot be controlled. However, an efficient method has been developed to tackle these disadvantages, namely atom transfer radical polymerisation (ATRP), which allows controlled radical polymerisation.

"Grafting onto" polymerisation. The "grafting onto" approach is done by firstly synthesising polymer chains, then functionalising their end group, and finally grafting them onto the lignin structure by the hydroxyl groups (Duval and Lawoko, 2014; Figueiredo et al., 2018). As this method is performed in three steps it is not as common as the "grafting from" method, but the synthesised chains can be much more easily modified prior to attachment (Duval and Lawoko, 2014).

2.5. Biological activity of lignin

The properties of lignin are hard to define as its great variety of sources, synthesis complexity, physical- and chemical heterogeneity, extraction processes, etc. all contribute and change the resulting properties. Generally, the molar mass of lignin varies greatly depending on source of extraction (Kai et al., 2017). It is an amorphous thermoplastic polymer with a T_g region and a thermal decomposition (T_d) region. It has a low solubility in most solvents, but as in the case of molar mass, the solubility varies depending on source and extraction process. Due to its highly branched polymer network structure and natural aromaticity, the biodegradability of lignin is low. Thus, only a few microorganisms such as specific fungi and bacteria can degrade lignin naturally. Additionally, lignin possesses several properties, which make it an interesting component for value-added applications, such as antioxidant, antimicrobial, and antifungal activity (Figueiredo et al., 2018; Thakur and Thakur, 2015). It can absorb UV-radiation and act as a fire-retardant (Figueiredo et al., 2018). The presence and quantity of different reactive functional groups allows for multiple modification routes of the polymer. Furthermore, studies have revealed that lignin possesses antigenotoxic and antimutagenic properties (Acosta et al., 2016).

2.5.1. Antimicrobial activity

Microbes, such as virus, fungi, bacteria, etc., can cause infections and health concerns (K. Li et al., 2023; Ullah et al., 2022). Many natural sources contain bioactive compounds, which can inhibit the harmful activities caused by microbes (Boarino and Klok, 2023; Ndaba et al., 2020). Examples of these types of compounds are polyphenols, terpenoids, tannins, amino acids, and flavonoids (Boarino and Klok, 2023). What all these compounds have in common, in addition to their antimicrobial activity, is that they are biocompatible, renewable, and biodegradable. However, the extraction processes of these compounds are typically complex with low yields of quantities. Thus, lignin has recently gained attention as a cheap and accessible alternative as raw material to inhibit the harm caused by microbes (Boarino and Klok, 2023; Ndaba et al., 2020).

In plants, lignin acts as an antimicrobial agent and inhibits growth of bacteria and fungi, preventing carbohydrates to decompose (Shu et al., 2021). For medical applications, extracted lignin has been utilised as an antimicrobial agent or additive against fungi, bacteria, and viruses (Boarino and Klok, 2023; Shu et al., 2021). The antimicrobial activity in lignin stems from phenolic structures, particularly isoeugenol structures with a methyl group in the C_γ position and a double bond in the $C_\alpha = C_\beta$ position on the side chain (Ullah et al., 2022). However, there are several contributors affecting the activity, such as lignin source, extraction method, molar mass, type of microbe, and concentration of lignin. Changing the extraction method or certain parameters, such as pH and temperature during the extraction, can change the antimicrobial activity (Ndaba et al., 2020).

2.5.2. Antioxidant activity

Lignin can be used as a natural antioxidant by neutralising or inhibiting the oxidation of reactive oxidised radicals or their derivatives (Lu et al., 2022; Sadeghifar and Ragauskas, 2022). Like the antimicrobial activity, the antioxidant activity of lignin varies greatly depending on source and method of extraction. However, the activity can be fairly well controlled by different pretreatments, modifications, and post-processing methods (Lu et al., 2022; Matos et al., 2021; Tagami et al., 2019). Tagami et al. (2019) investigated kraft lignins from different sources and how they affected the molar mass, structural features, and properties. In general, fractions with lower molar masses and a greater amount of short side chains attached to the phenolic rings showed increased antioxidant activity. Matos et al. (2021) studied different pyrolytic lignin fractions and how the fractionation method affected functional groups, linkages, molar mass, and different properties. The various fractions of the acetone:water fractionation process consisted of an insoluble, a precipitated, and a soluble fraction. The soluble fraction had the lowest molar mass and showed the greatest antioxidant activity, although all three fractions were reported to have a very strong antioxidant activity index. Additionally, the fractions showed antibacterial activity against bacteria *E. coli* and *S. aureus*. The minimum inhibitory concentration (MIC) was reported where the precipitated and the soluble fractions showed the lowest values.

There are two main methods for antioxidant assays, which are hydrogen atom transfer (HAT) (Eq. (1)) and single electron transfer (SET) (Eq. (2)) (Sadeghifar and Ragauskas, 2022).

$$\underline{\text{HAT}}: X\bullet + AH \rightarrow XH + A \quad (1)$$

$$\underline{\text{SET}}: X\bullet + AH \rightarrow X^- + AH^+ \quad (2)$$

In Eqs. (1) & (2) "X•" is a radical, "AH" is an antioxidant, "XH" is a protonated radical, "X" is an antioxidant radical or anion, and "AH^+" is a radical cation (Sadeghifar and Ragauskas, 2022). The abundant phenolic nature of the lignin structure indicates potential for phenoxy radical conversion. In addition to the phenolic nature, the antioxidant activity of lignin stems from the presence of para- and ortho-substituted methoxy groups, saturated propane chains, and propanoid chains with hydroxyl groups (Lu et al., 2022; Sadeghifar and Ragauskas, 2022). The general agreement based on studies is that lignin with low molar mass and high content of phenolic hydroxyl groups enhances the antioxidant activity (Lu et al., 2022).

3. Additive manufacturing

Additive manufacturing (AM), also known as 3D printing, is a manufacturing technique that enables the construction of three-dimensional objects with complex geometries (Ji et al., 2020; Shah et al., 2023; Xu et al., 2018). The manufacturing process is performed in a layer-by-layer manner according to 3D model data, constructing self-supporting objects with one or multiple materials (Ji et al., 2020). The model data allows rapid prototyping of objects of different kinds of materials (Xu et al., 2018), but simultaneously shifting more and more towards industrial series production. The versatility of AM technologies enables processing of these materials by extrusion, ink solidification, direct energy deposition, and photopolymerisation. The main technologies utilised for additive manufacturing of biomass-derived components are material extrusion (ME), direct ink writing (DIW), vat photopolymerisation (VPP), and binder jetting (BJ) (Ji et al., 2020). These technologies are illustrated in Fig. 13, and briefly introduced below.

Material extrusion. ME, commonly known as fused deposition

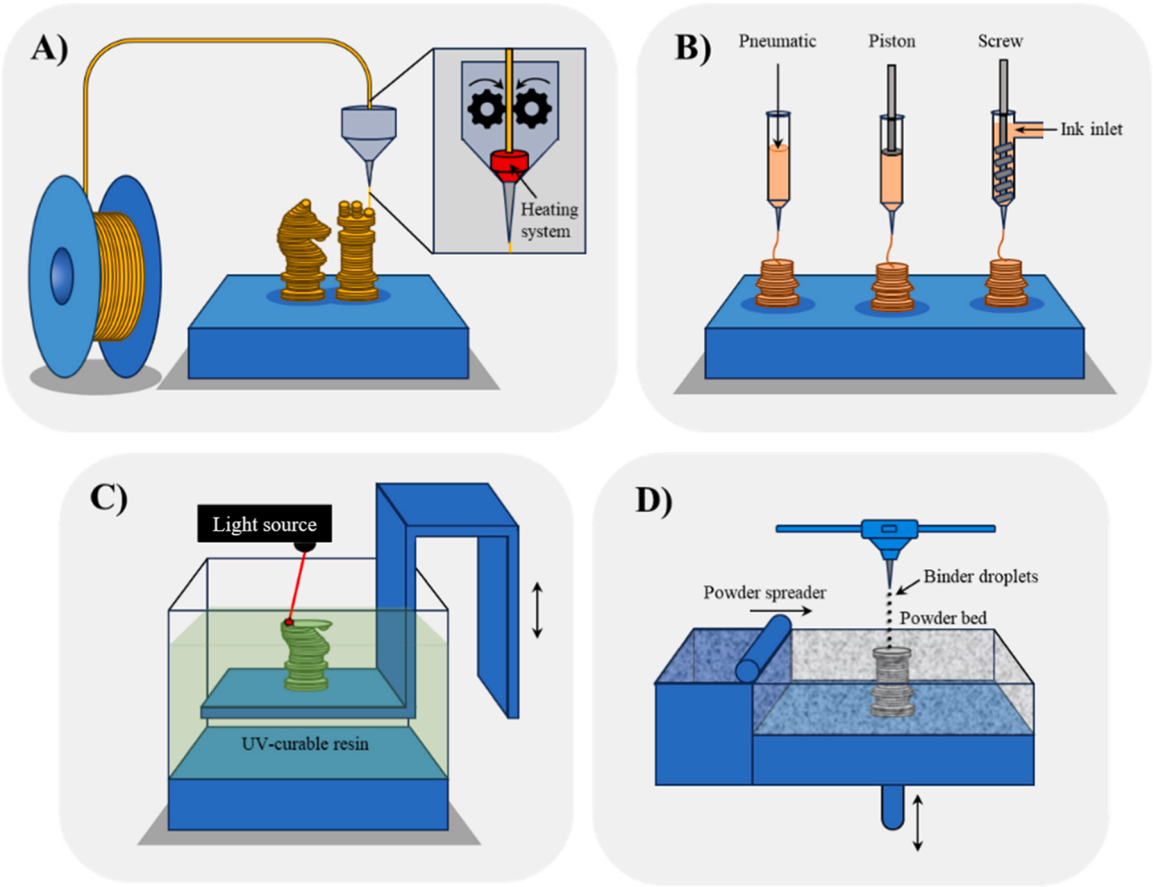


Fig. 13. Schematic illustration of AM technologies used for biomass derived components. **A)** Material extrusion, **B)** direct ink writing, **C)** vat photopolymerisation, and **D)** binder jetting.

modelling (FDM), is amongst the most used and inexpensive AM technologies (Tappa and Jammalamadaka, 2018). The manufacturing process involves a thermoplastic filament, which is fed to the printhead by an electrical or hydraulic motor-controlled roller mechanism (Daminabo et al., 2020). In the printhead the thermoplastic filament is melted and extruded through a nozzle, creating a two-dimensional pattern on the printing platform. As the molten extruded filament cools and solidifies, the layers fuse together (Xu et al., 2018). Additional two-dimensional layers are extruded one on top of each other to create the desired three-dimensional object (Daminabo et al., 2020). Different thermoplastics, such as polylactic acid (PLA), acrylonitrile butadiene styrene (ABS), poly-caprolactone (PCL), and ethylene-vinyl acetate (EVA), are commonly used for ME (Xu et al., 2018). Materials with suitable glass transition and melting temperatures can be incorporated into the thermoplastic filament for the manufacturing of composites.

Direct ink writing. DIW is also an extrusion-based AM technology which utilises viscoelastic materials as feedstock, such as polymer liquids, hydrogels, and colloidal suspensions (L. Li et al., 2019). It enables fabrication of complex structures at moderate costs (del-Mazo-Barbara and Ginebra, 2021). The desired object is constructed in a layer-by-layer manner by stacking the extruded filaments according to a digital model (Chen et al., 2019; del-Mazo-Barbara and Ginebra, 2021). A broad variety of nozzle sizes enables manufacturing of structures for several applications, ranging from 0.1 μm to several dm in diameter (del-Mazo-Barbara and Ginebra, 2021).

Successful DIW manufacturing stems from the rheological properties of the feedstock (del-Mazo-Barbara and Ginebra, 2021; Zhang et al., 2022). The ink must be extrudable through the nozzle and have proper self-support and shape-retention once extruded. Ideally, the feedstock has shear-thinning properties, meaning that it behaves fluid-like when subjected to applied stresses, but evinces an elastic behaviour when at rest (del-Mazo-Barbara and Ginebra, 2021). With proper rheological properties met, a smooth and continuous extrusion of the ink followed by a rapid transition from a liquid-like to a solid-like state can be achieved (Saadi et al., 2022).

Vat photopolymerisation. VPP is a polymerisation-based AM technology, creating three-dimensional structures by polymerising a photocurable resin one layer at a time with the aid of a light source (Chia and Wu, 2015; Melchels et al., 2010). Once a two-dimensional layer is complete, the printing platform lowers, allowing uncured resin to spread over the top, followed by the polymerisation of the sequential layer. This operational approach is referred to as the "bottom-up" approach, as seen in Fig. 13 "C)".

Another approach is referred to as the "top-down" approach, in which the curing light is projected from underneath the resin container (Chia and Wu, 2015; Melchels et al., 2010). The bottom of the container is transparent, allowing the projected light to pass through onto the printing platform, which is lowered into the resin bath. Once a layer is complete, the printing platform is raised to allow uncured resin to flow beneath it, followed by the curing of next layer. The "top-down" approach requires less resin than the "bottom-up" approach. Additionally, it removes the need for recoating the surface of the structure with uncured resin, and the structure is never exposed to the atmosphere during the process.

Binder jetting. Binder jetting is a powder-based AM technique (Mostafaei et al., 2021; Y. Wang et al., 2024; Ziaee and Crane, 2019). During the manufacturing process, a liquid binder is applied onto a powdered feedstock in the desired layer shape, forming a two-dimensional layer of the printed object. Solidification of the structure occurs through particle agglomeration across the layers (Y. Wang

et al., 2024). Once a layer is complete, a new layer of powdered feedstock is evenly spread across the powder bed with a rotatable roller, and the manufacturing of the next layer proceeds (Mostafaei et al., 2021; Y. Wang et al., 2024; Ziaee and Crane, 2019). Unbound powder acts as support for the structure during the manufacturing process, enabling the formation of internal volumes (Ziaee and Crane, 2019). To obtain a solid and durable part, a second process phase is needed where the "glued" powder solidifies through post-processing. This can be done, for instance, in a furnace.

3.1. Additive manufacturing of lignin-based composites

Recent studies conducted on the integration of lignin in additive manufacturing of composites are presented and briefly explained below. The reviewed studies are listed in Table 2 in order based on additive manufacturing technology. Both digital light processing (DLP) and stereolithography (SLA) presented in the list are vat photopolymerisation technologies.

Feng et al. (2017) prepared lignin-coated cellulose nanocrystals (L-CNC) filled methacrylate composites by SLA. The lignin-containing resin was prepared by directly mixing the L-CNC and methacrylate resin under stirring for 10 min, and then treated with ultrasonication for 6 min at 300 W. For the printing process, a "bottom-up" SLA approach was used. An increased resolution with a gradual increase of L-CNC at low concentrations into the methacrylate resin was reported. Additionally, both tensile strength and Young's modulus increased slightly with addition of up to 0.5 % L-CNC. Thermal stability improved as well with L-CNC introduced in the composites. Zhang et al. (2019) also incorporated softwood kraft lignin into methacrylate resin to manufacture lignin-reinforced composites by SLA printing. The lignin was purified and solution-blended with methacrylate resin in acetone to obtain lignin-methacrylate resin with various lignin concentrations. With only 0.4 wt percentage of lignin in the mixture, an increase of 64 % in tensile strength was reported.

In the work by Nguyen et al. (2018), hardwood lignin was incorporated into NBR41 and nylon 12 together with chopped carbon fibres as a reinforcing agent for the preparation of ME printable filaments. They concluded that organosolv hardwood lignin is more suitable for thermal processing than kraft softwood lignin, due to their structural differences and rheological properties. Likewise, nylon 12 showed more suitable thermal properties for ME printing. Composites of nylon 12 and hardwood lignin (6:4) incorporated with 4–16 wt% of carbon fibre as filler were successfully printed. The lignin-containing reinforced composites showed impressive improvements in both strength and toughness, and in printability, compared to neat nylon 12. Additionally, by introducing carbon fibres into the mixture, the thermal conductivity increased.

Vaidya et al. (2019) produced biorefinery lignin through enzymatic saccharification of high-temperature mechanical pretreated softwood pulp and utilised it as a non-reactive filler with polyhydroxybutyrate for ME composite manufacturing. An 8:2 ratio of poly polyhydroxybutyrate: lignin was determined to benefit printability, and the printed structures showed improved layer adhesion and decreased warpage compared to neat polyhydroxybutyrate.

A comparison of compatibility of kraft, organosolv, and lignosulphonate lignin with PLA for AM was investigated by Mimini et al. (2019). 5, 10, and 15 wt% of each lignin type was incorporated into PLA by mixing in a compounder. The obtained filaments were cut into pellets and run through the compounder once again to ensure homogeneity in the filaments. It was concluded that composites containing kraft lignin had poor compatibility compared to those containing organosolv lignin or lignosulphonate. While organosolv-based composites indicated the best compatibility, lignosulphonate-PLA blends showed great potential for additive manufacturing. Wasti et al. (2021) evaluated the influence addition of two different plasticisers, polyethylene glycol (PEG) and Struktol TR451, had on organosolv lignin/PLA composites. With addition of 2 % PEG in PLA/lignin composites with 20 % lignin, tensile strength was enhanced by 19 % and elongation at maximum load by 35 %. Addition of 0.5 wt% of Struktol TR451 enhanced elongation at maximum load by 24 %.

Ibrahim et al. (2019) enhanced the tensile strength of composites manufactured with DLP by introducing organosolv lignin and graphene nanoplatelets as reinforcing agents in photocurable polyurethane. The self-extracted organosolv lignin and 10 wt% of graphene nanoplatelets were mixed in a homogeniser prior to mixing with polyurethane resin to obtain the reinforced resin of various concentrations. Composites containing > 0.8 % lignin improved the tensile strength of the composites compared to printed structures of neat polyurethane. Likewise, lignin-graphene reinforced composites with > 0.8 % concentrations showed higher tensile strengths than structures of neat polyurethane and structures reinforced only by lignin. The highest achieved increase in tensile strength was 27 % higher than that of the reference sample of neat polyurethane. Mohan et al. (2021) used a similar approach reinforcing their composites with lignin-graphene blends. Lignin and graphene nanoplatelets were used as fillers in the preparation of acrylonitrile butadiene styrene (ABS) filaments for composite manufacturing using ME technology. Initially, lignin was isolated through the organosolv extraction method. Graphene nanoplatelets were added at different concentrations into the organoslov lignin solution to improve homogenisation in the matrix, after which the prepared solutions were oven-dried overnight. Prepared lignin-graphene blends of desired concentrations were mixed with ABS pellets and extruded into filaments for manufacturing of composites. Composites containing 5 wt % lignin and 0.5 wt% graphene nanoplatelets showed an increase in tensile strength by 29.17 % compared to identical samples printed of neat ABS. This increase was determined to stem from improved interlayer adhesion caused by lignin, and reinforcement from the graphene nanoplatelets.

In addition to mechanical properties, Domínguez-Robles et al. (2019) investigated value-added properties introduced in their composites by lignin. They reported antioxidant activity stemming from the presence of lignin, and antimicrobial activity when adding tetracycline into the composites. The printable filaments were prepared by initially coating PLA pellets with castor oil, and then coating the oily pellets with softwood kraft lignin powder. The pellets were extruded into printable filaments, and used for ME printing to manufacture meshes of different sizes. For the antioxidant activity measurement, a DPPH (2,2-diphenyl-1-picrylhydrozyl) radical was used to evaluate radical scavenging properties. Composites containing lignin reduced the content of DPPH over time, with greater reduction for composites with higher lignin content. Antimicrobial properties were evaluated by bacterial adhesion. No significant changes were observed in composites containing 1 % lignin. Addition of the antibiotic compound tetracycline reduced the bacterial adhesion sufficiently.

A novel additive manufacturing approach for lignin-based composite manufacturing was attempted by Ajdary et al. (2021), as they utilised selective laser sintering (SLS) as printing technology. To the best of our knowledge, this is the only published research where SLS has been utilised for lignin-based additive manufacturing. SLS is a similar technique to binder jetting, differing in how the powdered feedstock is joined together. Instead of a liquid binder, a laser beam irradiates the powder bed, fusing the particles together (Chen et al., 2019). Selective laser melting (SLM) is by concept identical to SLS, but instead of sintering particles, the irradiation melts them together (Chen et al., 2019; Hwa et al., 2017). In the study, up to 60 vol% of alkali lignin was mixed with polyamide 12, preheated prior to printing to 175 °C, and manufactured into desired shapes (Ajdary et al., 2021). The composites containing 60 vol% lignin increased the Young's modulus by 16 %, but decreased tensile strength by 7 %, compared to reference samples of neat polyamide. A structure of complex geometry was successfully manufactured, and it was concluded that the orientation of the printed structure plays a vital role in mechanical properties.

Although lignin-based additive manufacturing utilising SLS

Table 2
Recent studies on lignin utilisation in additive manufacturing.

Printing technology	Feedstock	Lignin source	Technical lignin	Lignin modification	lignin content	Additional components	Composite properties	Ref.
DIW	Viscoelastic paste/ink	N/A	Dealkaline lignin	None	0.1–1.0 g/mL	Zein	Biodegradability.	(Lee et al., 2021)
DIW	High viscosity ink	N/A	Dealkaline lignin	Lignin nanotubes preparation	1–9 wt%	PU	UV-light responsive shape-memory, increased tensile strength, decreased Tg.	(Wang et al., 2023)
DLP	Photo-curable resin	Oil palm empty fruit fibres	Organosolv lignin	None	0.2–3 wt%	PU, graphene nanoplatelets	Tensile strength, deformation resistance, increased hardness.	(Ibrahim et al., 2019)
DLP	Photo-curable resin	*Betula Alba* bark	Organosolv lignin	None	0–4 wt%	pTSA-PANI, HDODA, TPO, EGPEA	Decreased surface roughness, improved hardness, higher wettability, increased electrical conductivity.	(Arias-Ferreiro et al., 2022)
DLP	Photo-curable resin	Hardwood	Hot water extracted alkaline lignin	Fractionation and laccase polymerisation prior to nanoparticle preparation and surface coating.	1–5 wt%	GGMMA, LAP	Antimicrobial activity, good structural stability and printing fidelity, biocompatibility.	(Wang et al., 2022)
DLP	Photo-curable resin	Birch, spruce, wheat straw	Hot water extracted alkaline lignin	Lignin allylation	Concentration of lignin dispersion: 1 wt %	PEGDA, LAP	Improved cross-linking and printing fidelity.	(L. Wang et al., 2024)
ME	Filament	Softwood, hardwood	Kraft (SW), organosolv (HW)	None	40–60 wt% HW lignin in either ABS or nylon 12	NBR41, ABS, PA 12, CF, (NBR41 + ABS = ABL)	Improved stiffness, tensile strength, printability, conductivity, and enhanced printing speed. Reduced melt viscosity.	(Nguyen et al., 2018)
ME	Filament	*Pinus radiata* softwood	HTMP extracted and enzymatically saccharificated 'biorefinery lignin'	None	10–50 wt%	PHB	Improved layer adhesion, reduced warpage.	(Vaidya et al., 2019)
ME	Filament	Pine, beech	Kraft (pine), organosolv, lignosulphonate	None	5–15 wt%	PLA	Increased impact strength, thermal resistance, flexural strength.	(Mimini et al., 2019)
ME	Filament	Hardwood	Organosolv lignin	None	5–20 wt%	PLA, PEG, struktol TR451	Increased tensile strength and elongation, improved printability, and increased layer adhesion.	(Wasti et al., 2021)
ME	Filament	Oil palm empty fruit fibres	Organosolv lignin	None	1–15 wt%	ABS, graphene nanoplatelets	Improved tensile stress and interlayer adhesion, increased surface roughness and water contact angle.	(Mohan et al., 2021)
ME	Filament	Softwood	Kraft lignin	None	0–3 wt%	PLA, castor oil, tetracycline	Antioxidant and antimicrobial activity.	(Domínguez-Robles et al., 2019)
ME	Filament	N/A	Alkali lignin	Microwave hydrophobisation	10–50 wt%	PLA	Improved compatibility, thermal stability and thermoplasticity. Antioxidant activity.	(Yao et al., 2021)
ME	Filament	Corn cob	Enzymatic lignin	None	0–50 wt%	TPU, CF	Increased tensile strength, elongation at break, and layer adhesion.	(Zhou et al., 2022)
ME	Filament	N/A	Biolignin (TM)	None	0.5–3.5 %	PBS, Ag, ZnO	Improved printing quality and dynamic moduli. Antioxidant and antimicrobial activity.	(Abdullah et al., 2022)
ME	Filament	N/A	N/A	Preparation of microspheres by a	0–0.75 wt%	PLA	Improved tensile strength, bending	(Hu et al., 2022)

(*continued on next page*)

Table 2 (*continued*)

Printing technology	Feedstock	Lignin source	Technical lignin	Lignin modification	lignin content	Additional components	Composite properties	Ref.
				solvent-anti-solvent method			strength, and impact strength.	
ME	Filament	N/A	Kraft lignin	None	20 wt%	Synthesized liquid crystalline elastomer (LCE), TPU	Thermomechanical shape-memory, enhanced melt flow index.	(Prathumrat et al., 2023)
ME	Filament	N/A	Enzymatic hydrolysis lignin	None	Up to 50 wt%	PLA, ATBC, TBC	Increased elongation, toughness, layer adhesion, and printability.	(Ren et al., 2023)
ME	Filament	N/A	Kraft lignin	Lignin & 2-ethyl-hexyl acrylate copolymerisation	2.5–15 wt%	PLA	Improved interfacial compatibility and weld energy, enhanced toughness and impact energy.	(Ding et al., 2023)
ME	Filament	N/A	Alkali lignin	Synthesising of lignin-g-maleic anhydride (LM) for LM-PLA copolymerisation	10–20 % + 3–5 % LMP	Maleic anhydride, BPO, PEG, PLA	Enhanced tensile strength, elongation, and toughness. Improved compatibility and layer adhesion. Antioxidant activity.	(Ye et al., 2023)
ME	Filament	Hardwood	Organosolv lignin	Demethylation	5–10 %	PA 12	Improved interfacial interaction, tensile strength, Young's modulus. Good anti-aging performance.	(Zhang et al., 2024)
SLA	Resin	N/A	Lignin-coated cellulose nanocrystals	None	0–1 % L-CNC containing 3–6 wt% lignin	Methacrylate resin containing monomer, oligomer and photoinitiator	Enhanced tensile strength, modulus and thermal stability.	(Feng et al., 2017)
SLA	Resin	Softwood	Kraft lignin	Purification step	0.2–1.0 wt%	Methacrylate resin	Increased tensile strength and Young's modulus.	(Zhang et al., 2019)
SLS	Powder	N/A	Alkali lignin	None	40 wt%	PA 12	Decreased degradation and tensile strength. Increased stiffness.	(Ajdary et al., 2021)

technology seemingly has been studied in only one research, multiple different thermoplastic materials have been processed into composites with this technology. In addition to polyamide (PA) 12, which has been used in several studies (Jing et al., 2017; R. Li et al., 2019; Zhao et al., 2018), examples of different plastics that have been utilised or characterised for SLS printing are PA 11 & 6 (Verbelen et al., 2016), polyurethane (PU) (Gan et al., 2019; Ouyang et al., 2022; Zhuang et al., 2020), polyether ether ketone (PEEK) (Chavez et al., 2022; Roskies et al., 2016; Shuai et al., 2016), styrene ethylene butylene styrene (SEBS) (He et al., 2021), polypropylene (PP) (Fang et al., 2019; He et al., 2021; Zhu et al., 2015), phenol formaldehyde (PF) resin (Z. Li et al., 2019; Wu et al., 2023), poly(ethylene terephthalate) (PET) (Bashir et al., 2018; Gu et al., 2019), PLA (Gayer et al., 2019; Xu et al., 2023; Yan et al., 2020), and polycaprolactone (PCL) (Chen et al., 2014; Du et al., 2015; D. Li et al., 2023).

Lee et al. (2021) developed an extrudable lignin and zein containing bioink for DIW printing. The use of plant-based substances enables complete degradation of the composites to their molecular subunits when released into the environment. The ink was prepared by dissolving zein powder in ethanol and water by sonication, after which dealkaline lignin granules were added to the mixture, which was further sonicated to obtain the ink. Printed structures self-cured through drying as the zein polymer precipitated onto the lignin granules, resulting in a rigid structure. Holders, caps, and circuit boards with attached electronic components were successfully printed with the zein-lignin bioink. Increased concentrations of lignin in the composites were reported to increase tensile strength.

In contrast to most of the research on additive manufacturing of lignin-based composites, which focuses on enhancing mechanical properties, Yao et al. (2021) found a modification approach to improve compatibility between PLA and lignin, allowing high contents of lignin incorporation in the manufactured composites. By a solvent- and catalyst-free microwave-assisted esterification process, the hydrophobicity and compatibility of alkali lignin with PLA were significantly enhanced. Acetylated and hexanoated lignin was produced with the aid of acetic anhydride and hexanoic anhydride as reagents. Yields of modified lignin varied between 31 % and 81 %, with acetylated lignin increasing the yield. A 1:5 lignin to anhydride weight ratio was added to a pressure sealable vessel and subjected to microwave irradiation. After the reaction, water and methanol were used to precipitate the modified lignin product, followed by stirring for 24 h. After stirring, the product was obtained through suction filtration, washed to remove unreacted anhydride, and dried for 48 h in a vacuum oven. The modified lignin was then blended in an extruder together with dried and shredded PLA to obtain printable filaments for additive manufacturing. The esterification process allowed incorporation of up to 50 wt% of lignin in the composites while still maintaining good printability. 50:50 lignin-PLA composites sustained mechanical properties in the same range as neat PLA with only a slight decrease. Additionally, the acetylated lignin showed improved UV-shielding and antioxidant properties.

Lignin extracted through organosolv fractionation with acetic acid and hydrochloric acid as solvents was used in the work by Arias-Ferreiro et al. (2022) as a filler in the manufacturing of photocurable conductive composites. Para-toluene sulphonic acid (pTSA) polymerised with polyaniline (PANI) and lignin was incorporated as fillers in a resin containing ethylene glycol phenyl ether acrylate as a monomer, 1,

6-hexanediol diacrylate as a crosslinker, and diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide as a photoinitiator. Synthesis of pTSA-PANI was performed by adapting an emulsion polymerisation method described in the work by Dopico-García et al. (2014), but with pTSA as a dopant instead of dodecyl benzenesulphonic acid. The obtained feedstock was a photo-curable resin with pTSA-PANI and varying concentrations of lignin as fillers, which was used to manufacture composites with a DLP printer. Incorporation of lignin in the composites improved dispersion of the conductive filler, reduced surface roughness, and increased the conductivity by an order of magnitude.

Zhou et al. (2022) introduced thermoplastic polyurethane (TPU) to regulate the rheological properties of enzymatic lignin for ME printing. Additionally, carbon fibres were added to the composites to enhance mechanical properties of the printed structures. For the preparation of composite feedstock, lignin and TPU were oven-dried overnight, mixed with reinforcing carbon fibre, melt-blended in a twin extruder, and ground to pellets. The pellets were further extruded in a single screw extruder to obtain printable filaments. Printable filaments with up to 50 wt% of lignin were achieved, and with the addition of 0.5 wt% of carbon fibre in the composites the mechanical properties were significantly enhanced. Tensile strength increased by 67 % and elongation at break by 138 %, compared to composites without carbon fibre. The addition also densified the structures and enhanced bonding.

Development of nanocoated lignin-based composites with antioxidant and antimicrobial properties for potential biomedical applications was performed by Abdullah et al. (2022). A homogeneous mixture of lignin and polybutylene succinate (PBS) was obtained through a solvent-casting method, initiated by dispersing lignin in chloroform by sonication. PBS pellets were added to the dispersion under continuous stirring until the pellets completely dissolved. The solution was cast by evaporation and pelletised for the manufacturing of filaments by extrusion. The presence of lignin promoted printing quality, dynamic moduli, and antioxidant activity of PBS in the ME manufactured structures. Antimicrobial properties were further enhanced by applying a nanocoating of silver oxide, zinc oxide, or both on the surface of the printed structures. Composites with the highest concentration of lignin and coated with both silver and zinc oxide showed antimicrobial activity against up to five different microorganisms.

Hu et al. (2022) reinforced PLA with lignin microspheres for ME manufacturing. The microspheres were prepared by completely dissolving lignin in either methanol, ethanol, or n-propanol, after which deionised water was slowly added and the mixture was stirred at a constant temperature to evaporate the solvent. After solvent evaporation, the mixture was centrifuged, ultrasonically dispersed, and freeze-dried to obtain the lignin microspheres. The optimal solvent was determined to be n-propanol with an evaporation temperature of 60 °C, resulting in microspheres with a particle size distribution between 800 and 1000 nm. Blending of PLA and solvent-anti-solvent modified lignin was done with a twin-screw extruder. The batch was then dried before extruding ME printable filaments from it. The n-propanol modified lignin/PLA composites with 0.375 wt% of lignin content showed improved mechanical strength, glossiness, and printing accuracy. Tensile strength was increased by 49.8 %, bending strength by 25 %, and impact strength by 112.64 % compared to neat PLA.

Prathumrat et al. (2023) applied ME printing to manufacture shape memory liquid crystalline thermoplastic elastomeric composites containing lignin and thermoplastic polyurethane. Initially, liquid crystalline elastomer (LCE) was synthesised by dissolving RM257 monomers in toluene and adding PETMP, a crosslinking agent, and DPA, a catalyst, to the mixture. The mixture cured at room temperature through polymerisation and was further mixed with polyurethane in a batch mixture at 190 °C to obtain the liquid crystalline thermoplastic elastomers (LCTPE). Kraft lignin was added towards the end of the mixing process to obtain the LCTPE/lignin composite material, containing a 40:40:20 mass ratio of LCE, TPU, and lignin, respectively. Printable filaments of both LCTPE and LCTPE/lignin were produced by a single-screw extruder to utilise in ME printing. A shape memory behaviour was observed for the printed structures of both LCTPE and LCTPE/lignin composites, which were able to return to their original shape after temporarily reshaping them. Additionally, since the addition of lignin into the composites enhanced processability of the material, it was concluded that lignin incorporation can enhance processability and printability of shape memory materials for different industrial and engineering applications.

In the study by Ren et al. (2023), two different plasticisers, namely acetyl tributyl citrate (ATBC) and tributyl citrate (TBC), were utilised to reduce the brittleness of PLA and enable higher loadings of enzymatic hydrolysis lignin. Different compositions of the components were prepared into ME printable filaments, including filaments of pure PLA, PLA/lignin filaments containing no plasticiser, and PLA/lignin filaments containing either ATBC or TBC. Printed structures lacking plasticisers became more fragile with the addition of lignin due to poor compatibility between PLA and lignin, while plasticiser-containing structures, especially ATBC-containing structures, lowered the T_g of PLA and made processing easier by enhancing molecular mobility of the PLA. ATBC-containing structures showed better thermal stability than those containing TBC as plasticiser. The utilisation of ATBC as a plasticiser in the composites allowed up to 50 wt% of lignin to be incorporated in the structures while still maintaining proper toughness and good elongation at break. Additionally, these structures showed a shape memory behaviour and a light-responsive shape memory when reshaped and exposed to heat and laser illumination, respectively.

Another study that evaluated shape memory behaviour of lignin-based composites was done by Wang et al. (2023). Instead of PLA, they used polyurethane for its great flexibility, shape memory ability, and biocompatibility, and mixed it with synthesised lignin nanotubes as a UV-absorbent. The preparation of lignin nanotubes was performed by dissolving 5 wt% of dealkalised lignin in a 20 % tetrahydrofuran aqueous solution. Into the mixture, 0.1 mol/L NaCl electrolyte was added, after which the solution was dialysed for 48 h. By freeze-drying, the lignin nanotubes were acquired. The DIW printable ink was prepared by initially dissolving polyurethane in dimethyl sulphoxide (DMSO) to obtain a solution containing 34 wt% of polyurethane. The solution was then mixed with lignin nanotubes by planetary stirring and inserted into a syringe, which underwent centrifugal defoaming treatment prior to printing. The printed structures were post-treated by soaking them in absolute ethanol to remove the DMSO, and then placed in a freeze-dryer to obtain the polyurethane/lignin nanotube composites. Different lignin nanotube contents between 1 and 9 wt% were tested, of which composites of 5 wt% increased the tensile strength of the composites by 131 % compared to neat polyurethane. The increase in lignin content simultaneously decreased the T_g, making processability of the feedstock easier. UV-stimulated shape memory tests were performed on the composites by irradiating them with UV-light and bending them into a temporary “U”-formed shape. By removing the UV-light, the structures hardened and stayed in the U-shape without external forces applied. By then irradiating the structure again, the shape memory recovery began, and the process was evaluated. It was concluded that composites containing lignin nanotubes recovered almost completely during 15 min of UV irradiation, while structures of pure polyurethane showed poor recovery.

To overcome compatibility issues between PLA and lignin, Ding et al. (2023) modified kraft lignin to improve the compatibility, layer adhesion, and molecular mobility of ME printed PLA/lignin composites. Modified “e-lignin” by copolymerising ethylhexyl acrylate monomers onto lignin was obtained by initially dissolving NaCl in DMSO and then adding the kraft lignin to dissolve in the mixture. When dissolved, 2-ethylhexyl acrylate (EHA) and hydrogen peroxide (H_2O_2) were added to the solution and left under stirring for 24 h. The mixture was then poured into hydrochloric acid (HCL), filtered, washed with methanol, and set to dry to obtain the e-lignin. Printable filaments were prepared by mixing different contents of the modified lignin with PLA pellets, and printed

structures of the different filaments were evaluated. It was concluded that the copolymerised e-lignin improved interfacial compatibility with PLA and enhanced toughness of the composites. Composites containing 10 wt% of e-lignin increased both impact energy and toughness of the printed composites by 200 %, compared to pure PLA. Additionally, layer adhesion showed improvements with an increased weld energy of approximately 138 %.

Another approach towards compatibility enhancement between PLA and lignin by modification was studied by Ye et al. (2023), where lignin-g-maleic anhydride-g-PLA (LMP) was prepared to act as a compatibilizer in lignin/PLA composites. The modification process began by mixing alkali lignin in deionised water and adding 1 mol/L NaOH solution to the mixture until reaching a pH of 12. After centrifugation of the solution, 1 mol/L HCl solution was added to the lignin mixture until reaching a pH of 2, precipitating the lignin. The lignin precipitate was centrifuged and dialysed to neutral before dispersing it in dimethyl formaldehyde (DMF) and adding maleic anhydride to the solution. The solution was further washed with water, centrifuged, and dried to obtain lignin-g-maleic anhydride (LM). Copolymerisation of LM and PLA was performed with the aid of dibenzoyl peroxide (BPO) as an initiator by manually blending all the components in a self-sealing bag. The presence of BPO initiated copolymerisation between PLA and LM through "grafting onto" polymerisation, resulting in the modified LMP compatibilizer. The compatibilizer was then utilised in blends of PLA and lignin of different contents to produce ME printable filaments. Although tensile strength of lignin/LMP/PLA composites was lower than that of pure PLA, they exceeded PLA in elongation at break and toughness in composites containing PLA and 20 % lignin, and an additional 5 wt% of LMP. Enhanced compatibility of these composites was also achieved. Additionally, the printed composites of optimised component concentrations showed great antioxidant properties with a radical scavenging rate of up to 91 %, and a temperature-dependent shape memory behaviour.

Zhang et al. (2024) applied a demethylation method to hardwood organosolv lignin in their study to increase the concentration of phenolic hydroxyl groups in the lignin structure, and thus enhance adhesion and compatibility between PA12 and the modified lignin. Demethylation of lignin was performed by dissolving lithium bromide in deionised water in a three-neck flask and adding the organosolv lignin to the solution. Subsequently, hydrobromic acid was added, and the mixture was stirred for 4 h at 100 °C. After the reaction, the temperature was decreased to room temperature by immersing the flask in an ice bath, followed by vacuum filtration. The obtained lignin was then washed properly to neutralise the pH, freeze-dried, and lastly oven-dried in a vacuum oven overnight. Filaments of both modified and unmodified lignin with PA12 pellets were prepared by blending the components and extruding filaments with a twin-screw extruder. The obtained filaments were pelletised and extruded again to ensure proper dispersion of lignin in the polymeric matrix. It was concluded that the interfacial adhesion in the composites was enhanced by the modification of lignin, and both tensile strength and Young's modulus improved, compared to neat PA12. These composites also showed good anti-aging properties when subjected to elevated temperatures of 140 °C for 100 h, maintaining approximately the same tensile strength as before.

In the study by Wang et al. (2022), lignin was fractionated, modified, and surface-embedded with silver nanoparticles to be utilised as a high-performance antimicrobial reagent in a photo-crosslinkable polymeric matrix resin. In addition to the usage of a wood-based component as the antimicrobial reagent, the fabricated polymeric matrix was also wood-based, containing methacrylated *O*-acetyl galactoglucomannan (GGMMA). For the preparation of the hybrid silver-lignin nanospheres, purified lignin was initially fractionated by a sequential three-step solvent fractionation using isopropanol, ethanol, and methanol as solvents. The fractions were then polymerised by laccase and formed into nanospheres by a solvent shifting method prior to synthesising the silver-lignin nanospheres. The final step of surface-embedding the lignin nanospheres with silver was performed by mixing a silver ammonia solution with dispersed lignin nanospheres, which was then kept in an orbital shaker at 30 °C and 200 rpm for 4 h. The silver coated lignin nanospheres were then collected by centrifugation and purified. The final polymeric resin was prepared by mixing dispersed lignin-silver nanospheres with a photoinitiator and dry GGMMA powder, which was then additively manufactured into desired three-dimensional objects using DLP printing technology. It was found that the incorporation of lignin-silver nanospheres in the polymeric matrix improved structural stability and both lateral and axial printing fidelity. Additionally, the synthesised resin showed bactericidal ability suitable for biomedical applications.

The DLP printing technology was also utilised in another study by L. Wang et al. (2024) to additively manufacture lignin-based honeycomb hydrogel scaffolds. In this study, lignin from three different sources was used to evaluate their suitability as a component in a photo-curable bio-based resin, namely spruce, birch, and wheat straw lignin. Each lignin type was modified by grafting allyl glycidyl ether (AGE) onto the lignins, followed by dialysis to remove unreacted reactants. The obtained reaction products were lignin dendritic colloidal microparticles (lignin-DCMs). Each lignin-DCM type was further mixed with poly (ethylene glycol) diacrylate (PEGDA) and lithium phenyl-2,4,6-trimethylbenzoylphosphinate (LAP) using a vortex to obtain a homogeneous resin. It was concluded that the incorporation of lignin-DCMs reduced light penetration depth and enhanced crosslinking through free-radical reactivity and photo-absorption. As a result, the incorporation of lignin-DCMs in the PEG hydrogel improved the printing fidelity.

3.2. *Challenges and potential strategies*

The utilisation of lignin in various AM technologies is a trending topic within the scientific community. However, the process is not as straightforward as it may seem due to the complexity of the biopolymer. Similar challenges to those identified already in the early stages of lignin research, particularly in developing thermoplastic and thermosetting systems through polymer blending or modifications, are also present in AM-related lignin research today (Ebers et al., 2021). This stems from the structural diversity of different lignin types and the variations of extracts from different extraction methods and isolation protocols (Glasser, 2019). However, there is a slight misconception regarding the complexity of lignin. Industrial-scale isolation protocols are conducted under consistent and invariable conditions, producing uniform and unchanged lignin extracts. The extracts differ from one pulp mill to another but remains unchanged when produced following the same invariable delignification protocol. This underscores the importance of selecting a suitable type of lignin, extracted in a specific manner, for the intended application as the first step to overcome material-related challenges.

The structural variations among different lignin types and extracts lead to distinct structural characteristics, as well as differences in viscoelastic and physicochemical properties (Ebers et al., 2021). While some of these features may be desirable for certain AM technologies, others may cause processability complications. For instance, AM technologies that operate by melting the feedstock rely on heat-induced flowability properties, while vat photopolymerisation technologies would face failure if the photo-curable resin started developing phase separation. Furthermore, some of the technologies that operate with powders as feedstock relies heavily on the powder particle size, thermal behaviour, and flowability (Kusoglu et al., 2021), while the rheological properties are the most important for direct ink writing (del-Mazo-Barbara and Ginebra, 2021; Zhang et al., 2022). Common to all AM technologies regarding the processing of lignin-based composites is that the miscibility, such as compatibility or solubility between the different components of the feedstock, must be sufficient (Ebers et al., 2021).

The great variability of lignin naturally results in inconsistencies in

material properties. AM technologies rely heavily on the consistent quality of the feedstock, which means that inconsistencies in the printed material can cause issues during the printing process. Another crucial aspect of the printing process is achieving sufficient layer adhesion. Commercially available feedstock has been engineered to avoid such delamination, but the incorporation of lignin into these kinds of materials may decrease the interlayer adhesion. Additionally, different AM technologies process the feedstock in different ways, some by heat-inducing, others by photopolymerisation, binding, extruding, etc. Thus, the material processing during the printing process may entail miscibility, structural deviation, or irreversible reactions of the feedstock. This could, for instance, be phase separation of the feedstock components in photopolymerisation-based processes, or thermal degradation in heat-inducing AM processes.

To successfully overcome the challenges related to AM processing of lignin-based materials, the correlation between the feedstock and the used AM technology must be thoroughly evaluated and optimised. This is where chemical modification or fractionation of lignin comes in handy, as the feedstock can be fine-tuned to meet the requirements of the used AM technology and resolve miscibility issues between the feedstock components. For instance, through esterification, reactive carboxylic groups can be introduced to the lignin structure, improving its compatibility with PLA (Hong et al., 2021). Additionally, phenolation of lignin has also been shown to improve the compatibility between lignin and PLA (Frasca et al., 2024). Furthermore, fractionation of lignin yields low molecular weight fractions that are highly reactive, which was utilised in a study by Yang et al. (2024) where a combination of ethanol fractionation and grafting of long-chain alkenes and photosensitive group double bonds to the lignin structure was performed to obtain urethane acrylated lignosulphonate (UALS). The modification enhanced solubility of the UALS in 4-acryloylmorpholine (ACMO) used as a reactive diluent, and imparted photosensitivity to the lignin. Thus, improved compatibility for vat photopolymerisation processing of the lignin was achieved. In general, research suggests that various lignin modifications not only enhance specific properties of the manufactured composite, but also enable greater amounts of the polymer to be dispersed within the respective matrices (Ebers et al., 2021).

Currently, heat-induced AM technologies, especially ME-based technologies, are the most used for lignin-based materials. These technologies, which thermally melt the material, could cause degradation of the feedstock. However, the thermal degradation temperature interval for lignin is often higher than the temperature at which these AM technologies operate. For instance, thermal degradation of a few lignin types was evaluated in a study by Bartkowiak and Zakrzewski (2004), in which they concluded that the dynamic thermal degradation interval of lignin is between 350 and 450 °C. Simultaneously, it should be noted that a few of the samples tested showed a thermal degradation interval starting below the typical operating temperature of ME printers, highlighting the importance of analysing and choosing a suitable type of lignin for the intended AM technology.

For the manufacturing of biocomposites, lignin can be used, for instance, as a filler material, copolymer, compatibilizer, nucleating agent, or coupling agent (Sethupathy et al., 2022). However, the utilisation of native lignin typically decreases the mechanical strength and reactivity of composites due to factors such as low solubility, instability to UV-radiation, high glass transition temperature, and high polydispersity. Once again, the importance of selecting a suitable type of lignin extract for the intended application is crucial to ensure proper compatibility. Furthermore, it has been established that these issues can be resolved by various functionalisation, modification, or depolymerisation techniques, but on a larger scale this complicates its utilisation. This highlights the importance of lignin research in developing cost-effective and scalable solutions, as this may contribute to the optimisation of the future concepts for biorefineries, tailored to overcome the multiple requirements in AM of lignin-based composites.

4. Conclusion and future outlook

The importance of additive manufacturing is continuously increasing in various fields of the society. Simultaneously, the need for renewable, greener, and sustainable alternatives to substitute fossil fuel derived materials is constantly increasing. Lignin has recently emerged as a promising candidate to substitute petroleum-based materials due to its non-toxicity, renewability, abundancy, and biological activity. Although the availability of lignin is high and the costs are reasonably low, the complexity of this biopolymer still hinders its usability to a larger extent. To overcome these issues, especially the ones related to additive manufacturing of lignin-based composites, such as poor miscibility, compatibility, printability, and acquiring proper mechanical or chemical properties in the final lignin-based products, source of lignin, extraction method, and possible modifications must be considered and chosen accordingly. Shifting towards greener and renewable fossil fuel substituents promotes circular economy principles, where lignin as a typical by-product waste material could be utilised in value-added applications of biomass derived materials with reduced environmental impacts, enhancing sustainability of supply chains.

The greatest concern hindering the applicability of lignin stems from the great variability and complexity in its composition and structure, which differs substantially depending on source, extraction method, and processing technique. As a result, chemical and mechanical properties changes, obstructing the usage of lignin as such in certain applications. Regarding additive manufacturing, consistency in printability, quality, and both mechanical and chemical performance is therefore difficult to achieve, as the consistency of the feedstock varies. However, in smaller quantities, mainly with the aim of targeting certain properties or property enhancements, lignin opens great opportunities by altering the composition of the polymer by different modifications or functionalisation. When larger quantities are desired, the essential modification approaches required are aimed to enhance compatibility between lignin and additional components, such as different thermoplastics, for the manufacturing of lignin-based composites.

Despite the drawbacks of consistency when utilising lignin, the future of lignin valorisation in AM looks bright as research is continuously conducted to enable the possibilities it entails. Since the potential of lignin was recognised, rapid developments and advances in extraction technologies and processes has been made to produce technical lignin with improved purity and tailored properties for targeted applications. Additionally, an increased interest towards lignin in the research community promotes continuous development in modification and functionalisation approaches to eventually industrialise lignin in various fields. As presented in Table 2, lignin-based composite manufacturing by AM has mainly been done with the ME technology, but the trend seems to be shifting towards utilisation of different AM technologies to expand the usage area of this biopolymer. As in the case of variety in composition and structure of lignin, different AM technologies offer a broad variety of processing opportunities for a great range of materials and feedstock of different states. Thus, future research on lignin utilisation in different AM technologies is essential to reveal the full potential of lignin, shifting the current ME oriented focus towards a broader application spectrum.

CRediT authorship contribution statement

Valter Georgs: Writing – review & editing, Writing – original draft, Conceptualization. **Heidi Piili:** Writing – review & editing. **Jan Gustafsson:** Writing – review & editing, Supervision, Conceptualization. **Chunlin Xu:** Writing – review & editing, Supervision, Conceptualization.

Declaration 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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Data availability

Data will be made available on request.

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