The role of NMR spectroscopy in lignocellulosic biomass characterisation: A mini review

Jelena Parlov Vuković [a],[*], Marina Tišma [b],[*]

[a] *NMR Centre, Ruđer Bošković Institute, Bijenička cesta 54, HR-10 000 Zagreb, Croatia*
[b] *Josip Juraj Strossmayer University of Osijek, Faculty of Food Technology Osijek, Franje Kuhača 18, HR-31000 Osijek, Croatia*

ARTICLE INFO

ABSTRACT

Lignocellulosic biomass (LB) is promising feedstock for the production of various bio-based products. However, due to its heterogenous character, complex chemical structure and recalcitrance, it is necessary to know its structural composition in order to optimize pretreatment process and further (bio)conversion into bio-based products. Nuclear Magnetic Resonance (NMR) spectroscopy is a fast and reliable method that can provide advanced data on the molecular architecture and composition of lignocellulosic biomass. In this brief overview, characteristic examples of the use of high-resolution NMR spectroscopy for the investigation of various types of LB and their structural units are given and the main drawbacks and future perspectives are outlined.

1. Introduction

In recent decades, much attention has been paid to the search for synergies between modern societies, growing economies and environmental protection (Mujtaba et al., 2023). A promising renewable raw material for the production of high-quality products, including biofuels and value-added products, to replace the dependence on fossil resources is LB (Li, Yang, Jiang, Jin, & Wu, 2023). LB has many favourable properties such as biodegradability, renewability, wide availability, non-toxicity and low cost. It mostly comes from agriculture (crops and harvest residues) and forestry and wood technology, but can also be found among the by-products or residues of the food industry. Among all types of LB, woody biomass plays a crucial role in development of lignocellulosic biorefineries as it does not compete with food production. In general, production of LB worldwide is about 181.5 billion tons and only 8.2 billion tons are used in various applications (Mujtaba et al., 2023).

A detailed understanding of composition and properties of LB is crucial for its correct application which is the reason why the field of lignocellulose chemistry has attracted much attention in recent years. Many researches worldwide are focused on finding fast and accurate methods for determination of lignocellulose chemical composition. LB mainly consists of three types of biopolymers: cellulose, hemicellulose and lignin that are interconnected and form a very complex network structure. The quantities and ratios of the biopolymers depend on the

type and origin of the biomass. In addition, lignocellulose contains small amounts of pectin, protein, extractives, and inorganic compounds (Tišma, Bucić-Kojić, & Planinić, 2021). Lignin is the most abundant aromatic biopolymer found in plant cell walls. The structure and composition of lignin depends on the origin of the lignin, i.e. the type of wood, the tissue and the cell wall layer. Lignin is usually classified according to the origin of the wood or the isolation process. According to lignin origin, wood can be divided into three categories: hardwood, softwood and grass. Softwood species consist of 27–32 % of lignin and contain mainly guaiacyl units (G) and traces of *p*-hydroxyphenyl units. The lignin content in hardwood species is usually between 18 and 30 % of the dry wood mass and contains syringyl (S), guaiacyl (G) and a small amount of *p*-coumaryl units (H). Grass lignin consists of G, S and H units as well as ferulates and coumarates (Argyropoulos, Pajer, & Crestini, 2021; Happs et al., 2021). Grass species include 10–30 % of lignin (García, Alfaro, Loaiza, Lozano-Calvo & López, 2022). Due to its chemical structure, lignin is a suitable renewable feedstock to substitute crude oil aromatics (Strassberger, Tanase, & Rothenberg, 2014) and wide range of chemicals and energy sources (Argyropoulos et al., 2021; Guo, Zhao, Chang, & Lee, 2023) such as e.g. bio-oil, vanillin, and phenolic resin (Bajwa, Pourhashem, Ullah, & Bajwa, 2019). Understanding the lignin structure and properties as well as methods of isolation is crucial for its industrial application (Wen, Sun, Xue, & Sun, 2013). The polysaccharide cellulose is the most abundant lignocellulosic biopolymer which is consisted of linear polymer chains of several

---

* Corresponding authors.

E-mail addresses: jparlovv@irb.hr (J.P. Vuković), marina.tisma@ptfos.hr (M. Tišma).

hundred to many thousands of glucose molecules linked by β-1,4-glycosidic bonds. The molecular structure of cellulose reveals properties like high reactivity due to the presence of OH group units, chirality, hydrophilicity and degradability of the amorphous region of cellulose (El Hariri El Nokab et al., 2022). There are four different polymorphs of cellulose: native, regenerative, amorphous and cellulose obtained by treating the amorphous type with glycerol at very high temperatures. Depending on the chemical nature of the cellulose, it can be divided into cellulose esters, which are obtained from natural cellulose with organic acids, anhydrides or acid chlorides, and cellulose ethers, which are produced by chemical modification of cellulose soluble in aqueous or organic media. Cellulose and cellulose derivatives can be used in many areas, e.g. in the paper, pulp and sensor industries as well as in the production of biofuels and in the food industry (Dhingra, Michael, Rajput, & Patil, 2012). Cellulose is also used in nanocomposites, nano-adsorbents for proteins, bone tissue engineering, biomedical applications, drug delivery and wound healing (Joseph, Sagarika, Sabu, Kalarikkal, & Thomas, 2020). Hemicellulose is an amorphous heterogeneous polymer (hetero-polysaccharides) present in the primary and secondary cell wall of plants (Hu, Fang, Du, Luo, & Guo, 2020). It consists of different monosaccharides such as pentoses (xylose, arabinose), hexoses (mannose, glucose, galactose) and sugar acids (galacturonic, glucuronic) in various amounts or traces dependent on the natural source (Peng et al., 2012). It has potential to be used for many high-value purposes like adsorbent, thickeners, binders in the food industry, as well as in pharmaceutical and cosmetic industries (Huang, Ma, Ji, Choi, & Si, 2021).

Many classical and instrumental analytical techniques such as elemental analysis, high-pressure liquid chromatography (HPLC),"incorporated pyrolysis with successive gas chromatography and mass spectrometry,, (Py-GC/MS), Fourier transform infrared spectroscopy (FTIR), etc. have been involved in investigation of lignocellulose composition and properties (Agarwal, 2019; Huang & Lo, 2020; Javier-Astete, Jimenez-Davalos, & Zolla, 2021; Kline et al., 2020).

Since its discovery in the last century, NMR spectroscopy has seen unparalled growth as an analytical method with various applications. It is one of the most powerful tools for identification and structure elucidation of compounds. NMR is based on the interaction of radiofrequency electromagnetic radiation with nuclei of atoms immersed in a strong magnetic field. NMR-active nuclei detectable by NMR spectroscopy are those with $I \neq 0$ (I being spin quantum number). Almost every atom has NMR active nuclide, but the most frequently observed are ^1H, ^{13}C, ^{15}N and ^{31}P. Hence, when NMR active nucleus in a magnetic field is irradiated with a short radiofrequency pulse the energy of the rf is absorbed by the nuclear spins if it matches the resonance frequency of the nucleus. The excited spins will relax and emit the absorbed energy which is detected as NMR spectrum. Today NMR spectroscopy is highly developed and technologically advanced method and one of the principal structural techniques for chemists to study organic and inorganic molecules as well as biomolecules (Günther, 2013). It is employed in different scientific fields such as physics, chemistry, material science, biology, biochemistry, medicine for identification of physical and chemical properties of atoms and molecules, determination of composition and purity of various types of samples, monitoring of reactions and study metabolism in cells. Furthermore, it has found a widespread use in industrial applications such as pharmaceutical, food, oil or biorefinery. One of the big advantages of NMR is the fact that it is non-destructive technique that can operate both, in the liquid and the solid-state. Today, there are literally thousands of one- and multi-dimensional NMR experiments that can be executed to acquire different types of information.

NMR has also found a widespread use to characterize lignocellulosic biomass structure and composition for more than 30 years (Manders, 1987; Hawkes, Smith, Utley, Vargas, & Viertler, 1993). In general, NMR experiments can be performed both, in solution and solid state, while the combination of the two is being used more frequently. A number of

research groups studied biomass structure by employing one- and two-dimensional NMR methods (Argyropoulos et al., 2021; Cipriano et al., 2020; Happs et al., 2021; Mansfield, Kim, Lu, & Ralph, 2012; Vidal, Rahimi, Kroetsch, & Martinez, 2023). NMR spectra can be recorded from isolated parts or whole LB, such as wood and wood extracts (Wieczorek, Żyszka-Haberecht, Kafka, & Lipok, 2022). In addition, there is a considerable amount of research that deals with the direct analysis of lignin-carbohydrate binding by NMR techniques (Balakshin, Capanema, Gracz, Chang, & Jameel, 2011; Del Río et al., 2016; Du, Gellerstedt, & Li, 2013; Giummarella et al., 2018, 2019).

In this paper, the application of high field NMR spectroscopy in the analysis of the whole LB and/or its structural units (lignin, cellulose, hemicellulose) in the last decade has been reviewed focusing on NMR solution and solid-state methods. It has been demonstrated that the NMR spectroscopy can provide a wealth of information about structure of lignin and polysaccharide units of LB. Recent results on: a) lignin structural units such as syringyl, guaiacyl, *p*-hydroxybenzoate, *p*-coumarate, ferulate, β-O-4 ethers and metoxyl group as well as lignin interunit bonding motifs; b) side chain regions, α- and β- cellulose crystal structure, paracrystalline cellulose; and c) xylosyl and manosyl units from hemicellulose have been collected and analysed.

2. Preparation of lignocellulosic biomass for NMR analysis

2.1. Lignocellulose pretreatment

It is important to know the chemical composition of lignocellulosic biomass not only in its fresh form, but also during pretreatment and/or (bio)conversion into desire bio-based products, while appropriate utilisation of the biomass depends on its chemical composition. Due to the complex chemical composition of the biomass, pre-treatment is a crucial step in converting the LB into a less recalcitrant form. During the last decades various pretreatment procedures were developed (Banu et al., 2021; Meng et al., 2018) which are generally divided into physical, chemical, physico-chemical and biological processes. The physical methods usually include milling, extrusion, ultrasonic and microwave methods. Chemical pretreatment includes fractionation of lignocellulosic biomass by ionic liquids or organic solvents and alkaline or acidic solution (Mora-Sandi, Ramirez-González, Castillo-Henriquez, Loppreti-Correa, & Vega-Baudrit, 2021). Organosolv pretreatment uses organic or aqueous solvent mixtures, such as methanol, ethanol, acetone tetrahydrofurfuryl alcohol and ethylene glycol to solubilize and fractionate lignocellulose, obtaining a pure cellulose residue. Tetrahydrofuran has been identified as a useful solvent to achieve higher yields of sugars and other fuel precursors. In addition, tetrahydrofuran is biodegradable, which is desirable for the environment (Fowles et al., 2013). A new generation pretreatment process, Cosolvent Enhanced Lignocellulose Fractionation (CELF) uses mixtures of tetrahydrofuran and H_2O. Recently, deep eutectic solvents (DESs), the new type of ionic liquids used for LB fractionation have emerged as a promising solvents (Panić et al., 2021; Šalić et al., 2023). DESs are environmentally acceptable ionic liquids, easily prepared from two or three hydrogen bond acceptors and hydrogen bond donors. They are generally made from inexpensive and "green" compounds. They have outstanding properties such as simple preparation, biodegradability and non-toxicity, non-volatility and non-flammability, thermal and chemical stability. DESs have potential to dissolve different types of organic and inorganic compounds (Ee, Tan, Miao, Chu, & Li, 2023; Petračić, Sander, & Parlov Vuković, 2022; Verevkin et al., 2015) whereas many researces have been done on lignin extraction by DESs (Hong, Shen, Xue, Sun, & Yuan, 2020). A group of authors developed a green, cost-effective, mild, and efficient process for the extraction of lignin in high purity from coconut coir. It has further been valorised for the production of valuable chemicals by using a series of choline chloride (ChCl)-carboxylic acid based DESs to extract lignin from coconut coir under microwave irradiation (Mankar, Pandey, & Pant, 2022).

Physicochemical methods combine chemical and physical pre-treatments to break down the internal bonds between lignin and cellulose (Brodeur et al., 2011; Kumar & Sharma, 2017; Mora-Sandi, Ramirez-Gonzalez, Castillo-Hentiquez, Loppreti-Correea, Vega-Baudrit, 2021). There are many chemical and physico-chemical pretreatment technologies but some of them are expensive and not environmentally friendly. Steam explosion is one of the most promising mechanical-physical–chemical pretreatment processes since has lower environmental impact, lower costs and lower energy consumption compared to more commonly used autohydrolysis and pulping (Ahmad & Pant, 2018; Brodeur et al., 2011; Kumar & Sharma, 2017; Li, Gellerstedt, & Toven, 2009; Ziegler-Devin, Chrusciel, & Brosse, 2021). Biological pretreatment uses microorganisms like bacteria, fungi, microbial consortium or enzymes, which are generally considered environmentally friendly, but are time-consuming (Baksi et al., 2023; Tišma et al., 2021).

All of the above pretreatment methods have certain limitations as well as advantages and the choice of the appropriate pretreatment is still a challenge for researchers (Chen & Davaritouchaee, 2023; Mankar et al., 2021; Zhang et al., 2023).

The efficiency of the pretreatments can be measured by various analytical methods that indicate structural changes in LB composition, crystallinity (e.g., by FTIR and X-ray), pore size (e.g., by Simon staining), surface properties (e.g., by SEM, TEM, and AFM), degree of polymerization (Karimi & Taherzadeh, 2016).

2.2. Preparation of lignocellulosic biomass for chemical composition measurement by solution state NMR

The preparation of the LB for NNR spectroscopy is one of the most important steps to achieve reliable results. Solution state NMR techniques require solubilization of the sample before analysis. The preparation of the sample starts with the removal of waxes, fats, salts, non-volatile hydrocarbons, etc. by solvent extraction. Milling procedure is also an important step because particle size and large surface area are required for effective dissolution of the biomass in solvent systems (e.g. DMSO, ionic liquids, organic electrolytes). The detailed LB characterization of by solution state NMR requires a sufficiently dissolved or swollen biomass sample. Solvents are generally divided into non-derivatizing and derivatizing solvents. Non-derivatizing solvents can disrupt intermolecular interactions and can be devided into three categories: a) aqueous solvents, such as transition metal complexes with amines or tartaric acid ammonium hidroxydes, NaOH, NaOH/urea, NaOH/thiourea, etc., b) organic solvents like N-methylmorpholine-N-oxide mono-hydrate (NMMO) or N,N-dimethylacetamide (DMAc)/ lithium chloride system; and c) ionic liquids (low-melting-point and thermally stabile salts, e.g. 1-butyl-3-methylimidazolium chloride) (Alexandridis, Ghasemi, Furlani & Tsianon, 2018) and, in recent years, DESs. E.g., reusable acidic ternary deep eutectic solvents (TDES) composed of alanine, lactic acid, and ethylene glycol are used for fractionation of high-purity lignin and augmentation of LB (Ee et al., 2023). Derivatizing solvents disrupt intermolecular bonding of the cell wall material and form ether, ester or acetyl derivatives that are more suitable for dissolution in wide range of common solvents (Foston, Samuel, Heb, & Ragauskas, 2016). On the other hand, there are solvents that lead to swelling (gelling) of the biomass. Dissolution methods for whole plant cells used in solution state NMR can be divided according to derivatizing (solvent systems: DMSO/TBAF or DMSO/NMI and derivation in ionic liquids) and non-derivatizing (solvent systems DMSO-d_6, DMSO-d_6/ pyridine-d_5, or DMSO-d_6/NMI-d_6, ionic liquids and organic electrolyte) approaches. Fu and Ralph (2011) developed the first protocol for whole cell wall structural analysis after ball- milling using two binary solvent systems, dimethyl sulfoxide/tetrabutylammonium fluoride (DMSO/ TBAF) and dimethyl sulfoxide/N-methylimidazole (DMSO/NMI), without component separation or degradation, using high resolution solution state NMR (Lu & Ralph, 2011).

2.3. Preparation of lignocellulosic biomass for chemical composition measurement by solid state NMR

Generally, solid state NMR does not require solubilization of the lignocellulose biomass and lignocellulosic biopolymer prior to analysis. NMR rotors are filled with dried and ground LB samples or previously separated lignocellulosic biopolymers by already mentioned pretreatment processes. This method allows analysis of intact plant tissues (Munson, Gao, Mortimer, & Murray, 2022). It was demonstrated that general mechanical milling and ultrafine grinding could initiate different mechanochemical effects such as depolymerization and deacetylation of cell wall polymers (Qu et al., 2017). It has been proved by NMR methods that application of different milling conditions can cause different structural changes in inter-and intramolecular linkages.

3. Application of solution state NMR method in lignocellulose biomass analysis

The continuous technical development of NMR spectroscopy has made solution state NMR an important tool for the characterization of LB (Lu & Ralph, 2011). Cellulose, hemicellulose and lignin are soluble in commonly used NMR solvents directly or after derivatization, which allows detailed structural analysis of these samples by NMR in solution (Lu & Ralph, 2011). The most commonly used solvents are DMSO-d_6, D_2O and $CDCl_3$.

The most frequently used NMR techniques in the solution state for structural elucidation of LB as well as for cellulose, hemicellulose and lignin are one-dimensional ^{1}H, ^{13}C and ^{31}P and two-dimensional heteronuclear single quantum coherence (HSQC) and heteronuclear multiple bond correlation (HMBC) NMR techniques. Table 1 summarizes characteristic examples of the use of different solution state NMR techniques in the investigation of lignocellulosic samples, including the analysis of whole LB as well as lignocellulosic biopolymers, over the past decade.

The examples listed in Table 1 demonstrate that NMR spectroscopy is frequently used for characterisation of lignocellulosic samples providing a wealth of structural information. Hence, chemical structure, molecular weight and polydispersity have been determined and reported in the literature displayed in Table 1. Furthermore, the ^{1}H and ^{13}C NMR spectra can provide qualitative and quantitative information on different types of lignocellulose and their constituents. ^{1}H NMR spectroscopy was used to investigate quality and degradation status of lipids in cold-pressed cakes from soybean, rapeseed and sunflower before and after long-term storage (Vidal et al., 2023). Traditionally, oilseeds such as soybeans, rapeseed and sunflowers are a common source of edible oil. Cold-pressed cakes from seeds such as pumpkin, rapeseed, hemp, flax and sunflower are a natural source of LB rich in crude protein, dietary fibbers, essential amino acids and lipid content. The composition of cakes depends on the plant variety, cultivation conditions and oil extraction process. Oilseed cakes are produced when the oil is extracted from the seed by mechanical pressing, extraction or by some advanced green processes (Castro, Strætkvern, Romero-García, & Martín, 2023). The cakes consist mainly of de-oiled seeds and are a suitable raw material for numerous value-added products. Oilseed cakes may also contain antinutritive factors (ANFs) that are undesirable for human and animal consumption. Different types of oilseed cakes are promising candidates for the production of biodegradable plastics and biofuels (Mirpoor, Giosafatto, & Porta, 2021). Sometimes lipid degradation can lead to handling problems during long storage. Vidal et al. (2023) analysed both types of samples, fresh and stored for 12 months, by proton NMR spectroscopy after extraction of lipids from oilseed cake flower (Vidal et al., 2023). Using the NMR data, the authors calculated the content of the glyceride components, the acyl groups and the fatty acid composition. In addition, they determined the content of lipid oxidation products for samples with long-term storage. Furthermore, ^{13}C NMR experiments revealed valuable information on non-acetylated

Table 1

The characteristic examples of solution state NMR techniques in lignocellulosic analysis.

Source	NMR techniques	Main findings	Reference
Whole lignocellulosic biomass			
Spruce wood (*Picea abies*)	2D HSQC	evidence for the existence of structurally different lignins associated to hemicelluloses (xylan and glucomannan) and cellulose in spruce wood, information on some of the chemical linkages between the polymers	Du et al., 2014
Sesame seed (*Sesamum indicum L.*)	^{31}P	profile of phosphorous translocation in germinating sesame seed	Cai et al., 2018
Bracken (*Pteridium aquilinum* (L.) Kuhn) and bluebell (*Hyacinthoides non-scripta* (L.)	^{31}P	composition of P (phosphorus) forme in soils and plants	Ebuele et al., 2016
wheat (*Triticum aestivum*)	^{31}P	composition of all plant parts (root, stem, leaf, chaff/pod and seed) and rates of P application	Noack et al., 2014
birch	^{31}P, 2D HSQC	„monitoring" of mild protocol for quantitative fractionation of lignin – carbohydrate complexes	Giummarella et al., 2016
pine (softwood), poplar (hardwood),and corn stover (grass)	2D HSQC (gel state)	S/G ratios for a series of biomass samples, bond linkage information and aromatic moieties present in lignin	Happs et al., 2021
populous (*Populous trichocarpa* × *deltodies*) and switchgrass (*Panicum virgatum*), cellulose, hemicellulose (oak wood) and lignin (poplar)	^{31}P	quantification of various hydroxyl groups of biomass and its components, including aliphatic, condensed phenolic, guaiacyl phenolic, p-hydroxyl phenyl and carboxylic hydroxyl groups in the biomass components	Ben et al., 2018
wheat bran	^{1}H, ^{13}C, 1D NOESY, 2D COSY, 2D HSQC, 2D HMBC	development of a reliable qualitative and quantitative platform using a ^{1}H NMR-based metabolomics approach, followed by the discovery and obtainment of distinct chemical profiles between the wheat varieties in multivariate analyses	Kil et al., 2022
leaf litters and crop residues from para rubber, cocoa, oil palm and banana plantations	^{31}P	Identification and quantification of the various phosphorus species	Nanganoa & Njukeng, 2018
eucalyptus (*Eucalyptus grandis x Eucalyptus. urophylla,*	2D HSQC	characterization of the lignin-carbohydrate complex structures and linkages	Zhao et al., 2018
olive pomace	^{1}H, ^{13}C	characterization of the single isolated lignin and the acetylated lignin	Abid et al., 2020
(a)emergent plants, water oats (*Zizania caduciflora Turcz, Gramineae*) and branch smartweed (*Polygonum divaricatum Linn*); (b)floating plants, water caltrop *Trapa bispinosa* and water poppy (*Nymphoides peltata* (c) submerged plants, watermilfoil (*Myriophyllum verticillatum Linn.*) and waterthyme (*Hydrilla verticillata (Lf)*	^{31}P	detailed identification and quantification of phosphorus species in NaOH–EDTA extracts of plants	Liu et al., 2017
leaves from 199 trees of 31 species in the wet season	^{31}P	^{31}P NMR-based metabolic method to study species-specific P-allocation to different biologic functions in contrasting plant communities (due to inorganic phosphates, orthophosphate monoesters and diesters, phosphonates and organic polyphosphates)	Gargallo-Garriga et al., 2020
oilseed cakes (lipid composition)	^{1}H	identification of the most abundant phenolics present in the extractable polyphenolsfraction of the oil seed cakes	Vidal et al., 2022
brewer's spent grain	^{1}H	structural characterisation of brewer's spent grain	Zeko-Pivač et al., 2022
oilseed cake flours from soybean, canola and mid oleic-sunflower	^{1}H	lipid quality profile in terms of lipid composition, hydrolysis, and oxidation status, lipid stability after long-term storage before and after low-moisture extrusion, quantification of the glyceride components, acyl groups and fatty acid composition, and lipid oxidation products	Vidal et al., 2023
lignin			
Norway spruce wood	2D HSQC	relations between important interunit bonding motifs: β-O-4′ (H_α of std. motif), β-O-4′ (H_β incl. ox. der.), β-O-4′ (C_2-H of ox. der.), β-5′ (H_α), β-1′ (H_β), 5,5′-α,β-O-4′ (H_β), cinnamyl alcohol, (H_γ), β-β' (H_α)	Sette et al., 2013
sisal (*Agave sisalana*) and abaca (*Musa textilis*)	2D HSQC	structural characterisation of lignin-carbohydrate complexes: glucan-lignin and xylan-lignin, information on β-O-4′ alkyl-aryl ether linkages	Del Río et al., 2016
sugarcane bagasse	2D HSQC	characterisation of sugarcane bagasse, results suggested that syringyl units were more easily degraded and dissolved under low temperature soda-oxygen pulping conditions	Yue et al., 2016
loblolly pine and white spruce	2D HSQC	a total of twelve guaiacyl-type dimeric compounds, including six β-5, two β-1, two β-β, one 4-O-5, and one 5-5, released by thioacidolysis from softwood lignins have been verified and quantified with synthesized standard compounds, β-β products from pinoresinol structures in softwood lignins were verified and quantified for the first time, the most accurate information about carbon–carbon and diaryl ether units in various lignins that can be released by β-ether cleaving reactions	Yue et al., 2017
crude bamboo (*Neosinocalamus affinis*)	2D HSQC	differences in structural characterisation of lignin-carbohydrate complex between milled wood lignin of 2- and 24-month-old crude bamboo	Yue et al., 2017
Japanese red pine (*Pinus densiflora*)	2D HSQC, 2D HMBC, 2D HSQC-TOCSY	first direct proof of covalent bonding between plant cell-wall polysaccharides and lignin, observation the long-range correlations through an α-ether bond between lignin and the primary hydroxyl group of a mannose residue in glucomannan, complete signal assignment of the cognate structural units, identification of lignin–carbohydrate bonds by complete connectivity analysis from the phenylpropane unit to the carbohydrate moiety	Nishimura et al., 2018

Table 1 (*continued*)

Source	NMR techniques	Main findings	Reference
spruce	2D HSQC	quantitative method for fractionation of lignin carbohydrate complexes, fractionation of hemicelluloses of relatively high purity enabling for the first time estimates of hemicelluloses fractions not chemically bound to lignin in wood	Giummarella & Lawoko, 2016
lignin	[31]P	complete quantitative analysis of hydroxyl groups with small amounts of sample (~30 mg) within a relatively short experimental time (~30–120 min), measuring hydroxyl groups in a single spectrum with high signal resolution	Meng et al., 2019
Chinese Quince (*Chaenomeles sinensis*) Fruit	[31]P, 2D HMQC	structural characterisation of chinese quince fruits after subcritical water treatment, chemical linkages in the milled wood lignin (MWLs) were mainly β-O-4′ ether bonds, β-5′ and β-β′, and the units were principally G- S- H- type with small amounts of ferulic acids	Wang et al., 2021
kraft lignin (50 % Accacia spp. and 50 % mixed hardwood: Quercus spp. + other hardwood 1:1)	[31]P, 2D HMQC	determination of lignin substructures, hydroxyl (phenolic + aliphatic) contents, and carboxyl contents in kraft lignin (KL) prepared from mixed hardwoods, better understanding of the structural features of hardwood KL	Mun et al., 2022
lignin-based carbon fiber	^{1}H, ^{13}C, ^{31}P, 2D HSQC, 2D HMBC	detailed characterization of qualifying lignin-based carbon fiber for automotive mass production, the major reactions during conversion of lignin to carbon fiber	Mainka et al., 2015
silver birch (*Betula pendula*) chips	^{13}C, ^{31}P, 2D HSQC	detailed structural characterization of AqSO (AquaSolv Omni process) lignins	Schlee et al., 2023
rice husk waste	[1]H, 2D NOESY, DOSY	mechanistic understanding of the delignification process and lignin structural transformation	Ee et al., 2023
corncob	2D HSQC	two-step process to degrade corncob into xylose and glucose under mild conditions, confirmation of high pure lignina by 2D NMR	Zhang et al., 2023
spruces	^{13}C, ^{31}P, 2D HSQC	reactivity of lignin during a cyclic organosolv extraction process adopting physical protection strategies, deeper insights into lignin structure and the reactivity during the ethanol-based organosolv performed in cyclic mode	Karlsson et al., 2023
kraft lignin	^{1}H, ^{13}C, 2D HSQC	structural characterisation before and after enzymatic reaction	Gouveia et al., 2018
soda and kraft lignin	^{31}P, 2D HSQC	monomer/oligomer distribution, determination of structure and functionalities of the oligomers, quantifying changes within the G-, S- units and C-O, C-C linkages	Ročnik Kozmelj et al., 2024
Cellulose			
nanocellulose	^{1}H, ^{13}C, 2D HSQC, DOSY	characterization of poly(methyl methacrylate)-grafted cellulose nanocrystals (PMMA-g-CNCs), quantification of the degree of incorporation of the methyl methacrylate monomer to the bulk anhydrous glucose units, calculation of graft length and graft density	King et al., 2018
cellulose	[1]H	advantages of using a polar non-deuterated ionic liquid, 1,3-dimethy-limidazolium methyl methylphosphonate, as a cellulose solvent to prevent vanishing of the signals of hydroxyl groups (C–OHs) by hydrogen–deuterium exchange, the signals of the C–OHs at 2-, 3-, and 6-position were independently observed and strong interaction between C–OH at the 6-position and ILs was confirmed to be a key step for dissolution of cellulose	Kuroda et al., 2014
bacterial cellulose	2D TOCSY, 2D HSQC-TOCSY, 2D COSY	rough determination of the degree of polymerisation (DP) of a sample for low-DP celluloses by the integration of non-reducing chain ends C1 versus polymeric cellobiose C1, identification of residual xyloses and mannoses for high-purity pulps (pre-hydrolysis kraft and sulfite)	Holding et al., 2016
Hemicellulose			
sweet sorghum (Sorghum bicolor (L.) Moench)	[1]H, [13]C	structural characterisation of hemicellulose from sweet sorghums samples, 4-O-methylglucuronoarabinoxylans were the major constituents of the hemicellulosic polymers	Peng et al., 2012
Bamboo shavings from the stems of *P. pubescens*	^{1}H, ^{13}C, 2D HSQC	detailed structural characterization of naturally acetylated hemicelluloses from bamboo shavings	Huang et al., 2017
corn bran hemicellulose	2D, COSY, 2D TOCSY, 2D HMBC, 2D HSQC	monosaccharide sequence, glyosidic linkages: t-xylp, 1,2,3,4-β-D-xylp, t-α-L-araf, 1,2-α-L-araf, 1,4-β-D-xylp were indentified and several linkage fragments: t-araf → 2-araf → 2-O-(1,3,4-xyl), t-araf → 2-araf → 3-O-(1,2,4-xyl), t-araf → 2-araf → 3-araf, and t-gal → 2-arain were deduced in purified corn fibre gum	Kang et al., 2019
bleached hardwood kraft pulp	^{1}H, ^{7}Li, 2D-HSQC	structural analysis of the regenerated hemicellulose, linear skeleton of regenerated hemicellulose consisting of (1 → 4) linked β-d-xylopyranosyl units which were substituted by a small number of α-l-arabinofuranosyl units and 4-O-methyl-α-d-glucuronic acid	Gong et al., 2024

lignin structure such as the content of different β-O-4 linkages, different guaiacyl and syringyl moieties, condensed and uncondensed aromatic and aliphatic carbons (Choi & Faix, 2011; Wen et al., 2013), Abid, Bouhtoury, & Gabsi, 2020). Also, quantitative ^{13}C NMR spectra of acetylated lignin provided data on the amount of primary, secondary and phenolic hydroxyl groups.

While ^{1}H and ^{13}C NMR spectra of complex mixture usually suffer from overlapping signals, ^{31}P NMR owing to a large chemical shift range, usually exhibits more cleaner spectra and different chemical groups can be assigned straightfordwly (Araneda, Burton, Paleologou,

Riegel, & Lecler, 2022). Hence, the ^{31}P NMR spectroscopy was used to measure different chemical forms of plant phosphorus both qualitatively and quantitatively (Wieczorek et al., 2022). Phosphorus is one of the most important essential macronutrient for plants and a key factor in bolstering plant resilience against damaging environmental conditions (Khan, Bakar Siddique, Shabala, Zhou & Zhao, 2023). It is important for appropriate physiological and biochemical conditions in plants. Knowledge of the role of phosphorus in the mechanisms of plant physiological responses to abiotic stresses is crucial for sustainability of agricultural production. The total phosphorus content in organic and inorganic forms in plant material ranges from 0.5 to 10 g kg^{-1} (Nanganoa & Njukeng, 2018). Inorganic phosphorus is present in plants in the form of orthophosphates (H$_3$PO$_4$, H$_2$PO$_4^{4-}$, HPO$_4^{2-}$ and PO$_4^{3-}$), pyrophosphates and polyphosphates (Nanganoa & Njukeng, 2018). Organic phosphorus in plants is usually in the form of phosphate monoesters and diesters, α- and β-glycerophosphates and organic polyphosphates. The ^{31}P NMR can identify and quantify most of the organic and inorganic forms of phosphorus. Generally, aqueous and acidic solvents are used for extraction of inorganic phosphate, sugar phosphates, and phytate, while organic solvents are used to extract phospholipids and nucleotides from plant tissues (Wieczorek et al., 2022). Typical ^{31}P NMR spectrum of lignocellulosic sample after NaOH-EDTA extraction using previously described procedure is shown in Fig. 1 (Liu et al., 2017).

Usually, ^{31}P NMR spectrum of NaOH-EDTA extracts provides data about the presence of orthophosphate monoesters (phytate, glycerophosphates, mononucleotides) and orthophosphate diesters. One group of authors used both liquid and solid ^{31}P NMR techniques to monitor sesame seeds germination (Cai et al., 2018). Paramagnetic compounds were removed and a novel sample preparation procedure to achieve better quantitively was established. In this way, they proposed a quantitative time evolution of phosphorus metabolism during the entire course of seed germination. Araneda et al. (2022) compared quantitative results obtained by ^{31}P benchtop NMR spectroscopy with high-field NMR data (Araneda et al., 2022). They performed phosphitylation of lignin with the most often used phosphitylation reagent 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) for lignin hydroxyl group analysis to form phosphitylated derivative. The reaction was obtained in a mixture of pyridine and chloroform. The pyridine whit liberated HCl form a pyridine-HCl salt to prevent decomposition to the derivatized compounds that could cause liberated HCl. Argyropoulos' s research group was a pioneer in ^{31}P NMR in the field of biomass chemistry with a focus on determination of hydroxyl groups in different lignocellulosic samples (Argyropoulos, 1995). Phosphitylation reagent TMDI proposed by this group was widely used reagent for hydroxyl

groups analysis in biomass and edible oil samples (Araneda et al., 2022; Melone, Saladino, Lange, & Crestini, 2013; Melone, Saladino, Lange, & Crestini, 2013; Meng et al., 2019). In conclusion, the ^{31}P NMR spectroscopy offers major advances in the determination of hydroxyl groups in a single spectrum with high signal resolution compared to conventional wet chemical methods. The phenolic hydroxyl groups attached to syringyl, guaiacyl and *p*-hydroxyphenyl units can be distinguished in a short experimental time with small sample amounts (Meng et al., 2019). However, this method has some limitations, such as the presence of amine groups, which can interfere with the quantification of hydroxyl groups in some cases. Tha advantage of ^{31}P NMR has been underlined by the group of autors in cases when the form of phosphorus and the dynamics of phosphorus transformation in the body of living beings are investigated. Phosphorus compounds in plant tissues have been determined qualitatively and quantitatively by using simple colourimetric procedures and gas chromatography–mass spectrometry (GC–MS), high-performance liquid chromatography (HPLC), Flame atomic absorption spectrometry (FAAS), Inductively coupled plasma atomic emission spectrometry or inductively coupled plasma optical emission spectrometry (ICP-AES/ICP-OES) and ^{31}P NMR spectroscopy (Wieczorek et al., 2022). They concluded that each analytical problem related to the determination of phosphorus requires an individual approach and tecniques. ^{31}P NMR was found to be the most appropriate analytical tool allowing determination of various chemical forms (organic and inorganic) of plant phosphorus qualitatively and quantitatively, at the same time.

Due to severe signal overlapping, a complete assignment of ^{1}H and ^{13}C NMR spectra of lignocellulosic samples is almost impossible. Nowadays, the application of 2D NMR techniques provides more detailed signal assignment of natural polymers. It was demonstrated the usefulness of solution-state 2D HSQC NMR technique for the whole plant cell wall compositional characterization (Mansfield et al., 2012). This method provided information on polysaccharide components profile, lignin composition and interunit linkage distribution, acetylated and native call walls. The NMR profiles of the whole cell walls observed using mentioned approach represented a progress in the structural characterization of plant cell wall structures. Many researchers used this method for further analysis of native cell walls.

Generally, a cellulosic material has excellent properties such as low cytotoxicity, biocompatibility, good mechanical properties, high chemical stability and low cost, which makes them perfect candidates for many different applications (Blessy, Sagarika, Chinnu, Nandakumar, & Sabu, 2020). One problem with crystalline cellulose materials is their low solubility in most solvents. A group of authors described dissolution procedure and NMR analysis of different technical cellulosic pulps in the
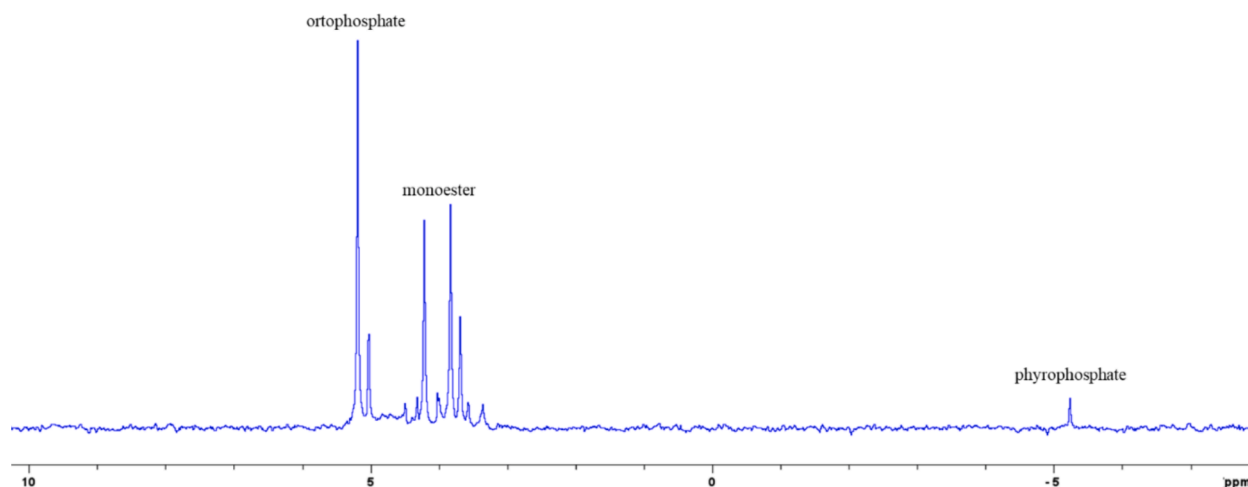

Fig. 1. Typical ^{31}P NMR spectrum of lignocellulosic sample after NaOH-EDTA extraction.

ionic liquid electrolyte methyl trioctylphosphonium acetate ([P8881]-[OAc]):DMSO-d_6 (Holding et al., 2016). The obtained results facilitated the development of a quantitative liquid-phase NMR method for the characterization of unsubstituted and low-substituted celluloses. King et al. (2018) demonstrated the NMR characterization of poly (methyl methacrylate) (PMMA)-grafted cellulose nanocrystals (CNCs) using the electrolyte tetrabutylphosphonium acetate ([P4444][OAc]):DMSO-d_6 (King et al., 2018). They used ^{1}H and HSQC NMR techniques to identify the signals of the polymer PMMA and those of the low molecular weight components originating from the solvent system. The ratio of methyl methacrylate monomer to anhydroglucose unit was determined by HSQC and quantitative ^{13}C NMR. DOSY (Diffusion-ordered spectroscopy) NMR technique was used to determine the average self-diffusion coefficient and molecular weight of the grafts (King et al., 2018). DOSY is a pseudo two-dimensional NMR pulse sequence where one dimension is proton and the other one represents translation diffusion coefficients. It has frequently been used to study complex chemical mixtures such as crude oil samples or food and drinks and can provide data on molecular masses and hydrodynamic radios of mixture constituents (Jagatić Korenika et al., 2024; Parlov Vuković et al., 2020; Raljević et al., 2021). Recently, an advanced diffusion NMR method PSYCHE-iDOSY (Pure Shift Yielded by CHirp Excitation DOSY) was applied in the analysis of lignocellulose (Zhao et al., 2023). It was shown that ultrahigh resolution DOSY technique is capable of detecting and separating the mixture components of C5/C6 sugar conversion products and its derivatives from lignocellulose biomass. Pure shift NMR can greatly improve the signal dispersion by suppressing ^{1}H–^{1}H couplings and reduce signal overlap. Combination of Pure Shift Yielded by Chirp Excitation and DOSY NMR improves spectral purity and sensitivity and does not introduce complications with spatially non-uniformpulsed field gradient (Foroozandeh et al., 2016; Zhao et al., 2023). Therefore, it has great potential for the study of LB polymers.

Meng et al. (2018) reported CELF lignin precipitation from hardwood poplar by HSQC and ^{31}P NMR and observed changes in molecular weights, hydroxyl group content and monolignol composition compared with untreated native lignin. NMR analysis indicated that CELF lignin's β-O-4 interunit linkages were extensively cleaved after CELF pretreatment. A decrease in aliphatic OH groups due to the oxidation of lignin side chains was observed, while the content of total phenolic OH groups in CELF lignin significantly increased due to cleavage of interunit linkages. They concluded that the CELF process yields high-purity lignin feedstock that has the potential to be processed into fuels, chemicals and materials in biorefineries (Meng et al., 2018). Using HMQC NMR technique in the analysis of kraft lignin (KL) produced from mixed hardwoods, lignin substructures such as stilbene (β-1 and β-5) and vanillin were identified (Mun, Pe, & Mun, 2022). These substructures were previously not detected by 1D NMR but were confirmed after 2D NMR data analysis. Li et al. (2009) applied steam explosion process to various wood species. The lignin fraction extractable by aqueous alkali solution was quantified and analysed by TGA, SEC, FTIR, UV, ^{13}C, HSQC and ^{31}P NMR, GC and SEC to evaluate their potential for the production biodiesel or chemicals. Several groups of authors investigated possibilities to use tropic fruits such as avocado, banana and mango peel and guava seeds for the production of high value added products based on biorefinery approach. (Mora-Sandi et al., 2021). HSQC NMR spectra of whole plant cell walls were recorded directly in the NMR tube for gel sample obtained by dissolving in DMSO (Kim, Ralph, & Akiyama, 2008). The spectra provided structural fingerprint of the polysaccharide and lignin components of the wall without solubilization and structural modification. The samples prepared in this way does not require the use of complex solvents, filtering and drying with no significant loss of information on the cell wall structure (Kim et al., 2008; Kohler & Heinze, 2007). The compositional analysis of different lignocellulosic materials processed using OrganoCat pretreatment allowed for investigation of the relationships between the plant wall compositions as well as role in acidic pretreatment (Weidener et al., 2020). Structural and compositional changes of OrganoCat extracted lignin compared to untreated material were monitored by HSQC-NMR spectroscopy and the results were compared to those reported in the previous studies (Cheng, Sorek, Zimmermann, Wemmer, & Pauly, 2013; Grande et al., 2019; Wen, Xue, Sun, & Sun, 2013). The obtained results were used to calculate the generic correlation coefficients between the measured chemical and structural features and the different OrganoCat product yields and quality. Furthermore, the combination of several 2D NMR techniques such as homonuclear correlation spectroscopy (COSY), total correlation spectroscopy (TOCSY), HSQC and HMBC were employed to identify and confirm different types of linkanges (t-xylp, 1,2,3,4-β-D-xylp, t-α-L-araf, 1,2-α-L-araf and 1,4-β-D-xylp) of a purified corn bran hemicellulose (Kang, Guo, & Shi, 2019). A group of authors studied covalent bonding between plant cell-wall polysaccharides and lignin by using HMBC and HSQC,-TOCSY. They detected correlation signals between the C-6 position of the β-mannose residue in glucomannan and the α position of lignin that indicate the presence of an α ether bond between them (Nishimura, Kamiya, Nagata, Katahira, & Watanabe, 2018).

4. Application of solid state NMR in lignocellulose biomass analysis

Despite all efforts to understand the structural architecture of lignocellulose, there are still many details to be clarified, and its structure and composition are still the subject of research. Nowadays, modern solid state NMR technologies can provide valuable information about the structure of lignocellulose and the mechanisms governing different lignocellulosic processes. The main advantage of solid state NMR is that it measures polymers in its native state compared to liquid state NMR analysis where solvents can interfere (Giummarella, Pu, Ragauskas, & Lawoko, 2019). Currently, various solid state NMR techniques are employed in structural and mechanistic studies of LB. Table 2 displays characteristic examples of the use of 1D and 2D NMR techniques for the investigation of lignocellulosic samples of various origins over the past decade.

The examples listed in Table 2 demonstrate the progress made in the application of solid state NMR techniques for the characterization of lignocellulosic samples. According to the literature, progress has been made recently in using ^{13}C CP/MAS NMR to determine lignin content in LB without destroying its native structure (Cipriano et al., 2020; Fu et al., 2015; Gao, Laskar, Zeng, Helms, & Chen, 2015). Most of other methods for the lignin content determination are time-consuming, require dissociation or degradation step and generate a lot of chemical residues. Gao et al. (2015) developed alternative methodology for lignin content of different kinds of LB samples using solid state ^{13}C CP MAS NMR with an internal standard. Further, one group of authors used ^{13}C CP MAS NMR spectra to study the lignin content in different types of biomass, including wood samples, fruit shells and lignocellulosic residues (Cipriano et al., 2020). For this purpose, the integrated intensity of the deconvoluted signal of methoxy groups in the ^{13}C NMR spectra was used for the assessment of the lignin content. NMR results were compared to those obtained by Klason method, one of the standard methods of lignin quantification. It was concluded that NMR spectroscopy was a good alternative to Klason method when the complete hydrolysis of carbohydrates is not possible. Lignin is mainly composed of aromatic components that vary in composition and structure depending on wood origin. Aromatic lignin composition, especially S/G ratio is very important parameter in biochemicals and biofuel production. Happs et al. (2021) compared a few methodologies used to determine aromatic lignin content as syringyl/guaiacyl (S/G) ratio for a various biomass samples. Authors performed gel- and solid-state NMR spectroscopy to measure S/G ratios. For gel-state NMR experiments Mansfield procedure was used while S/G ratios in solid-state were measured by Manders method and solid-state NMR spectral deconvolution (Happs et al., 2021; Mansfield et al., 2012; Manders, 1987). It was shown that different methods led to different results and that spectral deconvolution

Table 2

The characteristic examples of the use of solid state NMR techniques to study lignocellulosic samples over the last decade.

Source	NMR techniques	Main NMR Findings	Reference
Whole lignocellulosic biomass			
Arabidopsis (*Arabidopsis thaliana*)	^{13}C CP MAS, 2D HETCOR, 2D PDSD, MELODI HETCOR	structural role of pectins in plant primary cell walls	Wang et al., 2015
series of biomass samples including pine (softwood), poplar (hardwood), and corn stover (grass)	^{13}C CP MAS, 2D HSQC (gel state)	comparison of S/G lignin unit ratios obtained by solid- and liquid state NMR, thyioacidolysis and pyrolysis-molecilar beam mass spectrometry (py-MBMS) (HSQC is better for hardwood and grass)	Happs et al., 2021
(a) emergent plants, water oats (*Zizania caduciflora Turcz, Gramineae*) and branch smartweed (*Polygonum divaricatum Linn*); *(b)* floating plants, water caltrop (*Trapa bispinosa* and water poppy (*Nymphoides peltata; (c)* submerged plants, watermilfoil (*Myriophyllum verticillatum Linn.*) and waterthyme (*Hydrilla verticillata (Lf)*	^{13}C CP MAS	better understanding plant release, degradation and environmental behaviour in lake ecosystems	Liu et al., 2017
hardwoods: eucalyptus (*Eucalyptus grandis*) and poplar (*Populus × canadensis*), softwood: spruce (*Picea abies*)	^{1}H CP MAS, ^{13}C CP MAS,2D HSQC, 2D INADEQUATE,2D RFDR	better understanding of the principles of polymer interactions underlying the heterogeneous architecture of lignocellulose	Kirui et al., 2022
ginkgo cell walls (*Ginkgo biloba L.*)	^{13}C CP MAS	deep insights in structure of lignin–carbohydrate complexes (ketal and ether linkages were formed between the C-α of lignin side chains and carbohydrates)	Zhang et al., 2021
sugarcane bagasse	^{13}C Multi CP	alternative method for determination of cellulose crystallinity index directly within sugar-cane bagasse samples	Bernardinelli et al., 2015
various wood samples, fruit	^{13}C CP MAS	detailed assignment of signals in CP MAS ^{13}C NMR spectra of	Kostryukov et al., 2021

Table 2 (*continued*)

Source	NMR techniques	Main NMR Findings	Reference
shells, andother plant materials		different wood samples, determination of the total ratio of cellulose and hemicelluloses to lignin	
dicotyledonous and grass families (*Arabidopsis thaliana, Brachypodium distachyon*, and *Zea mays*)	^{13}C MAS, 2D ^{13}C–^{13}C correlation MAS	better understanding the three-dimensional structural network formed by polysaccharides in intact primary cell walls of several model plants of the dicot and grass families and mechanism of wall loosening	Wang et al., 2016
olive tree trimming (feedstockand hydrochar samples)	^{13}C CP MAS	one possible way of explanation of hydrochar properties	Calucci & Forte, 2023
Norway spruce secondary cell (*Picea abies Karst.*)	^{13}C CP MAS, CP INADEQUATE	model of softwood molecular architecture which explains the origin of the different cellulose environments observed in the NMR experiments	Terrett et al., 2019
almond shell (*Prunus dulcis*)	^{13}C CP MAS	methodology for a fast quantification of carbohydrate polymers	Modica et al., 2020
brewer's spent grain	^{13}C CP MAS	structural characterisation of brewer's spent grain	Zeko-Pivač et al., 2022
Lignin			
lignin modified with polyethylene glycol	^{13}C CP MAS	finding that polyethylene glycol (PEG) was grafted onto lignin after modification of lignin with PEG during steam explosion	Feng et al., 2017
lignin from *Pinus elliottii* sawdust	^{13}C CP MAS	detailed analysis of Pinus elliottii lignin	Bortoluz et al., 2019
Cellulose			
cellulose (Norway spruce (*P. abies* L. Karst.)	^{13}C CP MAS	discrimination of samples with different geographical provenance	Santoni et al., 2015
bacterial nanocellulose	^{13}C CP MAS,2D INADEQUATE	assignment signals for all carbon atoms in regenerated cellulose	Idström et al., 2016
cellulose nanocrystals	^{13}C CP MAS, ^{19}F CP MAS	structural characterisation of heterogeneous cellulose nanocrystals-based dirhodium(II) catalyst, spectra confirmed a chemical bond between the dirhodium(II) moiety and carboxyl groups	Liu et al., 2015
cellulose in cotton polyester blends	^{13}C CP MAS	quantification of the composition of cellulose and polyester in textile	Haslinger et al., 2019

Table 2 (*continued*)

Source	NMR techniques	Main NMR Findings	Reference
untreated and the enzyme treated natural cellulose	^{13}C CP MAS	blends, determination of the crystallinity of cellulose in cotton polyester blended textiles degradation of the amorphous region of cellulose-microfibril due to enzymatic treatment	Ghosh et al., 2019
carboxymethyl cellulose	^{13}C CP MAS	structural analysis of carboxymethylated bacterial cellulose samples with varying degree of substitution	Casaburi et al., 2018
tobacco cellulose	^{13}C CP MAS	method for the quantitative determination and structure analysis of cellulose in tobacco	Zhu et al., 2016
Hemicellulose hemicellulose (corn *Zea mays*)	^{13}C CP MAS, DDF-INADEQUATE	identification of hemicellulosic signals of lignocellulosic mixtures	Komatsu & Kikuchi, 2013

can be applied to many hardwoods but it may not be the best choice for some grass samples.

Happs et al. (2021) demonstrated that HSQC spectra may provide a wealth of information on additional aromatic moieties and bond linkages in biomass samples. Compared to thioacidolysis, the solid-state NMR is non-destructive method and the preparation of samples for analysis is much easier. By using Py-MBMS and liquid and solid state NMR (deconvolution), it was possible to measure multiple cell wall phenotypes. Furthermore, the liquid state NMR provided additional information on lignin linkages. Obtaining a detailed insight into biomass chemical composition is of highest priority for utility of biomass in production of sustainable biorefinery products. An understanding of structural complexity of biopolymers is an important task in the biofuel production industry. The separation of biopolymers from biomass is a complex process and for developing the most efficient separation technique it is important to thoroughly characterize the plant cell walls structure. Also, removal of lignin is usually expensive process. Besides in biofuel and biorefinery industries, lignmocellulose can also find application in car industry. To meet EU and USA Environment Protection Agency (EPA) regulations, car manufacturers must focus on investigating advance lightweight materials to reduce the total vehicle's weight (Mainka et al., 2015). Materials like carbon fiber can reduce component weight more efficiently than steel and aluminium. Limiting factor of production of the carbon fiber is high production cost of polyacrylonitrile which is the most often used precursor for production of this material. Using alternative precursor like lignin, costs can be significantly reduced. Mainka et al. investigated hardwood lignin, pre-treated sample pellets, lignin fiber and stabilized fiber by using a combination of solution and solid state NMR techniques. The HSQC and HMBC spectra were used to identify the primary structures of the investigated lignin derivatives. Subsequently, ^{31}P NMR was preformed to quantify the hydroxyl and phenolic groups in lignin. For detailed structural characterisation of samples ^{13}C CP MAS spectral analysis was performed next (Mainka et al., 2015).

Tian et al. investigated conformations and intermolecular interactions in cellulose/silk fibroin blend films using solid-state NMR spectroscopy (Tian et al., 2017). By using ^{1}H–^{13}C HETCOR NMR experiments they measured the content of the β-sheet structure and indicated the strong hydrogen bonding interaction between the SF and

cellulose. The presence of nanoheterogeneity in the cellulose/SF blend film was registered. Valuable information gained from those studies could contribute to elucidation of molecular origin of the enhanced mechanical properties of the blend film. Idström et al used ^{13}C CP MAS and ^{13}C–^{13}C refocused incredible natural abundance double quantum transfer experiment (INADEQUATE) and proton driven spin diffusion (PDSD) experiments to perform detailed assignment of ^{13}C signals for all carbon atoms in regenerated cellulose. Authors first biosynthesized ^{13}C-enriched bacterial nanocellulose and dissolved and coagulated the sample as highly crystalline cellulose II (Idström, Schantz, Sundberg, Chmelkad, Gatenholm, & Nordstierna, 2016).

Typical ^{13}C CP MAS NMR spectrum of lignocellulose sample is displayed in Fig. 2.

Kita et al. investigated structure of the surface of plate like cellulose II oligomer crystals (CIIOCs) by ^{13}C CP MAS NMR and 2D ^{13}C double quantum/^{13}C single quantum homonuclear correlation spectroscopy. Obtained results indicated that CIIOC and its derivatives can be used to reinforce polymeric materials and as nucleating agents for crystalline polymers (Kita et al., 2020). A group of authors employed ^{13}C CP MAS NMR and developed a protocol for the quantification and structural characterization of cellulose in cotton polyester blends (Haslinger, Hietala, Hummel, Maunu, & Sixta, 2019). They measured different blend concentrations to obtain a calibration function and make a validation by analyzing commercially available textiles and postconsumer garments. Near infrared (NIR) spectroscopy has been frequently used in textile industry. In comparison with NIR, solid-state NMR enabled more precise measurements that were not disturbed by different particle sizes, dyes and surface structures. NMR spectra have helped to gain fundamental insights into the crystallinity of cellulose and hemicelluloses. Generally, solid-state ^{13}C NMR have been widely used to determine the cellulose crystallinity index (CI). By splitting the C4 region of the spectrum into crystalline and amorphous parts it was possible to calculate CI. (Newman, 2004; Park, Baker, Himmel, Parilla, & Johnson, 2010). Recently, Bernardinelli et al. developed a method to determine CI by directly measuring inside sugarcane biomass after chemical pretreatment (acid + alkaline) or enzymatic hydrolysis using ^{13}C Multi CP solid state NMR (Bernardinelli, Lima, Rezende, Polikarpov, & deAzevedo, 2015).

A group of authors studied a role Li + played in the LiOH/urea/cellulose system. 3D interaction model of LiOH/urea/cellulose system was established by solid state NMR experiments employing ^{13}C CP MAS NMR, ^{6}Li CP MAS NMR, ^{6}Li single-pulse NMR, 2D heteronuclear ^{1}H–^{13}C and ^{1}H–^{6}Li correlation NMR (LGHETCOR) (Huang et al., 2021). By combining Arabidopsis molecular genetics and various solid state NMR experiments it was concluded that xylene interacted intimately with cellulose by adopting a twofold helical screw conformation (Simmons et al., 2016). This was the first direct experimental evidence for the atomic-scale arrangement of two distinct polymers within plant cell wall biomass.

According to the literature summarized in this review, it has been evidenced that solid state NMR has become a promising non-destructive technique that provides a wealth of information on the structure, conformation, packing and polymorphism of LB and thus can serve as reliable technique for lignocellulose characterization for the purposes of various industries, such as industry of biofuels production, biorefineries, car manufacturing, textile industry.

5. Conclusion and future prospective

In recent decades, the field of lignocellulose science has become frequently studied. There is no single analytical method that can provide a detailed (full) structural characterization of lignocellulose and its heterogeneous chemical composition.

It has been demonstrated here that high field NMR spectroscopy can provide valuable information and give insights into the structure and chemistry of lignocellulose. Although great progress has been made in
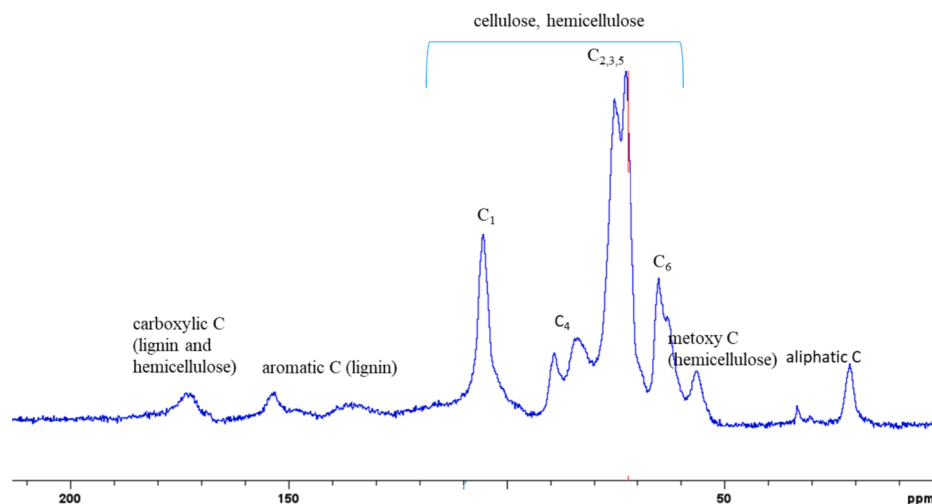
Fig. 2. Typical ^{13}C CP MAS NMR spectrum of lignocellulose sample.

the field of plant cell wall characterisation, many open questions still remain. Due to a complex, insoluble and disordered lignocellulose biomass structure, further improvements in sample preparation and characterization are expected. Advancements in modern liquid- and solid-state NMR methods will enable further steps to clarify and elucidate unresolved structural data, polymorphism architecture, water-matrix interactions and packing of LB. Since LB represents the most promising feedstock for the future biofuels and value-added products production, their detailed structural characterisation will be even more important.

CRediT authorship contribution statement

Jelena Parlov Vuković: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Conceptualization. **Marina Tišma:** Writing – review & editing, Funding acquisition, Conceptualization.

Declaration of competing interest

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

Data availability

No data was used for the research described in the article.

Acknowledgments

References

Abid, A., Bouhtoury, F.-C.-E., & Gabsi, S. (2020). Recovery of residues from olive industry: Characterization of simple and acetylated lignin. *IIETA International Information and Engineering Technology Association, 44*, 327–332. https://doi.org/10.18280/acsm.440504

Agarwal, P. U. (2019). Analysis of cellulose and lignocellulose materials by Raman spectroscopy: A rewiew of the current status. *Molecules, 24*, 1659. https://doi.org/10.3390/molecules24091659

Ahmad, E., & Pant, K. K. (2018). Chapter 14 - Lignin conversion: A key to the concept of lignocellulosic biomass-based integrated biorefinery. *Waste Biorefinery*, 409–444. https://doi.org/10.1016/B978-0-444-63992-9.00014-8

Alexandridis, P., Ghasemi, M., Furlani, E. P., & Tsianou, M. (2018). Solvent processing of cellulose for effective bioresource utilization. *Current Opinion in Green and Sustainable Chemistry, 14*, 40–52. https://doi.org/10.1016/j.cogsc.2018.05.008

Araneda, J. F., Burton, I. W., Paleologou, M., Riegel, S. D., & Lecler, M. C. (2022). Analysis of lignins using 31P benchtop NMR spectroscopy: Quantitative assessment of structures and comparison to high-field NMR. *Canadian Journal of Chemistry, 100*, 799–808. https://doi.org/10.1139/cjc-2022-0041

Argyropoulos, D. S. (1995). ^{31}P NMR in wood chemistry: A review of recent progress. *Research of Chemical Intermediates, 21*, 373–395. https://doi.org/10.1007/BF03052265

Argyropoulos, S. D., Pajer, N., & Crestini, C. (2021). Quantitative ^{31}P NMR analysis of lignins and tannins. *Journal of Visualized Experiments, 174*, Article e62696. https://doi.org/10.3791/62696

Bajwa, D. S., Pourhashem, G., Ullah, A. H., & Bajwa, S. G. (2019). A concise review of current lignin production, applications, products and their environmental impact. *Industrial Crops and Products, 139*, Article 111526. https://doi.org/10.1016/j.indcrop.2019.111526

Balakshin, M., Capanema, E., Gracz, H., Chang, H., & Jameel, H. (2011). Quantification of lignin–carbohydrate linkages with high-resolution NMR spectroscopy. *Planta, 233*, 1097–1110. https://doi.org/10.1007/s00425-011-1359-2

Baksi, S., Saha, D., Saha, S., Sarkar, U., Basu, D., & Kuniyal, J. C. (2023). Pre-treatment of lignocellulosic biomass: Review of various physico-chemical and biological methods influencing the extent of biomass depolymerization. *International Journal of Environmental Science and Technology, 20*, 13895–13922. https://doi.org/10.1007/s13762-023-04838-4

Banu, J. R., Sugitha, S., Kavitha, S., Kannah, R. Y., Merrylin, J., & Kumar, G. (2021). Lignocellulosic biomass pretreatment for enhanced bioenergy recovery: Effect of lignocelluloses recalcitrance and enhancement strategies. *Frontiers in Energy Research, 9*, Article 646057. https://doi.org/10.3389/fenrg.2021.646057

Ben, H., Chen, X., Han, G., Shao, Y., Jiang, W., Pu, Y., & Ragauskas, A. J. (2018). Characterization of whole biomasses in pyridine based ionic liquid at low temperature by ^{31}P NMR: An approach to quantitatively measure hydroxyl groups in biomass as their original structures. *Frontiers in Energy Research, 6*, Article 13. https://doi.org/10.3389/fenrg.2018.00013

Bortoluz, J., Cemin, A., Bonetto, L. R., Ferrarini, F., Esteves, V. I., & Giovanela, M. (2019). Isolation, characterization and valorization of lignin from Pinus elliottii sawdust as a low-cost biosorbent for zinc removal. *Cellulose, 26*, 4895–4908. https://doi.org/10.1007/s10570-019-02399-9

Bernardinelli, O. D., Lima, M. A., Rezende, C. A., Polikarpov, I., & deAzevedo, E. R. (2015). Quantitative ^{13}C MultiCP solid-state NMR as a tool for evaluation of cellulose crystallinity index measured directly inside sugarcane biomass. *Biotechnology for Biofuels andBioproducts, 8*, 110. https://doi.org/10.1186/s13068-015-0292-1

Blessy, J., Sagarika, V. K., Chinnu, S., Nandakumar, K., & Sabu, T. (2020). Cellulose nanocomposites: Fabrication, characterization and biomedical applications. *Journal of Bioresources and Bioproduct, 5*, 223–237. https://doi.org/10.1016/j.jobab.2020.10.001

Brodeur, G., Yau, E., Badal, K., Collier, J., Ramachandran, K. B., & Ramakrishnan, S. (2011). Chemical and physicochemical pretreatment of lignocellulosic biomass: A review. *Enzyme Research, 2011*, 1–17. https://doi.org/10.4061/2011/787532

Cai, H., Chuang, W. G., Cui, X., Cheng, R. H., Chiu, K., Chen, Z., & Ding, S. (2018). High resolution ^{31}P NMR spectroscopy generates a quantitative evolution profile of phosphorous translocation in germinating sesame seed. *Scientific Report, 8*, 359. https://doi.org/10.1038/s41598-018-31645-6

Calucci, L., & Forte, C. (2023). Influence of process parameters on the hydrothermal carbonization of olive tree trimmings: A 13C solid-state NMR study. *Applied Sciences, 13*, 1515. https://doi.org/10.3390/app13031515

Casaburi, A., Montoya Rojo, Ú., Cerrutti, P., Vázquez, A., & Foresti, M. L. (2018). Carboxymethyl cellulose with tailored degree of substitution obtained from bacterial cellulose. *Food Hydrocolloids, 75*, 147–156. https://doi.org/10.1016/j.foodhyd.2017.09.002

Castro, E., Strætkvern, K. O., Romero-García, J. M., & Martín, C. (2023). Pretreatment and bioconversion for valorization of residues of non-edible oilseeds. *Agronomy, 13*, Article 2196. https://doi.org/10.3390/agronomy13092196

Chen, S., & Davaritouchaee, M. (2023). Nature-inspired pretreatment of lignocellulose – Perspective and development. *Bioresource Technology, 369*, Article 128456. https://doi.org/10.1016/j.biortech.2022.128456

Cheng, K., Sorek, H., Zimmermann, H., Wemmer, D. E., & Pauly, M. (2013). Solution-State 2D NMR spectroscopy of plant cell walls enabled by a dimethylsulfoxide- d6/1-ethyl-3-methylimidazolium acetate solvent. *Aalytical Chemistry, 85*, 3213–3221. https://doi.org/10.1021/ac303529v

Choi, J. W., & Faix, O. (2011). NMR study on residual lignins isolated from chemical pulps of beech wood by enzymatic hydrolysis. *Journal of Industrial and Engineering Chemistry, 17*, 25–28. https://doi.org/10.1016/j.jiec.2010.10.004

Cipriano, D. F., Chinelatto, L. S., Jr., Nascimento, S. A., Rezende, C. A., de Menezes, S. M. C., & Freitas, J. C. C. (2020). Potential and limitations of ^{13}C CP/MAS NMR spectroscopy to determine the lignin content of lignocellulosic feedstock. *Biomass and Bioenergy, 142*, Article 105792. https://doi.org/10.1016/j.biombioe.2020.105792

Del Río, J. C., Prinsen, P., Cadena, E. M., Martínez, Á. T., Gutiérrez, A., & Rencoret, J. (2016). Lignin-carbohydrate complexes from sisal (Agave sisalana) and abaca (Musa textilis): Chemical composition and structural modifications during the isolation process. *Planta, 243*, 1143–1158. https://doi.org/10.1007/s00425-016-2470-1

Dhingra, D., Michael, M., Rajput, H., & Patil, R. T. (2012). Dietary fibre in foods. *Journal of Food Science and Technology, 49*, 255–266. https://link.springer.com/article/10.1007/s13197-011-0365-5.

Du, X., Gellerstedt, G., & Li, J. (2013). Universal fractionation of lignin-carbohydrate complexes (LCCs) from lignocellulosic biomass: An example using spruce wood. *The Plant Journal, 74*, 328–338. https://doi.org/10.1111/tpj.12124

Du, X., Pérez-Boada, M., Fernández, C., Rencoret, J., Del Rio, J. C., Jimenez-Barbero, J., Li, J., Gutierrez, A., & Martinez, A. T. (2014). Analysis of lignin–carbohydrate and lignin–lignin linkages after hydrolase treatment of xylan–lignin, glucomannan–lignin and glucan–lignin complexes from spruce wood. *Planta, 239*, 1079–1090. https://doi.org/10.1007/s00425-014-2037-y

Ee, L. Y., Tan, Y. K., Miao, J., Chu, H. T., & Li, S. F. Y. (2023). High-purity lignin from selective biomass fractionation with ternary deep eutectic solvents. *Green Chemistry, 25*, 3137–3151. https://doi.org/10.1039/d3gc00080j

Ebuele, V. O., Santoro, A., & Thoss, V. (2016). Phosphorus speciation by ^{31}P NMR spectroscopy in bracken (Pteridium aquilinum (L.) Kuhn) and bluebell (Hyacinthoides non-scripta (L.) Chouard ex Rothm.) dominated semi-natural upland soil. *Science of the Total Environment, 566–567*, 1318–1320. https://doi.org/10.1016/j.scitotenv.2016.05.192

El Hariri El Nokab, M., Habib, H. M., Alassmy, A. Y., Abduljawad, M. M., Alshamrani, M. K., & Sebakhy, O. K. (2022). Solid state NMR a powerful technique for investigating sustainable/renewable cellulose-based materials. *Polymers, 14*, 1049.

Feng, Y., Lan, J., Ma, P., Dong, X., Qu, J., & He, H. (2017). Chemical structure and thermal properties of lignin modified with polyethylene glycol during steam explosion. *Wood Science and Technology, 51*, 135–150. https://doi.org/10.1007/s00226-016-0870-9

Foroozandeh, M., Castañar, L., Martins, L. G., Sinnaeve, D., Poggetto, G. D., Tormena, C. F., Adams, R. W., Morris, G. A., & Nilsson, M. (2016). *Angewante Chemie International Edition, 55*, 15579. https://doi.org/10.1002/ange.201609676

Foston, M., Samuel, R., Heb, J., & Ragauskas, A. J. (2016). A review of whole cell wall NMR by the direct-dissolution of biomass. *Green Chemistry, 18*, 608–621. https://doi.org/10.1016/j.copbio.2014.02.002

Fowles, J., Boatman, R., Bootman, J., Lewis, C., Morgott, D., Rushton, E., van Rooij, J., & Benton, M. (2013). A review of thee toxicological and environmental hazard risks of tetrahydrofuran. *Critical Review Toxicology., 43*(10), 811–828. https://doi.org/10.3109/10408444.2013.836155

Fu, L., McCallum, S. A., Miao, J., Hart, C., Tudryn, G. J., Zhang, F., & Linhardt, R. J. (2015). Rapid and accurate determination of the lignin content of lignocellulosic biomass by solid-state NMR. *Fuel (London), 141*, 39–45. https://doi.org/10.1016/j.fuel.2014.10.039

Gao, X., Laskar, D. D., Zeng, J., Helms, G. L., & Chen, S. (2015). A ^{13}C CP/MAS-based nondegradative method for lignin content analysis. *ACS Sustainable Chemistry and Engineering, 3*, 153–162. https://doi.org/10.1021/sc500628s

García, J. C., Alfaro, A., Loaiza, J. M., Lozano-Calvo, S., & López, F. (2022). Cold alkaline extraction of Elephant grass for optimal subsequent extraction of hemicelluloses and energy production. *Biomass Conv Bioref, 14*, 8307–8320. https://doi.org/10.1007/s13399-022-03054-3

Gargallo-Garriga, A., Sardans, J., Llusià, J., Peguero, G., Asensio, D., Ogaya, R. I., Urbina, I., Van Langenhove, L., Verryckt, L. T., Courtois, E. A., Stahl, C., Grau, O., Urban, O., Janssens, I. A., Nolis, P., Pérez-Trujillo, M., Parella, M., & Peñuelas, T. J. (2020). ^{31}P-NMR metabolomics revealed species-specific use of phosphorous in trees of a french guiana rainforest. *Molecules, 25*, 3960. https://doi.org/10.3390/molecules25173960

Ghosh, M., Prajapati, B. P., Suryawanshi, R. K., Dey, K. K., & Kango, N. (2019). Study of the effect of enzymatic deconstruction on natural cellulose by NMR measurements. *Bioresource Technology*.

Chemical Physics Letters, 727, 105–115. https://doi.org/10.1016/j.cplett.2019.04.063

Giummarella, N., Gioia, C., & Lawoko, M. (2018). A one-pot biomimetic synthesis of selectively functionalized lignins from monomers: A green functionalization platform. *Green Chemistry, 20*, 2651. https://doi.org/10.1039/C8GC01145A

Giummarella, N., & Lawoko, M. (2016). Structural basis for the formation and regulation of lignin–xylan bonds in birch. *ACS Sustainable Chemistry and Engineering, 4*(10), 5319–5326. https://doi.org/10.1021/acssuschemeng.6b00911

Giummarella, N., Pu, Y., Ragauskas, A. J., & Lawoko, M. (2019). A critical review on the analysis of lignin carbohydrate bonds. *Green Chemistry, 21*, 1573–1595. https://doi.org/10.1039/C8GC03606C

Giummarella, N., Zhang, L., Henriksson, G., & Lawoko, M. (2016). Structural features of mildly fractionated lignin carbohydrate complexes (LCC) from spruce. *RSC Advances, 6*, 42120. https://doi.org/10.1039/C6RA02399A

Gong, R., Liu, C., Wu, M., Tian, R., Yu, G., Luo, X., Li, B., Peng, F., & Tang, Y. (2024). Efficient fractionation of pure hemicellulose with high DP from bleached hardwood pulp using LiBr·3H2O and co-production of dissolving pulp. *Green Chemistry*. https://doi.org/10.1039/d4gc00335g

Gouveia, S., Otero, L. A., Fernández-Costas, C., Filgueira, D., Sanromán, Á., & Moldes, D. (2018). Green binder based on enzymatically polymerized eucalypt kraft lignin for fiberboard manufacturing: A preliminary study. *Polymers, 10*, 642. https://doi.org/10.3390/polym10060642

Grande, P. M., Weidener, D., Dietrich, S., Dama, M., Bellof, M., Maas, R., Markus, P., Leitner, W., Klose, H., & de Maria, P. D. (2019). OrganoCat fractionation of empty fruit bunches from palm trees into lignin, sugars, and cellulose-enriched pulp. *ACS Omega, 4*, 14451–14457. https://doi.org/10.1021/acsomega.9b01371

Guo, H., Zhao, Y., Chang, J.-S., & Lee, D.-J. (2023). Lignin to value-added products: Research updates and prospects. *Bioresource Technology, 384*, Article 129294. https://doi.org/10.1016/j.biortech.2023.129294

Gŭnther, H. (2013). *NMR spectroscopy basic principles, concepts, and applications in chemistry* (3rd ed.). Wiley-VCH.

Happs, R. M., Addison, B., Doeppke, C., Donohoe, B. S., Davis, M. F., & Harman-Ware, E. (2021). Comparison of methodologies used to determine aromatic lignin unit ratios in lignocellulosic biomass. *Biotechnology for Biofuels, 14*(58), 1–16. https://doi.org/10.1186/s13068-021-01897-y

Haslinger, S., Hietala, S., Hummel, M., Maunu, S. L., & Sixta, H. (2019). Solid-state NMR method for the quantification of cellulose and polyester in textile blends. *Carbohydrate Polymers, 207*, 11–16. https://doi.org/10.1016/j.carbpol.2018.11.052

Hawkes, G. E., Smith, C. Z., Utley, J. H. P., Vargas, R. R., & Viertler, H. (1993). A comparison of solution and solid state ^{13}C NMR spectra of lignins and lignin model compounds. *Holzforschung, 47*(4), 302–312. https://doi.org/10.1515/hfsg.1993.47.4.302

Holding, A. J., Mäkelä, V., Tolonen, L., Sixta, H., Kilpeläinen, H., & King, A. W. T. (2016). Solution-state one- and two-dimensional NMR spectroscopy of high-molecular-weight cellulose. *ChemSusChem, 9*, 880–892. https://doi.org/10.1002/cssc.201501511

Hong, S., Shen, X.-J., Xue, Z., Sun, Z., & Yuan, T.-Q. (2020). Structure–function relationships of deep eutectic solvents for lignin extraction and chemical transformation. *Green Chemistry, 22*, 7219–7232. https://pubs.rsc.org/en/content/articlelanding/2020/gc/d0gc02439b.

Hu, L. S., Fang, X. Z., Du, M. H., Luo, F., & Guo, S. H. (2020). Hemicellulose-based polymers processing and application. *American Journal of Plant Sciences, 11*, 2066–2079. https://doi.org/10.4236/ajps.2020.1112146

Huang, L.-Z., Ma, M.-G., Ji, X.-X., Choi, S.-E., & Si, C. (2021). Recent developments and applications of hemicellulose from wheat straw: A review. *Frontiers in Bioengineering and Biotechnology, 9*, Article 690773. https://doi.org/10.3389/fbioe.2021.690773

Huang, J. Q., Qi, R. T., Pang, M. R., Liu, C., Li, G. Y., & Zhang, Y. (2017). Isolation, chemical characterization, and immunomodulatory activity of naturally acetylated hemicelluloses from bamboo shavings. *Journal of Zhejiang University Science B, 18*, 138–151. https://doi.org/10.1631/jzus.B1500274

Huang, Y.-F., & Lo, S.-L. (2020). Predicting heating value of lignocellulosic biomass based on elemental analysis, 191, 116501. DOI: 10.1016/j.energy.2019.116501.

Idström, A., Schantz, S., Sundberg, J., Chmelkad, B. F., Gatenholm, P., & Nordstierna, L. (2016). ^{13}C NMR assignments of regenerated cellulose from solid-state 2D NMR spectroscopy, 151, 480–487. https://doi.org/10.1016/j.carbpol.2016.05.107.

Jagatić Korenika, A.-M., Jeromel, A., Tomaz, I., Jednačak, T., Rončević, S., Nemet, I., Primožič, I., Hrenar, T., & Novak, P. (2024). Deep reinforcement learning classification of sparkling wines based on ICP-MS and DOSY NMR spectra. *Food Chemistry, 21*, Article 101162. https://doi.org/10.1016/j.fochx.2024.101162

Javier-Astete, R., Jimenez-Davalos, J., & Zolla, G. (2021) Determination of hemicellulose, cellulose, holocellulose and lignin content using FTIR in Calycophyllum spruceanum (Benth.) K. Schum. and Guazuma crinita Lam.. *PLoS ONE 16*(10), 1–12, e0256559. https://doi.org/10.1371/journal. pone.0256559.

Joseph, B., Sagarika, V. K., Sabu, C., Kalarikkal, N., & Thomas, S. (2020). Cellulose nanocomposites: Fabrication and biomedical applications. *Journal of Bioresources and Bioproducts, 5*, 223–237. https://doi.org/10.1016/j.jobab.2020.10.001

Kang, J., Guo, Q., & Shi, Y.-C. (2019). NMR and methylation analysis of hemicellulose purified from corn bran. *Food Hydrocoloids, 94*, 613–621. https://doi.org/10.1016/j.foodhyd.2019.03.048

Karimi, K., & Taherzadeh, M. J. (2016). A critical review of analytical methods in pretreatment of lignocelluloses: Composition, imaging, and crystallinity. *Bioresource Technology, 200*, 1008–1018. https://doi.org/10.1016/j.biortech.2015.11.022

Karlsson, M., Romson, J., Elder, T., Emmer, Å., & Lawoko, M. L. (2023). Structure and reactivity in the organosolv process studied by NMR spectroscopy, mass spectrometry, and density functional theory. *Biomacromolecules, 24*, 2314–2326. https://doi.org/10.1021/acs.biomac.3c00186

Khan, F., Bakar Siddique, A., Shabala, S., Zhou, M., & Zhao, C. (2023). Phosphorus Plays Key Rolesin Regulating Plants' Physiological Responses to Abiotic Stresses. *Plants, 12*, 2861. https://doi.org/10.3390/plants12152861

Kil, Y.-S., Han, A.-R., Hong, M.-J., Kim, J.-B., Park, P.-H., Choi, H., & Nam, J.-W. (2022). 1H NMR-based chemometrics to gain insights into the bran of radiation-induced colored wheat mutant. *Fronier in Nutrition, 8*, Article 806744. https://doi.org/10.3389/fnut.2021.806744

Kim, H., Ralph, J., & Akiyama, T. (2008). Solution-state 2D NMR of Ball-milled plant cell wall gels in DMSO-d 6. *Bio Energy Research, 1*, 56–66. https://doi.org/10.1007/s12155-008-9004-z

King, A. W. T., Mäkelä, V., Kedzior, S. A., Laaksonen, T., Partl, G. J., Heikkinen, S., Koskela, H., Heikkinen, H. A., Holding, A. J., Cranston, E. D., & Kilpeläinen, I. (2018). Liquid-state NMR analysis of nanocelluloses. *Biomacromolecules, 19*, 2708–2720. https://doi.org/10.1021/acs.biomac.8b00295

Kirui, A., Zhao, W., Deligey, F., Yang, H., Kang, X., Mentink-Vigier, F., & Wang, T. (2022). Carbohydrate-aromatic interface and molecular architecture of lignocellulose. *Nature Communications, 13*, 538. https://doi.org/10.1038/s41467-022-28165-3

Kita, Y., Kusumi, R., Kimura, T., Kitaoka, M., Nishiyama, Y., & Wada, M. (2020). Surface structural analysis of selectively 13C-labeled cellulose II by solid-state NMR spectroscopy. *Cellulose, 27*, 1899–1907. https://doi.org/10.1007/s10570-019-02896-x

Kline, L. M., Voothuluru, P., Lenaghan, S. C., Burris, J. N., Soliman, M., Tetard, L., Stewart, C. N., Jr., Rials, T. G., & Labbe, N. (2020). A robust method to quantify cell wall bound phenolics in plant suspension culture cells using pyrolysis-gas chromatography/mass spectrometry. *Frontier in Plant Science, 11*, Article 574016. https://doi.org/10.3389/fpls.2020.574016

Kohler, S., & Heinze, T. (2007). New solvents for cellulose: Dimethylsulfoxide/ammonium fluorides. *Macromolecular Bioscience, 7*, 307–314. https://doi.org/10.1002/mabi.200600197

Komatsu, T., & Kikuchi, J., (2013). Selective signal detection in solid-state NMR using rotor-synchronized dipolar dephasing for the analysis of hemicellulose in lignocellulosic biomass. The Journal of Physical Chemistry Letters. 4, 2279-2283. dx.doi.org/10.1021/jz400978g.

Kostryukov, S. G., Petrov, P. S., Kalyazin, V. A., Masterova, Y. Y., Tezikova, V. S., Khluchina, N. A., Labzina, L. Y., & Alalvan, D. K. (2021). Determination of lignin content in plant materials using solid-state 13C NMR spectroscopy. *Polymer Science, 63*, 544–552. https://doi.org/10.1134/S1560090421050067

Kumar, A. K., & Sharma, S. (2017). Recent updates on different methods of pretreatment of lignocellulosic feedstocks: A review. *Bioresources and Bioprocessing, 4*, 1–19. https://doi.org/10.1186/s40643-017-0137-9

Kuroda, K., Kunimura, H., Fukaya, Y., & Ohno, H. (2014). 1H NMR analysis of cellulose dissolved in non-deuterated ionic liquids. *Cellulose, 21*, 2199–2206. https://doi.org/10.1007/s10570-014-0271-x

Li, J., Gellerstedt, G., & Toven, K. (2009). Steam explosion lignins; their extraction, structure and potential as feedstock for biodiesel and chemicals. *Bioresorce Tehnology, 100*, 2556–2561. https://doi.org/10.1016/j.biortech.2008.12.004

Li, P., Yang, C., Jiang, Z., Jin, Y., & Wu, W. (2023). Lignocellulose pretreatment by deep eutectic solvents and related technologies: A review. *Journal of Bioresources and Bioproducts, 8*, 33–44. https://doi.org/10.1016/j.jobab.2022.11.004

Liu, J., Plog, A., Groszewicz, P., Zhao, L., Xu, Y., Breitzke, H., Stark, A., Hoffmann, R., Gutmann, T., Zhang, K., & Buntkowsky, G. (2015). Design of a heterogeneous catalyst based on cellulose nanocrystals for cyclopropanation: synthesis and solid-state NMR characterization. *Chemistry A European Journal, 21*, 12414–12420. https://doi.org/10.1002/chem.201501151

Liu, S., Zhu, Y., Wu, F., Meng, W., Wang, H., He, Z., Guo, W., Song, F., & Giesy, J. P. (2017). Using solid 13C NMR coupled with solution 31P NMR spectroscopy to investigate molecular species and lability of organic carbon and phosphorus from aquatic plants in Tai Lake, China. *Environmental Science and Pollution Research, 24*, 1880–1889. https://doi.org/10.1007/s11356-016-7954-9

Lu, F., & Ralph, J. (2011). Solution-state NMR of lignocellulosic biomass. *Journal of Biobased Matererial and Bioenergy, 5*(2), 169–180. https://doi.org/10.1166/jbmb.2011.1131

Mainka, H., Hilfert, L., Busse, S., Edelmann, F., Haak, E., & Herrmann, A. S. (2015). Characterization of the major reactions during conversion of lignin to carbon fiber. *Journal of Material Research and Technology, 4*, 377–391. https://doi.org/10.1016/j.jmrt.2015.04.005

Manders, W. F. (1987). Solid-state 13C NMR determination of the syringyl/guaiacyl ratio in hardwoods. *Holzforschung, 41*(1), 13–18. https://doi.org/10.1515/hfsg.1987.41.1.13

Mankar, A. R., Pandey, A., & Pant, K. K. (2022). *Bioresource Technology, 345*, Article 126528. https://doi.org/10.1016/j.biortech.2021.126528

Mansfield, D. S., Kim, H., Lu, F., & Ralph, J. (2012). Whole plant cell wall characterization using solution-state 2D NMR. *Nature Protocols, 9*, Article 1579. https://doi.org/10.1038/nprot.2012.064

Melone, F., Saladino, R., Lange, H., & Crestini, C. (2013). Tannin structural elucidation and quantitative 31P NMR analysis. 2. Hydrolyzable tannins and proanthocyanidins. *Journal of Agricultural and Food Chemistry, 61*, 9316–9324. https://doi.org/10.1021/jf401664a

Melone, F., Saladino, R., Lange, H., & Crestini, C. (2013). Tannin structural elucidation and quantitative 31P NMR analysis. 1. Model compounds. *Journal of Agricultural and Food Chemistry, 61*, 9307–9315. https://doi.org/10.1021/jf401477c

Meng, X., Aakash, P., Seemala, B., Kumar, R., Pu, Y., Christopher, P., Wyman, C. E., Cai, C. M., & Ragauskas, A. J. (2018). Chemical transformations of poplar lignin during cosolvent enhanced lignocellulosic fractionation process. *ACS Sustainable Chemical & Engineering, 6*, 8711–8718. https://doi.org/10.1021/acssuschemeng.8b01028

Meng, X., Crestini, C., Ben, H., Hao, N., Pu, Y., Ragauskas, A. J., & Argyropoulos, D. S. (2019). Determination of hydroxyl groups in biorefinery resources via quantitative 31P NMR spectroscop. *Nature Protocols, 14*, 2627–2647. https://doi.org/10.1038/s41596-019-0191-1

Mirpoor, S. F., Giosafatto, C. V. L., & Porta, R. (2021). Biorefining of seed oil cakes as industrial co-streams for production of innovative bioplastics. A review. *Trends in Food Science & Technology, 109*, 259–270. https://doi.org/10.1016/j.tifs.2021.01.014

Modica, A., Rosselli, S., Catinella, G., Sottile, F., Catania, C. A., Cavallaro, G., Lazzara, G., Botta, L., Spinella, A., & Bruno, M. (2020). Solid state 13C-NMR methodology for the cellulose composition studies of the shells of prunus dulcis and their derived cellulosic materials. *Carbohydrate Polymers, 2020*(240), Article 116290. https://doi.org/10.1016/j.carbpol.2020.116290

Mora-Sandi, A., Ramirez-González, A., Castillo-Henriquez, L., Loppreti-Correa, M., & Vega-Baudrit, J. R. (2021). Persea American agro-industrial waste biorefinery for sustainable high-value-added products. *Polymers, 13*, Article 1727. https://doi.org/10.3390/polym13111727

Mujtaba, M., Fernandes Fraceto, L., Fazeli, M., Mukherjee, S., Savassa, S. M., Araujo de Medeiros, G., do Espírito Santo Pereira, A., Donnini Mancini, S., Lipponen, J., & Vilaplana, F. (2023). Lignocellulosic biomass from agricultural waste to the circular economy: A review with focus on biofuels, biocomposites and bioplastics. *Journal of Cleaner Production, 402*, Article 136815. https://doi.org/10.1016/j.jclepro.2023.136815

Mun, J. S., Pe, J. A., III, & Mun, S. P. (2022). Characterization of kraft lignin prepared from mixed hardwoods by 2D HMQC and 31P NMR analyses. *BioResources, 17*, 6626–6637. https://ojs.cnr.ncsu.edu/index.php/BRJ/article/view/22110/80.

Munson, C. R., Gao, Y., Mortimer, J. C., & Murray, D. T. (2022). Solid-state nuclear magnetic resonance as a tool to probe the impact of mechanical preprocessing on the structure and arrangement of plant cell wall polymers. *Frontiers in Plant Science, 12*, Article 766506. https://doi.org/10.3389/fpls.2021.766506

Nishimura, H., Kamiya, A., Nagata, T., Katahira, M., & Watanabe, T. (2018). Direct evidence for α ether linkage between lignin and carbohydrates in wood cell walls. *Scientific Reports, 8*(6538), 1–11. https://doi.org/10.1038/s41598-018-24328-9

Nanganoa, L. T., & Njukeng, J. N. (2018). Phosphorus speciation by 31P NMR spectroscopy in leaf litters and crop residues from para rubber, cocoa, oil palm, and banana plantations in the humid forest zone of Cameroon. *Journal of Applied Chemistry*, 1–8. https://doi.org/10.1155/2018/6290236

Newman, R. H. (2004). Homogeneity in cellulose crystallinity between samples of Pinus radiata wood. *Holzforschung, 58*, 91–96. https://doi.org/10.1515/HF.2004.012

Noack, S. R., McLaughlin, M. J., Smernik, R. J., McBeath, T. M., & Armstrong, R. D. (2014). Phosphorus speciation in mature wheat and canola plants as affected by phosphorus supply. *Plant and Soil, 378*, 125–137. https://doi.org/10.1007/s11104-013-2015-3

Panić, M., Andlar, M., Tišma, M., Rezić, T., Šibalić, D., Cvjetko Bubalo, M., & Radojčić Redovniković, I. (2021). Natural deep eutectic solvent as a unique solvent for valorisation of orange peel waste by the integrated biorefinery approach. *Waste Management, 120*, 340–350. https://doi.org/10.1016/j.wasman.2020.11.052

Park, S., Baker, J., Himmel, M., Parilla, P., & Johnson, D. (2010). Cellulose crystallinity index: Measurement techniques and their impact on interpretingcellulase performance. *Biotechnology for Biofuels, 3*(1), 10. http://www.biotechnologyforbiofuels.com/content/3/1/10.

Parlov Vuković, J., Novak, P., Jednačak, T., Kveštak, M., Kovačević, D., Smrečki, V., Mikulandra, I., Djetelić Ibrahimpašić, M., Glanzar, S., & Zangger, K. (2020). Magnetic field influence on asphaltene aggregation monitored by diffusion NMR spectroscopy: Is aggregation reversible at high magnetic fields? *Journal of Dispersion Science and Technology, 41*, 179–187. https://doi.org/10.1080/01932691.2018.1561302

Peng, F., Bian, J., Peng, P., Guan, Y., Xu, F., & Sun, R.-C. (2012). Fractional separation and structural features of hemicelluloses from sweet sorghum leaves. *BioResources, 7*(4), 4744–4759. https://bioresources.cnr.ncsu.edu/resources/fractional-separation-and-structural-features-of-hemicelluloses-from-sweet-sorghum-leaves/.

Petračić, A., Sander, A., & Parlov Vuković, J. (2022). Deep eutectic solvents for deacidification of waste biodiesel feedstocks: An experimental study. *Biomass Conversion and Biorefinery, 12*(1), S3–S23. https://doi.org/10.1007/s13399-021-01511-z

Qu, T., Zhang, X., Gu, X., Han, L., Ji, G., Chen, X., & Xiao, W. (2017). Ball milling for biomass and pretreatment with aqueous hydroxide solutions. *ACS Sustainable Chemistry & Engineering, 5*, 7733–7742. https://doi.org/10.1021/acssuschemeng.7b01186

Raljević, D., Parlov Vuković, J., Smrečki, V., Marinić Pajc, L., Novak, P., Hrenar, T., Jednačak, T., Konjević, L., Pinević, B., & Gašparac, T. (2021). Machine learning approach for predicting crude oil stability based on NMR spectroscopy. *Fuel, 305*, Article 121561. https://doi.org/10.1016/j.fuel.2021.121561

Ročnik Kozmelj, T., Bartolomei, E., Dufour, A., Leclerc, S., Arnoux, P., Likozar, B., Jasiukaitytè-Grojzdek, E., Grilc, M., & Le Brech, Y. (2024). Oligomeric fragments distribution, structure and functionalities upon ruthenium-catalyzed technical lignin depolymerization. *Biomass and Bioenergy, 181*, Article 107056. https://doi.org/10.1016/j.biombioe.2024.107056

Santoni, I., Callone, E., Sandak, A., Sandak, J., & Dirè, S. (2015). Solid state NMR and IR characterization of wood polymer structure in relation to tree provenance. *Carbohydrate Polymer, 2015*(117), 710–721. https://doi.org/10.1016/j.carbpol.2014.10.057

Schlee, P., Tarasov, D., Rigo, D., & Balakshin, M. (2023) Advanced NMR characterization of Aquasolv Omni (AqSO) biorefinery lignins/lignin-carbohydrate complexes, ChemSusChem 16, e202300549 (2 of 12) https://doi.org/10.1002/cssc.202300549.

Sette, M., Lange, H., & Crestini, C. (2013). Quantitative HSQC analyses of lignin: A practical comparison. *Computational and Structural Biotechnology Journal, 6*, Article e201303016. https://doi.org/10.5936/csbj.201303016

Simmons, T. J., Mortimer, J. C., Bernardinelli, O. D., Pöppler, A.-C., Brown, S. P., deAzevedo, E. R., Dupree, R., & Dupree, P. (2016). Folding of xylan onto cellulose fibrils in plant cell walls revealed by solid-state NMR. *Nature Communications, 7*, Article 13902. https://www.nature.com/articles/ncomms13902.

Strassberger, Z., Tanase, S., & Rothenberg, G. (2014). The pros and cons of lignin valorisation in an integrated biorefinery. *RSC Advances, 4*, 25310–25318. https://pubs.rsc.org/en/content/articlelanding/2014/ra/c4ra04747h.

Šalić, A., Ljubić, A., Marčinko, T., Jurinjak Tušek, A., Cvjetko Bubalo, M., Tišma, M., & Zelić, B. (2023). Shifting the natural deep eutectic solvent based liquid lipase extraction from batch to continuous for more efficient process performance. *Journal of Cleaner Production, 405*, Article 136899. https://doi.org/10.1016/j.jclepro.2023.136899

Terrett, O. M., Lyczakowski, J. J., Yu, L., Iuga, D., Franks, W. T., Brown, S. P., Dupree, R., & Dupree, P. (2019). Molecular architecture of softwood revealed by solid-state NMR. *Nature Communications, 10*, 4978. https://doi.org/10.1038/s41467-019-12979-9

Tian, D., Li, T., Zhang, R., Wu, Q., Chen, T., Sun, P., & Ramamoorthy, A. (2017). Conformations and intermolecular interactions in cellulose/silk fibroin blend films: A solid-state NMR perspective. *The Journal of Physical Chemistry B, 121*, 6108–6116. https://pubs.acs.org/doi/10.1021/acs.jpcb.7b02838.

Tišma, M., Bucić-Kojić, A., & Planinić, M. (2021). Bio-based products from lignocellulosic waste biomass: A state of the art. *Chemical and Biochemical Engineering Quarterly, 35*, 139–156. https://doi.org/10.15255/CABEQ.2021.1931

Verevkin, S. P., Sazonova, A. Y., Frolkova, A. K., Zaitsau, D. H., Prikhodko, I. V., & Held, C. (2015). Separation performance of BioRenewable deep eutectic solvents. *Industrial and Engineering Chemistry Research, 54*, 3498–3504. https://doi.org/10.1021/acs.iecr.5b00357

Vidal, N. P., Rahimi, J., Kroetsch, B., & Martinez, M. M. (2023). Quality and chemical stability of long-term stored soy, canola, and sunflower cold-pressed cake lipids before and after thermomechanical processing: A ^{1}H NMR study. *LWT-Food Science and Technology, 173*, Article 114409. https://doi.org/10.1016/j.lwt.2022.114409

Vidal, N. P., Roman, L., Swaraj, V. J. S., Ragavan, K. V., Simsek, S., Rahimi, J., Kroetsch, B., & Martinez, M. M. (2022). Enhancing the nutritional value of cold-pressed oilseed cakes through extrusion cooking. *Innovative Food Science and Emerging Technologies, 77*, Article 102956. https://doi.org/10.1016/j.ifset.2022.102956

Yue, P.-P., Hu, Y.-J., Fu, G.-Q., Sun, C.-X., Li, M.-F., Peng, F., & Sun, R.-C. (2017). Structural differences between the lignin-carbohydrate complexes (LCCs) from 2- and 24-month-old bamboo (Neosinocalamus affinis). *International Journal of Molecular Sciences, 19*, 1. https://doi.org/10.3390/ijms19010001

Yue, F., Lan, W., Hu, S. G., Chen, K. L., & Lu, F. C. (2016). Structural modifications of sugarcane bagasse lignins during wet-storage and sodaoxygen pulping. *ACS Sustainable Chemistry Engineering, 4*, 5311–5318. https://doi.org/10.1021/acssuschemeng.6b00726

Yue, F., Lu, F., Regner, M., Sun, R., & Ralph, J. (2017). Lignin-derived thioacidolysis dimers: Reevaluation, new products, authentication, and quantification. *Chemistry Sustainability Energy Material, 10*, 830–835. https://doi.org/10.1002/cssc.201700101

Weidener, D., Dama, M., Dietrich, S. K., Ohrem, B., Pauly, M., Leitner, W., de María, P. D., Grande, P. M., & Klose, H. (2020). Multiscale analysis of lignocellulose recalcitrance towards OrganoCat pretreatment and fractionation. *Biotechnology Biofuels, 13*(155), 1–13. https://doi.org/10.1186/s13068-020-01796-8

Wang, T., Park, Y. B., Cosgrove, D. J., & Hong, M. (2015). Cellulose-pectin spatial contacts are inherent to never-dried arabidopsis primary cell walls: Evidence from solid-state nuclear magnetic resonance. *Plant Physiology, 168*, 71–884. https://doi.org/10.1104/pp.15.00665

Wang, T., Phyo, P., & Hong, M. (2016). Multidimensional solid-state NMR spectroscopy of plant cell walls. *Solid State Nuclear Magnetic Resonance, 78*, 56–63. https://doi.org/10.1016/j.ssnmr.2016.08.001

Wang, W.-Y., Qin, Z., Liu, H.-M., Wang, X.-D., Gao, J.-H., & Qin, G.-Y. (2021). Structural changes in milled wood lignin (MWL) of Chinese Quince (Chaenomeles sinensis) fruit subjected to subcritical water treatment. *Molecules, 26*, 398. https://doi.org/10.3390/molecules26020398

Wen, J.-L., Sun, S.-L., Xue, B.-L., & Sun, R.-C. (2013). Recent advances in characterization of lignin polymer by solution-state nuclear magnetic resonance (NMR) methodology. *Materials, 6*, 359–391. https://doi.org/10.3390/ma6010359

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. *Journal of Chemical Technology and Biotechnology, 88*, 1663–1671. https://doi.org/10.1002/jctb.4017

Wieczorek, D., Żyszka-Haberecht, B., Kafka, A., & Lipok, J. (2022). Determination of phosphorus compounds in plant tissues: From colourimetry to advanced instrumental analytical chemistry. *Plant Methods, 18*(22), 1–17. https://doi.org/10.1186/s13007-022-00854-6

Zeko-Pivač, A., Bošnjaković, A., Planinić, M., Parlov Vuković, J., Novak, P., Jednačak, T., & Tišma, M. (2022). Improvement of the nutraceutical profile of brewer's spent grain after treatment with Trametes versicolor. *Microorganisms, 10*, 2295. https://doi.org/10.3390/microorganisms10112295

Zhang, S., Duan, Y., Teng, C., Quan, H., Yang, X., Li, H., Li, X., & Yan, L. (2023). Fast and selective degradation of biomass for xylose, glucose and lignin under mild conditions. *Molecules, 28*, 3306. https://doi.org/10.3390/molecules28083306

Zhang, R., Gao, H., Wang, Y., He, B., Lu, J., Zhu, W., Peng, L., & Wang, Y. (2023). Challenges and perspectives of green-like lignocellulose pretreatments selectable for low-cost biofuels and high-value bioproduction. *Bioresource Technology, 369*, Article 128315. https://doi.org/10.1016/j.biortech.2022.128315

Zhang, K., Liu, Y., Cui, S., & Xie, Y. (2021). Elucidation of the structure of lignin-carbohydrate complexes in Ginkgo CW-DHP by [13]C–[2]H dual isotope tracer. *Molecules, 26*, 5740. https://doi.org/10.3390/molecules26195740

Zhao, B. C., Xu, J. D., Chen, B. Y., Cao, X. F., Yuan, T. Q., Wang, S. F., Charlton, A., & Sun, R. C. (2018). Selective precipitation and characterization of lignin-carbohydrate complexes (LCCs) from Eucalyptus. *Planta, 247*, 1077–1087. https://doi.org/10.1007/s00425-018-2842-9

Zhao, Q., Pedersen, C. M., Wang, J., Liu, R., Zhang, Y., Yan, X., Zhang, Z., Hou, X., & Wang, Y. (2023). NMR diffusion analysis of catalytic conversion mixtures from lignocellulose biomass using PSYCHE-iDOSY. *Green Energy & Environment, 8*, 1409–1416. https://doi.org/10.1016/j.gee.2022.02.003

Zhu, X., Dai, Y., Wang, C., & Tan, L. (2016). Quantitative and structure analysis of cellulose in tobacco by ^{13}C CP/MAS NMR. *Spectroscopy, 27*, 126–135. https://doi.org/10.1515/cttr-2016-0014

Ziegler-Devin, I., Chrusciel, L., & Brosse, N. (2021). Steam explosion pretreatment of lignocellulosic biomass: A mini-review of theorical and experimental approaches. *Frontiers in Chemistry, 9*, Article 705358. https://doi.org/10.3389/fchem.2021.705358