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Utilisation of Lignins in the Bioeconomy: Projections on Ionic Liquids and Molecularly Imprinted Polymers for Selective Separation and Recovery of Base Metals and Gold

Peter Papoh Ndibewu and Pierre Gerard Tchieta

Additional information is available at the end of the chapter

Abstract

A brief review has been herein done of technologies involved in the exploitation of lignin, in order to provide an introduction to the subject from the perspective of a fast technologically advancing economy. Lignocellulosic materials and biomass have historically been utilised from since time memorial, but a new conversation is emerging on the role of these materials in modern bioeconomies. This new discourse needs to help us understand how technologies for managing and processing lignocellulosic materials both as biosynthetic moieties, biogenic wastes or simply renewable biopolymer—both established and novel—should be deployed and integrated (or not) to meet developmental requirements of the sustainability paradigm. The world is caught in the middle of green technology advocating for more and more focus on renewable sources of manufacturing raw materials and that of the molecularly imprinted/synthesised or genetically engineered ones. The utilisation of lignins (from renewable sources) in both the industry as the base for the formulation of ionic liquids (with yet a wider industrial applications), and also is a potential scaffold material for functionally modified imprinted polymers (LCIPS) for the selective recovery of base metals and gold, respectively, evidently incorporates the bioeconomy aspirations.

Keywords: lignins, ionic liquids, polyelectrolytic polymers, gold, bioeconomy

1. Introduction

Lignins [1–10], in particular, and in general lignocellulosic materials (LCMs) [11–16] and biomass [17–20], respectively, have historically been utilised since time memorial, but a new conversation is emerging on the role of these materials in modern bioeconomies [21–25]. Due to the nature of the molecule(s) as a novel commodity for many interesting natural and manufactured products [26–29], a modern bioeconomy [30–33] is not simply a rerun of former ones. This new discourse needs to help us understand how technologies [34–38] for managing and processing lignocellulosic materials both as biosynthetic moieties [39–49], biogenic wastes [50–58] or simply renewable biopolymer [59–69]—both established and novel—should be deployed and integrated (or not) to meet developmental requirements of the sustainability paradigm [70–75]. More so, in a closed-loop and resource-security agendas that undoubtedly sits behind the bioeconomy aspirations now being voiced by many schools of thought in many countries and regions of a so fast technologically advancing world [76–87]. The world of which is caught in the middle of green technology [88–92] advocating for more and more focus on renewable sources [93–98] of manufacturing raw materials and that of the molecularly imprinted/synthesised or genetically engineered ones [99–102].

The utilisation of lignins [103–106] (from renewable sources) in both the industry as the base for the formulation of ionic liquids (with yet a wider industrial applications) and as a potential scaffold material for functionally modified imprinted polymers (LCIPS) [107–114] for the selective recovery of base metals and gold, respectively, evidently incorporates the bioeconomy aspirations. Further, one new trend in lignin research is to steer biosynthetic pathways towards the biosynthesis of molecules that, upon incorporation into the lignin polymer, will improve lignin degradation, has been echoed by some researchers [5].

The name for lignin was derived from the Latin word for "wood" [94]. Lignin is a complex biopolymer based on 4-hydroxyphenylpropanoids [8] and is synthesised by almost all terrestrial plants [115] and also in some algae [116]. It is known to be the second most abundant natural polymer on Earth, just after cellulose [94]. It is one major structural component of higher plants' cell wall [94], contributing significantly to the recalcitrance of the woody biomass [117] that provides mechanical structure and resistance to environmental stress and microbial decay [94]. Lignin, as a second most abundant biopolymers present in terrestrial ecosystems is reported to contain organic carbon 30%, approximately [6]. Structurally, lignin in its native state is defined as protolignin [118], and can be defined as an amorphous, polyphenolic material arising from an enzyme-mediated dehydrogenative polymerisation of three phenylpropanoid monomers. That is, namely monolignols, namely coumaryl, coniferyl, and sinapyl alcohols, which corresponds, respectively, to p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S), forming the lignin structures (**Figure 1**) [118].

As seen in the lignin biosynthesis (**Figure 1**), it can act as building blocks in phenylpropanoid pathway, and thus helps in precipitation of lignin in the presence of acidic solutions [119, 120].

The lignin structure consists of three dimensional cross-linked macromolecules, hereunder illustrated (**Figure 2**) depicts the three sub-divisions of alcohols namely: sinapyl, coniferyl and p-coumaryl alcohol (**Figure 1**), with various lignin residues constructed from the three monolignols as illustrated in **Figure 3**.
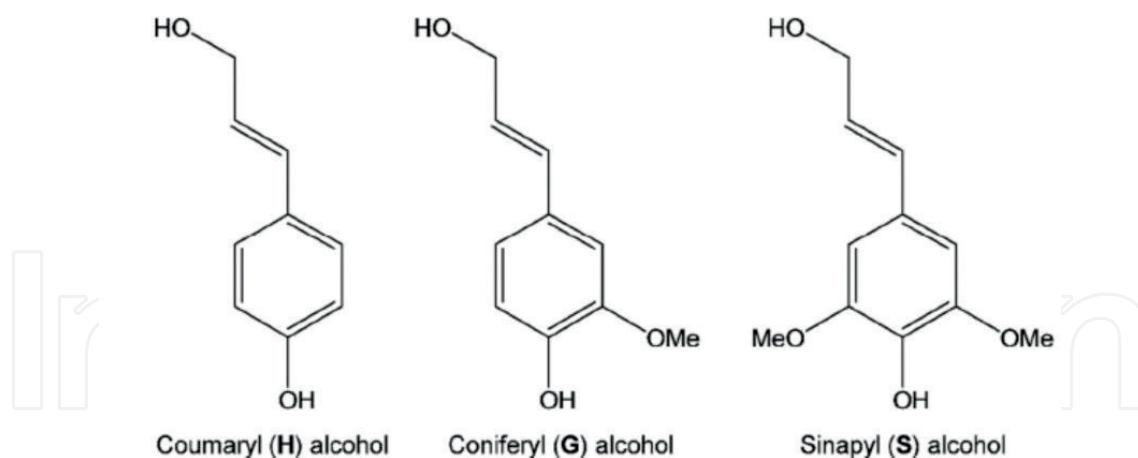
**Figure 1.** Phenylpropanoid precursors in lignin biosynthesis [118].
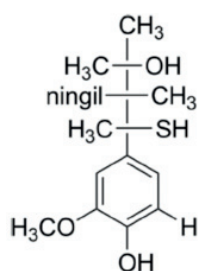
Figure 2. Structure of lignin [1].

Lignin can be considered essential "glue" that holds three polymers (lignin, cellulose, and hemicellulose) together in the plant cell wall (**Figure 2**) and is linked to polysaccharides, creating stable lignin-carbohydrate cross-linkages [121]. This is one of the main reasons for preventing selective separation of the biomass components in a biorefinery process [121]. Currently, it is understood that lignin, cellulose, and hemicellulose are not just individual units in a plant cell wall but are intimately interrelated and associated.

The chemical structure of cellulose has been clearly elucidated as a polysaccharide consisting of a linear chain of $\beta(1 \rightarrow 4)$ linked D-glucose units, from several hundred to many thousands (**Figure 5A**) [94]. Cellulose is embedded in the primary cell wall as protection (**Figure 4**), in fact, its regular structure makes it strong and resistant to most hydrolysis treatments [121].

On one hand, the cellulose polymers are arranged in microfibrils that are organised in fibrils; combined with cellulose fibres, which are responsible for the fibrous nature of lignocellulosic biomass [11, 12, 16] cell walls. On the other hand, hemicellulose is a branched polysaccharide composed of several different heteropolymers, such as arabinoxylans and glucomannans [12].

It is composed by a mixture of different pentoses (xylose and arabinose) and hexoses (glucose, mannose and galactose), respectively, containing C_5 and C_6 atoms (**Figure 5B**). It should be noted that hemicelluloses in deciduous woods (hardwoods) and agricultural herbaceous products like wheat straw, corn stover and switch grass predominantly consist of D-xylose units (xylans),
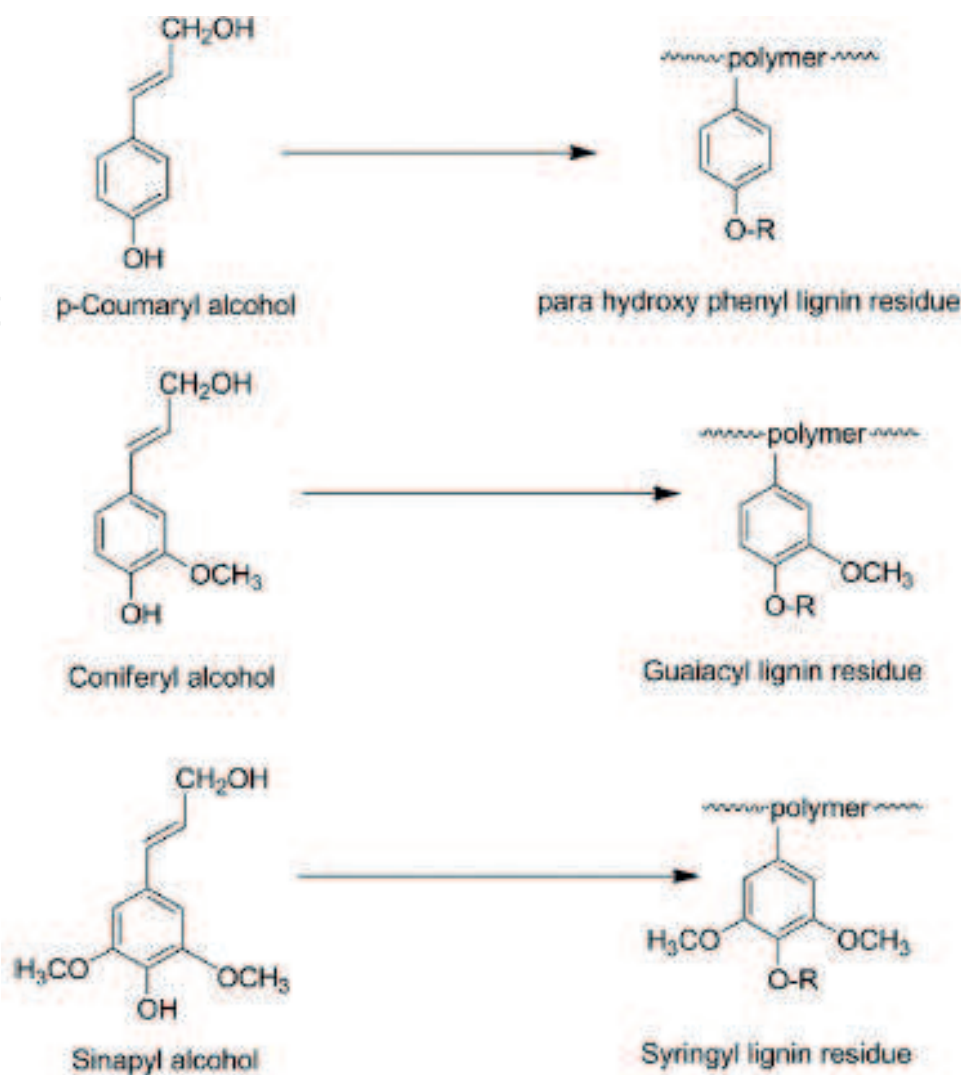
Figure 3. Structure of lignin residues from the three monolignols [1].

whereas coniferous (softwood) hemicellulose is mainly made up of D-mannose (mannans), L-arabinose (arabinans) and D-galactose (galactans) [123]. While they make up 30% of the cell wall material, xylans are the main hemicelluloses in hardwood, and predominate in annual plants and cereals making. Its structure is less regular than cellulose, and as such its resistance is also lower, while its role in the cell wall is to bind together different cellulose fibres together.

According to Huang [124], lignocellulosic biomass can be roughly classified into virgin bio-mass (e.g. trees and grasses), agricultural and forestry waste biomass (e.g. straws, sugarcane bagasse and paper mill discards) and energy crops (e.g. *Arundo donax* and switch grass). Some examples of different biomass type composition are shown in **Table 1**.

Lignocellulose that refers to the plant biomass accounts for more than 60% of the total biomass [11]. Authors [125, 126] clarify that this includes, but not limited to, the wood residues (saw-dust and paper mill discards), grasses, wastepaper, agricultural residues (straw, stover, peel-ings, cobs, stalks, nutshells, non-food seeds and bagasse), domestic wastes (lignocellulose garbage and sewage), food industry residues and municipal solid wastes (MSWs). These
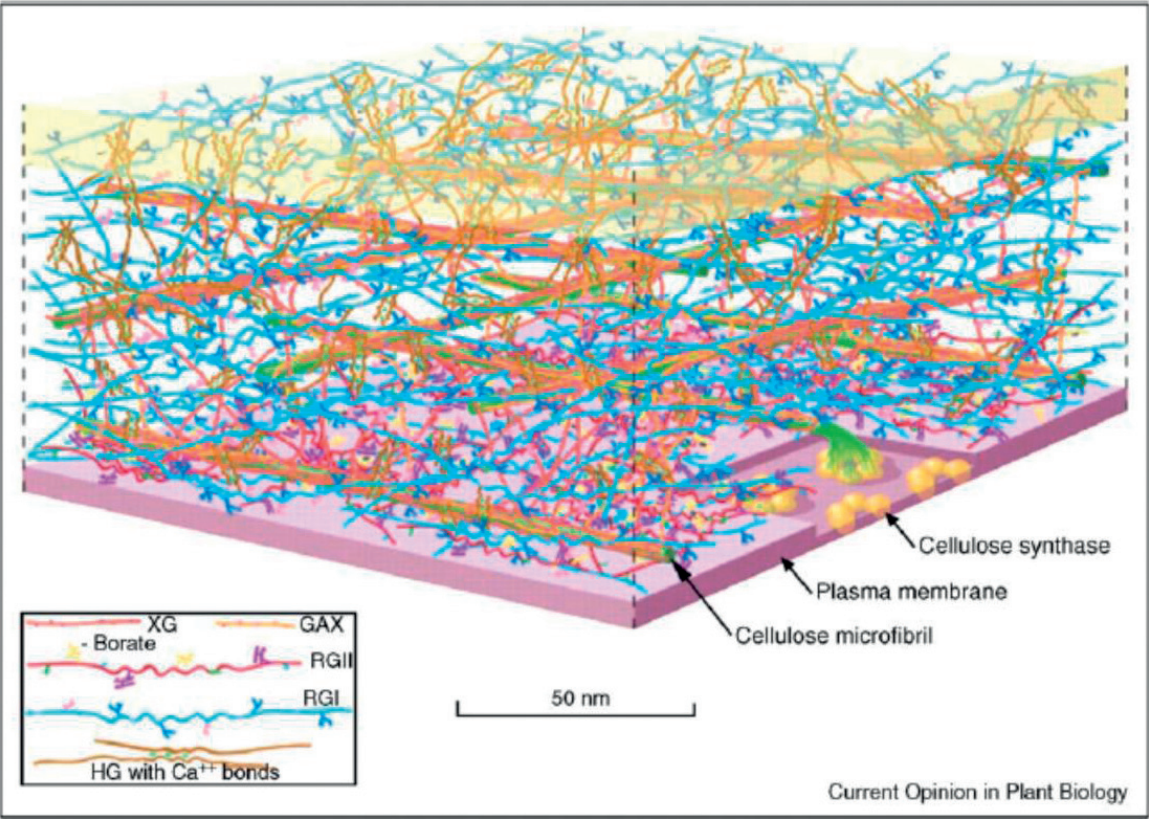
Figure 4. Schematic representation (Adapted from [8]) depicting the complexity of the plant cell wall [122].
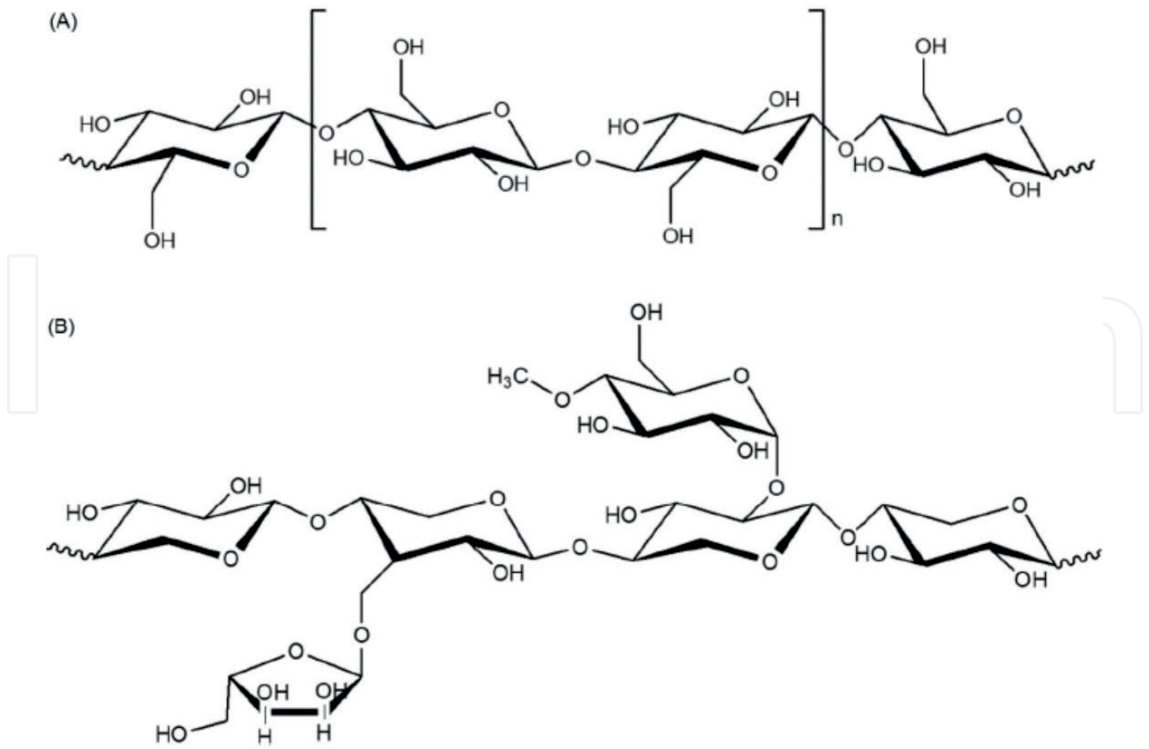

Figure 5. Structure of cellulose (A) and hemicellulose (B) [94].

composition constitutes the bulk of lignocellulosic materials (LCMs) of some importance in bioeconomic transformation [21]. In their review, Bilal et al. [11] provided an excellent detailed compositional profile of various previously reported LCMs herein summarised in **Table 2**. It is reported in the literature [94] that lignocellulosic biomass is essentially the inedible component of a plant, mainly composed of carbohydrate (cellulose and hemicellulose) and phenolic (lignin)-based polymers, chemically bounded together. From its composition viewpoint, these three main components represent from 85 to 95% by weight of the overall biomass; while the remaining part includes other components such as proteins, silica, fatty acids, pectin and salts.

Lignin samples have been fully characterised [127] with respect to lignin and sugar content and the amount of hydroxyl and carboxyl groups elucidated (**Table 3**).

It is a well-known fact that biomass was the main source of energy and materials prior to the industrial revolution. But following the exploitation of fossil fuels during the 1900s, biomass utilisation had declined sharply [52], except for a few cases that is worth mentioning. For example, during and after the aforementioned period, biomass usage was constant or even on the increased in the timber and fibre industries [128], during the 1930s agricultural surplus in the USA [129] and during World War II petroleum shortages in Europe [130]. As one of the twenty-first century human goal to reduce society's climate footprint and other environmental burdens, there is now a renewed interest in biomass, sparked by the aim to achieve a more secure supply of resources and to encourage the bioeconomy [21, 25, 30, 32]. Unfortunately, activities designed to achieve those aims are at the centre of a battlefield where recent food versus fuel and deforestation debates reveal that the source of the biomass being exploited is an important consideration. Thus, attention should be paid to the effective exploitation of renewable materials (unavoidable organic and biogenic wastes), including lignins and LCMs that might otherwise go unused or potentially be landfilled or cause disposal problems. The biotransformation and/or green treatment of lignins and LCMs with a focus on making new ionic liquids and molecularly imprinted polymers for selective separation and recovery of base metals and gold will result in tremendous gains in the bioeconomy loop.

The Dutch government's initiative in the 1920s of composting municipal solid waste (MSW) for land-expansion in Europe apparently was sparked by the concept of bioeconomy and these efforts was later followed by much wider interest in utilising MSW [131] much more sustainably. In recent times, many nations have designed very attractive strategies or roadmaps with clear settings on how they plan to approach the bioeconomy in their own respective countries

	Cellulose (% of d.m.)	Hemicellulose (% of d.m.)	Lignin (% of d.m.)	Other (% of d.m.)
Corn Stover	38	26	19	17
Soybean	33	14	-	53
Wheat Straw	38	29	15	18
Rye Straw	31	25	-	44
Switchgrass	37	29	19	15
Miscanthus	43	24	19	14
Forage Sorghum	34	17	16	33
Sweet Sorghum	23	14	11	52
Bagasse	40	30	20	10

Note: d.m. = dry matter

Table 1. Composition of main lignocellulosic biomasses [124].

Lignocellulosic materials	Carbohydrate composition (% dry wt.)		
	Lignin	Cellulose	Hemicellulose
Agricultural residues	5–15	37–50	25–50
Banana waste	14	13.2	14.8
Bagasse	23.33	54.87	16.52
Barley hull	19	34	36
Barley straw	6.3–9.8	36–43	24–33
Bamboo	23	49–50	18–20
Corn straw	8.2	42.6	21.3
Corn cobs	15	45	35
Corn stover	19	38	26
Cotton seed hairs	0	85–95	5–20
Coffee pulp	15.6–19.1	33.7–36.9	44.2–47.5
Douglas fir	15–21	35–48	20–22
Eucalyptus	29	45–51	11–18
Grasses	10–30	25–40	25–50
Horticultural waste	36	34.5	28.6
Hardwood	18–25	40–55	24–40
Olive tree biomass	19.1	25.2	15.8
Jute fibers	21–26	45–53	18–21
Leaves	0	15–20	80–85
Nut shells	30–40	25–30	25–30
Newspaper	18–30	40–55	25–40
Oilseed rape	14.2	27.3	20.5
Oat straw	10–15	31–35	20–26
Poplar wood	10–21	45–51	25–28
Pulp and paper sludge	16	23.4	8.6
Pine	23–29	42–49	13–25
Rice Straw	18	32.1	24
Rice husk	15.4–20	28.7–35.6	11.96–29.3
Sugar cane bagasse	20	42	25
Sweet sorghum	21	45	27
Softwood	25–35	45–50	25–35
Sponge gourd fibers	15.46	66.59	17.44
Sorted refuse	20	60	20
Solid cattle manure	2.7–5.7	1.6–4.7	1.4–3.3
Swine waste	NA	6	28
Sugar beet	NA	5	5.5
Tamarind kernel	NA	10–15	55–65
Winter rye	16.1	29–30	22–26
Wheat straw	16–21	29–35	26–32
Water-hyacinth	3.55	18.4	49.2
Wheat bran	8.3–12.5	10.5–14.8	35.5–39.2

Table 2. Compositional analysis of representative common lignocellulosic feedstocks [11].

Sample number	Raw material	Lignin type (commercial name)	Sample code	Lignin content (%)	COOH (mmol/g)	Phenolic OH (mmol/g)	Total sugars (%)
1	Hemp	Soda	He	Nd	2.1	1.58	2.4
2	Sisal	Soda	Si	Nd	1.18	2.29	7.7
3	Abaca	Soda	Ab	Nd	1.14	2.73	5.5
4	Straw	Soda	St	Nd	2.1	2.43	Nd
5	Jute	Soda	Ju	Nd	1.78	2.38	Nd
6	Flax	Soda	Fl-1	87.8	1.9	1.1	1.7
7	Softwood	Lignosulfonate (Borresperse 3A)	SW-LS-1	Nd	3.5	1.1	1.3
8	Softwood	Kraft (Indulin AT)	SW-Kr-1	90.0	2.5	1.8	2.06
9	Softwood	Lignosulfonate (Wafex P)	SW-LS-2	Nd	1.2	1.1	24.5
10	Flax	Soda (Bioplast)	Fl-2	87.8	1.9	1.1	1.7
11	Flax	Soda, oxidised	Fl-ox	92.1	1.8	0.9	1.6
12	Softwood	Kraft (Curan 100)	SW-Kr-2	88.6	1.7	0.8	2.26
13[a]	Softwood	Soda, precipitation high pH	SW-SF-1	64.7	Nd	Nd	1.77
14	Softwood	Kraft	SW-Kr-3	96.8	2.0	2.5	0.71
15	Mixed hardwoods	Organosolv (Alcell)	HW	96.5	0.78	2.4	0.32
16	Softwood	Soda, precipitation low pH	SW-SF-2	99.2	1.4	1.0	0.65
17	Softwood	Kraft (Curan 2711P)	SW-Kr-4	80.3	2.7	1.6	2.58

Nd, not determined.
   [a] Lignin 13 contains about 40% ash.

Table 3. Chemical characteristics of lignin samples [127].

or regions. From thence, there are undoubtedly new opportunities in exploiting biogenic wastes, of which lignins and lignocellulosic materials are some of the important prospect. This desire to valorise wastes and to holistically move waste treatment (and resources) up the waste hierarchy in an eco-friendly manner should contribute to a renewed vitality that is likely to nurture the bioeconomy [52]. Well, the valorisation of wastes happening so quickly and catalysed by technological and industrial developments, is an emerging subject going beyond energy applications. A good selection of recent ideas in the field of biotransformation of waste biomass into high value biochemicals has been exemplified by Brar et al. [132]. Typically, there is interest in generating higher value substances and products from biogenic waste, such as pigments, phenolics and nutrients, and so captivating can be the make new ionic liquids and molecularly imprinted polymers for the selective separation and recovery of base metals and gold, for industry applications and environmental pollution controls.

This chapter briefly reviews many of the key technological ingredients in the bioeconomy that are being explored for the utilisation of lignins and lignocellulosic materials (LCMs), as well as a brief description of biogenic wastes as a resource. Creating a categorical scheme for describing these renewable resources towards their potential to be explored in the manufacturing of a new range of ionic liquids (e.g. polyelectrolytic polymers) and bio-based imprinted polymers (e.g. molecularly imprinted polymers, MIPs) for selective separation and recovery of base metals and gold is increasingly an interesting avenue of research. Today's world of which is caught in the middle of green technology advocating for more and more focus on renewable sources for manufacturing raw materials is attempting desperately to meet up with the aspirations of bioeconomy. In this regard, the discussion herein presented in this chapter articulates well this new sustainability paradigm focusing on lignins and lignocellulosic materials. The utilisation of lignins (from renewable sources) in both the industry as the base for the formulation of ionic liquids (with yet a wider industrial applications) and as a potential scaffold material for functionally modified imprinted polymers (LCIPS) for the selective recovery of base metals and gold, respectively, evidently incorporates the bioeconomy principles. Further, one new trend in lignin research is to steer biosynthetic pathways towards the biosynthesis of molecules that, upon incorporation into the lignin polymer, will improve lignin

degradation [5]. Due to the nature of the molecule(s) as a novel resourceful commodity for many interesting natural and manufactured products, a modern bioeconomy in this niche area may not simply be a rerun of former ones. This discourse spelled out in this chapter, although not very critically, needs to help understand how technologies for managing and processing lignins and lignocellulosic materials both as biosynthetic moieties, biogenic wastes or simply renewable biopolymers—both established and novel—should be deployed and integrated (or not) to meet developmental requirements of the so much emphasised sustainability paradigm. More so, in a closed-loop and resource-security agendas that undoubtedly sits behind the bioeconomy aspirations now being voiced by many schools of thought in many countries and regions of the so fast technologically advancing world. This is the foremost reason that many countries, including international agencies at large, are working towards ensuring sustainable development [54].

2. The bioeconomy

To understand the term bioeconomy [22], two main schools of thoughts have conceptualise it and have tried to explain profoundly the aspirations behind the concept, irrespective from its origin [30]. The first school of thought widely publicised in the literature [133–136] defines the concept based on the understanding that bioeconomy will rely on renewable biomass instead of finite fossil inputs for the production of a wide range of value-added products such as food, feed, bio-based products and bioenergy. Secondly, proponents in the second school of thoughts, also available from the literature [23, 136, 137] advocates that these products will be produced in biorefineries following a cascade principle in order to maximally valorise the available biomass. Giurca and Metz [138] articulates that, from these two conceptualised definitions, the bioeconomy can be understood as a cross-sectoral concept, where different sectors (e.g. food, feed, chemistry, energy, fuel and pharmaceutical sectors) are expected to cooperate in order to derive products from renewable biological resources stemming from agricultural-, forest- and fishery-sectors [22, 23]. What this entails is that initially, biomass is processed into high value products such as chemicals and pharmaceutical active ingredients, and the residues are then used in downstream processes for lower value applications until a minimum of waste remains at the end of the process [139–141]. Some other co-workers [23, 137] has summarised the principle of the bioeconomy to be one which can thus be considered a collection of sectors and subsectors (e.g. food, feed, chemistry, energy, fuel and pharmaceutical sector), all working in conjunction to derive products from renewable biological resources originating from agriculture, fisheries and forestry. In this context, lignins and lignocellulosic materials, considered renewable and resourceful agricultural wastes are good candidates for consideration in further research, development and application. Another author [52] stated that "bioeconomy" shares a lot in common with the aims of "sustainability" and the use of biomass and renewables. This author exemplifies that in this regard, bioeconomy could be understood as an economy in which food, chemicals, energy and materials largely come from plants and animals—essentially bio-based. Thus, in agreement with the fundamental principle of bioeconomy emphasising an economy established on biomass instead of fossil fuels, signalling a significant shift in socio-economic, agricultural, energy and technological systems since from its inception in the twentieth century. This alignment of the

objectives of bioeconomy with those of sustainability may be able to create new directions and opportunities for meeting some of the requirements for sustainability [52]. As both scholars and policy-makers strongly assert that innovation plays a central role in ensuring a sustainable bioeconomy transition, both on the supply side, citing the need for new technologies and products, and on the user side, emphasising the consumption and waste patterns [22, 142–144], it must then be globally agreed that a multitude of different renewable resource-based technologies and innovation structures would have to come into play under the broad concept of "bioeconomy" [144] for this to happen. Technology Innovation Systems (TIS) perspectives [145, 146] can be regarded as a catalyst for the technology and innovation back-up.

In conclusion, it is widely ascertained, particularly in agreement with the views of both policy scholars and makers and scholars that the transition towards a bioeconomy is increasingly as one of the primary ways to reduce our dependency on fossil resources. However, research to provide the very complete myriad of economically viable technologies and biotransformation solutions of the total biomass (including lignins and lignocellulosic materials) remains scarce. This can be unarguably true of the socio-economic research on the transition towards the bioeconomy at the firm-level. This chapter serves a multiple purpose of creating the spark for more focussed research (lignin-biotransformation, lignin-based ionic polyelectrolytic polymers for industry usage, e.g. food, chemical and pharmaceutical, lignin-imprinted polymers for applications in gold and precious metals recovery and environmental remediation, just to name a few).

3. Lignins structure and functional properties

3.1. Structure

3.1.1. Lignin biosynthesis and distribution

Comprehensive approaches of the lignin biosynthetic pathway have been described in the literature [8]. It is common knowledge that the distribution and family expansion of the lignin biosynthetic genes in a few non-wood plants (rice, poplar and Arabidopsis, for example) exhibit a comparative genome expressive of the biosynthesis of lignin. Apparently, the complete lignin biosynthetic pathway first appeared in the lower plant (the moss). More so, the correlation between the expansion of lignin biosynthetic gene families and the substrate diversity is highly significant ($p < 0.05$). Furthermore, these authors observed that lignin biosynthetic genes expansion within the different families in terms of was very rapid. This observation could be a suggestion of a possible effective translation of transgenic lignin modification strategies from Arabidopsis (used as model species) to a more relevant plant with genetically differentiated biomass feedstocks only if it occurred between closely related species. A general reaction scheme for lignin biosynthesis is shown in **Figure 6** [8].

Chemically, lignins are synthesised via oxidative coupling between monomers of p-hydroxy-cinnamyl alcohols and other related molecules [6, 10, 147]. As illustrated in **Figure 6**, lignin is derived from three predominant p-hydroxycinnamyl alcohols, the monolignols: p-coumaryl, coniferyl and sinapyl alcohols. It is presumed [148] that all the enzymes required for monolignols biosynthesis are known, namely: phenylalanine ammonia lyase (PAL), cinnamate

4-hydroxylase (C4H), 4-coumarate-CoA ligase (4CL), shikimate hydroxycinnamoyl transferase (HCT), coumarate 3-hydroxylase (C3H), caffeoyl-CoA 3-O-methyltransferase (CCoAOMT), cinnamoyl-CoA reductase (CCR), cinnamyl alcohol dehydrogenase (CAD), ferulate 5-hydroxylase (F5H) and caffeic acid/5-hydroxyferulic acid O-methyltransferase (COMT). According to Vanholme et al. [5], the main biosynthetic route towards the monolignols p-coumaryl, coniferyl and sinapyl alcohol, adapted from Boerjan et al. [6, 10] is presented in **Figure 7**.

Obviously (**Figure 8**), the main building blocks of lignin are the hydroxycinnamyl alcohols (or monolignols), coniferyl alcohol and sinapyl alcohol, with typically minor amounts of p-coumaryl alcohol [149]. From the literature [150], biosynthetic pathway for the monolignols shows that they are synthesised from Phe through the general phenylpropanoid and monolignol-specific pathways. Whereas, Phe is derived from the shikimate biosynthetic pathway in the plastid [150]. Maybe, it is worth mentioning here that certain enzymes of the lignin biosynthetic pathway, like the cytochrome P450 enzymes cinnamate 4-hydroxylase (C4H), p-coumarate 3-hydroxylase (C3H), and ferulate 5-hydroxylase (F5H), are typically membrane proteins, presumably active at the cytosolic side of the endoplasmic reticulum [151, 152].
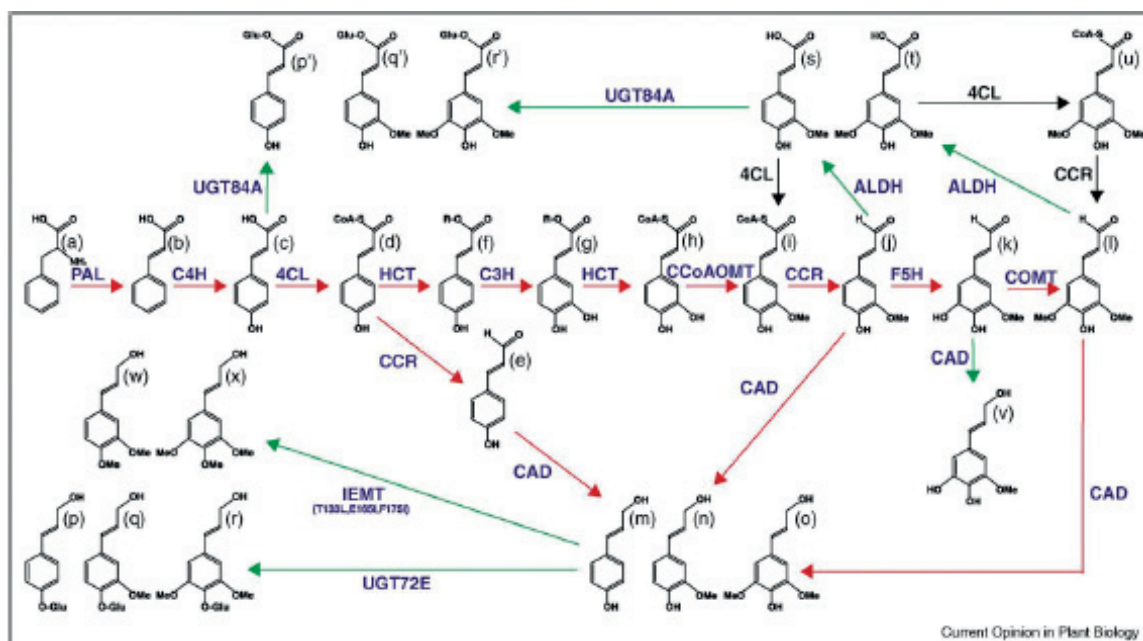

Figure 6. A schematic depiction of the known lignin biosynthesis pathways. 4CL, hydroxycinnamate-CoA/5-hydroxyferuloyl-CoA ligase; ALDH, hydroxycinnamaldehyde dehydrogenase; C3H, 4-hydroxycinnamate 3-hydroxylase; C4H, cinnamate 4-hydroxylase; CAD, hydroxycinnamyl alcohol dehydrogenase; CCoAOMT, S-adenosyl-methionine caffeoyl-CoA/5-hydroxyferuloyl-CoA-O-methyltransferase; CCR, hydroxycinnamoyl-CoA:NADPH oxidoreductase; COMT, caffeate O-methyltransferase; F5H, ferulic acid 5-hydroxylase; HCT, hydroxycinnamoyl-CoA shikimate/quinate hydroxycinnamoyl transferase; IEMT (T133 L, E165I, F175I), monolignol 4-O-methyltransferase (isoeugenol 4-O-methyltransferase carrying T133 L, E165I, F175I mutations); OMT, S-adenosyl-methione-caffeate/5-hydroxyferulate-O-methyltransferase; PAL, phenyl ammonia lyase; UGT84A, UDP-glucose: hydroxycinnamate glucosyltransferases; UGT72A, UDP-glucose:hydroxycinnamate 4-O-glucosyltransferase-like; a, phenylalanine; b, cinnamic acid; c, p-coumaric acid; d, p-coumaroyl-CoA; e, p-coumaraldehyde; f, p-coumaroyl shikimic acid/quinic acid; g, caffeoyl shikimic acid/quinic acid; h, caffeoyl-CoA; i, feruloyl-CoA; j, coniferaldehyde; k, 5-hydroxyconiferaldehyde; l, sinapaldehyde; m, p-coumaryl alcohol; n, coniferyl alcohol; o, sinapyl alcohol; p, p-coumaryl alcohol 4-O-glucoside; q, coniferyl alcohol 4-O-glucoside (coniferin); r, sinapyl alcohol 4-O-glucoside (syringin); s, ferulic acid; t, sinapic acid; u, sinapoyl-CoA; v, 5-hydroxy-coniferaldehyde; w, 4-methoxy-coniferyl alcohol; x, 4-methoxy-sinapyl alcohol; p0, p-coumaroyl glucose-ester; q0, feruloyl glucose-ester; r0, sinapoyl glucose-ester [8].

However, it remains unknown whether the other pathway active enzymes are also part of the metabolic complexes at the endoplasmic reticulum, although metabolic linkages has been shown between phenylalanine ammonia-lyse (PAL) and C4H [153, 154]. After synthesis, lignin monomers are exported into the plant cell wall where they will diffuse until they are oxidised by laccases or peroxidases and polymerised within the secondary plant cell wall [8]. The possible modes of export mechanism of the monolignols are illustrated in **Figure 7**.

Notwithstandingly the several proposed mechanisms (**Figure 8**), the exact mechanism of monolignol export from the cytosol to the apoplast still remains relatively unknown. The current up-to-date hypothesis suggests the exportation of free monolignols into the apoplast via plasma
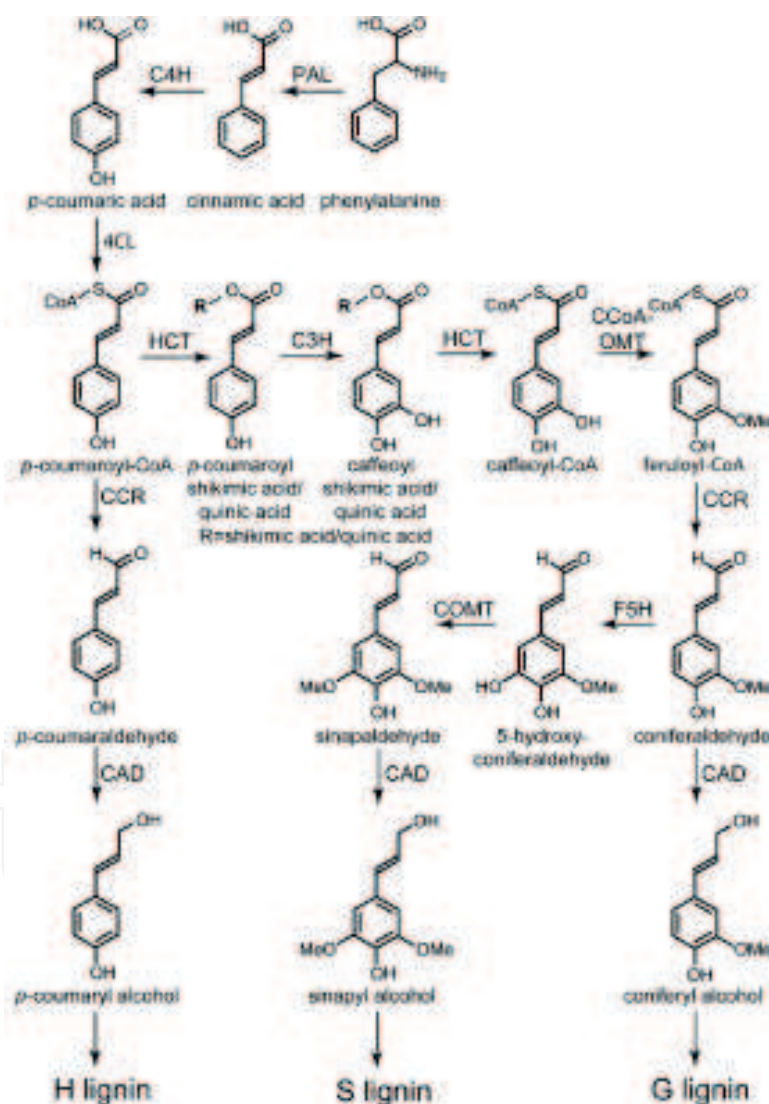
Figure 7. The main biosynthetic route towards the monolignols p-coumaryl, coniferyl, and sinapyl alcohol [6, 10]. PAL, phenylalanine ammonia-lyse; C4H, cinnamate 4-hydroxylase; 4CL, 4-coumarate: CoA ligase; C3H, p-coumarate 3-hydroxylase; HCT, p-hydroxycinnamoyl-CaA: Quinate/Shikimate p-hydroxycinnamoyl transferase; CCoAOMT, caffeoyl-CoA O-methyl transferase; CCR, cinnamoyl-CoA reductase; F5H, ferulate 5-hydroxylase; COMT, caffeic acid O-methyltransferease; CAD, cinnamyl alcohol dehydrogenase. Adapted from Vanholme et al. [5].
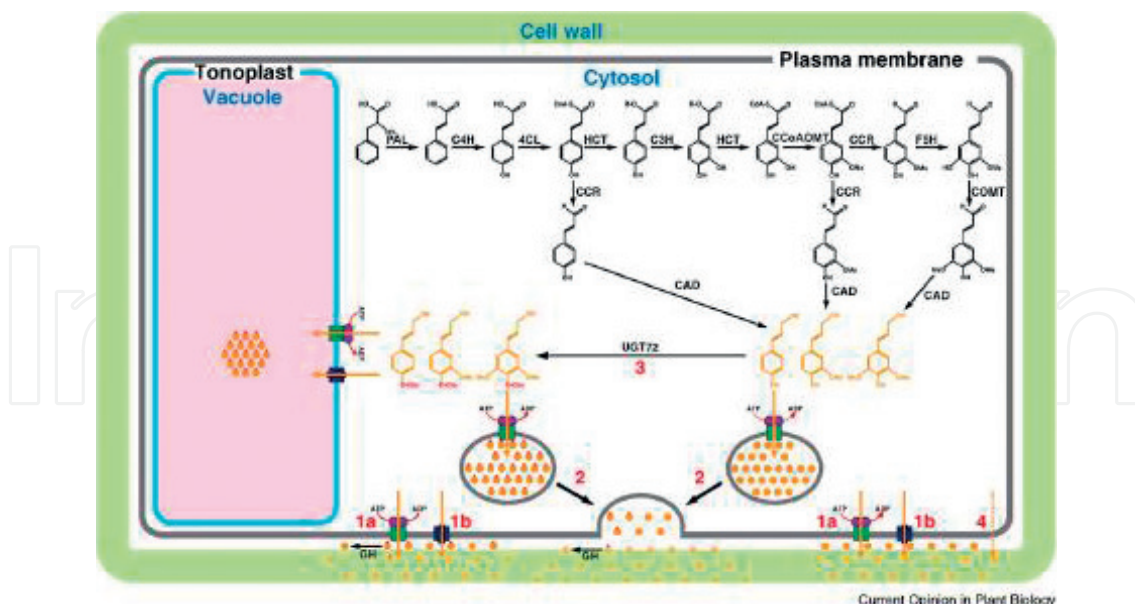
Figure 8. Schematic representation depicting lignin biosynthesis and possible modes of export mechanism of the monolignols: (1a) and (1b) protein-mediated transport mechanisms at the plasma membrane: (1a) active transporter (primary and secondary transport system) and (1b) facilitator protein; (2) secretion via vesicular export; (3) export of glycosylated monolignols (via a plasma membrane transporter or via vesicular export); (4) passive diffusion through the plasma membrane [8].

membrane transporters [155]. This is evidenced by the fact that feeding radiolabelled phenylalanine to lignifying cells did not show any vesicular accumulation of labelled monolignols [8, 155].

The most abundant renewable resource containing aromatic structures is lignin [156–158]. Lignin is the generic term for a large group of aromatic polymers resulting from the oxidative combinatorial coupling of 4-hydroxyphenylpropanoids [6, 10, 147]. Predominantly, these polymers are deposited in the thickened walls of secondary cells, resulting in their rigidity and making them impervious. Apart from the natural development via biosynthetic pathways and deposition of lignin, induced biosynthesis upon various biotic and abiotic stress conditions (e.g. wounding, pathogen infection, metabolic stress and perturbations in cell wall structure) have also been reported [159, 160]. As mentioned in the introduction, the protective characteristic of lignin, firmly protecting the cell wall polysaccharides from microbial degradation, and as a result imparting resistance to decay (recalcitrance), it thus presents one of the most important limiting factors in the conversion of plant biomass to pulp or biofuels. Extraction of lignin from plant biomass is a costly process. In recent times, research efforts are aimed at designing plants (bioengineering) that can either deposit less lignin or produce lignins that are more amenable to chemical degradation [161–163].

To conclude this section, one most recalls that the distribution of lignin within the cell walls is not uniform [149]. Zhou et al. [164] ascertained that the concentration of lignin in the middle lamella and the primary wall is higher than the concentration in the secondary wall. Nonetheless, it is reported in the literature [149] that the majority of the total amount of lignin present in the plant (75–85%) is located in the secondary wall, owing to its considerable larger volume. Structurally, the amount of lignin present in the plant varies from species to species, and range

from 20 ± 4% in hardwoods to 28 ± 3% in softwoods and herbaceous angiosperms; monocots are less lignified (15 ± 4%) [121, 165].

3.1.2. Structure-dependent functional properties of lignins

Lignin (**Figure 1b**) is a highly abundant, low-cost biopolymer exhibiting phenylpropane units as a typical structural feature. This molecule is a major component of wood and annual plants. Lignin produced mainly as a waste product in the pulp industry on a scale of 40–50 million tons per year worldwide. Whereas, a considerable amount of lignin is burned so to recover as downstream chemicals from the pulping process, as well as provide process heat, only 2% of all lignins are utilised for rather low-value applications [166]. This picture has led to the general perception that lignin is just a waste product of the pulping process. As a result, this has restrained the research for value-added applications for lignin and lignin-based materials for quite some time. However, intensive research is now focused on seeking higher value products from lignin [167]. Traditionally, lignin has been derived from the kraft and sulphite processes that are ubiquitous in the pulp and paper industry from since time memorial [167]. It has been reported [166, 168, 169] that over 50 million tonnes are produced annually worldwide.

The structure of native remains unclear despite intensive studies [167] over several years. However, Kubo and Kadla [170] have reported several proposed structures purely based on the analysis of degradation products. This has been possible through the identification of the dominant linkages between the phenylpropane units and their abundance, as well as the abundance and frequency of certain functional groups [167](**Figure 9a** and **b**).
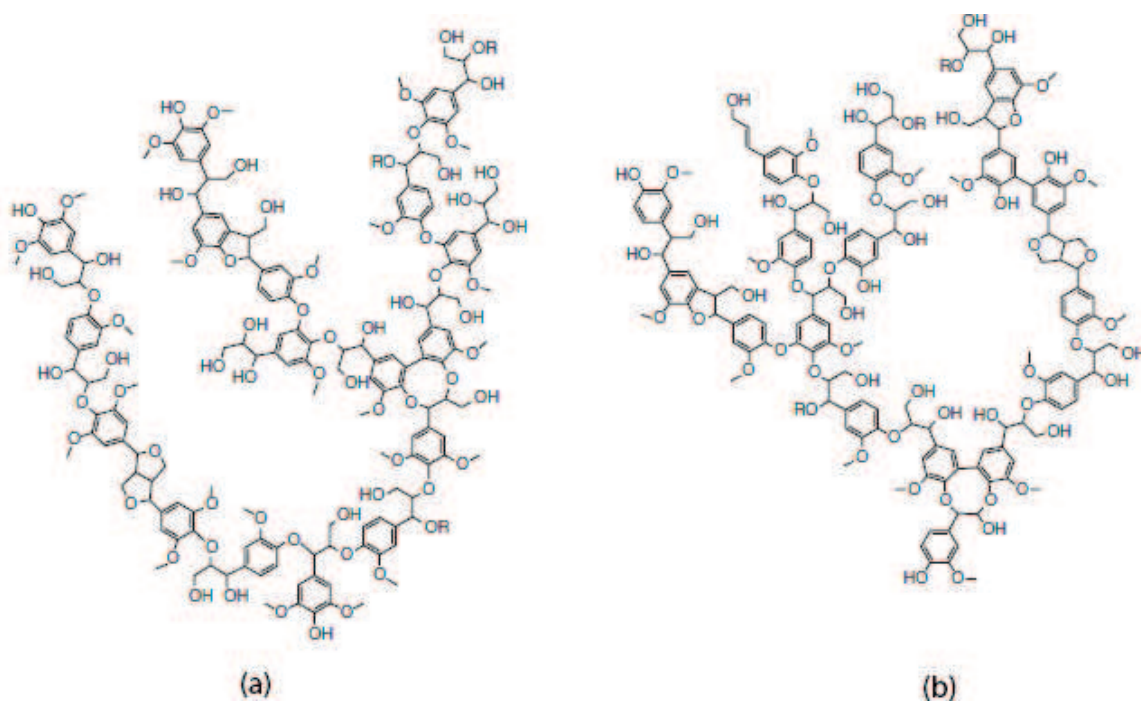
Figure 9. (a) Hardwood native lignin; R = H, alkyl, aryl [170] (adapted from [167]); (b) softwood native lignin; R = H, alkyl, aryl [170] (adapted from [167]).

The functional groups (R = H, alkyl and aryl) have some great impact on the reactivity of the lignin molecule. It should be recalled that the lignin molecule mostly contains methoxyl groups, phenolic and aliphatic hydroxyl groups, and a few terminal aldehyde groups [167], though most of the phenolic hydroxyl groups are not available because of the fact that they are occupied in interunit linkages.

3.1.3. Characterisation of lignins

Chemically, lignin samples have been characterised with respect to lignin and sugar content and the amount of hydroxyl and carboxyl groups (**Table 4**).

Structurally, the characterisation of lignin can be well illustrated by the work of Li and Ge [171]. These co-workers utilised the byproduct of a non-wood material for the extraction of lignin. The plant material investigated was sugar cane bagasse from where lignin was extracted via acidification of black liquor prior to characterisation. Firstly, the authors extracted sugar cane bagasse lignin (EBL) and then modified it by oxidation, hydroxymethylation and sulphonation into a water-soluble lignosulphonate (EBL-M) as a final product for characterisation. Techniques employed successfully were infrared spectroscopy (IR), ultraviolet-violet spectrophotometry (UV), gel-permeation chromatography (GPC) and elemental (C, H, O, N and S) analysis. A typical IR spectra of extracted bagasse liquid (soluble aqueous fraction) is shown in **Figure 10**.

The characterisation of molecular weight and sulphonic group's content of lignosulphonates were determined by employing GPC and an automatic potentiometric titrator, respectively.

According to Li and Ge [171], the relative contents of moisture, ashes and pure lignin content of extracted bagasse lignin, can be measured as follows: an appropriate amount of raw EBL is weighed and placed in an oven and heated to 105°C in air. The corresponding mass loss would

Sample number	Raw material	Lignin type (commercial name)	Sample code	Lignin content (%)	COOH (mmol/g)	Phenolic OH (mmol/g)	Total sugars (%)
1	Hemp	Soda	He	Nd	2.1	1.58	2.4
2	Sisal	Soda	Si	Nd	1.18	2.29	7.7
3	Abaca	Soda	Ab	Nd	1.14	2.73	5.5
4	Straw	Soda	St	Nd	2.1	2.43	Nd
5	Jute	Soda	Ju	Nd	1.78	2.38	Nd
6	Flax	Soda	Fl-1	87.8	1.9	1.1	1.7
7	Softwood	Lignosulfonate (Borresperse 3A)	SW-LS-1	Nd	3.5	1.1	1.3
8	Softwood	Kraft (Indulin AT)	SW-Kr-1	90.0	2.5	1.8	2.06
9	Softwood	Lignosulfonate (Wafex P)	SW-LS-2	Nd	1.2	1.1	24.5
10	Flax	Soda (Bioplast)	Fl-2	87.8	1.9	1.1	1.7
11	Flax	Soda, oxidised	Fl-ox	92.1	1.8	0.9	1.6
12	Softwood	Kraft (Curan 100)	SW-Kr-2	88.6	1.7	0.8	2.26
13[a]	Softwood	Soda, precipitation high pH	SW-SF-1	64.7	Nd	Nd	1.77
14	Softwood	Kraft	SW-Kr-3	96.8	2.0	2.5	0.71
15	Mixed hardwoods	Organosolv (Alcell)	HW	96.5	0.78	2.4	0.32
16	Softwood	Soda, precipitation low pH	SW-SF-2	99.2	1.4	1.0	0.65
17	Softwood	Kraft (Curan 2711P)	SW-Kr-4	80.3	2.7	1.6	2.58

Nd, not determined.
[a] Lignin 13 contains about 40% ash.

Table 4. Chemical characteristics of lignin samples [127].
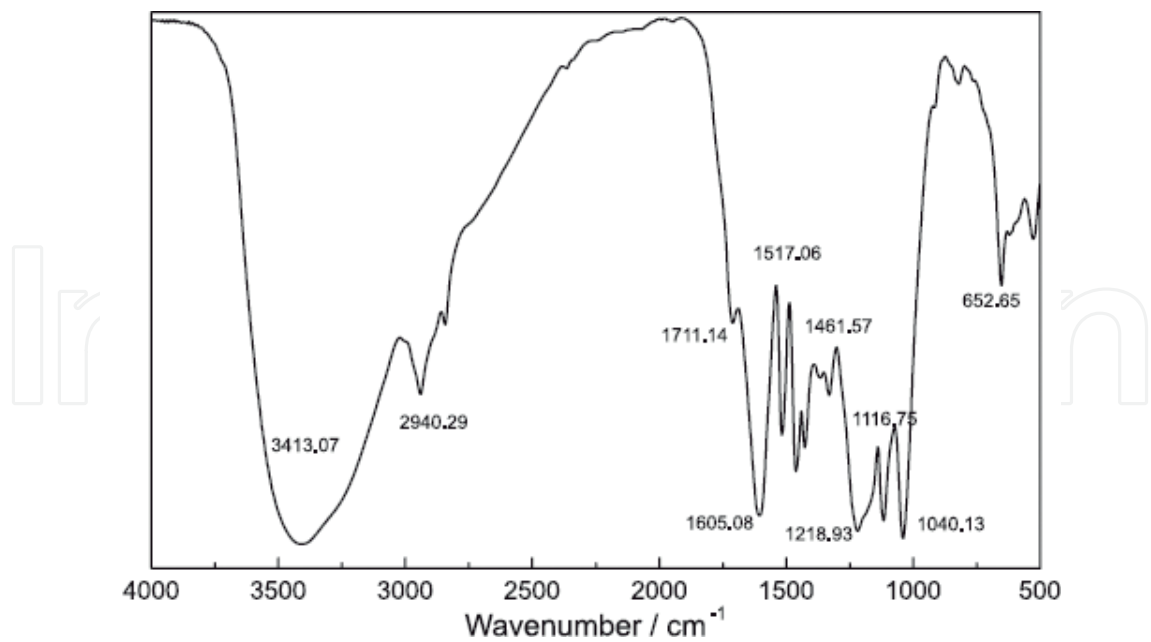
Figure 10. FT-IR spectrum of EBL-M [171].

be assigned as moisture. Another sample is placed in a muffle furnace and heated to 800°C in air. The remaining amount would be accounted as ashes. The pure lignin amount is subtracted from the moisture and ashes from the total amount of the sample. An example of the physico-chemical properties of extracted bagasse lignin (EBL) is shown in **Table 5**.

3.1.4. Trends and research avenues

From the literature, several reviews [37, 38, 172–174] have been published to cover various aspects of lignin, especially on processes aiming at its industrial applications and valorisation [149].

Extensive research has been conducted in the past decades in both the improvement of lignin extraction processes and the elucidation of its structure [127]. Such research efforts have been extended to cover works on the characterisation of chemical reactivity and functional properties, as well as the development of new applications of lignin [127]. In this regard, several co-workers [175–177] have shown that lignin is a versatile molecule endowed with multiple properties such as antioxidant (i.e. radical scavenger), UV-absorption, antifungal and antibiotic

Properties	EBL
Lignin source	Sugar cane bagasse pulping
Appearance	Light brown powder
Moisture / wt.%	5.2
Ashes / wt.%	2.9
Pure lignin / wt.%	91.9

Table 5. Properties of lignin extracted from sugar cane bagasse (EBL) [171].

activity. From the above, it is suggestive in agreement with the viewpoint of Boeriu et al. [127] that to enhance the industrial use of lignins, there is need for a continuous supply of lignin products with constant quality as related to purity, chemical composition and functional properties, meaning research is still to play central role to be able to meet the above goals.

As a conclusion and in alignment with the thoughts conceptualised by MacFarlane et al. [167], trends and research avenues focusing on lignins can be summarised within the following timeframes.

Firstly, economic studies must find a large market for lignin from the ubiquitous kraft process in the short term. The role that research can play in during this timeline is to intensify to improve on the quality and applications of kraft lignin as resins and adhesives. Penetration into this market is considered inevitable by Stewart [178].

It is predicted in the medium term that more lignin from unsulphonated sources will become available. As this lignin is likely to come abundantly from biorefinery platforms, owing to its uniqueness in properties compared to other feedstocks with a potential to uplift small-scale availability, research would have to stretch in that direction in the medium term. Initially, the resin and adhesives market may act as a catch-all for this more reactive lignin [167]. According to the same author, a product niche of high value and sufficient market size must be found for each lignin source, citing hydrophobic organosolv lignins as an example to hold the potential to add value to resins used for water resistant particleboard. Platform chemicals are an attractive medium-term market.

Finally, in the long term, biorefineries will be tuned to produce lignin for specific materials of high value, and lignin is expected to yield greater incomes than the other components of wood [167].

3.2. Renewable platform chemicals

3.2.1. Lignosulphonates

Lignosulphonate (**Figure 11**) is the sulphonated lignin that has been removed from wood by sulphite pulping. Hardwood lignosulphonate and softwood lignosulphonate are obtained from waste pulping liquor concentrate by the Howard process [179] after stripping and recovery of the sulphur [149]. They exhibit monomer molecular weights of 188 Da, and 215–154 Da, respectively [149].

Up to now, lignosulphonates are the only lignin products obtained from a pulping process that have found a considerable range of applications up to now are lignosulphonates (MacFarlane et al., 2013). These materials are endowed with excellent properties that, thus, are used as binders, emulsifiers and dispersants for a great variety of materials; and are non-hazardous. Good examples as binders are their common use for commodities like coal briquettes, ceramics, briquetting of mineral dust, and the production of plywood or particle boards, owing to their cheap cost. In addition, their ability to retain moisture and suppress dust makes them a useful tool for construction works, gravel roads, airports and sports facilities [180]. This material is an anti-settling agent that can prevent lumping, making lignosulphonates excellent
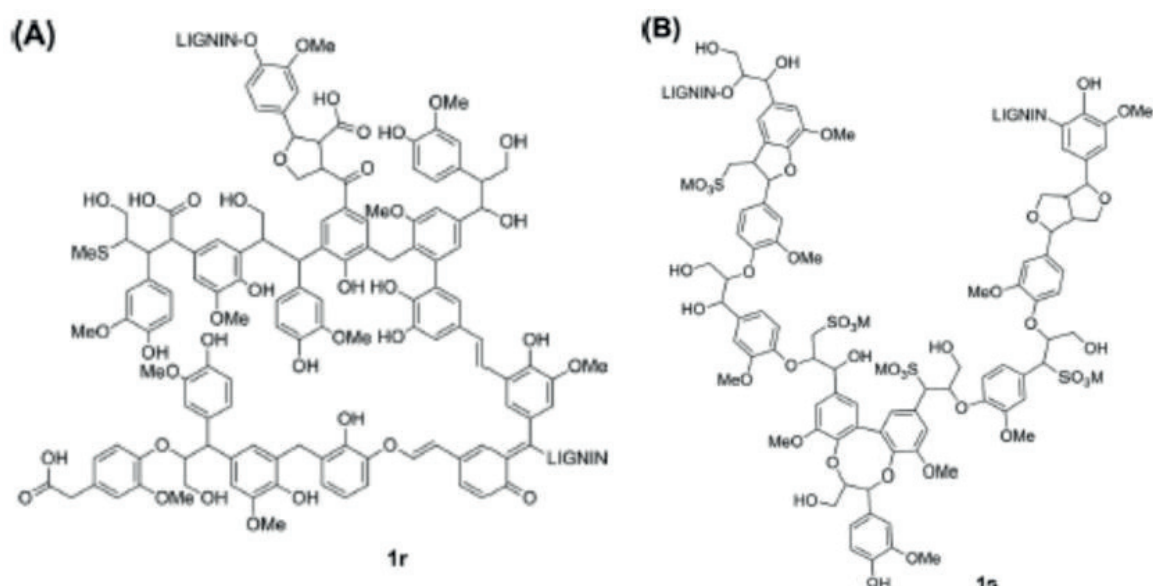
Figure 11. Structure of kraft lignin (A) and lignosulphonate (B) [149].

binders used in concrete mixtures, ceramics [180], gypsum-board production and for leather tanning. Lignosulphonates provide flowability and plasticity to cement [180]. These properties lends lignosulphonates as a replacement for more expensive materials that provide set retardation such as superplasticizers, gluconates and gluconic acid. In the wet-process, Portland cement mills lignosulphonates are utilised to increase the solids content of the raw slurries. It is stated [37, 38] that the demand for lignin-based concrete additives are on the increase with a market value worth as much as US $1.05–1.32/L as an aqueous solution. Nadif et al. [181] has also reported that sulphur-free lignin such as soda lignin has also been shown to improve flowability of mortar. It is known that lignosulphonates can also stabilise emulsions of immiscible fluids like asphalt emulsions, pesticide preparations, pigments and dyes [167]. Due to their low toxicity, they can be used as binders in animal feed and thereby improve the feed properties of pellets. In addition, lignosulphonates show the ability to keep micronutrients in solution which is useful for micronutrient transport or as a cleaning and decontaminating agent in water and soils [7, 181].

Apart from the usual (traditional) use of lignosulphonates as energy source and in leather tanning, these materials can now also be applied for polymer reinforcement, or as sequestrants (i.e. antioxidants). It has been suggested [176] that lignins can be applied for stabilisation of food and feed, due to their antioxidant and antifungal properties. Also, anti-carcinogenic and antibiotic activities of lignins have been reported [176]. When depolymerised, lignins can be used for the synthesis of valuable chemicals, such as vanillin.

3.2.2. Lignin oligomers

Chemically, lignin is viewed as a highly complex phenolic polymer, generally showing plant-specific compositions and linkage motifs [182, 183]. Very recent findings on milled wood lignin

samples are suggesting, however, that lignin exists as linear oligomers. Presumably, strongly interactive in such a way that traditional analyses of the molecular weights are biased, thus, a suggestion of the existence of higher molecular weight polymeric units [184]. Apparently and to the best of the current knowledge, these lignin oligomers lack a defined primary structure, but rather represent random phenylpropanoid (C_9) polyphenols, mainly linked by arylglycerol ether bonds between phenolic para-coumaryl alcohol (2) (H-type), coniferyl alcohol (3) (G-type) and sinapyl alcohol (4) (S-type) units [185, 186]. Depending on the plant-type, one of the different lignin types dominants. Lignin of gymnosperms consists almost entirely of G-type lignin (G-lignin); dicotyledonous angiosperms produce a mixture of G- and S-type lignins (GS-lignin). All three types of lignin can be found in quantities in monocotyledonous lignin (GSH-lignin) [149].

For the moment, there are a multitude of practical considerations that preclude further use of lignin as a monomer feedstock [156, 158] but actual developments on the level of low-cost catalysis and separation technologies could stimulate its future use [187].

4. Treatments and technologies towards renewable chemicals recovery

4.1. Treatments and technologies

4.1.1. Chemical treatments an advanced thermochemical recovery

There are several thermochemical methods reported in the literature that have been studied in the recent past in order to depolymerise lignin and to convert it into value-added chemicals. To name a few, pyrolysis, gasification, hydrogenolysis, chemical oxidation and hydrolysis under supercritical conditions are the major methods to produce pyrolytic oil, syngas or phenols. **Figure 12** shows an overview of these methods and the resulting products thereafter the treatments.

Lignins from trees, plants and agricultural crops with different chemical composition and properties can be obtained by use of several extraction methods. These include the commercial chemical pulping processes (sulphite and kraft process) to produce lignosulphonates and kraft lignins as residue. Recently, commercialised alkaline pulping-precipitation process supply sulphur-free, free-flowing lignins. The challenge resides, however, in practically isolating pure lignin quantitatively from cell walls in an intact state. The lignin isolated by known methods (physical, chemical or enzymatic treatments) is a mixture of degraded or solubilised lignin from various unidentified morphological regions [127].

4.1.2. Specialties base chemicals recovery

Roopan (2016) has stated that lignin is a best essential source for bio-pesticides. This author collected lignin compounds from fluidized bed pyrolysis reactor and investigated it for utilisation in bio-oil production. Other authors [188] have also collected lignin, cellulose and hemicellulose macromolecules from waste disposables and purified the lignin without any contaminants of macromolecules for test against various toxi-micro-organisms of fungi and bacterial species like *Xanthomonas campestris*, *Pythium ultimum*, *Sclerotinia sclerotiorum*, *Clavibacter michiganensis*, *Rhizoctonia solani* and *Streptomyces scabies*.
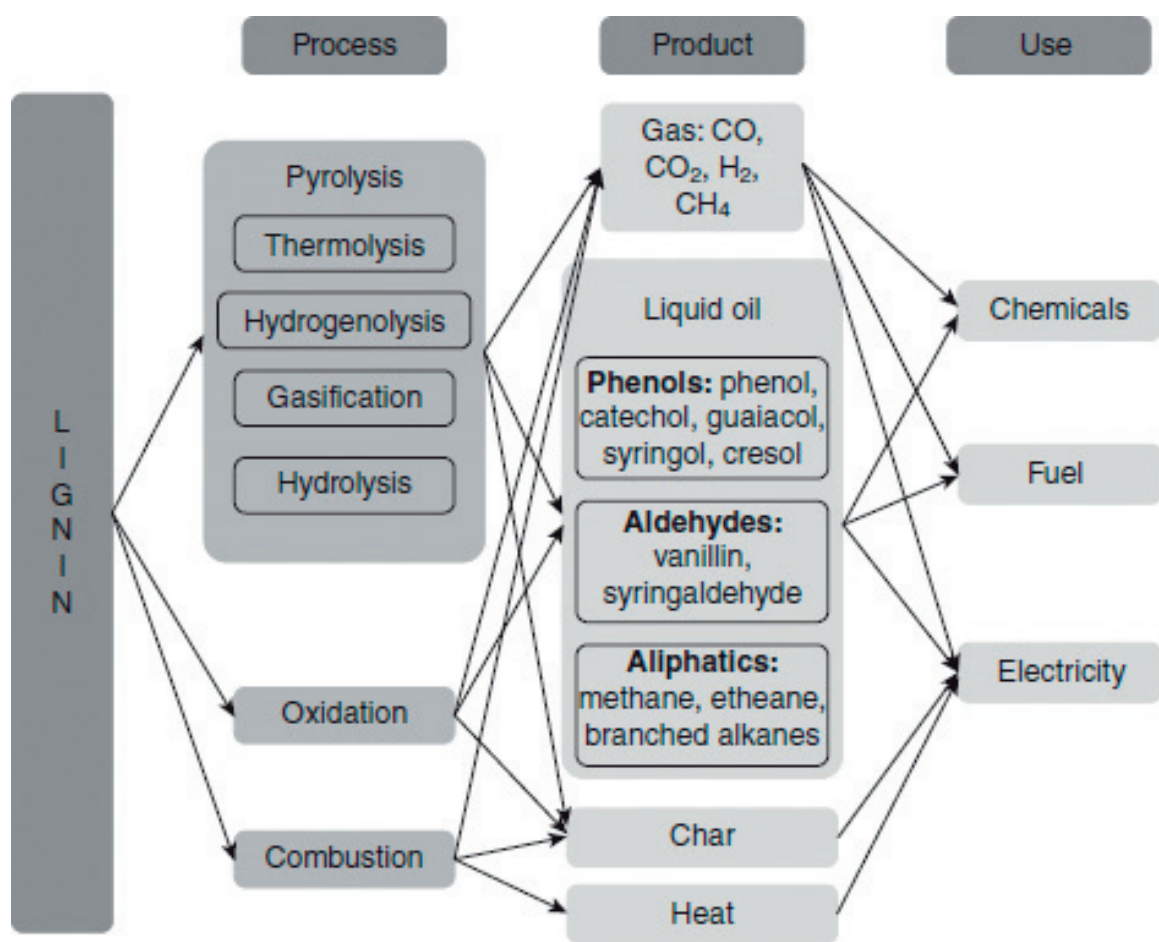
Figure 12. Major thermochemical lignin conversion processes and their potential products [167].
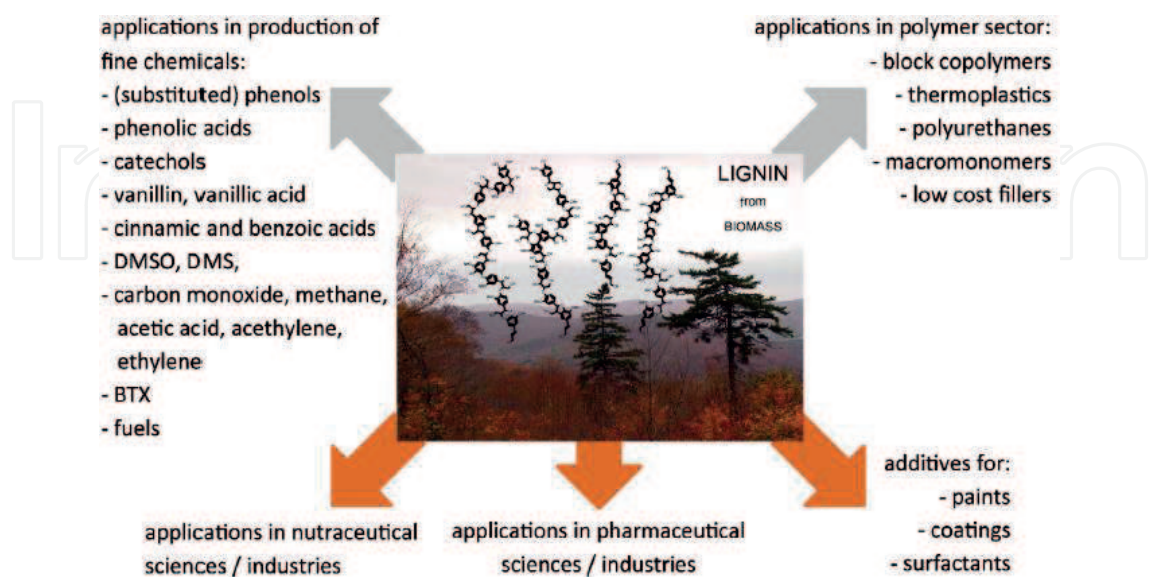

Figure 13. Existing and potential applications of lignin are summarised in [149].

Other specialty chemicals have been developed in recent times. Aromatic building blocks as platform chemicals in the field of polymer chemistry cannot are good examples, with scientific terms such as PET and bisphenol A becoming known to the general public. This is a result of their high production volumes, which were predicted to exceed 24 million tonnes [189] and 5.6 million tonnes [2], respectively, in 2015.

Since aromatic building blocks are to date being produced mainly from petroleum-based feedstocks, such as benzene, xylene and cumene, there is an ongoing quest for more sustainable and renewable sources for aromatic synthons evolving in both academia.

Llevot et al. [190] and Isikgor and Becer [191] and industry [192], using lignins. Some examples of bio-available aromatic systems include cardanol, originating from cashew nut shell liquid [193], hydroxymethylfurfural (HMF) obtained by carbohydrate dehydration.

Figure 13 summarises the speciality chemicals that can be obtained from lignins.

5. Separation and recovery of gold and other precious metals

5.1. Gold

5.1.1. Occurrence and fundamental properties of gold

Gold (Au) as a mineral usually occur in native forms associated with silver (Ag) along with copper (Cu), arsenic (As), iron (Fe), bismuth (Bi), tin (Sn) and zinc (Zn) [194]. The concentration of gold (Au) in the lithosphere is estimated to be $0.004~\mu g~g^{-1}$ in the rock, whereas in the soil it is about $0.001~\mu g~g^{-1}$ [195]. At the same time, its abundance in seawater and river is estimated at $0.05~\mu g~g^{-1}$ and $0.02~\mu g~g^{-1}$, respectively, much higher in the seawater and river [195]. Gold has been found in the atmospheric dust in a concentration as high as $440~mg~g^{-1}$, especially in the vicinity of gold mines [196]. Gold has a very high affinity for sulphur and often occurs as ultrafine solid solution inclusions in sulphide minerals [197]. The world distribution of gold is not with China as the leading country with 16.7% of the world production [198],

Precious metals such as gold (Au), silver (Ag), platinum (Pt), palladium (Pd), etc., are utilised in several manufacturing fields for various applications [180, 199]. These "noble" metals possess unique physical and chemical properties, thus, their high economic value.

Though the natural occurrence in the earth crust of precious metals and Au generally termed the platinum group elements (PGEs) is in very low abundance, their concentration and distribution in various types of rock formations have attracted enormous interest from miners in recent times. This is due to their rising demand in the technology sector owing to their applications as catalysts, biomedical tools (e.g. anticancer drugs), corrosion-resistant materials, high electrical conductivity materials, micro-electronics and also in jewellery manufacturing [200].

The fundamental properties of gold are indeed an interesting one. Gold (atomic number 79, mp 1065°C) is thence the noblest metal that is generally found in nature in the metallic state, and the only gold compounds that occur in a natural state are the telluride and stibnite

species, $AuTe_2$ and $AuSb_2$ [202]. The metal is soft, yellow and malleable, ductile and resistant to attack by common chemicals and light [201].

Yannopoulos [194] has reported 19 isotopes (ranging from [185]Au to [203]Au) although only the [197]Au isotope is known to occur naturally. Of a great significance to the extractive metallurgist is the chemistry of gold complexes in aqueous solutions, and this is a far broader subject beyond the scope of this chapter. Traditionally, it has been accepted that gold complexes in aqueous solution can exist in one of two oxidation states, the aurous (+1) or the auric (+3), and forming Au^+ and Au^{3+}, and that all the gold complexes of hydrometallurgical interest fall into these two groups [202]. The electron configuration of the element in the ground state is [Xe] $4f^{14}5d^{10}6s^1$. From this is deduced the monovalent ion: [Xe] $4f^{14}5d^{10}$ and the trivalent ion: [Xe] $4f^{14}5d^8$. Thermodynamics predicts that neither aurous (Au^+) nor auric (Au^{3+}) cations will be stable in aqueous solution, but will be reduced by water to metallic gold. Gold does not dissolve in either nitric acid (an oxidising agent) or hydrochloric acid (a complexing ligand), but dissolves quite easily in a mixture of the two ($HCl:HNO_3$, 3:1), aqua regia [203]. This is because the oxidation potential for transition Au^o to Au^{3+} is as high as 9.225 eV [204].

Thus, many of the known thermodynamic characteristics of gold complexes can be rationalised, providing some basis for the prediction of their behaviour. Chlorine (Cl) and bromine (Br) can also dissolve gold to generate Au^{3+} and under these reducing conditions, Au^{3+} species can easily be disproportionately converted from Au^o to Au^+. In water, Au^+ and Au^{3+} ions occur in a hydrated form. Nicol et al. [202] states that a useful first generalisation about the stability of gold complexes relates to the nature of the ligand donor atom, that is, the atom in the ligand that is bonded directly to the gold. From this, both gold(I) and gold(III) are B-type metal ions, meaning that the stability of their complexes tends to decrease as the electronegativity of the ligand donor atom increases (i.e. as the tendency of the atom to attract electrons increases). This leads to stability orders such as $I^- > Br^- > Cl^- > F^-$, where the order of electronegativities is $F^- > Cl^- > Br^- > I^-$.

5.1.2. Selective separation and recovery of gold from various secondary sources

Mining efforts of precious metals (Au, Ag, Pt, etc.) are currently being hampered owing to chemical ambiguities of mineralization. The need for the development of simple, fast and reliable recovery procedures is important.

5.2. Precious metals

As the name suggests, this group consists of precious metals out of which Au and Ag were probably the first metals ever extracted on earth [205], whereas the platinum group metals such as Pt and Pd are increasingly finding their role in modern products especially as auto catalysts used in the emission control system of passenger vehicles. These elements are also used in jewellery. Au and Ag, both have high electrical conductivity which makes them highly desirable in modern electronics apart from their historical use as investment and jewellery.

The fact the modern society depends intensively on metals utilisation, is the justification that metals are the basis of our infrastructure and the technology, without which it is hard to imagine modern life. Metals have been generated as a result of geological events spanning

over hundreds of millions of years. As such, metals are considered by some school of thoughts as non-renewable by nature as they which makes them a finite resource. This can be argued as true if metals, nevertheless, do not disappear after their consumption per se like some other resources like fuel minerals (e.g. oil, gas and coal due to their non-dissipative nature). Some-how, metals can be beneficiated by recycling them from urban mines, though with the product's long lifetimes and economic implications. Despite the above ascertainment, Bardi [205] and Prior et al. (2012) argue that despite the fact that the geological resources of metals are finite, their unprecedented extraction from the earth especially during the last two centuries has raised concerns regarding their long-term availability to meet the demand of future generations. Within the context of secure, uninterrupted and long-term availability of resources, a relatively new research field of resource criticality assessment got widespread popularity during the recent years [206].

Palladium (Pd) belongs to the precious metals group, that is, platinum group metals (PGMs), which are mainly used as catalysts in the automobile sector for pollution abatement. Other uses of PGMs are in fuel cells, petroleum refining, chemical industry, electronics, glass manufacturing, medical appliances, jewellery and as investment.

6. Concluding remarks

A brief review has been herein done of technologies involved in the exploitation of lignin, in order to provide an introduction to the subject from the perspective of a fast technologically advancing economy. Lignocellulosic materials and biomass have historically been utilised from since time memorial, but a new conversation is emerging on the role of these materials in modern bioeconomies. Due to the nature of the molecule(s) as a novel commodity for many interesting natural and manufactured products, a modern bioeconomy is not simply a rerun of former ones. This new discourse needs to help us understand how technologies for managing and processing lignocellulosic materials both as biosynthetic moieties, biogenic wastes or simply renewable biopolymer—both established and novel—should be deployed and inte-grated (or not) to meet developmental requirements of the sustainability paradigm, more so in a closed-loop and resource-security agendas that undoubtedly sits behind the bioeconomy aspirations now being voiced by many schools of thought in many countries and regions of the so fast technologically advancing world.

The world of which is caught in the middle of green technology advocating for more and more focus on renewable sources of manufacturing raw materials and that of the molecularly imprinted/synthesised or genetically engineered ones. **Figure 1** presents the main building blocks of lignin, from the hydroxycinnamyl alcohols (or monolignols) coniferyl alcohol and sinapyl alcohol, with typically minor amounts of p-coumaryl alcohol [6, 10].

The utilisation of lignins (from renewable sources) in both the industry as the base for the formulation of ionic liquids (with yet a wider industrial applications) and as a potential scaffold material for functionally modified imprinted polymers (LCIPS) for the selective recov-ery of base metals and gold, respectively, evidently incorporates the bioeconomy aspirations.

Further, one new trend in lignin research is to steer biosynthetic pathways towards the biosynthesis of molecules that, upon incorporation into the lignin polymer, will improve lignin degradation [5].

Acknowledgements

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