

## **Lignin: A review on properties, analytical techniques, and current sustainable fertilizer-based applications**

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**ABSTRACT-** Lignin is the second most abundant component of lignocellulose material after cellulose. The enormous tons of lignin produced as waste material in the pulp, biorefinery, brewery and other equally essential sectors make it critical for it to be used for sustainable applications. There are different types of lignin based on the extraction method and the biomass type. The properties, abundance and nature of lignin make it possible to quantify or elucidate it using several qualitative and quantitative analytical techniques; FT-IR, qNMR, gravimetric, thermogravimetric, and spectrophotometric approaches. The chemistry, abundance, hydrophobicity, toughness, and active sites of lignin make it a promising preferred target for medical, bioscience, environmental, energy, construction, and agricultural-based applications. The areas in agriculture where lignin is being applied include fertilizer-based, agrochemical delivery systems, and water retention ability. The fertilizer-based application is currently one of the most promising areas where lignin is utilized. These applications include synthesizing lignin-based hydrogel for slow-release nutrient and water retention, lignin-based magnetic nanoparticles for adsorbing phosphorus, and hydrophobic lignin-based bio-composite encapsulation of urea.

**Keywords:** Analytical techniques, Fertilizer-based, Lignin, slow-release fertilizer.

### **1. INTRODUCTION**

The need to move from petroleum-based products to renewable resources has been an environmentally friendly approach to safeguard the environment. Using fossil fuels in automobiles, machinery, and electrical energy to power household electrical appliances adds to the carbon prints in the environment [1]. Research has been funded and conducted in several institutions and countries to provide alternative approaches and renewable raw material sources from plants and other biological entities. Plant, bacteria, fungi, and other organisms have produced renewable materials. Plant biomass

comprises three main components: Cellulose, hemicellulose, and lignin [2]. Cellulose is the most abundant plant-based biomass on earth, followed by lignin [3]. Cellulose, the energy-rich part of plants, has been used for several applications, including biofuels [4], ethanol production, bioplastics, paper production, carbon nanomaterials, and carbon fibres. Lignin is a complex, hetero-polymeric component of a plant? It forms the outer layer of the plant cell wall, providing mechanical support, transport (xylem and phloem) due to their hydrophobicity, and protecting the plant's rich cellulosic component from microbial attack. The high thermal stability of lignin makes it an ideal candidate for biofuels. The chemical composition of lignin makes it a good source for synthesizing crucial materials and chemicals, including epoxy-resin, syringic acid, vanillin, and veratryl alcohol. Chemicals and materials synthesized in the laboratory may have environmental consequences because most raw materials are not renewable and could be depleted with time. The energy generation and synthesis of biomaterials and bio-based chemicals that use plant biomass (cellulose) as raw materials produce lignin as waste. These lignin waste produced are from industries ranging from pulp [5], cellulose fibre, and ethanol production. The high availability of secondary agro-waste materials provides a high source of lignin for several applications. The source of lignin comprises jute, hemp, cotton, and wood pulp [6].

This review will also discuss the source, chemistry, types of lignin, and the analytical techniques used to elucidate and extract lignin. Also, lignin as renewable raw material for current environmentally friendly applications in the agricultural sector will be discussed.

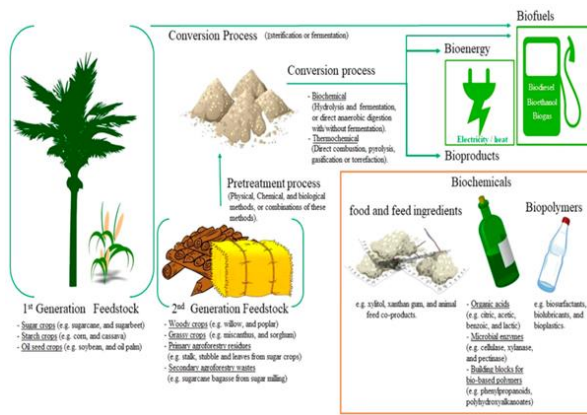


Figure 1: Schematic diagram of the applications of lignocellulose biomass. Reproduce from [7]

## 2. LIGNOCELLULOSE BIOMASS

Lignocellulose biomass comprises three main parts: cellulose, hemicellulose, and lignin. The cellulose component comprises complex sugars, the polymer of monomeric units joined by  $\beta$  1, 4 glycosidic bonds [8] and are either crystalline or non-crystalline. Cellulose comprises the most abundant biopolymer on earth, with about 30-80% composition across most lignocellulose types [5]. Hemicellulose is a polysaccharide that resembles cellulose but has branches in some aspects of its chains. It associates celluloses with lignin, and it is also amorphous. Unlike cellulose, hemicellulose is heterogeneous and made up of hexose (C6) and pentose (C5) sugars [9]. Their composition in hardwood and softwood are (15-30) % and (20) %, respectively [9]. Lignin is the second most abundant source of plant-based biomass and the most abundant natural aromatic biomass. Lignin acts as a barrier and connects the hemicellulose and cellulose in a plant cell wall.

Table 1: Major chemical composition of three primary lignocellulose biomass

Lignocellulose biomass	Chemical composition (%)			Reference
	Cellulose	Hemicellulose	Lignin	
Hardwood	40-44	15-35	18-25	[10]
Softwood	33-68	10-41	5	[11]
Grasses	34-39	30-35	6-25	[12]

## 3. PROPERTIES OF LIGNIN

### 3.1 Chemistry of lignin

The average percentage of lignin in most lignocellulose biomass is (15- 30) % [13]. Lignin is a poly-phenolic biopolymer complex with several non-straight linking structures [14]. The central forming units of lignin are p-hydroxyphenyl (H), syringyl (S), and guaiacyl (G) [15].

These monomer units are formed from their family units (coumaryl, coniferyl, and sinapyl) alcohol). The monomer units (H, S, and G) combine in several ratios to make the different plants biomass, i.e., hardwood, soft, wood and grasses. As seen in fig, lignin acts as a linker that joins the hemicellulose and cellulose part of the plants together. 2. According to [5], the chemical composition of lignin monomeric units reveals that about 50% is mainly aromatic rings. There are about five main chemical interactions that exist in lignin. Ether ( $\beta$ -O-4), phenyl coumaran ( $\beta$ -5), pinosresinol ( $\beta$ - $\beta'$ ), diphenyl ether (4-O5'), and diphenylmethane ( $\beta$ -1') are the significant bonds found in lignin structure [16], [17].

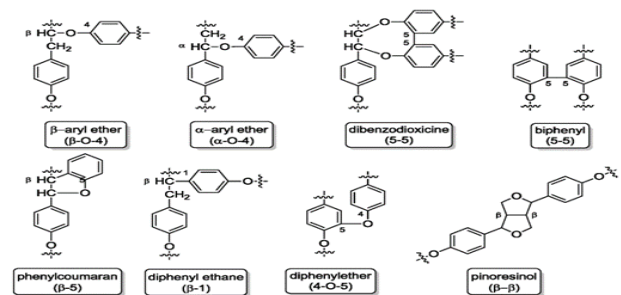


Figure 2: The different types of linkages in lignin structure [18]

### 3.2 Physical properties of lignin

Lignin is yellow and light or dark brown and has a glass transition and melting temperature of 97-167°C and 170°C, respectively. The density of lignin at 20°C is about 1,350-1,500 kg/m<sup>3</sup> [19]. Lignin can cement fibre cells. Lignin can withstand high temperatures without breaking. However, it can be readily deconstructed by UV [20]. Lignin is an intricate polyol with both straight-chain and benzene ringed components. They are also non-crystalline and do not dissolve readily in water. Lignin is insoluble in most solvents and cannot be broken down into monomeric units [20], [21]. The structure and morphological attributes of lignocellulose fibres are influenced [20]. The presence of lignin in plants provides structural support. Due to the presence of hydrophobic and hydrophilic functional groups in lignin, it is soluble in hot alkali solution and is readily oxidized [20]. Lignin can also be dissolved with phenol and cannot be hydrolyzed in an acidic solution.

## 4. TYPES OF LIGNIN

Lignin structure, chemical composition ratio, physical properties, and reactivity depend on biomass sources, extraction methods, and environmental factors. They include hardwood, softwood, and grasses for sources; kraft lignin [22], soda lignin [10], organosolv lignin [23], and lignosulphonate [24], and enzymatic liberation extraction methods.

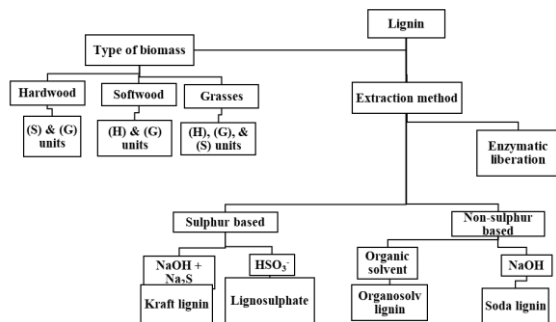


Figure 3: Type of lignin, based on source and extraction method.

#### 4.1 Lignin based on biomass type

Plants are characterized by the percentages of how the stem is strong, vascularity, ecosystem, and fruit and flower-bearing capabilities. Lignin comprises three major monolignols that combine in several ratios to form different types of lignin. This combination categorizes lignin into either hard, soft, or grasses. The combination between (H) and (G), (S) and (G), and (H), (S) and (G) forms softwood, hardwood, and grasses type lignin, respectively [25].

Table 2: Lignin monolignol composition (%)

Plant type	Monolignols (%)			Reference
	p-hydroxyphenyl (H)	Syringyl (S)	Guaiacyl (G)	
Hardwood	0-8	45-75	25-50	[25]
Softwood	<5	0	>95	[26]
Grasses	10-25	25-50	25-50	[27]

#### 4.2 Lignin based on the extraction method

##### 4.2.1 Sulphur-based

**4.2.1.1 Kraft lignin (KL).** The pulp industry uses the kraft process to rid lignin from woody conifers. The kraft process provides about 85 % of all lignin production globally [28]. The Kraft pulp process helps dissolve 95-98% of lignin and thus helps extract all the lignin content [28]. The conifers are dissolved in NaOH and Na<sub>2</sub>S and subjected to 160-170°C heat, forming a black liquor. The black liquor (BL) contains sulfur lignin. The kraft lignin (water-soluble) is precipitated with CO<sub>2</sub> at 65°C to gain a pH of 8.5. The BL lignin is filtered to get the water-soluble lignin [29].

##### 4.2.1.2 Lignosulphonate (LS).

The lignosulphonate process yields about 30-40% lignin [20]. Lignosulphonate comes from magnesium, sulfite, or calcium-based lignin with other hydrolyzed hemicellulose components. This method also uses black liquor from the pulp industry. The process involves precipitating lignin from the BL by acidifying H<sub>2</sub>SO<sub>4</sub> [30]. In [31], lignosulphonate was prepared from oil palm empty fruit bunches by acid hydrolysis of the fruit bunch in diluted H<sub>2</sub>SO<sub>4</sub>. After, the fruit bunch was used to extract the lignin in an alkaline solution using NaOH at 90°C for 80 min. After alkaline treatment, the solid portion of the fruit bunch was the cellulose and hemicellulose, and the liquid portion was BL. The pure lignin was precipitated from BL by acidifying the BL with 98% H<sub>2</sub>SO<sub>4</sub> to gain a pH of about 2. The precipitates were washed with deionized water. Sulphuration was achieved by treating the lignin with NaHSO<sub>3</sub> at 90°C for 4 hours [31]. The liquid phase of the mixture was then evaporated through boiling; the mixture was then concentrated with methanol, which caused precipitation of the bisulfite salt. The bisulfate was evaporated to concentrate the LS [31].

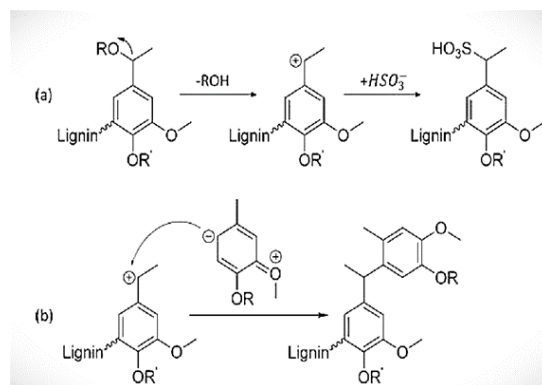


Figure 4. Sulphonation process. (A) sulphonation. (B) condensation pathway. Reproduced from: [32].

##### 4.2.2 Non-sulphur based

**4.2.2.1 Organosolv lignin (OL).** This type of lignin extraction is used to obtain low molecular weight lignin using a mild pretreatment process using an aqueous mixture of mineral acids and organic solvents. This method uses solvents such as phenol, acetic acid, butanol, or methanol [20]. An OL was prepared from walnuts [33]. Extractive-free fine powdered walnut was prepared by grinding the walnut with a mill several times and treating the powdered walnut with a mill several times and treating the powdered walnut with 98% toluene in a reflux system for 2 hrs. The extractive-free biomass was treated with a highly diluted H<sub>2</sub>SO<sub>4</sub> and 140 ml of preferred alcohol or organic solvent. The mixture was heated in a flask at 80°C for 4 hrs. The mixture is then filtered to the solid residue and concentrated using a rotary evaporator [33]. The extracts were dissolved in minimal acetone and mixed with water to precipitate lignin. Depending on the type of alcohol used, several purifications could be attained by using Na<sub>2</sub>SO<sub>4</sub> [33].

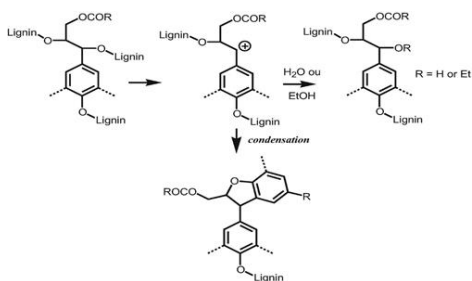


Figure 5. Organosolv lignin process. Reproduced from [34].

4.2.2.2 *Soda lignin (SL)*. Soda lignin typically has a lower molecular weight than Kraft lignin [35]. SL is also the purest of all the lignin extraction methods because it is sulfur-free [36]. The SL process is homologous to the KL process; the only difference is the sulfur addition process. Similarly, Lignocellulosic materials are treated with NaOH, producing soluble lignin with cellulose and hemicellulose as residue. The liquid portion is acidified with H<sub>2</sub>SO<sub>4</sub> to precipitate lignin [37].

#### 4.2.3 Enzymatic liberation.

The enzymatic liberation works on hydrolyzing the holocellulose component of the lignocellulose biomass. In this regard, only the lignin component will remain. This process is achieved by using cellulase, xylanase, and pectinases. This process is the best way of retrieving the native form of lignin since there is no severe chemical or depolymerization of the lignin form [21].

## 5. ANALYSES OF LIGNIN

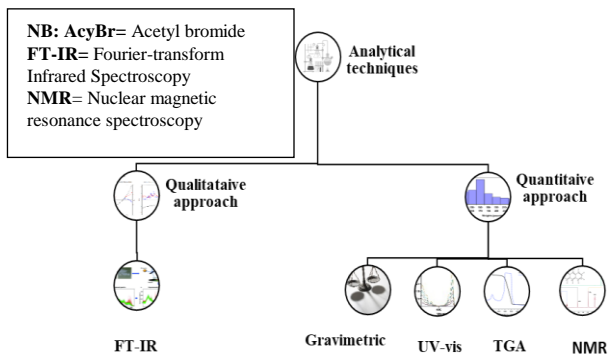


Figure 6. Schematic representation of the various type of techniques for analyzing lignin

### 5.1 Qualitative approach

#### 5.1.1. Fourier-transform infrared spectroscopy (FT-IR)

This technique obtains an infrared spectrum of material in its solid, liquid, or gaseous state. It provides absorption, emission, or photoconductivity as well. The wavenumbers and individual peaks often represent functional groups analogous to a specific material [38]. The wavenumber scan is normally from 400 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>. Lignin functional groups can be ascertained using FT-IR, where powdered samples will be subjected to IR spectroscopy [39]. The respective functional groups: (O-H) 3400-3415 cm<sup>-1</sup>, (CH<sub>3</sub> and CH<sub>2</sub>) 2950-2920

cm<sup>-1</sup>, (R-O=C-OH) 2865-2825 cm<sup>-1</sup>, (C=O) 1720-1710 cm<sup>-1</sup>, (aromatic) 1600-1420 cm<sup>-1</sup>, and (CO and C-O) stretching 1210-1220 cm<sup>-1</sup> and 1115-1120 cm<sup>-1</sup>, respectively. While (C-H) plane and aromatic plane deformation at 1030-1036 cm<sup>-1</sup> and 820-840 cm<sup>-1</sup>, respectively [40]. The respective functional groups are shown in table 3.

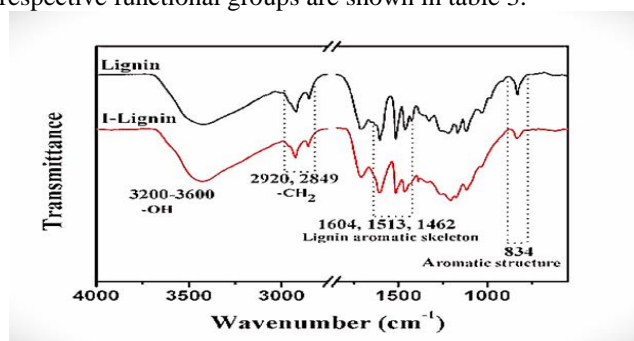


Figure 7. FT-IR spectra of pure lignin (black) and lignin treated with iodine (red). Reproduced from [50].

Table 3: FT-IR spectra information of lignin

Functional group Formula		Wavenumber cm <sup>-1</sup>	Reference
Free hydroxyl	-OH	3400–3600	[41]
Associated hydroxyl	-OH	3100–3400	[41]
Methylene/methyl	-CH <sub>2</sub> , -CH <sub>3</sub>	2820–2960	[42]
Carboxylic	R-O=C-OH	2920	[41], [42]
Methoxy methyl	R-O-CH <sub>3</sub>	2650–2890	[42]
Aromatics	C=O	1771	[43]
Unconjugated ketones, carbonyls, & ester groups	C=O	1700–1750	[44]
Aliphatic	C=O	1722	[43], [44]
Conjugated/p-substituent Carbonyl/ carboxyl	C=O	1650–1680	[42]–[44]
Benzene ring	C <sub>6</sub> H <sub>6</sub>	1500–1600, 1420–1430	[45], [46]
Plane and aromatic plane deformation	-CH <sub>2</sub> , -CH <sub>3</sub>	1450–1470, 1360–1370	[44], [46]
Syringyl ring	C-O	1325–1330, 1230–1235	[47]
Guaiacyl ring	C-O	1270–1275	[45], [47]
Ether	C-O	1215	[44]–[47]
Guaiacyl	C-H	1140–1145	[46], [48]
Syringyl	C-H	1130	[48]
Secondary alcohol and aliphatic ether	C-O	1085–1090	[49]
Aromatic ring and primary alcohol	C-O, C-H	1025–1035	[47], [48]
Aromatic ring	C-H	750–860	[49]

## 5.2 Quantitative

### 5.2.1 Gravimetric method

Gravimetric analyses help to quantify a material based on its mass or weight. It is the analytical technique where the quantity of a sample or extract is elucidated using a change in mass or mass itself [51]. According to [51], gravimetry is divided into four major types: precipitation, electro, volatilization, and particulate gravimetry. Determination of the quantity of pure or adulterated lignin can be elucidated using the gravimetric process.

Precipitation gravimetry separates lignin from its mixture with other soluble materials in a given solvent. The technique is based on the fact that the composite materials and lignin are readily soluble in each solvent. An example of such a method in recovering lignin is the Kraft lignin process, where NaOH and H<sub>2</sub>S are used to dissolve all the lignin components, and after precipitating the lignin by dropping the pH of the solution to 2-3 [29]. The volatilization technique comprises chemically or thermally decomposing a sample and finding the resultant change of mass [51]. When heat is applied in the decomposition process, the change in the material causes a change in a curve, and thus, the change in mass is elucidated [51]. This method of elucidating the content of a material in a matrix of others is termed thermogravimetry analyses (TGA) [28]. Lignocellulose materials subjected to thermal decomposition with an increase in temperature will cause the removal of less thermo-stable materials such as cellulose and hemicellulose with a specific change in curve. More thermo-stable components like lignin will decompose as the temperature increases and leave the final product [52]. The percentage at which the curve changes with temperature denotes the per cent composition of that material, as seen in Figure 13.

Similarly, dissolving a material in a solvent where some compositions dissolve while others cannot be used to elucidate the composition of the insoluble component in the matrix. Klason lignin KL (Insoluble lignin) can be elucidated from a lignocellulose material using the particulate gravimetry method. Unlike the precipitation gravimetry, no precipitation is required in the particulate gravimetry approach as the analyte or material in question is left insoluble in the solvent [52]. This method is used to quantify Klason lignin in lignocellulose materials. Extractive-free samples of the lignocellulose material are produced by treating them with 99% Acetone on a hot plate at 80°C for 3 hours to remove fatty acids, wax, resins, and other substances may interfere with the extraction process [2]. Alternatively, the TAPPI 222 om-02 method can eliminate all extractives by treating the sample with water, ethanol, and benzene sequentially using a Soxhlet reflux system for 16 hours each [53].

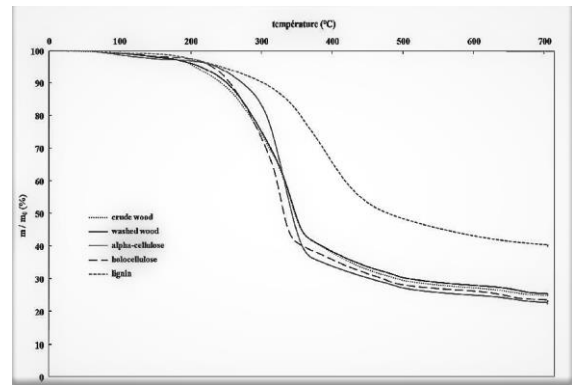


Figure 8. TGA curve of differently treated lignocellulose material; pure lignin, holocellulose,  $\alpha$ -cellulose, washed wood, and crude wood. Reproduced from [52].

The Klason method requires the treatment of extractive free lignocellulose material with H<sub>2</sub>SO<sub>4</sub> (72%, 3 ml / 0.5 g of biomass). This mixture is treated at a temperature of 30°C for 1 hour, after which the sample is diluted with about 83-85 ml of distilled water to obtain 3 % H<sub>2</sub>SO<sub>4</sub>. This diluted sample is autoclaved (121°C, 1.5 KPa, and 1 hour) or boiling the sample for 1 hour [53], [54]. The autoclaved sample is filtered to collect the dried residue (Klason lignin), and the mass is measured. Similarly, another method described in [2] suggests the treatment of extractive free lignocellulose pineapple leaves (1 g) with H<sub>2</sub>SO<sub>4</sub> (30 ml, 98%, room temperature, and 24 hours), after which the sample is boiled (100°C, 1 hour) then filtered hot (80°C), dried (105-110°C), and mass measured. This acid hydrolysis method of quantifying lignin has some drawbacks; accuracy is dependent on lignocellulose specie, lignin quantity is underestimated, and it is work-intensive [55]– [57].

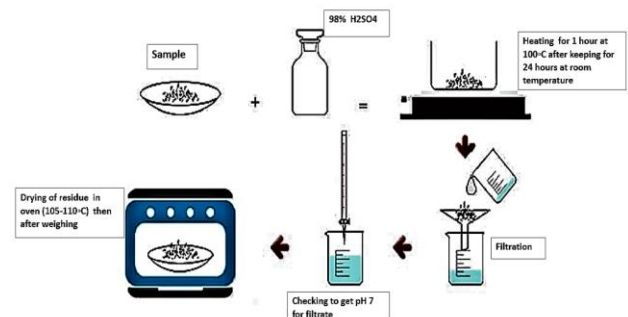


Figure 9. The Klason lignin extraction flow diagram is explained in [2]. Reproduced from [2]

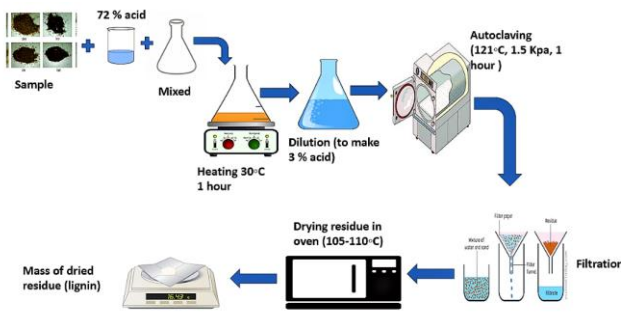


Figure 10. Flow chart for determination of Klason lignin using [53].

### 5.2.2 Spectrophotometric approach

5.2.2.1 Ultra-violet and visible absorption spectroscopy. This technique realizes that molecules or entities in a liquid sample can absorb UV-visible light [58]. The principle behind this technique is the Beer-Lambert law, where the absorbance of an analyte is directly proportional to the concentration, path length of the cuvette, and the absorptivity coefficient, as seen below (1) [59]. This indicates that the concentration of an analyte in the solution can be determined for a given path length.

$$A = \epsilon * C * L \quad (1)$$

where  $A$  = Absorbance

$\epsilon$  = Absorptivity coefficient

$C$  = Concentration

$L$  = Optical path length of the cuvette

This principle is applied in the determination of three types of lignin (i. e. acid-insoluble [53], acetyl bromide [57], and thioglycolic lignin [56]). In acid-insoluble lignin, the lignin that dissolved in the acid during the Klason lignin process is elucidated by measuring the filtrate's respective absorbance around 205 nm [55] using a spectrophotometer. However, the filtrate is diluted to get an absorbance reading ranging from 1.0-0.7 nm to ensure accuracy. Blanking is performed with 72% H<sub>2</sub>SO<sub>4</sub> diluted to 3%, like the treatment process. The mathematical formula for finding the mass and percentage mass in mg and %, respectively, is seen below (2) and (3), respectively [53].

$$\text{Lignin (g/L)} = \frac{A}{L * \epsilon} * D \quad (2)$$

Where  $A$  = Absorbance

$\epsilon$  = Absorptivity coefficient in g/L cm<sup>-1</sup> (110 g/L cm<sup>-1</sup> for wood)

$L$  = Optical path length in cm

$D$  = Dilution factor (if applicable)

$$\text{Lignin \%} = \frac{B * V * 100}{1000 * W} \quad (3)$$

Where  $B$  = mass of lignin in mg/L

$V$  = total volume used in the treatment in ml

$W$  = mass of the lignocellulose biomass used

One of the disadvantages of the acid-soluble lignin method is the absorption from polysaccharides that are also hydrolyzed by the acid.

Acetyl bromide lignin (ABSL) is another spectrophotometric approach to ascertaining lignin content in lignocellulose materials [60]. The chemistry of this method is the acetylation of non-substituted -OH groups and bromination of replaceable -OH groups in the lignin structure [61]. This causes the dissolution of lignin in the acetic acid medium [62]. According to [61], this method is not tissue-sensitive, results are accurate and consistent, and provides high recovery of the lignin content of several tissues. However, overestimating lignin content can occur due to hydrolysis of polysaccharides due to incubation at around 70 °C [61]. Extractives and polysaccharides from fine lignocellulose powder are removed to ensure accurate lignin content estimation. This is done by washing with several solvents in turns. These solvents include DMSO, acetone, 70% ethanol, chloroform, and distilled water [63]. This stage is to eliminate results obtained due to absorptions by proteins, wax, starch, and other forms of polysaccharides. In a study by [55], 25% acetyl bromide (25%, v/v) was diluted with glacial acetic acid in a chemical hood since the acetyl bromide is very toxic and the reaction produces many hazardous fumes.

In this method, 100 mg of extractive-free powder was treated with 25% acetyl bromide and incubated at 50°C for 2 hours in a Teflon cap glass test tube. At 30 minutes, the test tubes were shaken gently to cause complete dissolution of the lignin components. After NaOH (0.3 M, 2 ml) is added to stop the reaction, hydroxylamine hydrochloric acid (HAhc) (0.5 M, 1 ml) is also added before the reading is done on a spectrophotometer at a wavelength of 280 nm. Negative control was conducted by treating 100 mg of the same sample with all the solvents and conditions except the addition of acetyl bromide. A blank was also prepared with all the chemicals except the lignocellulose powder. Another method reported in [55] is using permanganate lignin (Perl), which uses Potassium permanganate instead of Acetyl Bromide. Spectrophotometric measurement is done in triplicates at 280 nm.

Another spectrophotometric approach is the thioglycolic method, where thioethers form because of the interaction between the thioglycolic acid and the benzyl alcohol components of the lignin. Lignin content results obtained from this method are under-represented due to the specificity of the acid to ether bonds present in lignin; thus, only the thioether components will dissolve [62]. The formula for estimating the percentage lignin component is seen below and adapted from [61].

$$\% \text{ ABSL} = \left( \frac{A^{280}}{\epsilon * L} \right) * \left( \frac{D}{m} \right) * 100 \quad (4)$$

Where  $A_{280}$  = Absorbance at 280 nm,  
 $\epsilon$  = Absorptivity coefficient in  $g/L\ cm^{-1}$   
 $L$  = Path length  
 $m$  = Mass of lignocellulose sample  
 $D$  = Dilution factor

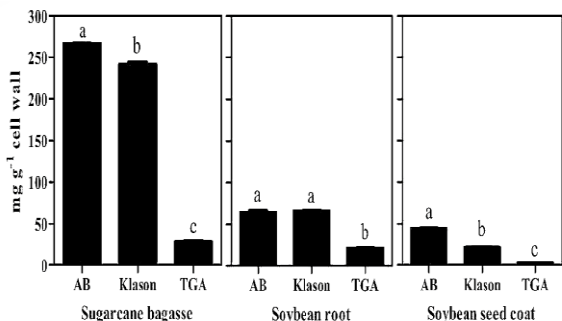


Figure 11. Lignin content composition in mg/g of soybean (bagasse, root, and seed coat) using the acetyl bromide (AB), Klason, and thioglycolic acid (TGA) lignin method. Reproduced from [62].

### 5.2.3 Nuclear Magnetic Resonance spectroscopy (NMR)

According to [64], using NMR as a quantitative technique is a very laudable approach to determining the content of an organic substance in a sample. This technique is based on the transfer and absorption of energies at radio frequencies possible for some nuclei ( $^1H$  and  $^{13}C$ ) [65]. These nuclei are electrically charged, and the application of external magnetic force causes energy transfer from the lower energy level to the high energy level. The release of this energy causes the nuclei to return to their base spin location, and the energy released is read using the same frequencies as the base energy and the energies released are read in a constant frequency (Radio frequencies). This generates specific signals of a particular molecule or nuclei [65]. One of the problems encountered with using quantitative nuclear magnetic resonance spectroscopy (qNMR) is the overlapping of some signals, inconsistencies in the polarization and transfer of energies between  $^1H$ - $^{13}C$  contents, and the high turnover time in terms of nuclei spin relaxation time.

Solid-state qNMR ( $^{13}C$ ) was used to quantify lignin composition in a biomaterial [66]. This study used 16 raw bio-based materials (wood samples, fruit shells, and other plant materials). The technique employed was the cross-polarization magic angle spinning (CP MAS). This method prepared standards using commercially available cellulose and kraft lignin. The two standard materials were mixed in several ratios to produce standard qNMR signals. The 16 samples were ground to very small pore sizes (i.e., 0.5 mm-0.1 mm), after which the samples were dried in an oven (105-110) °C for 24 hours to get rid of water molecules. The acid hydrolysis standard method was used to quantify the Klason lignin content for all sixteen samples. The qNMR was performed at the same frequency of 10 kHz in 4 mm zirconium dioxide rotors. The comparisons made between the signals, retention time and signal intensities between the standard

sample mixtures and the 16-lignocellulose content were used to elucidate the signals belonging to lignin and cellulose. The calibrated standard curve generated from the physical mixed standard materials was used to ascertain the percentage content of lignin (i.e., aromatic and the methoxy portion) [66]. The solid-state qNMR has been used to quantify lignin content in wood dating from 1984 based on calculation from the mean molecular weight of lignin [67]. Alternatively, the calibration curve method from the intensities of the signal corresponding to the methoxy component was also used to quantify lignin with others, such as qNMR of pure lignin [68]. The use of sodium salt of 3-(trimethylsilyl) propanoic acid as an internal standard is also reported to be used instead of lignin [69]. Results are typically compared to the standards and already published data available, as represented by the table adapted from [66] below.

Table 4. Lignin composition (%) of the different lignocellulose samples studied. Table adapted from [66]

SAMPLE	Lignin composition (%)			
	$^{13}C$ NMR		Acid hydrolysis Lignin	Published data
	Chromatic	Cmethoxy		
Spruce wood	27.2	29.5	28.7	27.9 [70]
Pinewood	19.7	20.1	20.1	20 [70]
Siberian larch wood	28.1	29.2	29.4	29.2 [71]
Aspen wood	18.2	20.6	21.5	19.5 [72]
Poplar wood	15.0	16.2	16.4	15.5-16.3[70]
Birchwood	22.7	16.2	22.1	22.4 [73]
Oakwood	24.3	24.2	24.5	24.1 [70]
Linden wood	23.6	22.8	23.5	28.3
Barley straw	7.8	7.4	8.3	6.3-9.8 [70]
Spent grain	3.3	5.4	5.5	16.9-27.8[72]
Sunflower seed shells	9.5	13.1	13.0	7.72-13.4[72]
Pumpkin seed shell	46.8	60.3	47.5	No data
Walnut shell	22.5	28.0	54.1	53.5 [72]
Peanut shell	33.0	40.2	32.5	28 [72]
Pistachio shell	6.5	8.0	30.2	29.4 [72]
Almond shell	22.2	27.5	28.1	36 [72]

Table 5. Summary of the analytical techniques used in lignin content determination of some lignocellulose materials.

Technique	Classification	Lignocellulose	Reference
Fourier transform infrared spectroscopy	Qualitative	Banana stem	[74]– [76]
		Date palm rachis	[77]
		Sorghum stem	[78]
		Sugar cane bagasse	[79], [80]
		Banana stem	[75], [76]
Klason acid-soluble lignin	Quantitative	Date palm rachis	[81]
		Sorghum stem	[82]
		Sugar cane bagasse	[74], [83]
Acetyl bromide lignin	Quantitative	Sugar cane bagasse	[62]
		Soybean root	[62]
		Soybean seed coat	[62]
		<i>Brachiaria brizantha cv Marandú</i>	[60]

Thioglycolic acid lignin	Quantitative	rice	[56]
		Soybean root	[62]
Thermogravimetric method	Quantitative	Soybean seed coat	[62]
		Japanese cedar leaves	[84]
		Wheat straw	[85]
		Pine bark	[85]
		Spruce bark	[85]
Quantitative nuclear magnetic resonance spectroscopy	Quantitative	Willow and poplar	[85]
		wood	[66], [71]
		Fruit shells	[66]
		Pistachio shell	[66]
		Spruce wood	[66]

Subject area	Environmental science	19
	Chemical engineering	15
	Energy	15
	Biochemistry, genetics, and Molecular Biology	13
	Agricultural Science	13
	Chemistry	11
	Materials science	10
	Medicine	5
Year range	2012-2022	62

NB: N/A means not applicable

6. APPLICATIONS OF LIGNIN

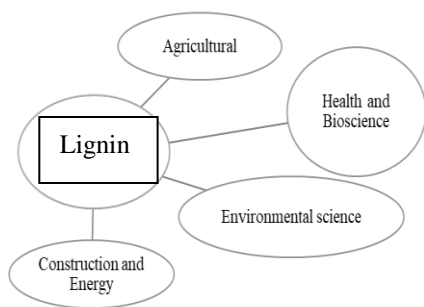


Figure 12. Significant industries utilize lignin as a biomaterial.

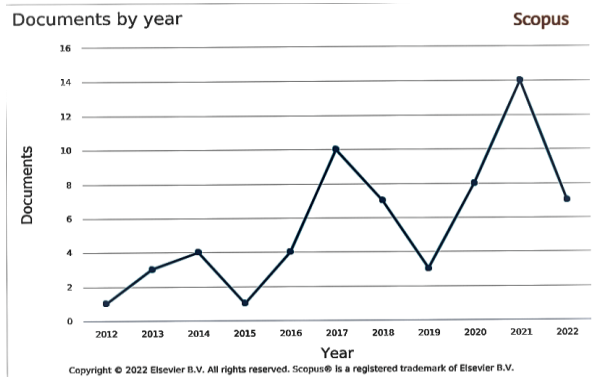


Figure 13. Trends in the number of publications with time (2012-2022) related to lignin using “Lignin as bioresource” as a keyword. Accessed from Scopus (2022).

Table 6. Summary of search criteria on Scopus (Keyword: Lignin as bioresource)

Search criteria	Name of criteria	No. of papers
Keyword	“Lignin as bioresource”	N/A
Type of Access	All Open Access	22
Paper type	Article	60
	Conference paper	2

Table 7. Specific industries and their lignin-based applications

Industry	Sub Industry	Material/product	Application	Reference
Agriculture	Chemical	Fertilizer, Pesticide delivery system, hydrogels	Improving soil properties and fertility	[86]–[91]
Health and bioscience	Nanomaterial, chemical	Nanoparticles, Lignin-based capsules, Chemicals	Drug delivery, Cancer treatment, Bio-imaging labelling	[92]–[97]
Environmental sciences	Nanomaterial, Chemical	Nanoparticles, carbon-based materials	Waste treatment, water treatment, Detection of heavy and toxic multivalent metals	[98]–[101], [102]–[106]
Construction	Material, composites	Additives, epoxy	Water retention, avoiding shrinkage, binder	[107]–[109]
Energy	Nanomaterials, Power, Battery	Nanocomposites, Carbon fibre	Energy storage, Sustainable energy,	[110]–[112]
Chemicals /Biofuel	Chemicals, Bio-based fuels.	Chemicals, lignin-based fuels	Sustainable energy is a renewable resource.	[113]–[117]

6.1 Agricultural applications

6.1.1 Fertilizer-based applications

Lignin provides a framework for chemically and thermally preparing slow-release organic nitrogen-based fertilizers (L-SRN). Slow-release nitrogen fertilizers prevent leaching and excessive loss of nitrogenous nutrients from the soil through seepage and run water. The use of organic materials

complexed with lignin under several conditions helped to produce a slow-released lignin nitrogen-based fertilizer [86]–[91], [118]. Lignin-based slow-release nitrogen was prepared using the ammoniation technique to incorporate nitrogen using ethylenediamine (EDA) via microwave heating [91]. The surface response methodology was utilized to ascertain the optimal conditions (content of EDA, time of microwaving, and temperature). The elemental analysis of the nitrogen content revealed that high levels of nitrogen (4.11-7.26) % were recorded for conditions; EDA content (4.0-8.0) g, temperature (60-80) °C, and time (10-40) minutes. Fourier-transform Infrared spectroscopy was used to ascertain the spectrum of the free lignin and the ammoniated lignin. Thermal analysis, zeta potential, contact angle, and scanning electromagnetic micrograph showed a slow release of nitrogen from the lignin-based nitrogen fertilizer using technical lignin. Lignin, a lignocellulosic material, is a good material for agricultural applications [91]. Similarly, an amination of biorefinery technical lignin was utilized to produce slow-release nitrogen fertilizers [90]. Unlike the [91], phenolation of the technical lignin (TL) was done under different ratios (phenol: TL; 1:1, 1:2, 1:4, and 1:6, respectively) and pretreated for 110°C for 20 min under acidic conditions using H<sub>2</sub>SO<sub>4</sub>. The phenolated lignin (5 g) was then ammoniated using three different nitrogen-based chemicals (40%; dimethylamine aqueous, ethylenediamine solution, or diethylenetriamine) and 37% formaldehyde solution. The mixture was treated under (60, 70, and 80) °C for (3, 4, and 5) hours [90]. Phenolation increased the active sites of the TL from 2.91 mmol/g to 8.26 mmol/g. The extent of ammoniation was reflective of the type of nitrogen-based reagent rather than the ratio of ammoniation. Under the optimal condition, high nitrogen content (10.13%) and low C/N ratio (6.08) were obtained. The leaching experiment conducted revealed that the SRL fertilizer prepared was good in preventing high leaching [90].

A hydrophobic lignin-based bio-composite, solvent-free coated, was prepared to use a slow-release nitrogen fertilizer [118]. Crosslinked sulphonated lignin (CSL) was prepared using epichlorohydrin at different concentrations. The different prepared CSLs were hydrophobized and esterified using N, N-dimethylformamide, pyridine, lauryl chloride, and glacial HCl. This optimized esterified crosslinked sulphonated lignin (ECSL) was used as a solvent-free coated material for urea (nitrogen content; 46.4%). This coated material was used as a slow-releasing nitrogen-based fertilizer (SRF) [118]. This ECSL helps encapsulate the urea for the application of fertilizers. Compared to other SRFs, this bio-polymeric thermoplastic material has the appropriate glass transition temperature and can slowly release nitrogen (86.9%, after 44 days) [118]. The co-application of lignin-based hydrogel was reported by [87] as a slow-release fertilizer and a water retention material from black liquor.

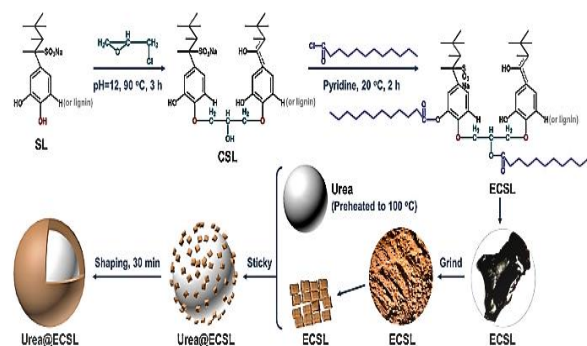


Figure 14. Schematic diagram showing the preparation steps for urea encapsulated by ECSL.

The co-application of lignin-based nanoparticles [88] as separation and recovering agent of phosphate and the onwards use as renewable magnetic fertilizers is also one of the innovative uses of lignin for agricultural benefits. The recovery and separation of phosphate enrich the nanoparticle with nutrients due to absorption. This nanoparticle can be applied as fertilizers for agricultural purposes [88]. The first amination of lignin prepared the magnetic lignin-based fertilizer (M/ALFe), and Fe<sub>2</sub>O<sub>3</sub> nanoparticles were loaded. The Fe<sup>3+</sup> was chelated on the aminated lignin. The (M/ALFe) prepared is used to absorb phosphorus, which is used as fertilizer [88]. The magnetic lignin is recovered using magnetic and reused to absorb phosphorus (reusing materials).

## 7. CONCLUSION

Lignin is a vital bioresource that can be accessed from various agricultural waste, biorefinery, and pulp industries. The various extraction methods used to extract lignin do not necessarily recover the entire lignin content in lignocellulose biomass. However, the most promising extraction is the enzymatic process, where the native form of the lignin is recovered. Due to the nature of the lignin polymer, several analytical tools are handy to concentrate lignin and thus very easy to validate the content quality of lignin in a sample. The potential of lignin as raw material for the eco-friendly and cheap synthesis of bio-based material stems from its chemical and chemical properties and its abundance in the environment compared to petroleum-based sources. The application of lignin to form fertilizer-based materials and delivery systems is a laudable bio-economic approach to safeguard the environment and ensure sustainable development.

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