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Comparison of lignin distribution, structure, and morphology in wheat straw and wood

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A R T I C L E I N F O

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A B S T R A C T

Agricultural fiber sources, such as wheat straw, are promising lignocellulosic feedstocks for the generation of renewable substitutes for synthetic materials (e.g., plastics, construction materials, biofuel, and other biorefinery products). The interest in the utilization of lignin has increased rapidly during the last years; the number of publications increased more than five times between 2000 and 2020. The number of publications concerning lignin from wheat straw follows the general trend with an increasing scientific interest in lignin but comprises less than 5% of the total lignin publications. The structure and morphology of lignin in straw and wood differ between the different species. The monolignol composition and spatial location in plant tissue are notably different, as well as the nature and abundance of lignin-carbohydrate linkages involving p-coumaric acid (pCA) and ferulic acid (FA) units in wheat straw lignin. To further enable the utilization of wheat straw as a resource for bio-based materials, a solid understanding of the wheat lignin structure and composition is required. This review aims to consolidate the state-of-the-art in wheat lignin and focuses on lignin and its distribution, fundamental chemical structures, and morphology in wheat straw and compares these features with lignin in wood cell walls.

1. Introduction

Agricultural fiber sources such as wheat straw, wheat bran, and oat hull are abundant resources of lignin, cellulose, and hemicelluloses. Although these fiber sources have a relatively lower value compared to wood and other plant fibers, their annual output is considerable. Wheat straw, for example, it is an abundant byproduct from wheat production. It is an annually renewable fiber resource that is available in large quantities in many regions of the world. Nearly 733 million tons hectares of wheat are estimated to be cultivated annually worldwide (FAO Cereal Supply and Demand Brief, 2016). This production generated 734 million metric tons of wheat in 2018 (FAOSTAT, 2018). Data from 2013 indicate that 0.85 kton of dry stalks of the cereal crops is produced per 1 kton of wheat. (NL Agency Mistry of Public Affairs, 2013). Hence, millions of tons of wheat straw, of which the majority are used for soil fertility, livestock feed, and incineration for energy production. Just as a comparison, the production of wood pulp in the same year was around 184 metric tons (Statista, 2021). Still, only a small

Abbreviations: CC, cell corner; CEL, cellulolytic enzyme lignin; CML, compound middle lamella=P + ML; DHP, dehydrogenate polymer; DMSO, dimethylsulfoxide; EDS, Energy-dispersive X-ray spectroscopy; FA, ferulic acid; G, guaiacyl lignin structure unit derived from coniferyl alcohol; H, p-hydroxyphenyl lignin structure unit derived from p-coumaryl alcohol; HPLC, high-performance liquid chromatography; LCC, lignin-carbohydrate complexes; LEH, hemicellulose-rich fractions from enzyme lignin; LEL, lignin-rich fraction from enzyme lignin; LMH, hemicellulose-rich fractions from MWL; LML, lignin-rich fraction from MWL; ML, middle lamella; M_w, weight-average molecular weight; MWL, milled wood lignin; P, primary wall; pCA, p-coumaric acid; PVF, percentage volume fraction; S, secondary wall that includes S1 outer layer of secondary wall S2 middle layer of secondary wall S3 inner layer of secondary wall; S, syringyl lignin structure unit derived from sinapyl alcohol; SEC, size exclusion chromatography; TBAH, tetrabutylammonium hydroxide.

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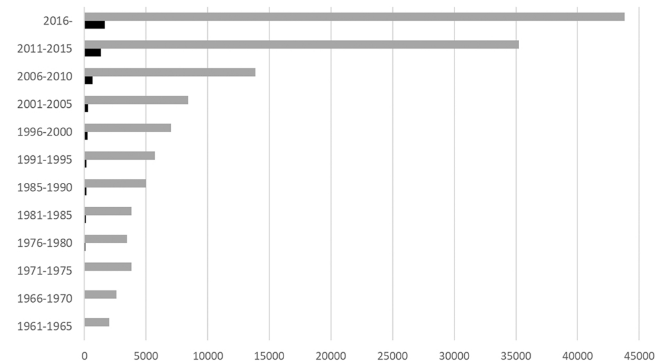

Fig. 1. Bibliometric summary on the number of publications from year 1961 to date in the research topic lignin. Gray columns represent the number of publications on lignin in general and black bars represent the number of publications on wheat straw lignin. *Source:* CAS SciFinder.

percentage of the wheat straw has been used as biorefinery feedstock for biobased materials, pulping, and fermentation (Sun et al., 2020). The use of wheat straw could open new markets for these agricultural crop residues and improve the rural agriculture-based economy.

The interest in lignin, including agricultural-sourced lignin, as a renewable feedstock (Jędrzejczak et al., 2021) has increased rapidly since the turn of the century, reflected in the number of scientific publications and patents in the area (Fig. 1). Successful utilization requires an in-depth understanding of the morphology, chemistry, and process-structure relationships. In the field of lignin, such a knowledge base is hitherto much more mature and widely explored for lignins from wood than for lignins from wheat and other cereals, motivating a consolidation of the current state of knowledge of wheat lignin. Comprehensive insights in the composition, structure, and morphology of wheat straw lignin will contribute to maximizing the exploitation of this important agricultural fiber source as a feedstock for biorefinery products.

Recent advances in characterization, especially NMR, new synthetic protocols for preparing tailor-made oligomeric lignin motifs, and tools for genetic modeling enabling transgenic plants have all paved the way for a deeper and broader understanding of the molecular features of lignin. Such new insights have spurred scientists within the field to revisit and re-evaluate the structure, composition, intra- and intermolecular linkages of lignins from terrestrial sources.

A schematic diagram of the wheat straw matrix showing the main contents is shown in Fig. 2. Lignocellulosic biomass, e.g., wood, straw, and grass are mainly composed of cellulose, hemicellulose, and lignin. In addition, agricultural fiber sources such as straw and hull also contain various other organic compounds such as proteins, small quantities of waxes, salts and insoluble ash, including silica (Sahoo et al., 2002; Toman and Chimidcogzol, 1988). Wheat straw and wood vary in chemical composition. Aside from origin, the composition is also affected by the specific cultivar, soil type, fertilizer treatment, and other growth conditions. In general, wheat straw contains 11–26% lignin, 32 – 45% cellulose, and 20 – 45% hemicelluloses (Trubetskaya et al., 2016; Del Río et al., 2012; Khan and Mubeen, 2012; Adapa et al., 2009; Harper and Lynch, 1981).

Lignin is primarily a structural material that adds strength and rigidity to cell walls in straw, wood or other natural woody plants. Between different biomass types, there are notable differences in the amount of lignin and its specific chemistry. Compared with wheat straw, wood usually have higher lignin contents (Table 1). Wheat straw contains some inorganics, mainly Si, and trace amounts of common minerals, including K and Ca (Biricik et al., 1999). Softwood has the highest lignin composition (Matsakas et al., 2019; Yu et al., 2017; Kumar et al., 2012), followed by hardwood (Fougere et al., 2016; Wen et al., 2013; Xiao et al., 2013; Zhou et al., 2012). However, there are some exceptions; for example, compression wood of softwoods may be comprised of up to 40% lignin, and tension wood fibers of hardwoods have a specialized gelatinous cell layer that contains almost no lignin (Novaes et al., 2010). It must also be noted that the detected lignin content, distribution, and structural composition, varies between scientific

Table 1
Cellulose, hemicelluloses, lignin, and other components of wheat straw, spruce, and birch (% of dry materials).

Composition	Wheat straw	Spruce (softwood)	Birch (hardwood)
Lignin	11–26	29–34	24–26
Cellulose	32–45	38–47	35–44
Hemicelluloses	20–45	18–22	26–30
Starch	0–3	–	–
Protein	2–6	–	–
Ash	0–2	–	–
References	(Trubetskaya et al., 2016; Del Río et al., 2012; Khan and Mubeen, 2012; Adapa et al., 2009; Harper and Lynch, 1981)	(Matsakas et al., 2019; Yu et al., 2017; Kumar et al., 2012)	(Wen et al., 2013; Xiao et al., 2013; Zhou et al., 2012)

- Not determined

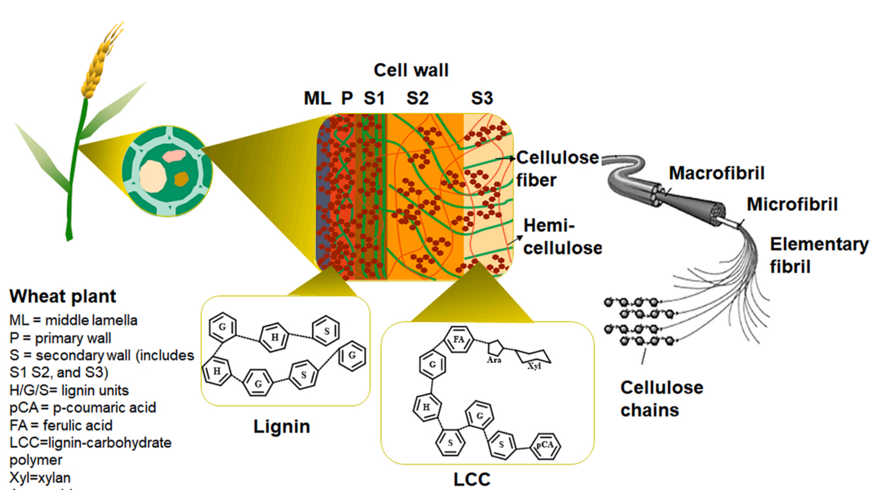

Fig. 2. Schematic diagram of the wheat straw matrix. Green lines represent cellulose fibers, orange lines represent hemicelluloses and red, dotted lines represent lignin.

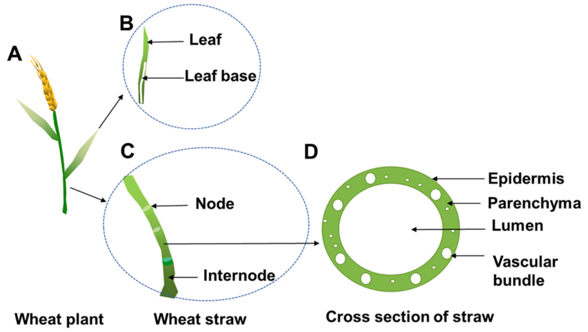

Fig. 3. Schematic diagram of (A) the wheat plant (head, stem, and leaves), (B, C) wheat straw (leaf, leaf base, node, and internode), and (D) cross section of wheat straw (epidermis, parenchyma, lumen, and vascular bundles).

studies based on the method of isolation. A number of isolation methods have been developed, including "milled wood lignin" (MWL), kraft lignin, soda pulp lignin, cellulolytic enzyme lignin (CEL), and organosolv lignin (Björkman, 1956; Chang et al., 1975; Paszner and Behera, 1985; El Hage et al., 2009; Wen et al., 2015; Duval et al., 2016). The isolation processes, involving more or less harsh mechanical and/or chemical treatments, alter the native structure, morphology, and molecular weight due to irreversible reactions. Process conditions affect the lignin structure and have implications on the lignin properties. Lignin may partly degrade during isolation due to thermal, oxidative, and chemical action, and combinations of the above (Huang et al., 2020). A higher amount of C-O linkages typically leads to a higher degree of disaggregation (Schutyser et al., 2018). Lignin may further hydrolyze under acidic conditions leading to a lower molecular weight and higher dispersity (Bose and Francis, 1999). As an example, organosolv extraction was reported to cause α-O-4 aryl-ether bond cleavage when acidic water/alcohol mixtures were used as media (Sturgeon et al., 2014; Jasiukaitytė-Grojzdek et al., 2020). The most common interunit linkage, the β-O-4 aryl-ether linkage (described in Section 3.3), is likewise susceptible to acid-induced cleavage (Sturgeon et al., 2014). Also, alkaline conditions, such as soda pulping, lead to depolymerization of lignin. Following aryl-ether interlinkage cleavage, restructuring and condensation are commons events, forming C-C bonds more resistant to further depolymerization. Hence, reported values on lignin contents, composition etc. can vary considerably in literature, even for the same species.

Wheat straw has been explored as a raw material for pulping in paper-making and a lignin-rich fraction, technical lignin, is generated in the process (Tian et al., 2017; Gillet et al., 2017; Huang et al., 2020). Alkaline processes such as soda, soda-anthraquinone, and kraft pulping, efficiently remove and depolymerize lignin. Degraded lignin fractions dissolve or disperse in the black liquor from which they can be isolated. Compared to soda-anthraquinone pulping, the soda-oxygen process preserved more of the native β-O-4 interunit linkages (described in Section 3.3) (Zhang et al., 2017). Said pulping processes also mediate cleavage of lignin-hemicellulose linkages (described in Section 4), facilitating liberation from the straw and further altering the structure of lignin. Organosolv pulping, of wood, grass, and agricultural biomass has been studied, typically using aqueous alcohol mixtures. Similarly, various polar solvents or solvent mixtures with varying polarity and alkalinity, and more recently ionic liquids, have been explored to fractionate lignin from wheat and other cereal straw. A series of technical lignins with various molecular weights and purity may then be isolated.

Table 2
Chemical composition of wheat straw determined by gravimetric analysis, expressed as a mass fraction of dry material (%) (Harper and Lynch, 1981).

Composition	Leaves	Leaf bases	Internodes	Nodes
Lignin	15	14	14	17
Cellulose	32	34	34	33
Hemicelluloses	38	33	45	38
Hot-water solubles	15	19	7	13
Ash	12	12	5	6

2. Anatomical structure of wheat straw and ultrastructure of wheat straw cell wall vs wood cell walls

2.1. *Anatomical structure of wheat straw vs wood*

2.1.1. *Wheat straw*

A wheat plant has four basic parts: the head, stem, leaves, and roots (Fig. 3A). The stem and leaves comprise the straw. The leaf portion (Fig. 3B) contains the leaf and leaf base, and the stem contains the node and the internode (Fig. 3C). The relative contents of the wheat straw components in leaves, leaf bases, nodes, and internodes are different (Harper and Lynch, 1981; Jacobs et al., 2000; Khan and Mubeen, 2012; Collins et al., 2014). Data from a representative study on wheat cultivar Huntsman are presented in Table 2. Literature data varies depending on the cultivar, the specific growth conditions, and, as discussed in the former section, depending on the pretreatments enabling composition analyses. An ambitious study compared six different cultivars of wheat and found significant differences in carbohydrate and lignin composition of component tissues (Collins et al., 2014). Overall, literature data agree in that there are higher concentrations of ash (in which silica is the main constituent) in the leaves and the leaf bases, carbohydrates (cellulose and hemicelluloses) in the internodes, and lignin in the nodes than in the other parts of the straw (Table 2). The main region of wheat straw is the internode.

The internode of wheat straw is a hollow cylinder (Figs. 3D and 4A), which is made up of essentially the parenchymatous ground tissue, the vascular bundles, and the epidermis (Xu, 2010; Singh et al., 2011; Motte et al., 2014; Ghaffar, 2018). Parenchyma ground tissue is composed of thin-walled cells and is shown in the Fig. 4A(b) and the lower right portion of Fig. 4B. Each vascular bundle is composed of phloem, xylem, and sclerenchyma (Fig. 4B). The phloem contains non-lignified, thin-walled sieve tubes with companion cells, whereas the xylem contains the earlier formed protoxylem and is later differentiated into metaxylem (Evert, 2006). Phloem and xylem work together to support the growth of wheat straw. The phloem is responsible for the transport of photosynthetic products such as sugars. Xylem is a reinforcing and conducting tissue that transports water and solutes (e.g., minerals). The phloem and xylem are surrounded by the sclerenchyma. The sclerenchyma contains fiber cells and sclereids, and there is usually a sheath on the outside of these two kinds of cells (Ilvessalo-Pfäffli, 1995). Fiber cells are often long slender cells, while sclereids vary in shape (Raven et al., 2007). Normally, the fiber cells close to the epidermis have a thick cell wall and are known as thick fibers, whereas fiber cells in the middle of straw have a much thinner cell wall and known as thin fibers (the comparison of cell wall thickness can be found in Table 3). The proportion of fiber cells in wheat straw is only 30%; others are nonfibrous cells, such as parenchyma, epidermis cells, and vessels (Singh et al., 2011). This needs to be considered in the utilization of wheat straw as a fiber resource.

2.1.2. *Comparison between wheat straw and wood*

Woods and wheat are vascular plants within the kingdom of plants. Softwoods belong to the division of conifers (Gymnosperms) and hardwood and grasses, including wheat, belong to Angiosperms. Within Angiosperms, hardwood (deciduous trees) belong to the Eudicotyledons and the grasses to the Monocotyledons. Wheat belongs to the

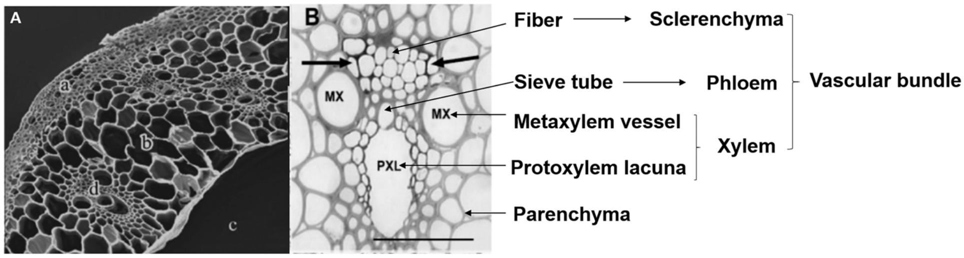

Fig. 4. (A) SEM image of the wheat straw internode cross section: (a) epidermis, (b) parenchyma, (c) lumen, and (d) vascular bundles (Yu et al., 2008). The original image was not marked with a scale bar, and the author speculates that the thickness of the cross section is approximately 200–300 μm. (B) A higher magnification of a vascular bundle from wheat straw surrounded by parenchyma (*Triticum aestivum* var. Westbred 936). Bar, 50 μm (Schirp et al., 2006).

Table 3
The PVF and thickness of various morphological layers in wheat straw fiber and spruce tracheid (adapted from Zhai and Lee, 1989).

Morphological layer	Wheat straw				Spruce tracheid (softwood)	
	Thick fiber		Thin fiber			
	Thickness (μm)	PVF (%)	Thickness (μm)	PVF (%)	Thickness (μm)	PVF (%)
CC	–	14.7	–	20.3	–	10.2
CML(ML+P)	0.1–0.2		0.06–0.12		0.05–0.1	
S1	0.1–0.3	83.5	0.2–0.3	80.7	0.15–0.2	89.8
S2	1.8–2.5		0.5–0.8		0.7–2.0	
S3	0.15–0.3		0.1–0.2		0.1	

PVF = percentage volume fraction

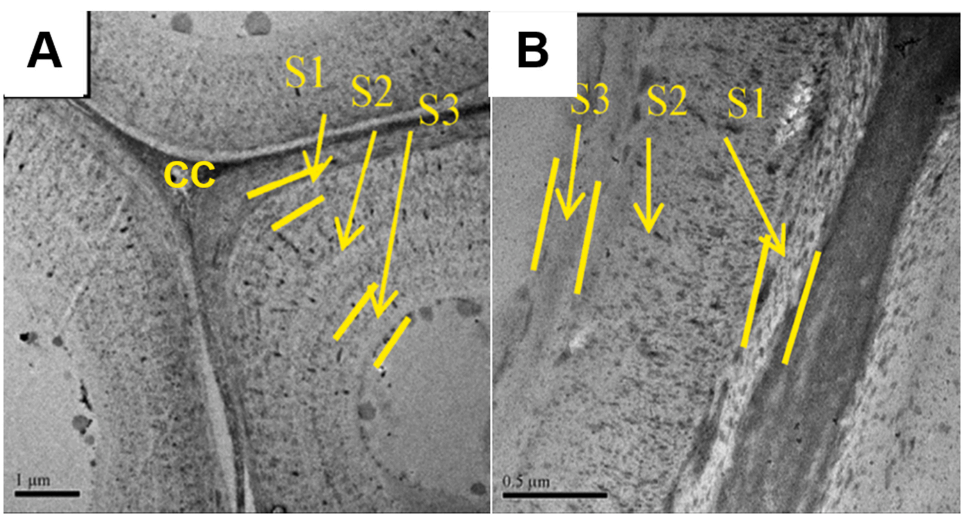

Fig. 5. TEM images of cross-sections from wheat straw fibers (A), and aspen wood (hardwood) fibers (B). TEM images of A and B were stained with $KMnO_4$. Samples were treated with sulfuric acid at 170 °C for 20 min and mechanically downsized using a Kumagai Riki Kogyo high-consistency disc-refiner (Kumagai Riki Kogyo, Tokyo, Japan) (Fougere et al., 2016). Scale bars are provided in the lower left for reference, and they are different in A and B. CC, cell corner; S, secondary wall, including S1, S2, and S3.

monocotyledon (monocot) group (Mauseth, 2008).

Softwood is simple in its anatomical features compared to wheat straw, over 90% of which are long and thin cells known as tracheids (The Wood Database, 2021.). Because of this, parenchyma cells are comparatively sparse. Many softwoods, e.g. pine and spruce, do not have any parenchyma at all (The Wood Database, 2021.). Therefore, the main fiber source in softwood is the tracheids. In sharp contrast to the relatively simple anatomy of softwoods, the hardwoods of the world are typically more complex. The types of wood cells in hardwood include fiber cells, tracheids, vessels, wood rays, and parenchyma cells (Britannica, 2021). Among these, fiber cells are the main support tissue and fiber source of hardwood, accounting for 60–80% of the total amount of hardwood cells. The proportion of fiber cells of softwood and hardwood are both higher than that of wheat straw.

In addition, the length of straw fiber cells is relatively short compared to softwood. The fiber cells of wheat straw are an average of 1.18 mm in length and 13.60 μm in width, (Singh et al., 2011), whereas softwood tracheids are approximately 3 mm in length and 20–35 μm in width. Fiber cells from hardwood are typically approximately 1 mm in length and not as thick as softwood fiber cells in width (Mini--Encyclopedia of Papermaking Wet-End Chemistry, n.d.).

2.2. *Ultrastructure of wheat straw cells vs wood cells*

2.2.1. *Wheat straw*

The fiber cells of wheat straw have an average cell wall thickness of around 4 μm. The parenchyma measures in average 445 × 124 μm, the epidermal cells measure 390 × 38 μm, and the vessels measure 96 × 57 μm (Singh et al., 2011). The cell wall of wheat straw is made of several layers; from the outside of the cell wall to the lumen, they are known as the middle lamella (ML), the primary wall (P), and the secondary wall (S) (Figs. 2 and 5). The ML is a thin layer that glues the individual cells together to form the tissue. Between three or four adjacent cells, there is a common area known as the cell corner (CC). The secondary wall is divided into three layers, namely, the outer layer (S1), middle layer (S2), and inner layer (S3) (Fig. 5A).

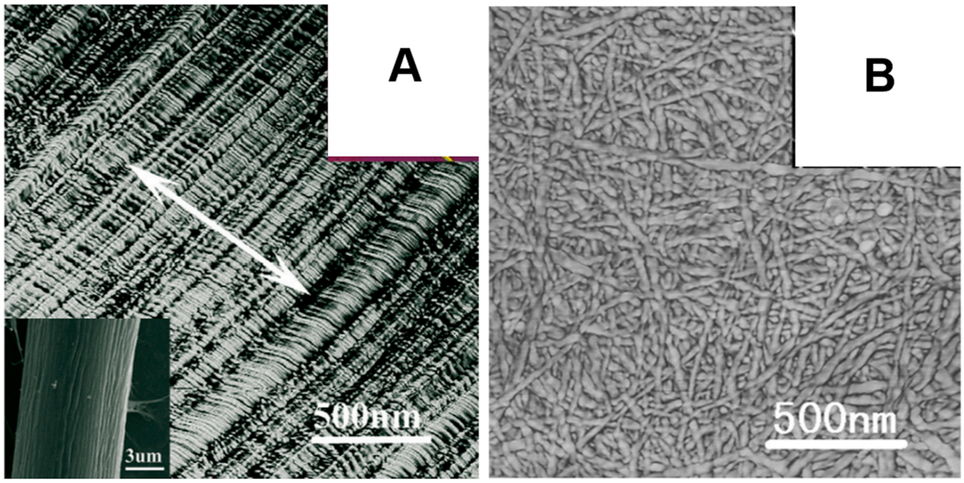

Fig. 6. AFM images of cellulose microfibrils of wheat straw showing cellulose arrangement in the (A) fiber cell and the (B) parenchyma cell. The double-head arrow indicates the longitudinal axis of the fiber (Yu et al., 2008).

2.2.2. Wood cells

Similar to wheat straw cells, the "normal" wood cells also consist of ML, P, S1, S2, and S3 (Fig. 5B). Sometimes the ML and P are fused together and called the compound middle lamella (CML). ML/CML has high concentrations of hemicelluloses and lignin; the P layer consists of cellulose, hemicelluloses, pectin, protein, and lignin. The thickest wall layer is S2 and is affected by the growing season, age, and morphological position (Xu, 2010). The structure of wood cell walls has been well studied and many special cases have been found. For example, "reaction" wood, which can be found on branches and leaning stems, changes its cell wall structure in response to gravity. In the cell wall of softwood "compression wood", the S3 layer is commonly absent and deep helical fissures tend to occur in the S2 layer (Altaner et al., 2010). In addition, the S3 layer is sometimes absent in hardwood (Xu, 2010) and often absent in compression wood (Donaldson, 2008).

2.2.3. Comparison between wheat and wood cells

The cell walls of wheat straw and wood are similar in layering, but the thicknesses of morphological layers in wheat straw are different from those in wood cells. A comparison of the thickness of different layers of cell walls and the corresponding percentage volume fraction (PVF) from wheat straw fiber and spruce tracheid are detailed in Table 3. Using thick fiber as an example, the CML thickness of wheat straw normally ranges from 0.1 to 0.2 μm. The S layer forms the main portion of the cell wall, accounting for 83.5% of the total cell wall. S1 is as thin as CML, and forms approximately 15% of the total cell wall. S2 is the thickest (1.8–2.5 μm), and determines the thickness of the cell wall. S3 is also a thin layer, approximately 15% of the total cell wall. The CML layer in wheat straw fiber is considered thicker than that of the spruce tracheid. Therefore, the total PVF of the S layer of wheat straw is lower than that in spruce tracheids. However, the S1 layer of wheat straw fiber is thicker than that of the spruce tracheid (Fig. 5; please note that the scale bars in Fig. 5A and B are different). The thick S1 layer coupled with relatively low lignin levels is believed to be a focal point of fracture in mechanically based processes (Fougere et al., 2016; Donaldson et al., 2001; Zhai and Lee, 1989). Fracture behavior has been studied closely in wood samples and several mechanisms for fracture propagation have been identified, including trans-wall and intra-wall breakage and propagation along the grains or through the S layers (Wang et al., 2020). The S1 layer in particular was identified to be associated with fracture surfaces in softwood, and it was hypothesized that this is due to uneven lignification (Donaldson, 1996). The understanding of the mechanisms governing response to mechanical load and fracture propagation is vital in product design, when a polymer matrix is to be used in a construction or commodity material.

In the cell walls, the parallel cellulose chains pack together to form microfibrils several nanometers in diameter and millimeters in length. It is known that the arrangement and orientation of cellulose microfibrils in the cell wall are very important because they determine the capacity and direction of deformation of the cell wall (Taiz and Zeiger, 2010). The orientation of cellulose microfibrils in each layer in wheat straw fiber cells is different from that in wood fiber cells. Both wheat straw and wood cells have irregular microfibril directions in the primary wall, which display a net-like texture. The S1 layer microfibrils in wheat straw fiber cells are oriented helically and almost perpendicular to the fiber axis. In the wood fiber S1 layer, the microfibrils irregularly wind around the cell at an angle between 50° and 75° to the cell axis. It has been proposed that the thicker S1 layer and the fibril orientation in wheat straw cause a higher recalcitrance toward delignification (Xu, 2010). The microfibrils in the wheat straw fiber cell S2 layer are densely packed, making an angle of only 20–30° with the cell axis, while the angle of wood fiber S2 is approximately 10–30° (Xu, 2010). Cellulose microfibrils in the parenchyma cell (Fig. 6) of wheat straw are observed with almost no preferred orientation (Liu et al., 2005).

Recently, Baison et al. (2019) showed by using genome-wide association studies on Norway spruce wood that many of the properties of the tracheid (such as dimensions, cell wall thickness, and microfibril angles) are controlled by the genome. To the best of the authors' knowledge, no such studies on genomic control of the structure of wheat straws are available.

2.3. Lignin distribution in the cell wall of wheat straw vs wood

Lignin distribution in the cell wall was studied using a variety of techniques, such as UV microscopy, bromination or mercurization combined with energy dispersive X-ray analysis (EDS), interference microscopy, and fluorescence microscopy (Donaldson et al., 2001). Confocal Raman microspectroscopy was also used to analyze the lignin distribution of wood fiber and *Miscanthus sinensis* (Ma et al., 2014; Ji et al., 2013); however, no references were found reporting the use of this technique to analyze wheat straw lignin.

2.3.1. Distribution in wheat straw cells

In wheat straw cells, epidermal cells have the lowest lignin concentration, followed by fiber cells, and parenchyma region has the highest lignin concentration. The low lignin concentration of epidermal cells is probably due to the higher silica content (Xu, 2010). The lignin concentration in all cell types in the wheat straw showed to be highest in the

Table 4
Lignin concentration in various morphological regions of wheat straw and wood fiber (adapted from Zhai and Lee, 1989).

Species	Fiber type/Tracheid	Lignin distribution (g/g)		
		S	ML	CC
Wheat straw	Thick wall fiber	0.2	0.4	0.6
	Thin wall fiber	0.2	0.3	0.7
Birch (hardwood)	Fiber	0.2	0.3–0.4	0.7–0.9
Spruce (softwood)	Earlywood tracheid	0.2	0.5	0.9
	Latewood tracheid	0.2	0.6	1

Table 5
Lignin distribution of the total amount of lignin (w, %) in different morphological regions (Zhai and Lee, 1989).

	Fiber type	Lignin distribution (w, %)		
		S	ML	CC
Wheat straw	Thick wall fiber	68	18	14
	Thin wall fiber	58	20	22
Birch (hardwood)	Fiber	78	11	11
Spruce (softwood)	Earlywood tracheid	72	16	12
	Latewood tracheid	82	10	8

Table 6
Functional groups in lignin (Ghaffar and Fan, 2013).

Biomass origin	Lignin isolation process	COO- (%)	OH Phenolic (%)	Methoxy (%)
Wheat straw	Alkaline	7.2	2.6	16
Hardwood	Organosolv	3.6	3.7	19
Softwood	Kraft	4.1	2.6	14

CC and the lowest in the secondary wall (Zhai and Lee, 1989). This distribution of lignin was later confirmed by using the autofluorescence intensity in confocal microscopy (Donaldson et al., 2001). The lignin concentrations and distributions in the fiber cells of wheat straw, birch, and spruce are shown in Table 4. The lignin concentration values in wheat straw are 0.57–0.66 g/g for the CC region, 0.34–0.41 g/g for the ML, and 0.15–0.17 g/g for the secondary wall. However, considering that the S layer has a larger PVF (Table 3), most lignin (58–68%) is distributed in the S layer.

2.3.2. Comparison of lignin distribution between wheat straw and wood cells

Wood fiber cells and wheat straw have the same trend in lignin distribution. The lignin concentration is the highest in the CC, followed by ML, and the lowest in the secondary wall. However, the PVF of the ML and the CC in wheat straw fiber (~15–20%) is larger than that in wood fiber (10%), resulting in the percentage of total lignin in the ML and the CC being greater for wheat straw fiber (~32–42%) than for wood fiber (birch ~22%, spruce ~18–28%) (Table 5). Donaldson et al. compared the lignin distribution between wheat straw and coppice poplar. They found that the lignin concentration in ML for wheat straw and hardwood poplar was higher (31% and 63%, respectively) than the lignin concentration in the fiber S wall (9% and 6%, respectively). However, the values reported by Donaldson are lower than the ones reported by Zhai et al. (Table 5), which likely is due to that different analytical techniques (interference microscopy and bromination and SEM-EDXA for Donaldson et al. and Zhai et al., respectively) were used.

3. Lignin chemical structure

3.1. Lignin functional groups of wheat straw and wood

The key chemical functional groups in both wheat straw and wood

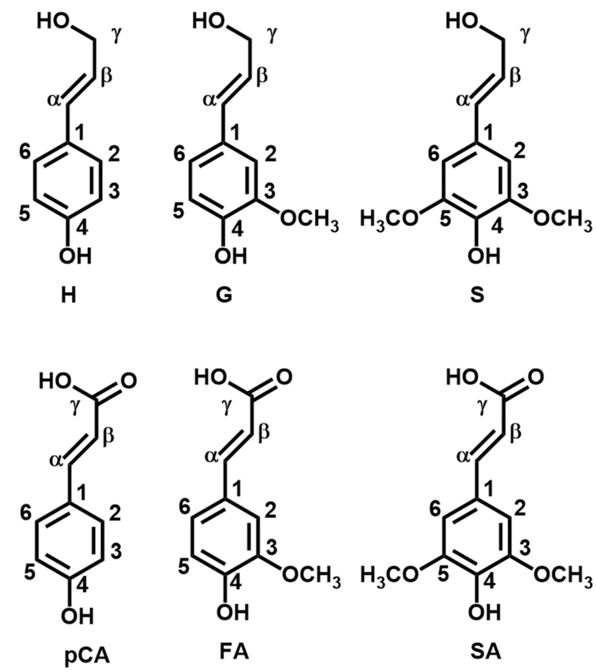

Fig. 7. Lignin structural units. H = p-coumaryl alcohol, G = coniferyl alcohol, S = sinapyl alcohol, pCA = p-coumaric acid, FA = ferulic acid, and SA = syringic acid.

lignin are hydroxyl (phenolic hydroxyl, alcoholic hydroxyl), methoxy, carbonyl, and carboxylic groups (Table 6). The carbonyl group in lignins can be determined by titration methods, which are based on the hydrogen ions released from the oxidation reaction with hydroxylamine hydrochloride (Lin and Dence, 1992). Total phenolic hydroxyl groups have been detected by many physical and chemical methods, such as UV spectroscopy, FTIR spectroscopy, and phosphorus NMR (Argyropoulos, 1994; Serrano et al., 2018). Methoxy groups can be quantified by conversion to iodomethane (CH_3I) and subsequently analyzed using gas chromatography (Goto et al., 2006; Lee et al., 2019). In general, softwood has a lower amount of methoxy groups than wheat straw and hardwood because of the absence of syringyl-type lignin. However, the relative quantities of these groups depend on the origin of the lignin and the isolation processes adapted. For example, the amount of phenolic OH groups in wheat straw increases slightly during the organosolv process, and the number of the total OH groups decreases as a function of the reaction time (Huijgen et al., 2014). Huijgen et al. (2014) also proved that the proportion of carboxyl groups in wheat straw is higher than that of hardwood lignin when separated by the same organosolv method.

3.2. Lignin structural units of wheat straw and wood

Lignin is a polyphenolic polyether with a complex macromolecular structure. The main monomers are the primary monolignols p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol (Fig. 7), giving rise to p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units, respectively, in the lignin polymer chain. The units are connected via diaryl and alkyl-aryl C–C bonds, as well as aliphatic ether bonds, which are illustrated in Section 3.3. The lignin composition depends on the botanical origin. The lignin structure of straws, grasses, and hardwood is primarily (G-S)-type lignin. Grasses have approximately 40% G, 40% S, and 20% derived from H and other aromatic derivatives, while hardwood lignin is generally derived 50% from G and 50% from S alcohols. Softwood contains (G)-type lignin, and over 90% of lignin is derived from coniferyl alcohol (Fougere et al., 2016). Table 7 shows the H/G/S ratios for wheat straw, spruce, and birch. Lignin units in wheat straw (small amount of H

Table 7
Ratio of lignin structural units in lignin from different sources (assuming the G unit = 1).

Derivation	NaOH dosage (%)	Heating time (h)	H	G	S	References
Wheat straw[a]	6	2	0.19	1	0.90	Tian et al. (2017)
	10	2	0.07	1	1.37	Tian et al. (2017)
	14	2	0.10	1	0.96	Tian et al. (2017)
	10	1	0.10	1	0.98	Tian et al. (2017)
	10	1.6	0.04	1	0.92	Tian et al. (2017)
Wheat straw[b]			0.05	1	0.59	Pereira et al. (2017)
Spruce (softwood)[b]	–	–	0.01	1	0	Pereira et al. (2017)
Birch (hardwood)[b]	–	–	–	1	0.77	Faleva et al. (2020)

[a] Wheat straw lignin was extracted by alkali cooking.
[b] MWL lignin from wheat straw, spruce, and birch.

Table 8
Hydroxycinnamic acid content of wheat straws, spruce, and poplar (%, w/w, Sun et al., 2001).

Derivation	pCA	FA	SA
Wheat straw[a]	0.66	1.24	-[b]
Spruce (softwood)	0.10	0.17	0.26
Poplar (hardwood)	0.10	0.17	0.26

[a] Sample was extracted in 4 M NaOH aqueous solution at 170 °C for 2 h.
[b] Not detectable

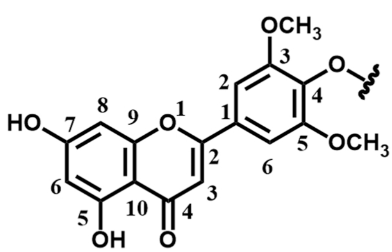

Fig. 8. Structure of tricin (5,7,4′-trihydroxy-3′,5′-dimethoxyflavone) end groups in lignin (Del Río et al., 2012).

and 1: ~1 in G/S units) are more similar to hardwood (1:1 in G/S units) than softwood (~ G units). However, wheat straw in the form of MWL (Björkman, 1956) seems to have a higher H-type lignin and a lower S-type lignin ratio than wood MWL. Huijgen et al. (2014) compared the organosolv wheat lignin with hardwood lignin and obtained the same conclusion.

Wheat straw lignin includes the three units (with still a comparatively low number of H-units), making its structure apparently more complex. Additionally, the hydroxycinnamic acids p-coumaric acid (pCA) and ferulic acid (FA) and their derived esters also occur widely in the structure of wheat straw lignins (Fig. 7) and other grass-like lignins (Ralph, 2010; del Rio et al., 2012). Another kind of hydroxycinnamic acid, syringic acid (SA), is found in some wood (such as spruce, poplar, Table 8) and grass materials (rice straw, Bunzel et al., 2003), but not in wheat straw (Sun et al., 2001). The amount of hydroxycinnamic acids, e.g., pCA and FA, in wheat straw lignin was reported to be 0.8–4.4% (Sun et al., 1997, 2001) but later studies indicate that the p-hydroxycinnamate units may be more common in grass lignins than previously estimated (Ralph, 2010). Meanwhile, the content of H-units may have been overestimated in lignin analysis (Ralph et al., 2019). The details of how pCA and FA link to lignin are discussed in Section 4.2. The content and composition of hydroxycinnamic acids are dependent on the morphological location and when the lignin is formed during the differentiation state. It has been reported that FA rapidly deposits in the cell walls at the early stage of lignification, subsequently pCA residues deposit continuously throughout lignification and become a predominant constituent of hydroxycinnamic acids (Sun et al., 2002).

Lignin from wheat straw is partially acylated (Crestini and Argyropoulos, 1997; del Rio et al., 2012). NMR studies indicate that primarily G-units are acylated at the γ-position by p-coumarates esterifying γ-OH groups.

An interesting feature of wheat straw lignin is that the flavone tricin is apparently incorporated into the lignins (Del Río et al., 2012). Tricin (5,7,4′-trihydroxy-3′,5′-dimethoxy-flavone) (Fig. 8) is a compound originally found to be incorporated as a chain end in grass lignin polymers via β–O–4 coupling and is not found in wood materials. Up to 8.0 units of tricin have also been detected in wheat straw lignin per 100 aromatic rings (Zeng et al., 2013). The tricin structure is expected to enhance the antibacterial properties of lignin (Zhou and Ibrahim, 2010; Del Río et al., 2020).

3.3. Linkages between lignin structural units of wheat straw and wood

Lignification starts with dehydrogenative dimerization or cross-coupling of two monolignol molecules and continues with further polymerization of the preformed dimers or oligomers and incoming monolignols so that lignin macromolecules are produced (Sangha et al., 2012; Vanholme et al., 2008). Lignification polymerization is a radical coupling pathway (Adler, 1977; Gani et al., 2019). The biosynthetic pathways for lignification have been reviewed in detail (Boerjan et al., 2003; Vanholme et al., 2010; Nguyen et al., 2016; Liu et al., 2018). During the lignification process, these monolignols produce a complex three-dimensional amorphous lignin polymer via C-C and C-O linkages (Fig. 9), hence lignin lacks the regular and ordered repeating motifs found in other plant biopolymers such as cellulose, starch, and hemicelluloses. The different types of interunit linkages form complex structures and render lignin macromolecules difficult to completely degrade (Reid, 1995).

Quantification analysis of lignin linkages (per 100 aromatic units) by HSQC NMR spectra is shown in Table 9. The percentage of C-C in wheat straw was measured to 19% and the percentage of C-O linkages was 81%. There are obviously fewer C-C connections in wheat straw lignin than in wood lignin (Table 9). C-C bonds are usually more resistant to chemical degradation during delignification during pulping than the C-O linkages (Holm and Niklasson, 2018). The predominant linkage in wheat straw lignin is alkyl-aryl ether β-O-4 linkage, constituting 79% of all interunit linkages in the MWL of wheat straw (Zeng et al., 2013). Other studies found that wheat straw lignin contains approximately 75% β-O-4, which indicates some variation in the reported values and should be seen as indications (Del Río et al., 2012; Lourenço and Pereira, 2018). The 5–5 linkage is usually found in so-called condensed lignin samples treated under conditions of extreme pH and temperature (Sannigrahi et al., 2008) and the amount is relatively low in native lignin (Katahira et al., 2018).

The distribution of linkages in wheat straw lignin differs from those in wood, where it is interesting to see that the types of bonds in wheat straw lignin are more similar in softwood than in hardwood, even if the lignin units in wheat straw are more similar to hardwood. The linkages in lignin can have a large influence on the potential branching of lignin chains and crosslinking between lignins and polysaccharides (Balakshin

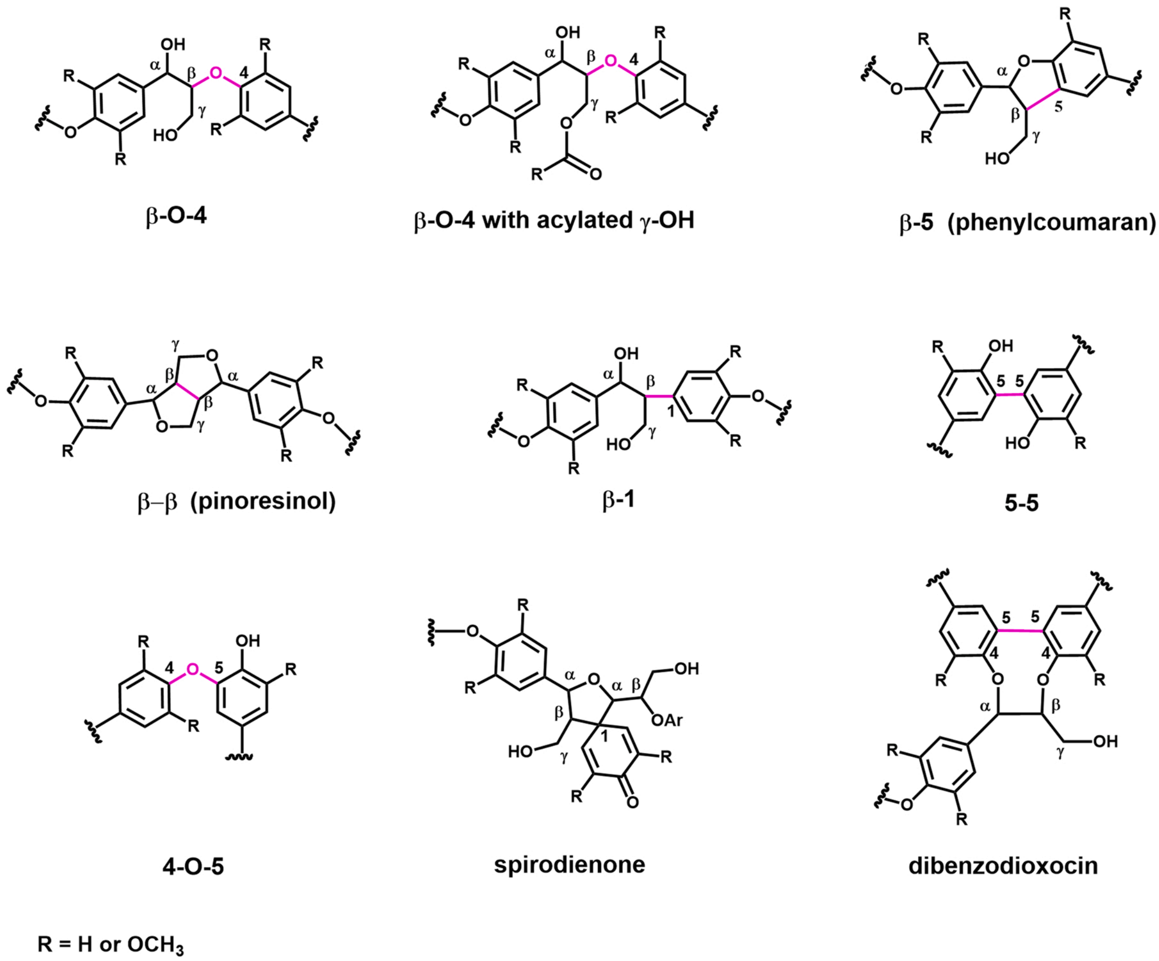

Fig. 9. Examples of lignin interunit linkages including C-C (β-1, β-5, 5–5, and β-β) and C-O (β-O-4, 4-O-5) connections (adapted from Lu and Ralph, 2010, Sette et al., 2011, and Del Río et al., 2012).

Table 9
Quantification analysis of lignin linkages (per 100 aromatic units) by HSQC NMR spectra and their relative percentage (adapted from Zeng et al., 2013).

Linkages		Wheat straw	Softwood	Hardwood
	Percentage of total C-C linkages (%)	19	21–23	32–35
C-C	Comprised of:			
	β-1	1.1	7.0–7.7	7.6–8.2
	β-5	14.4	6.0–6.6	10.6–13.0
	β-β	3.5	3.0–3.3	2.2–2.4
	5–5	0.5	4.5–5.0	11.2–12.0
C-O	Percentage of total C-O linkages (%)	81	77–80	65–68
	Comprised of:			
	α-O-4	1.3	6.6–8.0	7.1–8.7
	4-O-5	–	6.5–7.1	4.1–4.4
	β-O-4	79.3	63.7–65	52.2–56.5

et al., 2020). In particular, 5–5 and 4-O-5 linkages have been assigned as branching points (see further discussion in Section 3.4). Therefore, it is interesting to see that wheat straw lignin has fewer of these types of linkages than wood. The amount of 5–5 bonds increases as wheat straw < softwood < hardwood, whereas for the 4-O-5 linkage the order is wheat straw < hardwood < softwood.

3.4. Molecular structure of wheat straw and wood lignin

Model representations of the lignin macromolecule can be drawn based on the relative occurrence of structural units and linkage analysis, including between lignin and the polysaccharides, between the hydroxycinnamic acids and the polysaccharides or/and lignin. Lignin-carbohydrate linkages are further discussed in Section 4.2. Sun et al. (1997) provided an early tentative chemical structure of the wheat straw lignin-polysaccharide complex, based on the linkages between lignin and the polysaccharides (Fig. 10A). It should be noted that the schematic structure only shows how these compounds connect to each other and does not quantitatively represent the presence or percentages of linkages. A comparative model of a poplar lignin in Fig. 10B indicates representative difference between wheat straw and hardwood lignin in terms of monolignol composition and the relative occurrence of lignin linkages. Recent advances in lignin characterization, not in the least in NMR analysis, has revealed that p-hydroxycinnamates (FA and pCA units) occur more frequently than previously estimated in grass lignins, identified new structural units such as tricin in wheat, and provided a better understanding of the nature linkages, which motivates a modified model representation of wheat straw lignin (Fig. 10C) (Ralph, 2010; Del Río et al., 2012).

Over the years, there has been some ambiguities whether lignin is branched or not. The structural models of wheat straw lignin and hardwood lignin in Fig. 10a and b, respectively, are both branched structures. Indications of branching structures have been presented as well as results pointing toward a linear structure (Adler, 1977, 2019). Linkages of the 5–5 and 4-O-5 type have typically been anticipated to generate branching sites, however such linkages may be less commonly occurring than previously thought (Yue et al., 2016). Recent reports

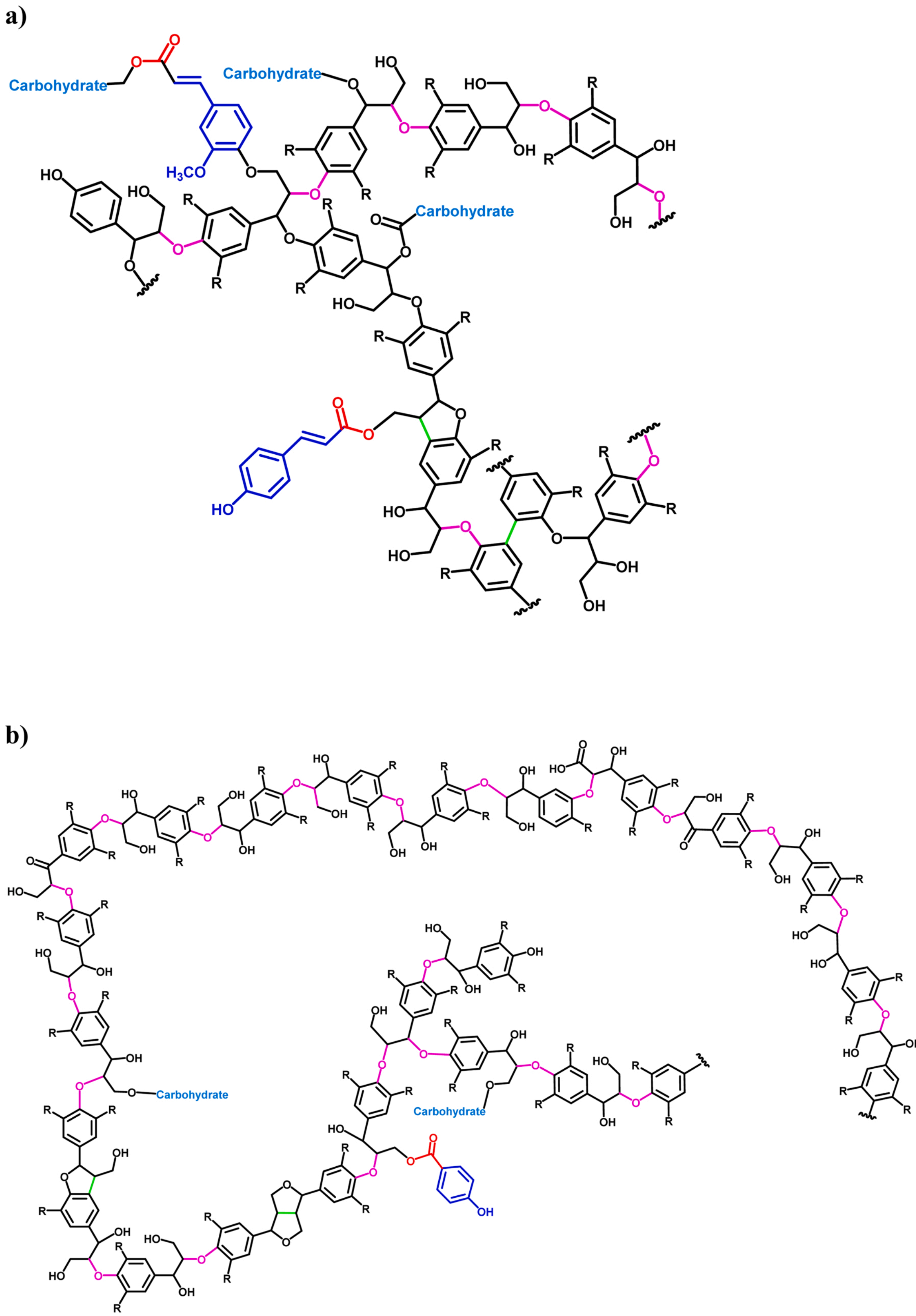

Fig. 10. (a) A tentative chemical structure of wheat straw lignin. (b) A structural model of lignin in 6-month-old poplar woods. (c) A structural model of lignin in monocotyledones, to which group wheat belongs. Black represents lignin structure units, light blue represents polysaccharides, dark blue represents hydroxycinnamic acids (FA/pCA); rose red represents ether linkages, green represents C-C linkages, and red represents ester bonds. R = H or OCH_3.
(a): Adapted from Sun et al. (1997). (b): Adapted from Wang et al. (2019). (c): Adapted from Ralph et al. (2019).

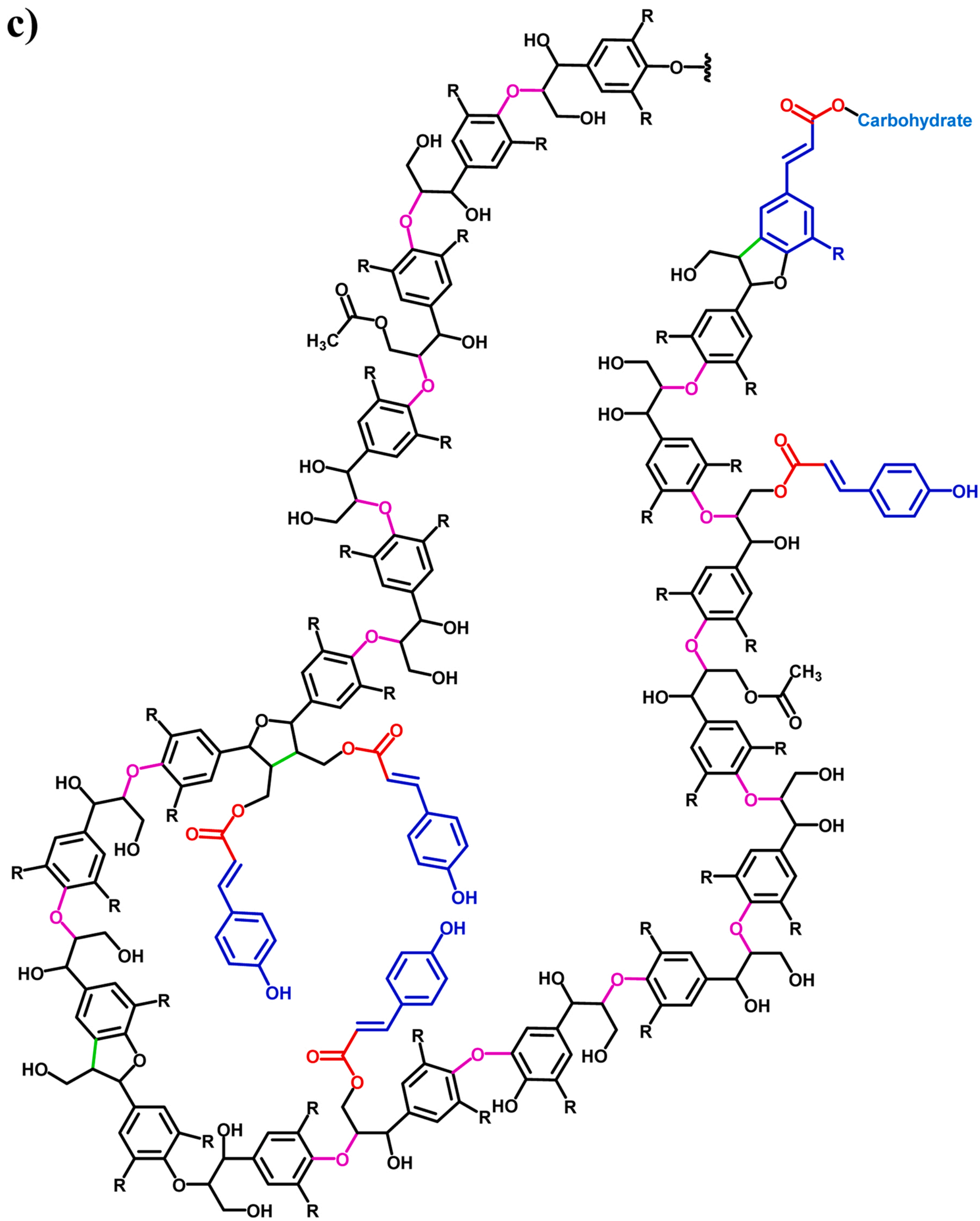

Fig. 10. (*continued*).

argue that wood lignin is branched and that there is evidence of branching by 5–5 etherified units and 4-O-etherified 5–5 units (Katahira et al., 2018; Balakshin et al., 2020; Sapouna and Lawoko, 2021). Again, wood lignins have been much more studied than agricultural-sourced lignin. In contrast, a recent study reports that wheat lignin is essentially a linear polymer (Karmanov et al., 2021) as illustrated in Fig. 10c.

4. Lignin-carbohydrate complexes (LCCs) of wheat straw and wood

4.1. LCC content in wheat straw and wood

Lignocellulose is composed of cellulose, hemicellulose, and lignin, forming a compact fibrous composite that is resistant to biological and chemical degradation, which is known as biomass recalcitrance (Zhang et al., 2016, 2014). It is generally believed that this recalcitrance can be explained to some extent by covalent linkages between the lignocellulosic polymers (originally proposed by Björkman et al., 1957). Many

Table 10
Chemical component analyses of LCC extracted from wheat straw, spruce, and birch (%, w/w).

LCC source	Wheat straw[a]	Spruce[b] (softwood)	Birch[c] (hardwood)
Relative content of total biomass	20.0	12.8	15
Comprised of (%):			
Glucose	15	8.9	2.2
Xylose	71	37.4	53.3
Arabinose	11	7.4	0.7
Mannose	–	1.8	0.7
Galactose	3	1.7	0.7
Rhamnose	–	–	1.2
Klason lignin	13.4	42.7	41.1
References	(Zikeli et al., 2016)	(Du et al., 2013)	(Balakshin et al., 2011)

[a] The LCC sample from wheat straw was extracted by dimethyl sulfoxide (DMSO) and tetrabutylammonium hydroxide (TBAH) and separated by a membrane.
[b] The LCC sample from spruce was extracted by DMSO and TBAH, and precipitated by a saturated $Ba(OH)_2$ solution. Samples were obtained by freeze-drying the solution after precipitation.
[c] The LCC sample from birch was extracted by 90% acetic acid and dried in a vacuum oven at 35 °C.

studies have indicated that lignin is covalently linked to hemicellulose units in so called lignin-carbohydrate complexes (LCCs) (Lawoko et al., 2003). The existence of analogous cellulose-lignin covalent linkages is still under debate.

Lignin/phenolic–carbohydrate complexes from wheat straw and wood may contain different amounts of lignin and carbohydrates. As shown in Table 10, a component analysis of LCC from wheat straw indicated that it contains 86.6% carbohydrates (among them, 15% glucose, 71% xylose, 11% arabinose, 3% galactose) and 13.4% Klason lignin (Zikeli et al., 2016). The types of sugars in LCC are mainly related to the types of hemicellulose in the species of wood materials and wheat straw. The principal sugars are D-xylose, L-arabinose, D-glucose, D-galactose, D-mannose, D-glucuronic acid, 4-*O*-methyl-D-glucuronic acid, and D-galacturonic acid. L-rhamnose, L-fucose, and various *O*-methylated neutral sugars are present to a lesser extent. The major hemicellulose in wheat straw is acetylated arabino-4-*O*-methylglucuronoxylan. The predominant softwood hemicelluloses are acetylated galactoglucomannans, and the predominant hemicelluloses in hardwood, such as birch, are partially acetylated acidic xylans (Sun et al., 2004). However, the relative sugar content is related to both the species and the separation method of LCCs. For example, Yao et al. (2016) studied the LCC fraction extracted from wheat straw and found the arabinose/xylose ratio of LCC is lower than that of hemicelluloses. This observation suggested that the side chains of hemicelluloses of LCC are degraded during extraction (Yao et al., 2016).

4.2. LCC structure and bonds of wheat straw and wood

Generally, lignin forms covalent bonds with hemicelluloses at the α-carbon site and C-4 in the benzene ring (Buranov and Mazza, 2008). Covalent bonds between lignin and hemicelluloses have been suggested to be of four main types: benzyl ethers, benzyl esters, phenyl glycoside bonds, and acetal linkages (Björkman, 1957; Zhao et al., 2020).

Most LCC linkages in wheat straw lignin are direct ether bonds to

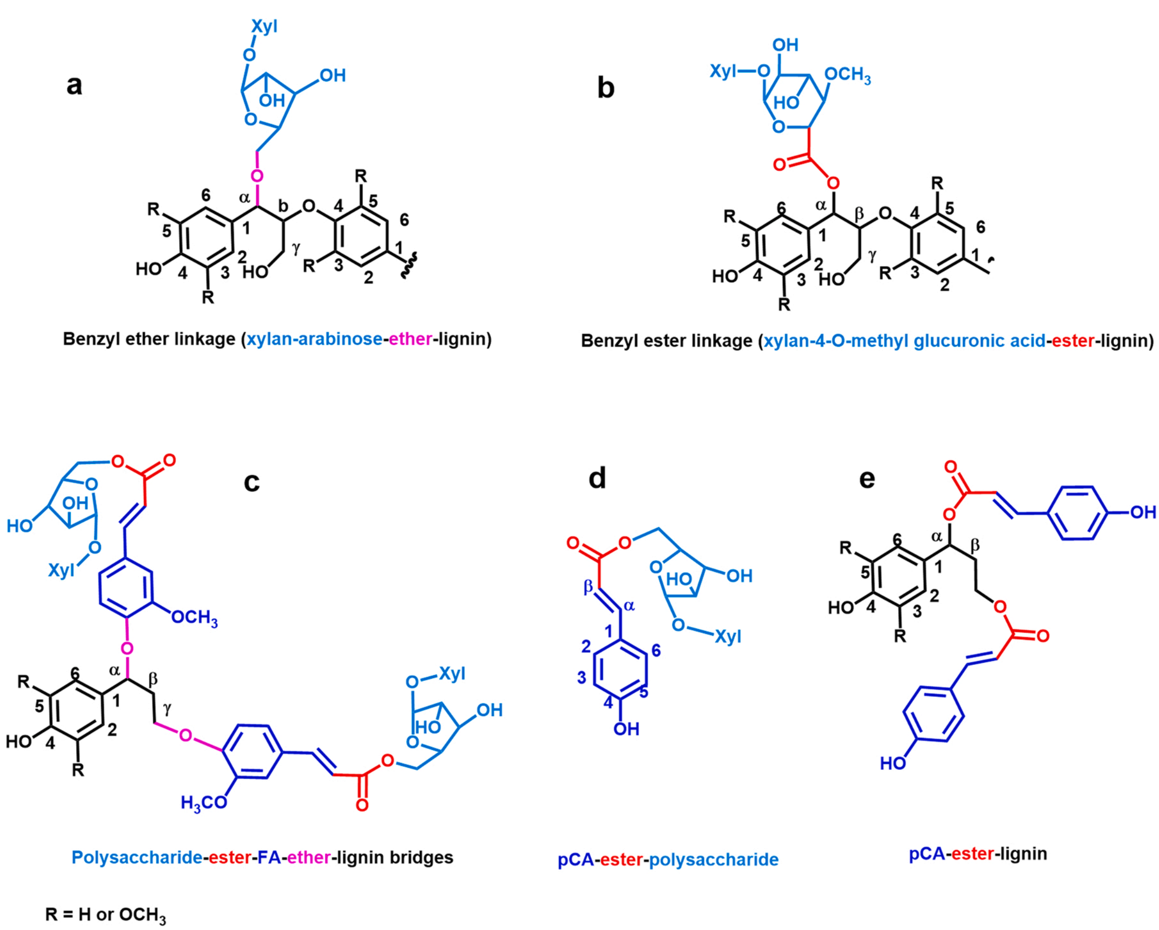

Fig. 11. Simple representative polysaccharide-lignin bridges (adapted from Sun et al., 1997): (a) benzyl ether linkage, (b) benzyl ester linkage, (c) polysaccharide-ester -FA-ester-lignin bridges, (d) pCA-ester-polysaccharide, and (e) pCA-ester- lignin.

Table 11
The content of hydroxycinnamic acids (%, w/w) in milled wheat straw lignin from four days ball-milled wheat straw (LMH and LML), and enzyme lignin fractions obtained from four-day ball-milled wheat straw and three days cellulose-treated residues (LEH and LEL) (Sun et al., 1997).

Fractions	pCA			FA		
	Total[a]	Ester-linked[a]	Ether-linked[b]	Total[a]	Ester-linked[a]	Ether-linked[b]
LMH[c]	0.16 ± 0.01	0.068 ± 0.003	0.092	0.61 ± 0.02	0.28 ± 0.01	0.33
LML[d]	0.74 ± 0.02	0.58 ± 0.01	0.16	2.72 ± 0.02	0.81 ± 0.01	1.91
LEH[e]	0.62 ± 0.01	0.48 ± 0.01	0.14	1.26 ± 0.01	0.40 ± 0.00	0.86
LEL[f]	1.40 ± 0.02	0.96 ± 0.02	0.44	3.02 ± 0.03	1.24 ± 0.02	1.78

[a] Mean ± S.E. based on duplicate of determinations.
[b] Difference between total and ester-linked hydroxycinnamic acids.
[c] LMH Hemicellulose- rich fractions from milled straw lignin
[d] LML Lignin-rich fraction from milled straw lignin
[e] LEH Hemicellulose-rich fractions from enzyme lignin
[f] LEL Lignin-rich fraction from enzyme lignin

arabinose side chains of xylan (Fig. 11A). Approximately 1% wheat straw lignin is also directly linked to glucuronic acid or 4-*O*-methyl-glucuronic acid by ester bonds (Fig. 11B). In wheat straw cell walls, hydroxycinnamic acids, mainly FA were proven to act as a bridge in the connections between lignins and hemicelluloses (Sun et al., 1997). Sun et al. showed that FA is ether-linked to lignin (52–68%) and ester-linked to hemicelluloses (32–48%) forming ester-ether bridges in the lignin fragments (Fig. 11C), while pCA in wheat straw is mainly ester-linked to lignin, with little ester-linked to hemicelluloses (Fig. 11D and E, Table 11). pCA cannot act as a bridge in the connection between lignin and hemicelluloses (Sun et al., 1997, 2001, 2002).

Softwood hemicelluloses constitute predominantly galactoglucomannan with smaller amounts of xylan. Studies on spruce and pine pulps, prepared by sulfite cooking, revealed that the LCC bonds were of the phenyl glycoside and γ–ester types and often involved xylan, probably due to that xylan sustained the harsh pulping conditions without severe degradation better than galactoglucomannan (Lawoko et al., 2006; Deshpande et al., 2018). In hardwood, acetylated 4-*O*-methylgluconoxylan is the main carbohydrate associated with lignins, and acetyl groups frequently acylate the C2 and C3 positions in the xylose units (Yuan et al., 2011). LCC can decrease the rate of delignification in chemical processes, decrease the yield of cellulosic ethanol via fermentation, and increase biomass recalcitrance during other biomass refinery processes (Nicholson et al., 2012). Therefore, studying the LCC structure is of great significance to biomass refinement.

5. Conclusion

The lignin distribution, structure, and morphology of wheat straw and wood were compared. The important points are the following:

1. In general, wheat straw contains less lignin than wood materials, but it is affected by soil type, fertilizer treatment, and sampling sites.
2. Both wood and wheat straw fibers consist of a middle lamella (ML), primary wall (P), and secondary wall (S). However, the S1 layer is thicker in wheat straw fiber than in wood fiber. S1 is believed to be a focal point of fracture in wheat straw in mechanically based processes.
3. Because the volume fraction of the ML and the CC in wheat straw fiber is larger than that in wood fiber, the percentage of total lignin in the ML and the CC is higher for wheat straw fibers than for wood fibers.
4. The structure of wheat straw lignin is a coumaryl-guaicyl-syringyl (H-G-S)-type lignin, while softwood is a guaiacyl (G)-type lignin and hardwood is a guaiacyl-syringyl (G-S)-type lignin. Wheat straw lignin also contains p-coumaric acid (pCA) and ferulic acid (FA).
5. A significant difference between wheat straw lignin and wood lignin is that the flavone tricin is incorporated into the wheat straw lignin. Up to 8.0 units of tricin have been detected in wheat straw lignin per 100 aromatic rings.
6. Monolignols in wheat straw and wood lignin are connected via C-C bonds (β-1, β-5, β–β, and 5–5) and C-O (β-O-4 and 4-O-5) bonds. There are fewer C-C connections in wheat straw lignin than in wood lignin
7. In wheat straw cell walls, the majority of wheat straw lignin is directly linked to arabinose side chains of xylan by ether bonds. p-Coumaric acid (pCA) in wheat straw is mainly ester-linked to the lignin while ferulic acid (FA) is ether-linked to lignin and ester-linked to hemicelluloses.

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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.

References

Adapa, P., Tabil, L., Schoenau, G., 2009. Compaction characteristics of barley, canola, oat and wheat straw. Biosyst. Eng. 104 (3), 335–344. https://doi.org/10.1016/j.biosystemseng.2009.06.022.
Adler, E., 1977. Lignin chemistry-past, present and future. Wood Sci. Technol. 11 (3), 169–218. https://doi.org/10.1007/BF00365615.
Altaner, C.M., Tokareva, E.N., Jarvis, M.C., Harris, P.J., 2010. Distribution of (1→4)-β-galactans, arabinogalactan proteins, xylans and (1→3)-β-glucans in tracheid cell walls of softwoods. Tree Physiol. 30 (6), 782–793. https://doi.org/10.1093/treephys/tpq021.
Argyropoulos, D.S., 1994. Quantitative phosphorus-31 NMR analysis of lignins, a new tool for the lignin chemist. J. Wood Chem. Technol. 14 (1), 45–63. https://doi.org/10.1080/02773819408003085.
Baison, J., Vidalis, A., Zhou, L., Chen, Z.-Q., Li, Z., Sillanpää, M.J., Bernhardsson, C., Scofield, D., Forsberg, N., Grahn, T., Olsson, L., Karlsson, B., Wu, H., Ingvarsson, P. K., Lundqvist, S.-O., Niittylä, T., García-Gil, M.R., 2019. Genome-wide association study identified novel candidate loci affecting wood formation in Norway spruce. Plant J. 100 (1), 83–100. https://doi.org/10.1111/tpj.14429.
Balakshin, M., Capanema, E., Gracz, H., Chang, H.M., Jameel, H., 2011. Quantification of lignin–carbohydrate linkages with high-resolution NMR spectroscopy. Planta 233 (6), 1097–1110. https://doi.org/10.1007/s00425-011-1359-2.
Balakshin, M., Capanema, E.A., Zhu, X., Sulaeva, I., Potthast, A., Rosenau, T., Rojas, O.J., 2020. Spruce milled wood lignin: linear, branched or cross-linked. Green Chem. 22, 3985–4001. https://doi.org/10.1039/D0GC00926A.
Biricik, H., Aköz, F., Berktay, I., Tulgar, A.N., 1999. Study of pozzolanic properties of wheat straw ash. Cem. Concr. Res. 29 (5), 637–643. https://doi.org/10.1016/S0008-8846(98)00249-X.
Björkman, A., 1956. Studies on finely divided wood. Part 1. Extraction of lignin with neutral solvents. Sven. Papp. 59, 477–485.
Björkman, A., 1957. Lignin and lignin-carbohydrate complexes. Ind. Eng. Chem. 49 (9), 1395–1398. https://doi.org/10.1021/ie50573a040.
Boerjan, W., Ralph, J., Baucher, M., 2003. Lignin biosynthesis. Annu. Rev. Plant Biol. 54, 519–546. https://doi.org/10.1146/annurev.arplant.54.031902.134938.
Bose, S.K., Francis, R.C., 1999. The role of β-O-4 cleavage in acidic organosolv pulping of softwoods. J. Pulp Pap. Sci. 25, 425–430.
Britannica, 2021. Available from: ⟨https://www.britannica.com/science/wood-plant-tissue/Microstructure⟩.
Bunzel, M., Ralph, J., Kim, H., Lu, F., Ralph, S.A., Marita, J.M., Steinhart, H., 2003. Sinapate dehydrodimers and sinapate−ferulate heterodimers in cereal dietary fiber. J. Agric. Food Chem. 51 (5), 1427–1434. https://doi.org/10.1021/jf020910v.
Buranov, A.U., Mazza, G., 2008. Lignin in straw of herbaceous crops. Ind. Crop. Prod. 28 (3), 237–259. https://doi.org/10.1016/j.indcrop.2008.03.008.
Chang, H.M., Cowling, E.B., Brown, W., Adler, E., Miksche, G., 1975. Comparative studies on cellulolytic enzyme lignin and milled wood lignin of sweetgum and

spruce. Holzforschung 29 (5), 153–159. https://doi.org/10.1515/hfsg.1975.29.5.153.

Collins, S.R.A., Wellner, N., Martinez Bordonado, I., Harper, A.L., Miller, C.N., Bancroft, I., Waldron, K.W., 2014. Variation in the chemical composition of wheat straw: the role of tissue ratio and composition. Biotechnol. Biofuels 7, 121. https://doi.org/10.1186/s13068-014-0121-y.

Crestini, C., Argyropoulos, D.S., 1997. Structural analysis of whet straw lignin by quantitative 31P and 2D NMR spectroscopy. The occurrence of ester bonds and α-O-4 substructures. J. Agric. Food Chem. 45, 1212–1219. https://doi.org/10.1021/jf960568k.

Crestini, C., Melone, F., Sette, M., Saladino, R., 2011. Milled wood lignin: a linear oligomer. Biomacromolecules 12 (11), 3928–3935. https://doi.org/10.1021/bm200948r.

Del Río, J.C., Rencoret, J., Prinsen, P., Martínez, A.T., Ralph, J., Gutiérrez, A., 2012. Structural characterization of wheat straw lignin as revealed by analytical pyrolysis, 2D NMR, and reductive cleavage methods. J. Agric. Food Chem. 60 (23), 5922–5935, 10.1021/jf301002n.

Del Río, J.C., Rencoret, J., Gutiérrez, A., Elder, T., Kim, H., Ralph, J., 2020. Lignin monomers from beyond the canonical monolignol biosynthetic pathway: another brick in the wall. ACS Sustain. Chem. Eng. 8, 4997–5012. https://doi.org/10.1021/acssuschemeng.0c01109.

Deshpande, R., Giummarella, N., Henriksson, G., Germgård, U., Sundvall, L., Grundberg, H., Lawoko, M., 2018. The reactivity of lignin carbohydrate complex (LCC) during manufacture of dissolving sulfite pulp from softwood. Ind. Crop. Prod. 115, 315–322. https://doi.org/10.1016/j.indcrop.2018.02.038.

Donaldson, L., 2008. Microfibril angle: measurement, variation and relationships – a review. IAWA J. 29 (4), 345–386. https://doi.org/10.1163/22941932-90000192.

Donaldson, L., Hague, J., Snell, R., 2001. Lignin distribution in coppice poplar, linseed and wheat straw. Holzforschung 55 (4), 379–385. https://doi.org/10.1515/HF.2001.063.

Donaldson, L.A., 1996. Clonal variation in the fracture properties of radiata pine wood. In: Donaldson, L.A., Singh, A.P., Butterfield, B.G. (Eds.), Recent Advances in Wood Anatomy. White-house. NZFRI Ltd, Rotorua, New Zealand, pp. 283–291.

Du, X., Gellerstedt, G., Li, J., 2013. Universal fractionation of lignin–carbohydrate complexes (LCC s) from lignocellulosic biomass: an example using spruce wood. Plant J. 74 (2), 328–338. https://doi.org/10.1111/tpj.12124.

Duval, A., Vilaplana, F., Crestini, C., Lawoko, M., 2016. Solvent screening for the fractionation of industrial kraft lignin. Holzforschung 70 (1), 11–20. https://doi.org/10.1515/hf-2014-0346.

El Hage, R., Brosse, N., Chrusciel, L., Sanchez, C., Sannigrahi, P., Ragauskas, A., 2009. Characterization of milled wood lignin and ethanol organosolv lignin from miscanthus. Polym. Degrad. Stab. 94, 1632–1638. https://doi.org/10.1016/j.polymdegradstab.2009.07.007.

Evert, R.F., 2006. Esau's Plant Anatomy: Meristems, Cells, and Tissues of the Plant Body: Their Structure, Function, and Development, third ed. John Wiley & Sons. Wiley Online Library.

Faleva, A.V., Belesov, A.V., Kozhevnikov, A.Y., Falev, D.I., Chukhchin, D.G., Novozhilov, E.V., 2020. Analysis of the functional group composition of the spruce and birch phloem lignin. Int. J. Biol. Macromol. 166, 913–922. https://doi.org/10.1016/j.ijbiomac.2020.10.248.

FAO, Food and Agriculture Organization of the Unites States, 2016. Cereal Supply and Demand Brief. Available from: ⟨http://www.fao.org/worldfoodsituation/csdb/en/⟩.

FAOSTAT, Food and Agriculture Organization of the Unites States (2018). Available from: ⟨http://www.fao.org/faostat/en/#home⟩.

Fougere, D., Nanda, S., Clarke, K., Kozinski, J.A., Li, K., 2016. Effect of acidic pretreatment on the chemistry and distribution of lignin in aspen wood and wheat straw substrates. Biomass Bioenergy 91, 56–68. https://doi.org/10.1016/j.biombioe.2016.03.027.

Gani, T.Z.H., Orella, M.J., Anderson, E.M., Stone, M.L., Brushett, F.R., Beckham, G.T., Román-Leshkov, Y., 2019. Computational evidence for kinetically controlled radical coupling during lignification. ACS Sustain. Chem. Eng. 7 (15), 13270–13277. https://doi.org/10.1021/acssuschemeng.9b02506.

Ghaffar, S.H., 2018. Wheat straw biomass and its anatomical characteristics. Food Nutr. Curr. Res. 1 (2), 61–66.

Ghaffar, S.H., Fan, M., 2013. Structural analysis for lignin characteristics in biomass straw. Biomass Bioenergy 57, 264–279. https://doi.org/10.1016/j.biombioe.2013.07.015.

Gillet, S., Aguedo, M., Petitjean, L., Morais, A.R.C., da Costa Lopes, A.M., Łukasik, R.M., Anastas, P.T., 2017. Lignin transformations for high value applications: towards targeted modifications using green chemistry. Green Chem. 19, 4200–4233. https://doi.org/10.1039/C7GC01479A.

Goto, H., Koda, K., Tong, G.L., Matsumoto, Y., Meshitsuka, G., 2006. Interference of carbohydrates in the determination of the methoxyl content of lignin in woody samples. J. Wood Chem. Technol. 26, 81–93. https://doi.org/10.1080/02773810600582277.

Harper, S.H., Lynch, J.M., 1981. The chemical components and decomposition of wheat straw leaves, internodes and nodes. J. Sci. Food Agric. 32 (11), 1057–1062. https://doi.org/10.1002/jsfa.2740321103.

Holm, A., Niklasson, R., 2018. The Effect on Wood Components During Soda Pulping; Pretreatment and Pulping of Forest Residues in a Biorefinery Concept (Master thesis). Chalmers University of Technology, Sweden.

Huang, D., Li, R., Xu, P., Li, T., Deng, R., Chen, S., Zhang, Q., 2020. The cornerstone of realizing lignin value-addition: exploiting the native structure and properties of lignin by extraction methods. Chem. Eng. J. 402, 126237 https://doi.org/10.1016/j.cej.2020.126237.

Huijgen, W.J.J., Telysheva, G., Arshanitsa, A., Gosselink, R.J.A., De Wild, P.J., 2014. Characteristics of wheat straw lignins from ethanol-based organosolv treatment. Ind. Crop. Prod. 59, 85–95. https://doi.org/10.1016/j.indcrop.2014.05.003.

Ilvessalo-Pfäffli, M.S., 1995. Fiber Atlas: Identification of Papermaking Fibers. Springer Series in Wood Science, Springer-Verlag Berlin Heidelberg, Germany. https://doi.org/10.1007/978-3-662-07212-7.

Jacobs, R.S., Pan, W.L., Fuller, W.S., McKean, W.T., 2000. Wheat straw: within-plant variation in chemical composition and fiber properties. In: Proceedings of the Pulping/Process and Product Quality Conference. Technical Association of the Pulp and Paper Industry (TAPPI), Canada.

Jasiukaitytė-Grojzdek, E., Huš, M., Grilc, M., Likozar, B., 2020. Acid-catalysed α-O-4 aryl-ether bond cleavage in methanol/(aqueous) ethanol: understanding depolymerisation of a lignin model compound during organosolv pretreatment. Sci. Rep. 10 (1), 11037. https://doi.org/10.1038/s41598-020-67787-9.

Jędrzejczak, P., Collins, M.N., Jesionowski, T., Klapiszewski, Ł., 2021. The role of lignin and lignin-based materials in sustainable construction – a comprehensive review. Int. J. Biol. Macromol. 187, 624–650. https://doi.org/10.1016/j.ijbiomac.2021.07.125.

Ji, Z., Ma, J.F., Zhang, Z.H., Xu, F., Sun, R.C., 2013. Distribution of lignin and cellulose in compression wood tracheids of *Pinus yunnanensis* determined by fluorescence microscopy and confocal Raman microscopy. Ind. Crop. Prod. 47, 212–217. https://doi.org/10.1016/j.indcrop.2013.03.006.

Karmanov, A.P., Kanarsky, A.V., Kocheva, L.S., Belyy, V.A., Semenov, E.I., Rachkova, N. G., Bogdanovich, N.I., Pokryshkin, S.A., 2021. Chemical structure and polymer properties of wheat and cabbage lignins - valuable biopolymers for biomedical applications. Polymer 220, 123571. https://doi.org/10.1016/j.polymer.2021.123571.

Katahira, R., Elder, T.J., Beckham, G.T., 2018. A brief introduction to lignin structure. In: Lignin Valorization: Emerging Approaches, Chapter 1. RSC, pp. 1–20. https://doi.org/10.1039/9781788010351-00001.

Khan, T.S., Mubeen, U., 2012. Wheat straw: a pragmatic overview. Curr. Res. J. Biol. Sci. 4 (6), 673–675.

Kumar, L., Arantes, V., Chandra, R., Saddler, J., 2012. The lignin present in steam pretreated softwood binds enzymes and limits cellulose accessibility. Bioresour. Technol. 103 (1), 201–208. https://doi.org/10.1016/j.biortech.2011.09.091.

Lawoko, M., Henriksson, G., Gellerstedt, G., 2003. New method for quantitative preparation of lignin carbohydrate complex from unbleached softwood kraft pulp: ligninPolysaccharide networks I. Holzforschung 57 (1), 69–74. https://doi.org/10.1515/HF.2003.011.

Lawoko, M., Henriksson, G., Gellerstedt, G., 2006. Characterization of lignin-carbohydrate complexes from spruce sulfite pulp. Holzforschung 60 (2), 162–165. https://doi.org/10.1515/HF.2006.026.

Lee, H., Feng, X., Mastalerz, M., Feakins, S.J., 2019. Characterizing lignin: combining lignin phenol, methoxy quantification, and dual stable carbon and hydrogen isotopic techniques. Org. Geochem. 136, 103894 https://doi.org/10.1016/j.orggeochem.2019.07.003.

Lin, S.Y., Dence, C.W., 1992. Methods in Lignin Chemistry. Springer Series in Wood Science, Springer-Verlag Berlin Heidelberg, Germany. https://doi.org/10.1007/978-3-642-74065-7.

Liu, Q., Luo, L., Zheng, L., 2018. Lignins: biosynthesis and biological functions in plants. Int. J. Mol. Sci. 19 (2), 335. https://doi.org/10.3390/ijms19020335.

Liu, R., Yu, H., Huang, Y., 2005. Structure and morphology of cellulose in wheat straw. Cellulose 12 (1), 25–34. https://doi.org/10.1023/B:CELL.0000049346.28276.95.

Lourenço, A., Pereira, H., 2018. Compositional variability of lignin in biomass. lignin-trends and applications. In: Poletto, M. (Ed.), Lignin - Trends and Applications. IntechOpen, London, pp. 65–98. https://doi.org/10.5772/intechopen.71208.

Lu, F., Ralph, J., 2010. Lignin. In: Sun, R.C. (Ed.), Cereal Straw as a Resource for Sustainable Biomaterials and Biofuels. Elsevier, Amsterdam, the Netherlands, pp. 169–207. https://doi.org/10.1016/C2009-0-06759-2.

Ma, J., Zhou, X., Ma, J., Ji, Z., Zhang, X., Xu, F., 2014. Raman microspectroscopy imaging study on topochemical correlation between lignin and hydroxycinnamic acids in *Miscanthus sinensis*. Microsc. Microanal. 20 (3), 956–963. https://doi.org/10.1017/S1431927614000658.

Matsakas, L., Raghavendran, V., Yakimenko, O., Persson, G., Olsson, E., Rova, U., Christakopoulos, P., 2019. Lignin-first biomass fractionation using a hybrid organosolv–Steam explosion pretreatment technology improves the saccharification and fermentability of spruce biomass. Bioresour. Technol. 273, 521–528. https://doi.org/10.1016/j.biortech.2018.11.055.

Mauseth, J.D., 2008. Botany: An Introduction to Plant Biology, fourth ed. Jones & Bartlett Publishers, Sudbury, USA.

Mini-Encyclopedia of Papermaking Wet-End Chemistry, n.d. Available from: ⟨https://projects.ncsu.edu/project/hubbepaperchem/FIBR.htm⟩.

Motte, J.C., Escudie, R., Beaufils, N., Steyer, J.P., Bernet, N., Delgenes, J.-P., Dumas, C., 2014. Morphological structures of wheat straw strongly impacts its anaerobic digestion. Ind. Crop. Prod. 52, 695–701. https://doi.org/10.1016/j.indcrop.2013.11.038.

Nguyen, T.-N., Son, S.-H., Jordan, M.C., Levin, D.B., Ayele, B.T., 2016. Lignin biosynthesis in wheat (*Triticum aestivum L.*): its response to waterlogging and association with hormonal levels. BMC Plant Biol. 16, 28. https://doi.org/10.1186/s12870-016-0717-4.

Nicholson, D.J., Duarte, G.V., Alves, E.F., Kiemle, D.J., Francis, R.C., 2012. Preliminary results on an approach for the quantification of lignin-carbohydrate complexes (LCC) in hardwood pulps. J. Wood Chem. Technol. 32 (3), 238–252. https://doi.org/10.1080/02773813.2012.659318.

NL Agency Mistry of Public Affairs, 2013. Rice straw and Wheat straw. Potential feedstocks for the Biobased Economy, Report, June 2013. ⟨https://english.rvo.nl/sites/default/files/2013/12/Straw%20report%20AgNL%20June%202013.pdf⟩.

Novaes, E., Kirst, M., Chiang, V., Winter-Sederoff, H., Sederoff, R., 2010. Lignin and biomass: a negative correlation for wood formation and lignin content in trees. Plant Physiol. 154 (2), 555–561. https://doi.org/10.1104/pp.110.161281.

Paszner, L., Behera, N.C., 1985. Beating behaviour and sheet strength development of coniferous organosolv fibers. Holzforschung 39, 51–61. https://doi.org/10.1515/hfsg.1985.39.1.51.

Pereira, A., Hoeger, I.C., Ferrer, A., Rencoret, J., Del Rio, J.C., Kruus, K., Rojas, O.J., 2017. Lignin films from spruce, eucalyptus, and wheat straw studied with electroacoustic and optical sensors: effect of composition and electrostatic screening on enzyme binding. Biomacromolecules 18 (4), 1322–1332. https://doi.org/10.1021/acs.biomac.7b00071.

Ralph, J., 2010. Hydroxycinnamates in lignification. Phytochem. Rev. 9 (1), 65–83. https://doi.org/10.1007/s11101-009-9141-9.

Ralph, J., Lapierre, C., Boerjan, W., 2019. Lignin structure and its engineering. Curr. Opin. Biotechnol. 56, 240–249. https://doi.org/10.1016/j.copbio.2019.02.019.

Raven, P.H., Evert, R.F., Eichhorn, S.E., 2007. The angiosperm plant body: structure and development. Biology of Plants, seventh ed. W.H. Freeman & Company/Worth Publishers, New York, pp. 510–527.

Reid, I.D., 1995. Biodegradation of lignin. Can. J. Bot. 73 (S1), 1011–1018. https://doi.org/10.1139/b95-351.

Sahoo, B., Saraswat, M.L., Haque, N., Khan, M.Y., 2002. Influence of chemical treatment of wheat straw on carbon–nitrogen and energy balance in sheep. Small Rumin. Res. 44 (3), 201–206. https://doi.org/10.1016/S0921-4488(02)00043-3.

Sangha, A.K., Parks, J.M., Standaert, R.F., Ziebell, A., Davis, M., Smith, J.C., 2012. Radical coupling reactions in lignin synthesis: a density functional theory study. J. Phys. Chem. B 116 (16), 4760–4768. https://doi.org/10.1021/jp2122449.

Sannigrahi, P., Ragauskas, A.J., Miller, S.J., 2008. Effects of two-stage dilute acid pretreatment on the structure and composition of lignin and cellulose in loblolly pine. Bioenergy Res. 1 (3–4), 205–214. https://doi.org/10.1007/s12155-008-9021-y.

Sapouna, I., Lawoko, M., 2021. Deciphering lignin heterogeneity in ball milled softwood: unravelling the synergy between the supramolecular cell wall structure and molecular events. Green Chem. 23, 3348–3364. https://doi.org/10.1039/D0GC04319B.

Schirp, A., Loge, F., Aust, S., Swaner, P., Turner, G., Wolcott, M., 2006. Production and characterization of natural fiber-reinforced thermoplastic composites using wheat straw modified with the fungus *Pleurotus ostreatus*. J. Appl. Polym. Sci. 102 (6), 5191–5201. https://doi.org/10.1002/app.24724.

Schutyser, W., Renders, T., van den Bosch, S., Koelewijn, S.F., Beckham, G.T., Sels, B.F., 2018. Chemicals from lignin: an interplay of lignocellulose fractionation, depolymerisation, and upgrading. Chem. Soc. Rev. 47, 852–908. https://doi.org/10.1039/C7CS00566K.

Serrano, L., Esakkimuthu, E.S., Marlin, N., Brochier-Salon, M.C., Mortha, G., Bertaud, F., 2018. Fast, easy, and economical quantification of lignin phenolic hydroxyl groups: comparison with classical techniques. Energy Fuels 32 (5), 5969–5977. https://doi.org/10.1021/acs.energyfuels.8b00383.

Sette, M., Wechselberger, R., Crestini, C., 2011. Elucidation of lignin structure by quantitative [2]D NMR. Chem. Eur. J. 17 (34), 9529. https://doi.org/10.1002/chem.201003045.

Singh, S., Dutt, D., Tyagi, C.H., 2011. Complete characterization of wheat straw (*Triticum aestivum* PBW-343 L. Emend. Fiori & PAOL.)–a renewable source of fibres for pulp and paper making. BioResources 6 (1), 154–177. https://doi.org/10.15376/biores.6.1.154-177.

Statista, 2021. Available from: ⟨https://www.statista.com/statistics/596035/pulp-production-distribution-worldwide-by-region/⟩.

Sturgeon, M.R., Kim, S., Lawrence, K., Paton, R.S., Chmely, S.C., Nimlos, M., Foust, T.D., Beckham, G.T., 2014. A mechanistic investigation of acid-catalyzed cleavage of aryl-ether linkages: implications for lignin depolymerization in acidic environments. ACS Sustain. Chem. Eng. 2, 472–485. https://doi.org/10.1021/sc400384w.

Sun, M., Xu, X., Wang, C., Bai, Y., Fu, C., Zhang, L., Wang, Y., 2020. Environmental burdens of the comprehensive utilization of straw: wheat straw utilization from a life-cycle perspective. J. Clean. Prod. 259, 120702 https://doi.org/10.1016/j.jclepro.2020.120702.

Sun, R., Lawther, J.M., Banks, W.B., 1997. A tentative chemical structure of wheat straw lignin. Ind. Crop. Prod. 6 (1), 1–8. https://doi.org/10.1016/S0926-6690(96)00170-7.

Sun, R., Sun, X.F., Wang, S.Q., Zhu, W., Wang, X.Y., 2002. Ester and ether linkages between hydroxycinnamic acids and lignins from wheat, rice, rye, and barley straws, maize stems, and fast-growing poplar wood. Ind. Crop. Prod. 15 (3), 179–188. https://doi.org/10.1016/S0926-6690(01)00112-1.

Sun, R.C., Sun, X.F., Zhang, S.H., 2001. Quantitative determination of hydroxycinnamic acids in wheat, rice, rye, and barley straws, maize stems, oil palm frond fiber, and fast-growing poplar wood. J. Agric. Food Chem. 49 (11), 5122–5129. https://doi.org/10.1021/jf010500r.

Sun, R., Sun, X.F., Tomkinson, J., 2004. Hemicelluloses and their derivatives. In: Hemicelluloses: Science and Technology. ACS Symposium Series 864, Chapter 1, pp. 2–22. DOI: 10.1021/bk-2004-0864.ch001.

Taiz, L., Zeiger, E., 2010. Cell walls: structure, biogenesis, and expansion. In: Taiz, L., Zeiger, E. (Eds.), Plant Physiology. Sinauer Associates, Sunderland, MA. Chapter 15.

The Wood Database,2021. Available from: ⟨https://www.wood-database.com/wood-articles/softwood-anatomy/⟩.

Tian, X., Wang, B., Wang, B., Li, J., Chen, K., 2017. Structural characterization of lignin isolated from wheat-straw during the alkali cooking process. BioResources 12 (2), 2407–2420. https://doi.org/10.15376/biores.12.2.2407-2420.

Toman, R., Chimidcogzol, A., 1988. L-Arabino-(4-O-methyl-D-glucurono)-D-xylan from the straw of the wheat Orchon (*Triticum bulgary* Z). Chem. Pap. 42 (5), 649–657.

Trubetskaya, A., Jensen, P.A., Jensen, A.D., Steibel, M., Spliethoff, H., Glarborg, P., Larsen, F.H., 2016. Comparison of high temperature chars of wheat straw and rice husk with respect to chemistry, morphology and reactivity. Biomass Bioenergy 86, 76–87. https://doi.org/10.1016/j.biombioe.2016.01.017.

Vanholme, R., Morreel, K., Ralph, J., Boerjan, W., 2008. Lignin engineering. Curr. Opin. Plant Biol. 11 (3), 278–285. https://doi.org/10.1016/j.pbi.2008.03.005.

Vanholme, R., Demedts, B., Morreel, K., Ralph, J., Boerjan, W., 2010. Lignin biosynthesis and structure. Plant Physiol. 153 (3), 895–905. https://doi.org/10.1104/pp.110.155119.

Wang, D., Lin, L., Fu, F., Fan, M., 2020. Fracture mechanisms of softwood under longitudinal tensile load at the cell wall scale. Holzforschung 74 (7), 715–724. https://doi.org/10.1515/hf-2019-0112.

Wang, H.M., Ma, C.Y., Li, H.Y., Chen, T.Y., Wen, J.L., Cao, X.F., Sun, R.C., 2019. Structural variations of lignin macromolecules from early growth stages of poplar cell walls. ACS Sustain. Chem. Eng. 8 (4), 1813–1822. https://doi.org/10.1021/acssuschemeng.9b05845.

Wen, J.L., Xue, B.L., Sun, S.L., Sun, R.C., 2013. Quantitative structural characterization and thermal properties of birch lignins after auto-catalyzed organosolv pretreatment and enzymatic hydrolysis. J. Chem. Technol. Biotechnol. 88 (9), 1663–1671. https://doi.org/10.1002/jctb.4017.

Wen, J.L., Sun, S.L., Yuan, T.Q., Sun, R.C., 2015. Structural elucidation of whole lignin from Eucalyptus based on preswelling and enzymatic hydrolysis. Green Chem. 17 (3), 1589–1596. https://doi.org/10.1039/C4GC01889C.

Xiao, L.P., Shi, Z.J., Bai, Y.Y., Wang, W., Zhang, X.M., Sun, R.C., 2013. Biodegradation of lignocellulose by white-rot fungi: structural characterization of water-soluble hemicelluloses. BioEnergy Res. 6 (4), 1154–1164. https://doi.org/10.1007/s12155-013-9302-y.

Xu, F., 2010. Structure, ultrastructure, and chemical composition. In: Sun, R.C. (Ed.), Cereal Straw as a Resource for Sustainable Biomaterials and Biofuels. Elsevier, Amsterdam, the Netherlands, pp. 9–47. https://doi.org/10.1016/B978-0-444-53234-3.00002-X.

Yao, L., Chen, C., Zheng, X., Peng, Z., Yang, H., Xie, Y., 2016. Determination of lignin-carbohydrate complexes structure of wheat straw using Carbon-13 isotope as a tracer. BioResources 11 (3), 6692–6707. https://doi.org/10.15376/biores.11.3.6692-6707.

Yu, H., Liu, R., Shen, D., Wu, Z., Huang, Y., 2008. Arrangement of cellulose microfibrils in the wheat straw cell wall. Carbohydr. Polym. 72 (1), 122–127. https://doi.org/10.1016/j.carbpol.2007.07.035.

Yu, J., Paterson, N., Blamey, J., Millan, M., 2017. Cellulose, xylan and lignin interactions during pyrolysis of lignocellulosic biomass. Fuel 191, 140–149. https://doi.org/10.1016/j.fuel.2016.11.057.

Yuan, T.Q., Sun, S.N., Xu, F., Sun, R.C., 2011. Characterization of lignin structures and lignin–carbohydrate complex (LCC) linkages by quantitative ^{13}C and 2D HSQC NMR spectroscopy. J. Agric. Food Chem. 59 (19), 10604–10614. https://doi.org/10.1021/jf2031549.

Yue, F., Lu, F., Ralph, S., Ralph, J., 2016. Identification of 4-O-5 units in softwood lignins via definitive lignin models and NMR. Biomacromolecules 17, 1909–1920. https://doi.org/10.1021/acs.biomac.6b00256.

Zeng, J., Helms, G.L., Gao, X., Chen, S., 2013. Quantification of wheat straw lignin structure by comprehensive NMR analysis. J. Agric. Food Chem. 61 (46), 10848–10857. https://doi.org/10.1021/jf4030486.

Zhai, H.M., Lee, Z.Z., 1989. Ultrastructure and topochemistry of delignification in alkaline pulping of wheat straw. J. Wood Chem. Technol. 9 (3), 387–406. https://doi.org/10.1080/02773818908050306.

Zhang, L., You, T., Zhang, L., Yang, H., Xu, F., 2014. Enhanced fermentability of poplar by combination of alkaline peroxide pretreatment and semi-simultaneous saccharification and fermentation. Bioresour. Technol. 164, 292–298. https://doi.org/10.1016/j.biortech.2014.04.075.

Zhang, L., You, T., Zhou, T., Zhang, L., Xu, F., 2016. Synergistic effect of white-rot fungi and alkaline pretreatments for improving enzymatic hydrolysis of poplar wood. Ind. Crop. Prod. 86, 155–162. https://doi.org/10.1016/j.indcrop.2016.03.041.

Zhang, L., Chen, K., Peng, L., 2017. Comparative research about wheat straw lignin from the black liquor after soda-oxygen and soda-AQ pulping: structural changes and pyrolysis behavior. Energy Fuels 31 (10), 10916–10923. https://doi.org/10.1021/acs.energyfuels.7b01786.

Zhao, Y., Shakeel, U., Rehman, M.S.U., Li, H., Xu, X., Xu, J., 2020. Lignin-carbohydrate complexes (LCCs) and its role in biorefinery. J. Clean. Prod. 253, 120076 https://doi.org/10.1016/j.jclepro.2020.120076.

Zhou, J.M., Ibrahim, R.K., 2010. Tricin—a potential multifunctional nutraceutical. Phytochem. Rev. 9, 413–424. https://doi.org/10.1007/s11101-009-9161-5.

Zhou, S., Liu, L., Wang, B., Xu, F., Sun, R., 2012. Microwave-enhanced extraction of lignin from birch in formic acid: structural characterization and antioxidant activity study. Process Biochem. 47 (12), 1799–1806. https://doi.org/10.1016/j.procbio.2012.06.006.

Zikeli, F., Ters, T., Fackler, K., Srebotnik, E., Li, J., 2016. Wheat straw lignin fractionation and characterization as lignin-carbohydrate complexes. Ind. Crop. Prod. 85, 309–317. https://doi.org/10.1016/j.indcrop.2016.03.012.