

# DeMANS: Design and manufacture of sustainable materials for additive manufacturing technologies

## Deliverable Report

### WP1: Material Selection and Pre-Processing

Deliverable D1.1 Report on perspectives of AM of biopolymers and sustainable solutions:

“Novel biopolymers derived from lignocellulosic biomass of potential additive manufacturing”

<b>Contributing Author(s)</b>	Anuj Kumar (LUKE), Risto Korpinen (LUKE), Michael Morris (TCD)
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## Version Control and History

Version	Date	Status and Description of Changes	Distribution
1.0	31 May 2022	Final Release Version	[PU]

## List of Abbreviations

<b>ABS</b>	Acrylonitrile butadiene styrene
<b>Ac-CW</b>	Acetylated Cell Walls
<b>AcOH</b>	Acetic Acid
<b>AM</b>	Additive manufacturing
<b>CEL</b>	Cellulolytic Enzyme Lignin
<b>CTs</b>	Condensed tannins
<b>DSC</b>	Differential Scanning Calorimetry
<b>EMAL</b>	Enzymatic Mild Acidolysis Lignin
<b>ETs</b>	Ellagitannins
<b>GTs</b>	Gallotannins
<b>HTs</b>	Hydrolysable tannins
<b>LCCs</b>	Lignin-carbohydrates complexes
<b>MAE</b>	Microwave Assisted Extraction
<b>MAL</b>	Mild Acidolysis Lignin
<b>MWEL</b>	Milled Wood Enzymatic Lignin
<b>MWL</b>	Milled Wood Lignin
<b>PLA</b>	Poly (lactic acid)
<b>PLE</b>	Pressurized Liquid Extraction
<b>RCEL</b>	Regenerated Cellulolytic Enzyme Lignin
<b>SCE</b>	Super Critical Extraction
<b>SFAs</b>	Suberin fatty acids
<b>SLE</b>	Solid-Liquid Extraction
<b>T<sub>g</sub></b>	Glass Transition Temperature
<b>UAE</b>	Ultrasonic-Assisted Extraction
<b>WE</b>	Water Extract

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## **Novel biopolymers derived from lignocellulosic biomass of potential additive manufacturing**

### **1. Introduction**

Additive manufacturing (AM), also known as three-dimensional (3D) printing became the leading manufacturing techniques to produce the wide range of tailored object geometries additively by depositing materials layer-by-layer [1]. AM techniques are becoming an important tool in producing materials and composites for wide range of areas , such as energy, biotechnology, medical devices and electronic goods etc. [2,3]. AM provides various advantages over the traditional methods (milling, casting, forging or welding processes), such as low consumables, control over object geometry, cost-effectiveness and rapid on-demand fabrication; further AM provide a high degree of automation and reproducibility to fabricate objects with complex structures [4].

Currently, different feedstocks for AM, such as polymers, composites, metals, ceramic, gypsum, sand and wax are being developed in various applications. Among them, polymers, such as acrylonitrile butadiene styrene (ABS) and polylactic acid (PLA) have been widely utilized as 3D printing materials [5,6]. There is an urgent need to reduce reliance on fossil fuel derived plastics. Many of the polymers used in AM (including PLA, ABS and the nylons) cannot be recycled due to additives within them as well as not being thermoplastic in nature and cross-linking that can occur during thermal processing; developing more sustainable and circular material approaches is an imperative. This international and intersectoral project has the ambitious goal of world-class innovation in the design and additive manufacture (AM) of parts, components and devices using sustainable (bio)polymer materials.

Various types of biobased polymers or materials have been used in AM, however most of them have been mixed with a fossil fuel derived plastic-based component via extrusion process to prepare the hybrid biobased polymer and plastic molecules. A recent material being heavily studied for 3D printing is cellulose, which is the most abundant natural polymer in nature, and a most potential candidate for 3D printing [7]. Traditionally, hemicellulose and lignin, as the other two main components of plant resources after cellulose, have a strong appeal for the preparation of 3D printing bio-feedstocks due to their environmental friendliness [8]. However, in this report we considered several other wood-derived biopolymers those are still underutilized in 3D printing along with lignin. Among them tannins, suberin fatty acids, lignin-carbohydrates complex's (LCCs), all these have tremendous potential to use in AM.

## 2. Novel biopolymeric materials and their properties

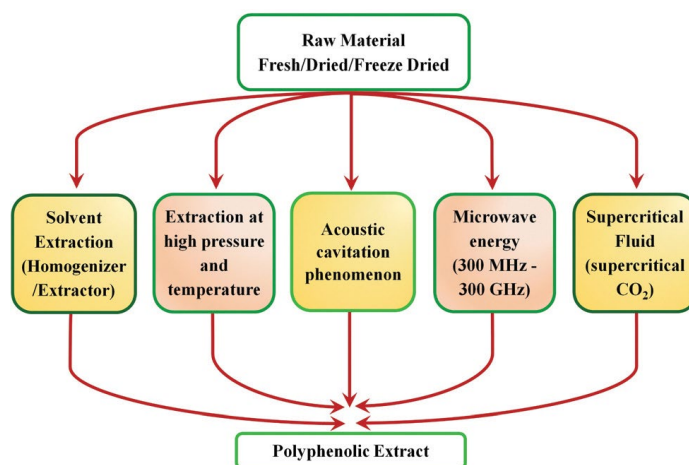
### 2.1 Tannins

Tannins are typically defined as water-soluble phenolic compounds that are able to bind and precipitate proteins and other macromolecules within aqueous solutions. Additionally, tannins are known to bind metals and to form, for example, blue to black complexes with iron(III)salts, and have molecular masses between 500 and 3000  $\text{gmol}^{-1}$  [9]. Tannins are the fourth most abundant form of terrestrial biomass extracted compounds right after cellulose, hemicellulose, and lignin [10]. Tannin is a plant-based highly reactive polyphenolic and it is the most prevalent source of natural aromatic macromolecules after lignin with a global industrial production of over 160,000 tons/year [11]. Tannins are considered polyphenols with high molecular weights. Thus, they possess typical features of the polyphenols group, but not only that. The presence of multiple functional groups in the chemical structure of tannins, such as hydroxyls, provides them with the ability to create bonds to reach a stable cross-linked association within different molecules, such as proteins or carbohydrates. This unique characteristic lets them be differentiated from the common group of polyphenols [12] [13].

According, the arrangement of their polyphenol groups, tannins are divided into two main groupings, hydrolysable tannin, and condensed tannin. However, the chemical reclassification and sources of extraction further divided tannins into five main categories; Gallotannins, ellagitannins, complex tannins, condensed tannins, and phlorotannins. Hydrolysable tannin, and condensed tannin are derived from higher plants mainly from hardwood species and these both types of tannin are produced and used commercially. So, in this report, we are explaining their important properties and potential application in additive manufacturing.

#### 2.1.1 Extractions of Tannins

The raw material is subjected to various extraction methods to obtain a polyphenolic extract as the product: solvent extraction (solid–liquid extraction, SLE), extraction at high temperature and pressure (pressurized liquid extraction, PLE), acoustic cavitation phenomenon (ultrasonic-assisted extraction, UAE), microwave energy (microwave assisted extraction, MAE), and supercritical fluid (super critical extraction, SCE).



**Fig. 1:** Schematic illustration of the different extraction methods. [14].

### 2.1.2 Hydrolysable tannins (HTs)

The hydrolysable tannin family perhaps is the most fascinating group of tannins, since they show both structural simplicity and complexity within both monomeric and oligomeric form. The HTs are secondary metabolites characterized by water solubility and molecular masses between 500 and 5000 Dalton; they give the usual phenolic reaction and precipitate alkaloids and proteins [15]. In regard, to chemical structures, HTs are multiple esters of gallic acid with glucose and products of their oxidative reactions. HTs are first divided into three subclasses such as simple gallic acid derivatives, gallotannins (GTs) and ellagitannins (ETs). Simple gallic acid derivatives contain five or less galloyl groups (Fig. 2) that are most commonly esterified to either glucose (monogalloyl and pentagalloyl glucoses) or quinic acid (monogalloyl quinic acid). Table 1 shows the important properties of HTs.

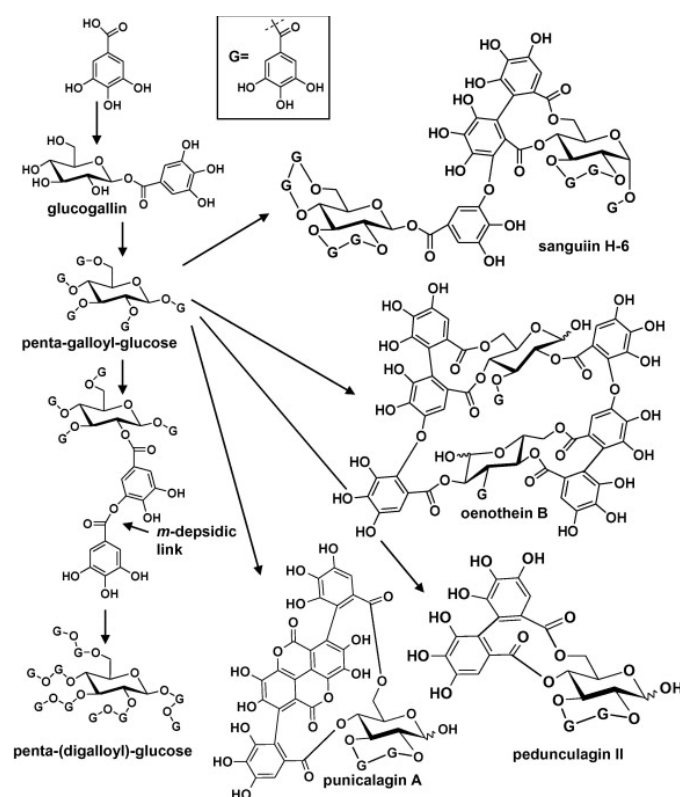


Fig. 2: Structures of Hydrolyzable Tannins [15]

### Properties of HTs

Table 1: Showing the important properties of HTs

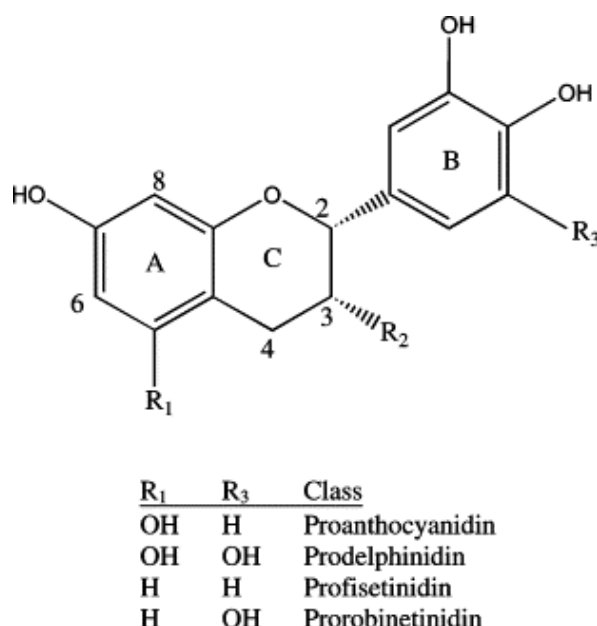
Name of HTs	Molecular formula	Molecular weight	Melting point	Solvents
Gallic acid	C <sub>7</sub> H <sub>6</sub> O <sub>5</sub>	170.12	258 to 265 °C	
Quinic acid	C <sub>7</sub> H <sub>12</sub> O <sub>6</sub>	192.7		
Gallotannin or tannic acid	C <sub>76</sub> H <sub>52</sub> O <sub>46</sub>	1701.2	200 °C	alcohol, acetone

## Current state of use of HTs in AM

The majority of HTs provide antibacterial, antiviral, anticancer and antifungal behaviour, and have proven useful in HIV treatment also [16]. So, HTs have proved to be significantly useful in biomedical and food applications. HTs have been only rarely used in AM except few recent studies. Zhu et al. 2021 [17] reported the preparation of high-performance 3D printing UV-curable resins derived from soybean oil and gallic acid. Tannic acid could provide the mussel-inspired polyphenol chemistry as well as the demand for low-cost analogues to polydopamine in adhesive design, it become a research focus because of its wide availability, health benefits and special chemical properties. As a natural building block, tannic acid could be used as a crosslinker either supramolecularly or chemically, ensuring versatile functional polymeric networks for various applications [18]. Because of all the excellent biopolymeric properties, HTs might be a suitable candidate for 3D printing materials intended for biomedical applications i.e., bone tissue engineering, drug delivery, and even in biomedical instruments also due to their anti-inflammatory nature. This may be particularly useful in AM because it combines individual design (e.g., for tissue and bone repair) with highly beneficial properties.

### 2.1.2 Condensed tannins (CTs)

Condensed tannins are polyphenolic compounds synthesized by plants in the phenylpropanoid pathway [19]. Condensed tannins have been defined as astringent, high molecular weight polyphenolic compounds that characteristically bind and precipitate proteins [20] as well as other organic compounds such as carbohydrates and minerals. Condensed tannins are characterized based on hydroxylation pattern, stereochemistry, functional groups and interflavan linkages [19,21]. They are called proanthocyanidins as they yield anthocyanidins when depolymerized under oxidative conditions. Different types of condensed tannins exist, such as the procyanidins, propelargonidins, prodelphinidins, profisetinidins, proteracacinidins, proguibourtinidins or prorobinetidins. All the above are formed from flavan-3-ols, but flavan-3,4-diols, called (leucoanthocyanidin) also form condensed tannin oligomers



**Fig. 3:** The basic repeating unit in condensed tannins. If,  $R_1=R_2=OH$ ,  $R_3=H$  then the structure is that for (-)-epicatechin. The groups at R1 and R3 for other compounds are indicated below the structure.  $R_2=O$ -galloyl in the catechin gallates. [22]

## Properties of CTs

In general, CTs are low-density amorphous non-crystalline pale yellow-slightly brown solid oligomer/polymers. Numerous tannins are optically active, while their stereochemistry is highly influenced by the C15 sequence. Dried tannin extracts are hygroscopic and exhibit a strong absorption in the UV-Vis region with several local maxima ( $\lambda_{\text{max}}$ : 250 and 290 nm). At room temperature, CT-extracts are mainly soluble in water, short-chain alcohols (methanol, ethanol), and acetone aqueous solutions, and yield an acid environment with a sharp “puckering” and “astringent” flavour. They yield colloids in water, where they form viscous solutions (e.g., 40-45 wt.%, 5 mPa/s at 20 °C) due to the strong hydrogen bridge formed between the -OH groups and the water molecules. The viscosity depends on the CT concentration, the dispersity, the topology and the relation of hydrophilic/hydrophobic domains. The viscosity of some tannin extracts is increasing the difficulty to formulate CT based materials or to spray CT based resins, especially in the wood-based composite industry. In addition, CTs are thermo- and UV- labile compounds prone to oxidation. The residual weight at 600 °C oscillates between 40-50 % as a consequence of decomposition processes between 150-300 °C. However, the thermal behaviour is strongly associated to the Mw and the chemical structure. Considering that CTs are biopolymers, the glass transition temperature ( $T_g$ ) is an important variable to be considered for CT-application in materials engineering. Their  $T_g$  is strongly associated to the Mw, the purity grade, and the moisture content. The  $T_g$  of native tannin varies between 120 and 180 °C. In general, it is difficult to detect the  $T_g$  in CT samples because of Mw and property distributions. In addition, the reproducibility for the values is very low, regardless of the experimental parameter variation using Differential Scanning Calorimetry (DSC).

## Chemical modification pathways of CTs to use in material engineering

García et al. [23] has reviewed the chemical pathways to convert CTs based polyphenols into polymeric materials. The applicability of condensed tannins is restricted by high reactivity and poor solubility in organic solvents. A strategy to overcome this limitation is to modify the chemical structure by derivatization reactions. Among many possibilities, acetylation and alkylation, and here especially O-acylation using acid chlorides or anhydrides and alkyl halures, are the most frequent reactions. They change the physicochemical properties of the derivatives for their effective use in the industry and for purification technologies. Condensed tannins modification with conventional chemicals (e.g., anhydrides and halides), and propylene oxide affects drastically the physicochemical properties of the derivatives and provide high performance micro building-blocks for material engineering.

## 2.2 Suberin fatty acids (SFAs)

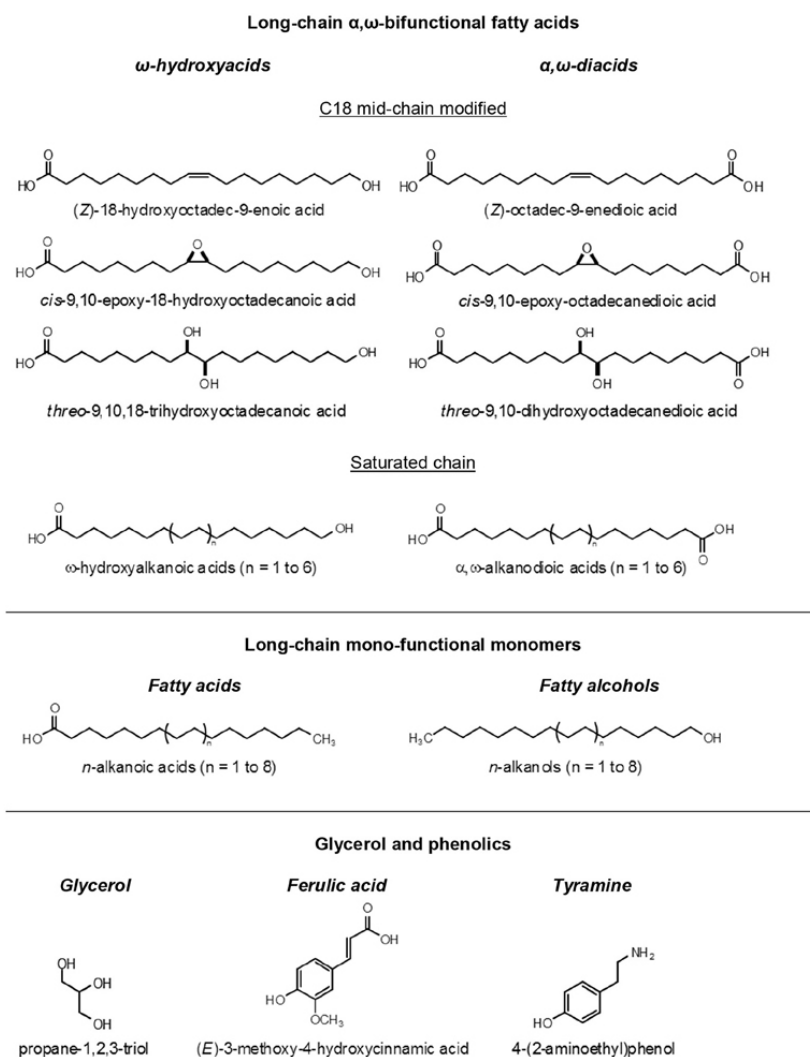
Suberin is a complex polyester built from poly-functional long-chain fatty acids (suberin acids) and glycerol. The suberin acids composition of a number of plant tissues and species is now established, but how the polyester macromolecule is assembled within the suberized cell walls is not known. Birch outer bark is rich in valuable biochemicals like the naturally occurring biopolyester suberin and the triterpenoids betulinol and lupeol [24,25]. The content of betulinol and lupeol in outer bark varies between 30%–35% and the content of suberin can be up to 40%–50% [26,27]. Birch bark containing both inner and outer bark from a pulp mill has been reported to contain 5.9% of suberin [28]. Suberin is a complex polymer, built by long-chain bifunctional  $\omega$ -hydroxyacids and  $\alpha,\omega$ -diacids that are both C18 midchain modified and saturated, long-chain monofunctional fatty acids, and fatty alcohols which are interlinked by ester-bonds to glycerol. When suberin is depolymerized, the main components are long-chain aliphatic acids as shown in Fig. 4, typically 80%–90% of depolymerisates

[29]. Suberin fatty acids are covalently linked through esterification to ferulic acid and neighboring lignin-like polyaromatics [29]. Suberin is believed to form partly orderly lamellar structures [29].

Due to its complex structure suberin is very difficult to isolate as an intact polymer but it needs to be hydrolysed into fatty acids [30] [31]. The suberin fatty acid composition after hydrolysis has been studied in detail [26]. Analysis of the suberin monomeric composition revealed that C18 and C22  $\omega$ -hydroxyfatty acids, including mid-chain epoxy- and dihydroxy-derivatives, followed by  $\alpha,\omega$ -dicarboxylic acids, are the main components in suberin, with 9,10-epoxy-18-hydroxyoctadecanoic, 18-hydroxyoctadec-9-enoic, 9,10,18-trihydroxyoctadecanoic and octadec-9-enoic acids as the major components, as seen in Table 2.

**Table 2:** Chemical composition of hydrolysed suberin.

Compound	(mg/g)
Hexadecanedioic acid	2
Octadecanedioic acid	2
Octadec-9-enedioic acid	29
Eicosanedioic acid	9
Docosanedioic acid	36
Alkanedioic acids	80
16-Hydroxyhexadecanoic acid	2
Dihydroxyhexadecanoic acid	20
18-Hydroxyoctadec-9-enoic acid	87
20-Hydroxyeicosanoic acid	20
20-Hydroxyeicos-10-enoic acid	11
22-Hydroxydocosanoic acid	93
24-Hydroxytetracosanoic acid	2
Hydroxyalkanoic acids	236
9,10-Epoxy-18-hydroxyoctadecanoic acid	220
9,10-Epoxyoctadecanedioic acid	10
9,10,18-Trihydroxyoctadecanoic acid	64
9,10-Dihydroxyoctadecanedioic acid	5
Epoxy derivatives	284
Total	600



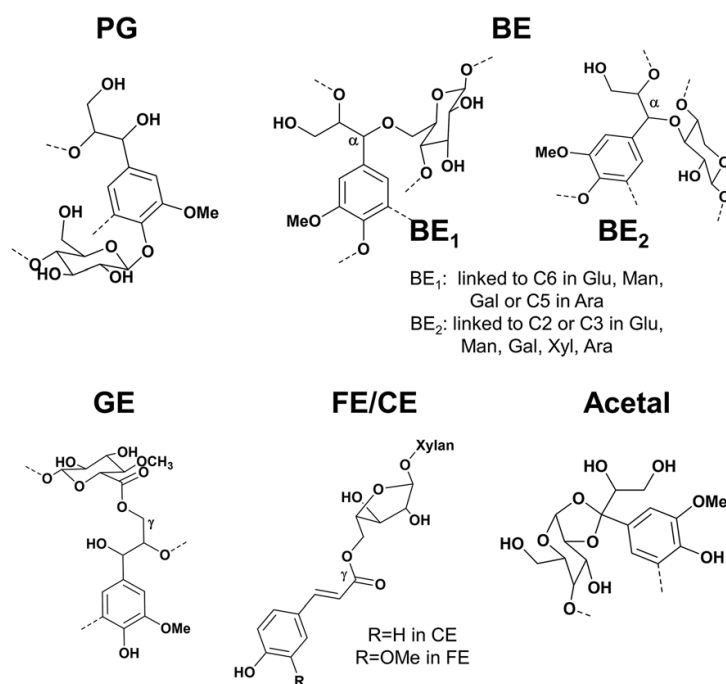
**Fig. 4:** Structural formula of the main suberin monomers [29].

### Properties of suberin fatty acids

SFAs must be considered as a rather non-polar material with surface properties that resemble those of its cork precursor, whose reported values of surface energy range between 30 and 40  $\text{mJ m}^{-2}$ . Given the broad temperature range associated with the melting or forming of these crystalline phases, and the very small size of the crystals, it seems likely that the SFAs components more apt to crystallize, because of their suitable structures, do so on an individual basis, at their respective freezing temperature, when the liquid mixture is slowly cooled down [32]. The result is therefore a set of microcrystals, each member belonging to a given dep-suberin component. Interestingly, the fact of having a rather complex mixture of compounds does not hinder the individual crystallization of some of them, most probably because the major driving force is associated with the ease of self-assembly among their long and linear aliphatic sequences [32]. SFAs showed a good thermal stability up to  $\sim 280$   $^{\circ}\text{C}$ , followed by a progressive weight loss, reaching a plateau at about 80% volatilization at 470  $^{\circ}\text{C}$  and leaving a carbonaceous residue [33]. Due to the microcrystalline nature SFAs, has been tried used as an additive to offset printing inks, in replacement of other waxy materials like PTFE oligomers [34]. All these inherited properties of SFAs make it an ideal biobased candidate of 3D printing either as additive or individual monomers.

## 2.3 Lignin-carbohydrates complex (LCCs):

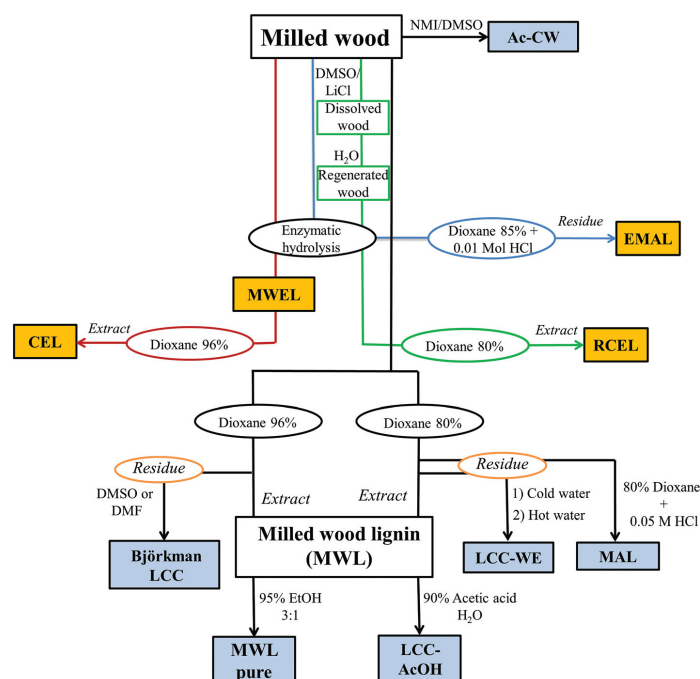
Covalent bonds between lignin and carbohydrates, forming a matrix referred to as lignin carbohydrate complexes (LCC), remain one of the most controversial topics in wood chemistry. A key issue is whether they are formed during chemical and mechanical pre-treatments of the compact wood structure or present in wood prior to isolation. A fundamental understanding of their origin and reactivity is vital to unravel their role in wood formation and recalcitrance. Recalcitrance, specifically, has affected the successful development of effective and clean fractionation of wood polymers. Different structures of LCCs seemingly exist depending on either structure of lignin or type/quantity of carbohydrate attached to lignin



**Fig. 5:** Suggested structures of lignin–carbohydrate bonds (LC) in wood and grass. In the figure, PG = phenyl glycosides, BE = benzyl ethers; GE =  $\gamma$ -esters; FE = ferulate esters; CE = coumarate esters [35].

### Extraction process of LCCs

Figure 6 dissipated the different extraction process of LCCs from woody biomass. In yellow: lignin protocol including both ball milling and enzymatic hydrolysis; in light blue: lignin isolated after ball milling. MWL = milled wood lignin, Ac-CW = acetylated cell walls, CEL = cellulolytic enzyme lignin, MWEL = milled wood enzymatic lignin, EMAL = enzymatic mild acidolysis lignin, RCEL = regenerated cellulolytic enzyme lignin, AcOH = acetic acid, WE = water extract, MAL = mild acidolysis lignin [35].



**Fig. 6:** Isolation protocol of lignin-carbohydrate complex (LCC) from wood [35].

### Sources and Properties of LCCs

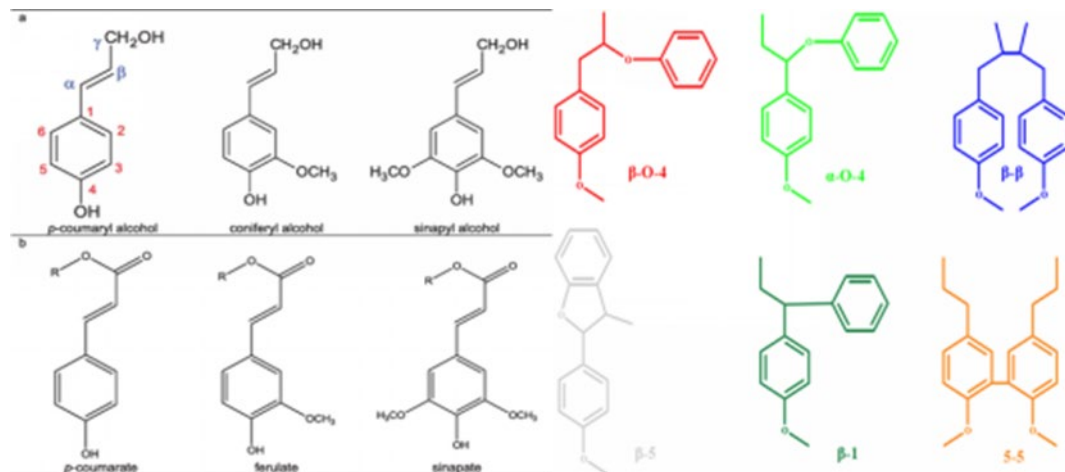
The LCCs can be extracted from all types of wood and non-wood lignocelluloses resources, as shown in Fig. 6, LCCs extracted from different process. Here are some of sources of LCCs: soft wood pulp, soft wood bark, hardwood pulp, LCCs from spend liquor from pulping industry grasses and plants.

The combination of rigid, hydrophobic lignin units, and flexible hydrophilic sugar moieties results in a good biological compatibility and strength in LCC material. Softwood and hardwood LCC preparations were successfully tested as biocarrier for liver cells' culturing. In addition, the high concentration of hydroxyl groups provides an opportunity to employ LCC materials for composite polymer production [36].

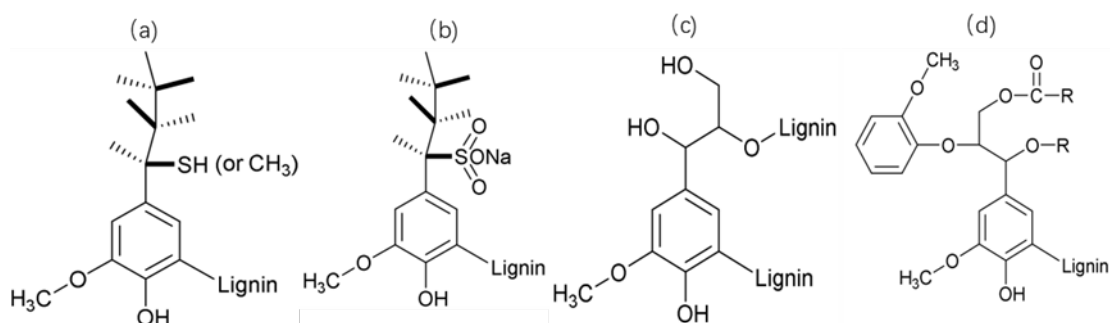
## 2.4 Lignin

Lignin is a polyaromatic biomolecule that exists in every lignocellulosic living worldwide, such as hardwood trees, softwood trees, agricultural crops, energy crops, and corn cone. Lignin consists of three different aromatic units with different ratios, they are crosslinked and combined into a complicated structure. [37]. As Figure 7 presents, lignin units contain an aromatic ring and a C3 chain, which differs in the number of methoxyl groups, and the lignin unit is divided by the chemical structure difference. The OH groups (phenolic and alcoholic hydroxyl group) in the three lignin units are considered as the most reactive functional group which used to connect lignin units. The functional groups (hydroxyl groups in the aromatic ring, main carbon chain, and methoxyl group) are the determination parameters when modifying the lignin, which affects the properties and characteristics of lignin. Bonding methods of lignin determine the difference between lignin compounds. Figure 7 also shows several common linkages between monomers, they can link through ether bond ( $\beta$ -O-4,  $\alpha$ -O-4) and carbon-carbon single bond ( $\beta$ - $\beta$ ,  $\beta$ -5,  $\beta$ -1, 5-5) to form a complicated network structure. Ether bonding has a higher utilization compared to the C-C bonding method, accounting for 56% linkages in lignin aromatic polymer [38]. Among industrial technical

lignin, kraft lignin occupied the highest share due to the well-developed paper industries. lignosulfonate lignin and Kraft lignin contain contaminant sulfur owing to the chemical treatment, while soda lignin and organosolv lignin are considered sulfur free (Figure 8).



**Fig. 7:** Three types of lignin monomers (a) and the hydroxycinnamates (b), R = H, and the several linkages between lignin monomers.

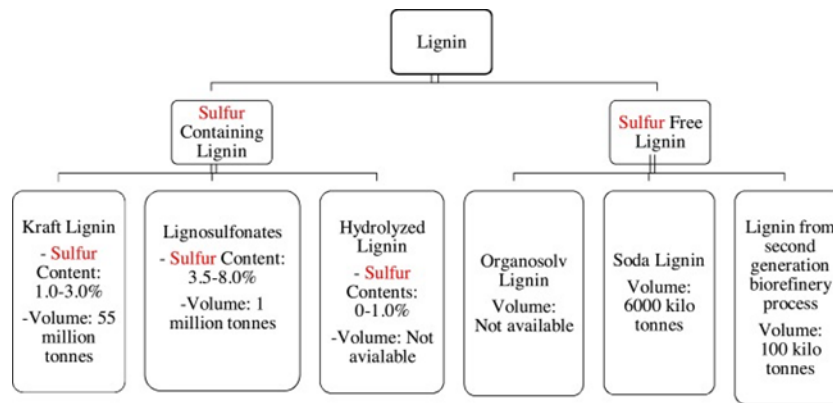


**Fig. 8:** Industrial technical lignin, (a) kraft lignin, (b) lignosulfonate lignin, (c) soda lignin, (d) organosolv lignin.

The lignin macromolecules are a complicated three-dimensional polymer without a regular structure. Researchers have shown that the lignin structure is diverse and heterogeneous because the complex linkages of lignin and various parameters that affects lignin synthesis process. Thus, the structure of lignin is determined by the lignocellulosic plants and obtaining methods.

### Lignin classification

Lignin difference can be identified as the lignin unit ratio, linkage formation, molecular weight, shape, size, and source, they are different between lignocellulosic materials and influenced by their surrounding environments, such as soil type, location, and climate.



**Fig. 9:** Lignin source and their volume [39].

Lignin can be classified as original lignin and technical lignin (Figure 9). Original lignin is in ideal form without any change in lignin structure. Naturally, original lignin cannot be obtained through extraction from lignocellulosic material, recycling from biorefineries by-products, or any modern processing method. Thus, the commercially accessible lignin source is the modified lignin varies in lignin manufacturing processes. The technical lignin can be grouped into sulfur-containing and sulfur-free lignin. They can be divided into different types according to the processing method, such as kraft lignin, organosolv lignin, lignosulfonates, soda lignin, and hydrolysis lignin. All these lignin types can be depolymerized into the same lignin fragment which improves the reactivity due to the increased reactive sites and functional groups. Therefore, the fragmented lignin has a better potential application and further workability [40]. Incorporating lignin in 3D printing materials decreases the reliance on typical petroleum-based plastic 3D printing materials. Doing so not only makes the 3D printing materials more environmentally friendly, but it also reduces costs as lignin is much cheaper than typical 3D printing materials.

### 3. Conclusion and new possibilities

3D printing has become an important digital tool in manufacturing of functional materials with a precise control over target design, which enable this technology for a wide range of new applications and reducing the waste of materials. This technique has been developing over the time and today it is being in manufacturing of smart materials; ceramics materials; electronics materials; biomaterials; and composite materials. In the DeMANS project we are dealing with several different types of material application more precise focus on consumable electronics good and functional biomaterials. There is an advantage of AM methods over conventional moulding techniques since these require careful control of properties and homogenous feedstocks. The ability to print shapes without moulds may then allow the use of these highly variable biopolymers thus enabling use of renewable materials over conventional fossil fuel derived systems.

The listed novel biopolymers are derived from natural and sustainable resources of forestry biomass. These biopolymers are not used significantly in fabrication of consumable electronics and functional biomedical materials. Most of these materials containing polyphenols as main building block of their structures, as discussed, these biopolymers already had several applications in food sector and biomedical sector. Suberin fatty acids are the biobased polyesters, and they could several applications in AM fabricated materials. Lignin carbohydrate complexes (LCCs) are the amorphous compound mixture of lignin and carbohydrates, which enables them in providing excellent behaviour such as rigid, hydrophobic nature, and flexible hydrophilic sugar moieties results in a good biological compatibility and strength.

There are some key factors and advantages of AM techniques for using these materials:

- 1) Enable the use of inexpensive, renewable materials in production thereby reducing reliance on fossil-fuel systems
- 2) Generate functional products that have inherent antimicrobial, binding or optical properties that may be useful in biomedical or packaging applications requiring controlled functionality
- 3) Increase the circularity and sustainability of manufacture through the use of renewable and biodegradable materials.
- 4) Increase the use of waste materials (e.g., tree thinnings) and enable bioeconomy and circular bio economies in countries/regions

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