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Lignin Valorisation

THE IMPORTANCE OF A FULL VALUE CHAIN APPROACH



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Summary Lignin Valorisation - the importance of a full value chain approach

Biomass plays an important role in food supply and in the transition towards a bio-based and circular economy. Concerns about biomass availability, competition with food supply, the pursuit of a circular economy and especially achieving sound business cases, force the bio-economy towards full valorisation of lignocellulosic biomass.

Lignocellulosic biomass consists of cellulose, hemicellulose and lignin. Especially lignin is a tough nut to crack. Already for decades the pulp industry is converting lignocellulose into valuable fibres from the (hemi)cellulose part, burning the lignin for energy. And also the more recent so-called second generation technologies are able to produce chemicals and biofuels only from the cellulose and hemicellulose fraction. The lignin fraction apparently is very difficult to turn into valuable products. With lignin making up about 20-35% of the dry mass of every tree or plant, the total lignin present in the biosphere exceeds 300 billion tonnes and annually increases by around 20 billion tonnes. A feedstock of such abundance clearly cannot be ignored and sound valorisation strategies are urgently needed.

The difficulty lays in the fact that there is not one such thing as 'lignin'. Indeed, there is no one unique, well-defined lignin molecule with certain characteristic properties and functionalities. The structure of lignin, and hence its properties, is dependent on its origin, external conditions during growth (e.g., season, climate and position in the field) and the isolation and pretreatment technology applied to isolate the lignin. It is also important to realise that lignins are presently not as such available in large quantities on the market. Most of the currently produced lignin streams are directly used for producing process energy (biofuel production) or for recovery of chemicals (paper industry).

What would be needed to improve lignin valorisation?

At first, there is not enough knowledge about the detailed structure of the many types of (technical) lignins and their physical and chemical properties (e.g., functionality and solubility) and the effects of pretreatment technology on structure and properties. A databank containing fingerprints of all kind of lignins (i.e., different kinds of origin, availability (current, future) and the effect of external conditions and pretreatment processes) would significantly support lignin application research and increase the chances for successful lignin-based value chains.

Secondly, it is advisable that research on valorisation of lignocellulosic biomass takes into account both valorisation of the cellulose/hemicellulose and the lignin fraction. Cost-effective technologies for cellulose isolation or conversion, not necessarily lead to lignin-streams that can be easily further converted to be used in high-value applications. In fact, all current commercially applied pretreatment methods lead to technical lignins of which the molecular structure is significantly altered with respect to native lignin, inevitably making the lignins more chemically recalcitrant towards depolymerisation and hence their valorisation. In the future other pretreatment technologies might produce lignin of a quality that allows it to be more easily converted to higher value applications. Moreover, research into lignin valorisation requires insight in the whole valorisation chain, connecting plant selection and adaptation to the biomass fractionation and lignin isolation process to downstream upgrading into materials or value-added chemicals or fuels, to ensure that the results are applicable to realistic value chains. In the ideal situation the lignin

isolation process would be adapted to generate the best possible lignin structure required for its application *without* compromising on the overall quality of the cellulose and hemicellulose fractions, which are to be valorized in other, integrated process within the biorefinery. In fact, biorefineries should strive to maximize the *combined* value-addition of the three main components, rather than optimize the valorization of one. This is currently not yet the case for many of the proposed biorefinery schemes, which need a high value for the lignin produced to break even, but actually use biomass pretreatment or fractionation processes that produce a lignin for which it is difficult to justify that value.

To conclude, full valorisation strategies require cross-sectoral partnerships between the forest-based sector, agro sector, and the frontrunners of the chemical industry. Only then sound cascading approaches can be developed that lead to an optimal valorisation of both the cellulose/hemicellulose fraction and the lignin fraction of the lignocellulosic biomass.

1. INTRODUCTION

Lignin, which makes up about 20-35% of the mass of every tree or plant, is the most abundant natural aromatic resource. The total lignin present in the biosphere exceeds 300 billion tonnes and annually increases by around 20 billion tonnes. Lignin, which lacks a well-defined structure, has unique properties including its highly aromatic nature and lower oxygen content compared to polysaccharides, making lignin a highly interesting bio-polymer to be converted into useful, renewable chemical building blocks and related fuels and materials. It is noted that the techno-economical application potential of lignin heavily depends on a proper appreciation of the lignin source, its availability, isolation technology, and the technical requirements of the foreseen applications. This requires full integration, on equal footing to the polysaccharides, of lignin into the value chains of bio-refinery operations. Future bio-refineries therefore should aim to produce no waste, including the proper use of the abundant lignin fraction of biomass. In this respect, a cascading approach, i.e., a multistep, gradual valorisation of all the carbon in the lignin structure is thought to be a particularly attractive way of adding value to this currently highly undervalued feedstock.

This *position paper* gives an overview of the different technical lignins available (i.e. those obtained and isolated during or after a whole biomass treatment process). The structural (e.g. molecular weight and morphology) and compositional (e.g. the number and nature of functional groups) differences between these technical lignins will be highlighted, as far as possible as the current knowledge on structure and composition of most lignins allows. These differences in structure and composition and, consequently, the physical properties as well as the projections of future lignin availability will be linked to the different requirements demanded by the various (potential) lignin applications. First, the types of lignin will be described followed by lignin availability and the processes from which these lignins will most likely be obtained. Subsequently, an attempt is made to link predicted lignin supply to the various applications and (future) markets. To conclude the paper will highlight some possible routes for lignin valorisation.

2. TYPES OF LIGNIN

Lignin is a complex cross-linked polymer containing mainly coumaryl- (H), coniferyl- (G) and sinapyl (S) phenolic structures (Figure 1).

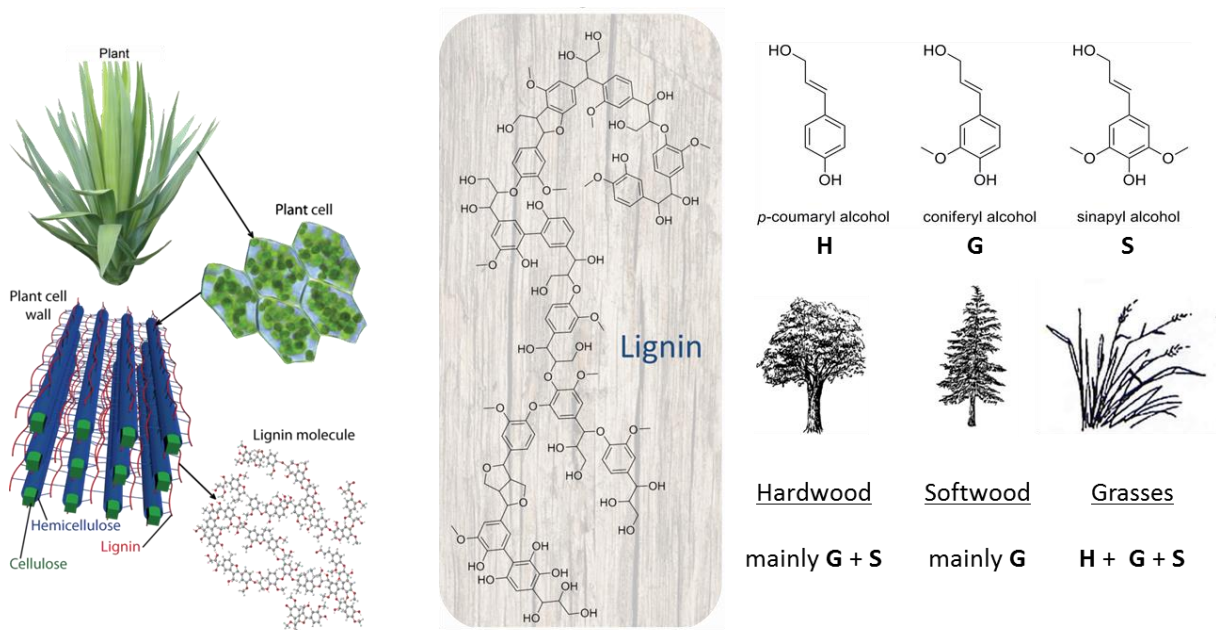


Figure 1. Schematic representation of the location and structure of lignin in lignocellulosic material, including a lignin fragment and the molecular structure of the three monolignol building blocks of lignin. Please note that the lignin fragment is just meant to show possible linkages between the monomers and by no means represents a 'repeat unit' of the polymer. Figure adapted from [refs.1,2]. Copyright American Chemical Society, 2010 and Wiley-VCH, 2016.

Lignin is formed in the cell walls of wood or agricultural crops and plants, to provide structural strength. Lignin can have a variety of specific structures and compositions, depending on the specific plant or tree species, the season, the climate and the plant age. Indeed, the composition of lignin will strongly depend on the plant species, both in terms H/G/S composition, as well as in relative abundance of the chemical linkages in the polymer (Figure 2).

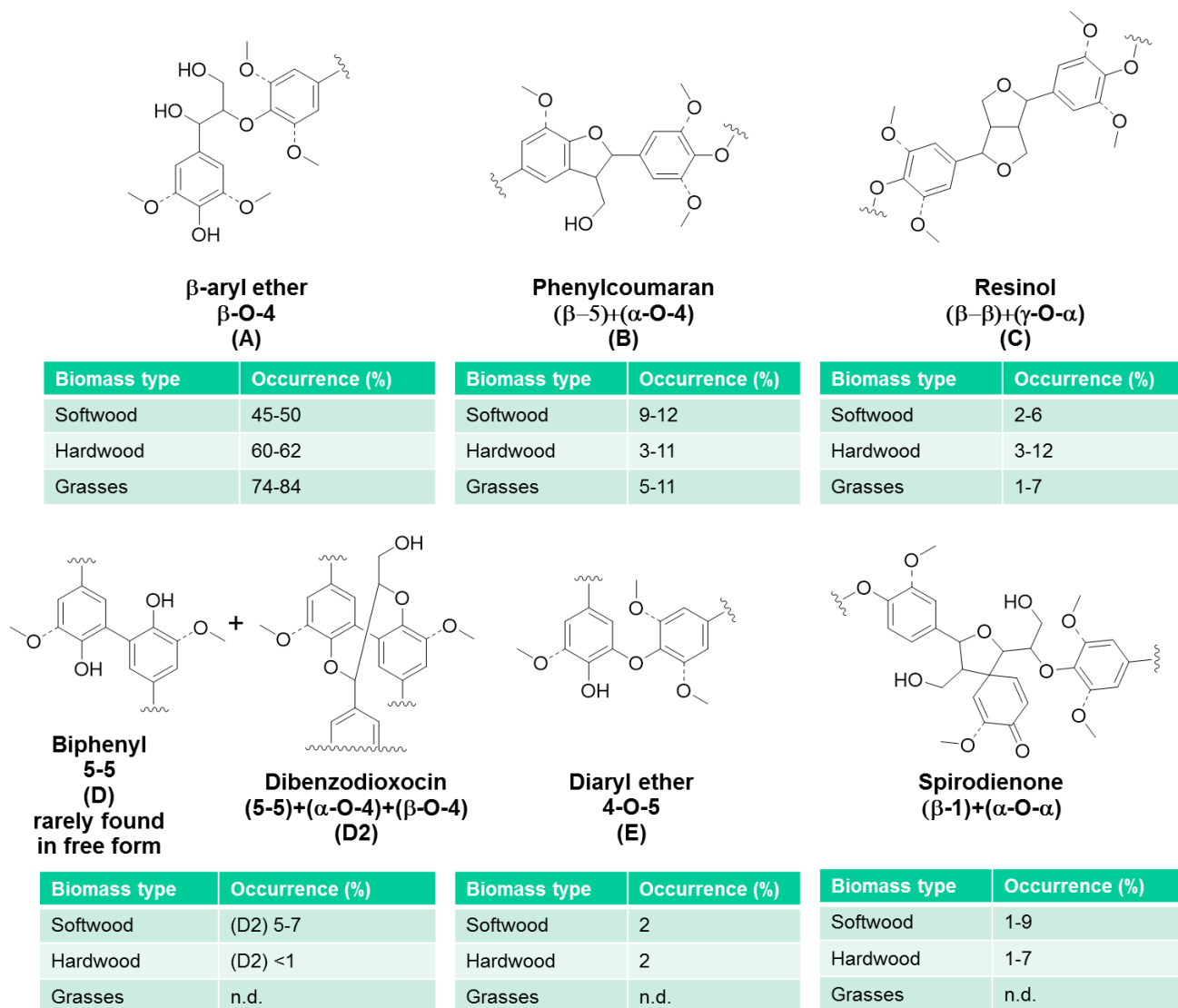


Figure 2. The relative occurrence of various typical (native) lignin linkages in soft- and hardwoods and grasses. Figure adapted from [ref.2]. Copyright American Chemical Society, 2010 and Wiley-VCH, 2016.

Importantly, the molecular structure of lignin will be invariably significantly altered by the process applied on the biomass to separate it into its components, and thus leading to lignin liberation ("technical lignins"). As a consequence the characteristics of the technical lignin are different: molecular weight, water solubility, degree of contamination (e.g. remaining covalently bound sugar residues or incorporation of non-native elements, such as sulfur), extent of condensation and functional group decoration of the macromolecule.

2.1 LIGNIN CHARACTERISATION

The technical lignins obtained by different pretreatment technologies thus differ in their chemical structure as well as in their physicochemical properties. As lignin analysis is inherently difficult given the complexity and highly heterogeneous nature of the macromolecule, a rather extensive number of parameters need to be determined in order to capture the characteristics of the particular lignin feed. Of particular interest are the overall chemical composition, i.e. the elemental composition including ash content, sulfur content as well as the amount of remaining sugars and the amount of other minor chemical species that can be chemically bound to lignin. Furthermore, macromolecular properties, such as solubility, molecular weight, as well as poly-dispersity, will greatly determine the possibilities for valorisation. From a more chemical point of view, it is important to determine the connectivity, i.e. the linkages between the original monolignols (e.g. β -O-4, β -5, β - β , and other linkages that might result from the applied pretreatment process), as well as the number and type of functional groups present in the macromolecule.

In this sense, it is important to note that even with advanced analytical methods, with arguably multidimensional NMR (Nuclear Magnetic Resonance) spectroscopy being the most informative, typically only a fraction of the bonds present between the constituent monolignols can be identified. Thus, data obtained from a combination of analytical techniques is required to get to the desired level of detail to guide valorisation strategies. Typical analytical methods include elemental analysis, residual carbohydrate content determination, ash determination, molar mass determination (e.g. by SEC – Size Exclusion Chromatography), analysis by advanced 1D and 2D NMR methods (optionally after derivatization), and vibrational and electronic spectroscopy/microscopy. For materials applications, physicochemical properties as determined by TGA (Thermogravimetric Analysis) and DSC (Differential Scanning Calorimetry), as well as functional group identification and density can also be valuable. With (catalytic) valorisation by lignin depolymerisation in mind, impurities will start to play an important role in the efficiency of the process. The impurities present in lignin will vary again with pretreatment method and can include remaining ash, metal-containing salts, residual sugars, or impurities introduced by the pretreatment method, e.g. sulfur incorporation in lignin in Kraft pulping processes. For a complete overview of all analytical techniques available for lignin characterization we refer to a recent review paper of Lupoi et al. [ref.3].

Table 1. Overview of the most important analytical techniques used in the analysis of lignin and lignin depolymerisation streams. For a complete overview of all analytical techniques currently available we refer the interested reader to the paper of Lupoi et al. [ref.3].

Technique	Measures	Restrictions
³¹ P NMR	Free hydroxyl/phenol/carboxylic acid functionalities H/G/S ratio	Limited to determination of end groups
HSQC NMR	H/G/S ratio (quantitative) linkage information Constituents other than the three monolignols (e.g. ferulates and tricins)	Limited to linkages containing C-H bonds Spectral crowding in some regions Assignments for non-native, technical lignin structures less developed
GPC	Hydrodynamic volume (molecular weight <i>by proxy</i>)	Molecular weights obtained depend highly on system and standards used Molecular weight severely underestimated if lignin is cross-linked
(GCx)GC(-MS)	Volatile monomers	Only low molecular weight products are detected Care should be taken with structural assignments based on library search

2.2 PRE-TREATMENT METHODS: EFFECTS ON LIGNIN CHARACTERISTICS

Several processes have been developed to disintegrate lignocellulosics into hemicellulose, cellulose and lignin fractions, most of them with the main goal to achieve high quality cellulose with lignin merely being regarded as by-product. Of the many different processes presented, only few are currently commercially applied. Others, mostly developed in the 1970s as alternatives for producing papermaking fibres, were abandoned as a result of bad cellulose pulp quality. With focus shifting from paper applications of the pulp to conversion to sugars by hydrolysis of the polysaccharides for further fermentation to bio-ethanol or to other bio-chemicals, some of these old processes are attracting renewed interest. This section provides an overview of common (pre)treatment technologies for lignocellulosic biomass. The way in which these technical lignins are produced will provide insight into the implications for the availability of these lignins and what can be expected for the structure and functional groups of the various lignins that may be produced in the future.

2.2.1. Acidic pulping of lignocellulose with excess aqueous (bi)sulfite together with either sodium-, magnesium-, calcium- or ammonium hydroxide. The lignin ends up dissolved in the pulping liquor (black liquor) as lignosulfonate together with some degraded carbohydrates and some

extractives. Lignosulfonates cannot be precipitated through change of pH and are instead isolated through complete evaporation of water. A crude lignosulfonate, containing substantial amounts of carbohydrate-derived products, can be isolated in powder form as a sodium-, calcium-, magnesium-, or ammonium salt, depending on the process. In most pulp mills, the fraction that contains the lignin and the pulp chemicals is evaporated to high dryness before being burnt to generate the necessary process energy, simultaneously recovering the chemicals to be returned to the process. As a result of improvements in pulp mill energy demands, black liquor volumes exceed energy demand, however, meaning that part of the lignin can be extracted and used for other purposes than energy generation.

2.2.2 Alkaline pulping utilizing either the Kraft process (i.e., with aqueous sodium hydroxide and sodium sulfide) or the soda process (i.e., with aqueous sodium hydroxide). Kraft is the dominant process representing over 95% of all chemical pulp produced. Like in acidic pulping, lignin is dissolved in the pulping liquor (black liquor) but in alkaline pulping lignin is present as lignin phenolate. Soda and Kraft lignins are highly poly-disperse with both low molecular mass phenols as well as high molecular mass lignins attached to carbohydrate residues being present. The alkaline pulping methods lead to extensive degradation of the native lignin structure. Importantly, Kraft lignin, in contrast to soda lignin, has sulfur species incorporated in its structure. The lignin in the black liquor is burnt for recovery of chemicals and energy production and thus not freely available. The **LignoBoost technology** was originally developed by *Innventia* and the Chalmers University of Technology (Sweden). LignoBoost aims at extracting high quality lignin from a Kraft pulp mill. It works in conjunction with evaporation, and the process begins by precipitating lignin from black liquor by lowering its pH with the help of CO₂. The precipitate is then dewatered using a filter press, similar to those used in the mining and energy sectors. Conventional filtering and sodium separation problems are overcome by re-dissolving the lignin in spent wash water and acid. The resulting slurry is dewatered again and washed, with acidified wash water, to produce cakes of quite pure lignin. Upon acidification all phenols and carboxylic acids become protonated. The lignin is highly pure with only a minor contamination of carbohydrates and ash, and 2-3 wt% of sulfur, half of which being chemically linked to the lignin. *Metso* acquired the technology in 2008 in its entirety and has developed it further, selling its first commercial plant for LignoBoost technology at the end of 2011 to *Domtar*. The unit – at a pulp mill in Plymouth (NC, USA) – began commercial operation in 2013 and produces 25.000 tonne of Kraft lignin. A second plant, which was sold to *Stora Enso*, produces 50.000 tonnes of dried lignin per year and was started up in the third quarter of 2015 in Sunila, Finland. A similar lignin is commercially produced by Mead-Westvaco in Charleston (USA) with an annual production of about 30.000 tonnes.

2.2.3 The Bergius-Rheinau process, using concentrated hydrochloric acid at low temperature, produces a lignin fraction that is solid, water insoluble, of high molecular weight and low in functional groups, all making it more difficult to convert into valuable products. Furthermore, the hydrolysed sugars and the lignin end up together with part of the hydrochloric acid, which must also be recovered. Separation of lignin and hydrochloric acid was historically done by water washing which required a lot of energy, making the process expensive. *HCL Cleantech* (later *Viridia* and now *Stora Enso*) was founded in Israel in 2007 and has been operating a pilot plant since April 2012 in Danville (VA, USA) based on the Bergius-Rheinau process, manufacturing refined sugars and lignin from softwood and hardwood. The refined lignin has

successfully been tested for combustion and for a number of added value products such as flame retardants and carbon fibres. Virdia recovers the HCl by using an extraction process with amines [ref.4]. *Avantium* is also developing a process based on the Bergius-Rheinau Process. It has developed proprietary sugar/acid and lignin/acid separation technology [refs.5,6]. *Avantium* is building its pilot plant in the Netherlands in 2016.

2.2.4 Steam explosion processing involves woody biomass pretreatment with steam at about 200 °C or higher and high pressure for a short period of time followed by a rapid decompression. The lignin can be obtained as a by-product by extraction of the exploded fibrous material with either aqueous alkali or an organic solvent. Also fermentation to ethanol can take place first followed by removal of the ethanol by distillation, leaving behind the lignin in the fermentation broth. For instance, *DSM-POET* (Emmetsburg, USA) is using steam explosion for refining corn stover producing an aqueous lignin stream as a by-product. The resulting lignin contains little carbohydrates and wood extractive impurities. With respect to functional group amount and composition it resembles the native lignin more than the other produced technical lignins. However, the molecular weight of the resulting lignin is significantly reduced.

2.2.5 Organosolv pulping is a fractionation technology that allows for relatively easy isolation of the lignin and comprises a class of processes in which lignocellulosic biomass is treated, often at elevated temperatures, in a mixture of an organic solvent and water. Ethanol, methanol, acetone, cyclic ethers or organic acids, such as acetic acid and formic acid or combinations thereof, are often used for organosolv processing. As a result, the cellulose is delignified, and the lignin dissolved in the extraction solvent. The process is acid-catalyzed, with the acid either being formed in-situ from the hemicellulose fraction, or added deliberately.

2.2.6 A direct method for separation of carbohydrates and lignin in biomass is by **hydrolysis** using a dilute acid, like sulfuric acid or hydrochloric acid. A sulfuric acid-based process, developed in a pilot scale facility by *Sekab* in Domsjö (Sweden), is also focused on the production of monomeric sugars for fermentation to ethanol. In this process the lignin is condensed into a highly insoluble polymeric material [ref.7].

2.2.7 Many new (catalytic) fractionation methods have been reported and are currently being explored at the lab scale [refs.7,8]. Such methods might make use of **Ionic Liquids** (ILs), **liquid salts** such as zinc chloride hydrate or **Deep eutectic solvents** (DES) to (selectively) dissolve lignin or cellulose from lignocellulosic biomass. Another method might be based on superheated steam [refs.9,10,11] and supercritical water [ref.12,13,14]. These types of pre-treatment are still in the laboratory or early pilot phase and the effect of these processes on the lignin characteristics is still unknown.

2.3 TYPES OF LIGNINS AND CHARACTERISTICS

The technical lignins that are, or at least in principle can be, isolated after a cascaded biomass pretreatment process vary widely in terms of chemical composition (including impurities), molecular structure, molecular weight and as a result in physical properties, such as solubility and hydrophobicity/hydrophilicity. As these characteristics will determine to a large extent, which strategies are viable for further valorisation, the physicochemical characteristics of some lignins are shortly listed below.

- 2.3.1 Lignosulfonates.** Lignosulfonates obtained from the (acidic) sulfite process are characterized by the sulfonate groups that are introduced mainly in the α -position of the propyl side chain. It should be noted here that this in contrast to sulfonated Kraft lignins, which have the sulfonate on the aromatic ring. As a result, the obtained lignin is water-soluble, setting it apart from the other types of technical lignins. The high density of functional groups endows lignosulfonates with unique colloidal properties, accounting for their use as stabilizers, dispersing agents, surfactants and adhesives. The lignosulfonates have a relatively high molecular weight and high ash content and still contain a significant amount of carbohydrates. Lignosulfonates are commercially available from hard- and softwoods.
- 2.3.2 Kraft lignin.** Kraft lignin is highly condensed, low in readily cleavable ether bonds and high in recalcitrant C-C bond linkages (e.g., biphenyl and methylene-bridged ones). In addition, sulfur species (mainly as thiols) are incorporated covalently into the structure and thus constitute important impurities that can have consequences for further valorisation (either in material applications or for catalytic depolymerisation with S being a known poison for many metal-containing catalysts). Kraft lignins are typically quite high in phenolic OH content. Kraft lignins are commercially available from hard- and softwoods.
- 2.3.3 Soda lignin.** Soda lignins differ from Kraft lignin and lignosulfonates in that no sulfur-containing reagents are used, rendering the lignin sulfur-free. The relatively harsh pulping conditions do cause the lignin to be rather condensed and recalcitrant. As do Kraft lignins, soda lignins contain small amounts of ash and carbohydrates and are of low to moderate purity. As opposite to Kraft lignins and lignins obtained under acidic conditions, vinyl ethers can be found in soda lignins. Soda lignins are commercially available from annual crops (and to some extent hardwoods).
- 2.3.4 Organosolv lignins.** The structure of the organosolv lignins depends to a large degree on the processing conditions under which they are obtained. Organosolv lignins are of high purity, often with very little carbohydrate and ash impurities. The wide-spread, general notion that organosolv lignins are also most similar in structure to native lignin and still contains a high fraction of easily cleavable aryl ether linkages (β -O-4) is generally not true, however, and only holds for organosolv lignins obtained under mild conditions at lab scale. While more homogeneous in overall structure, i.e. of lower molecular weight and polydispersity, organosolv lignins can be as chemically recalcitrant as soda or Kraft lignins. Organosolv lignins are being produced at both the pilot and demonstration plant scale from hard- and softwoods.

Table 2 shows an overview of characteristics of several types of lignins. The photographs in Figure 3 demonstrate the varieties in physical appearance of a number of typical technical lignins.

Table 2. Characteristics of several types of lignins. Adapted from [ref.15].

Type of lignin	Scale of Production	Separation Method	Pretreatment Chemistry	Sulfur Content	Purity
Kraft	Industrial	Precipitation (pH change) or ultrafiltration	Alkaline	Moderate	Moderate

Soda	Industrial	Precipitation (pH change) or ultrafiltration	Alkaline	Free	Moderate-low
Lignosulfonate	Industrial	ultrafiltration	Acid	High	Low
Organosolv	Pilot/demo	Dissolved air flotation, precipitation (addition of non-solvent)	Acid	Free	High
Hydrolysis	Industrial/Pilot		Acid	Low-free	Moderate-low
Steam Explosion	Demo/Pilot		Acid	Low-free	Moderate-low
AFEX	Pilot		Alkaline	Free	Moderate-low



Figure 3. Photographs showing the differences in physical appearance for a number of typical technical lignins.

3. LIGNIN SUPPLY

For every potential business case, the sustainable supply of a sufficient amount of lignin with physicochemical characteristics suitable for a specific technical application is key. This section provides insight into available lignin containing feedstock and side streams and a projection to future supply¹.

3.1 SOURCES IN NATURE

Lignin is present in the tissue of vascular plants where it adds to the mechanical strength and structural integrity of the cell wall. Softwoods have a lignin content of 25-30 wt% and hardwoods 20-25%, both with only small differences between the different parts of the trees (i.e., stem, roots, branches and tops). Various annual plants have a lower lignin content, e.g. flax (around 3 wt%), with large differences between different parts of the plant. Grasses typically contain up to 10% of lignin. The total amount of lignin present in the biosphere exceeds 300 billion tonnes and annually increases by around 20 billion tonnes [ref.16]. The lignin present in the biomass can, in principle, also be directed targeted for valorisation, i.e. without prior isolation of a technical lignin by one of the fractionation methods listed above. Such processes, which essentially concern a catalytic pretreatment aimed at combined depolymerisation and separation, are being intensively studied, but are at early stages of development. This 'lignin-first' approach offers the advantage of accessing the native lignin polymer, which still contains a high fraction of cleavable bonds, rather than having to work with the recalcitrant lignins that are obtained after biomass pretreatment. For such approaches, it is mandatory that the holocellulose that is left behind is still of sufficient quality to allow further processing.

3.2 INDUSTRIAL SOURCES

The forestry industry produces huge quantities of lignin in its pulping operations, of which the main objective is to liberate the cellulosic fibres present in wood or (in some countries) in annual plants for the production of paper. The annual production of Kraft pulp (softwood and hardwood) in the world is in the order of 130 million tonnes, corresponding to a total release of approximately 55 million tonnes of Kraft lignin [ref.17]. This lignin is mainly burnt in a recovery boiler to produce energy and recover the cooking chemicals. Only 2% of it was commercially used for products, such as dispersing or binding agents. It should be stressed in this respect that of these 55 million tonnes produced by pulping, only a very limited amount is actually isolated and available.

For example, today 75.000 tonnes of lignin is being isolated via the Lignoboost process.

Acidic pulping via the sulfite process results in lignosulfonates that are completely water-soluble and include about 50% of the total organic material in the spent pulping liquor. Currently about 1 million ton of lignosulfonates is produced annually (with Borregaard as the dominate producer), with major uses as dispersants and binders in a variety of applications. The pulp production via the sulfite process is declining due to the higher versatility of the Kraft process. This will also result in a lower availability of lignosulfonates in the future.

Lignin at present is also a by-product from 2nd generation bioethanol production. Four commercial plants each produce approximately 100 million litres of lignocellulosic ethanol, thus together annually producing around 200 kilo tonnes of lignin. The USA goal as part of the Renewable Fuels Standard is to produce 872 million litres of cellulosic biofuels in 2016, [ref.18]. This would lead to an amount of co-generated lignin of 120 million tonnes in 2022. This lignin is at present burnt for energy. As about only

¹ The focus is on lignin that is already being produced in moderate quantities. Small quantities that are being produced on lab scale by still immature pre-treatment technologies are not covered in this overview.

40% of the (dry) lignin produced is required to fully meet the heat/power required for the production of ethanol (e.g., pretreatment and processing) 60% lignin (72 million tonnes) could be considered as surplus in the USA (i.e. real waste if not valorised). At least this (unpurified) lignin could become available for higher value end products, when lignin characteristics meet the high value product requirements. Also for any future ethanol production in Europe, it can be estimated that roughly 0.5 kg of lignin per kg ethanol will be produced.

Table 3. Volume of several types of lignin (not complete for technologies in development such as Organosolve).

Lignin type	Scale of operation	Volume (kta)	Suppliers	References
Lignosulfonates	a) Commercial b) Commercial c) Commercial d) Commercial e) Commercial f) Commercial	a) 500 [1] b) 570 [1] c) 120 [c.w.] d) ? e) ? f) 45 [c.w.]	a) Borregaard LignoTech (NO, ww e.g. JV w Sappi SAF) b) TEMBEC (Can) c) Domsjo Fabriker (SE), now Aditya Birla (India) d) La Rochette Venizel (FR) now Saica (Esp) e) Nippon Paper Chemicals (Jpn) f) Cartiere Burgo (it)	a) www.borregaard.com b) www.tembec.com c) www.domsjo.adityabirla.com d) www.saica.com/en e) www.npchem.co.jp/english/product/lignin/ f) www.burgo.com/en/group/figures/ls
Kraft (softwood)	a) Commercial b) Demo c) Domtar d) Stora Enso e) Pilot f) Demo	a) 35 [1]; 60 [Gosselink] b) 8 [c.w.] c) 25 [c.w.] d) ?	a) Meadwestvaco b) Lignoboost/Metso c) Lignoboost license d) Stora Enso Lignoboost license e) Suzano f) West Fraser	a) www.mwv.com b) www.Metso.com c) www.domtar.com/en/pulp/ d) http://www.storaenso.com/rethink/new-kind-of-gold-from-nordic-forests e) www.suzano.com.br f) www.westfraser.com
Soda (wood)	a) Commercial	a) 6000	a) Green value SA	a) www.greenvalue-sa.com
Organosolv	a) Pilot b) Pilot c) Pilot d) Pilot	a)b) Bankrupt	a) CIMV b) Alcell c) Chempolis d) American Sc Techn	a) www.cimv.fr b) c) www.chempolis.com d) www.amsnt.com
High Acid	a) Pilot b) Weyland c) Pilot	b)Bankrupt	a) Stora Enso (Virdia) b) c) Avantium	a) www.storaenso.com b) c) www.avantium.com
Other a)ionic Liquid, b)ZnCl ₂ hydrate c) supercritical water	a) Mainly academic b) Pilot c) Pilot	b)Bankrupt	b) BiChem c) Renmatix	c) www.renmatix.com

4. PRODUCTS AND MARKETS

Today lignin is mainly used for energy generation as it has a relatively high caloric value of 26.5 MJ/kg for dry lignin. This is higher than the lignocellulose from which it is liberated as the hemicellulose and cellulose caloric value is only 16.7 MJ/kg. Incineration of lignin for energy recovery is mainly performed at the same site as Kraft pulping is performed, as the recovery boiler is also meant to recover the Kraft cooking chemicals. In fact, modern Kraft mills typically generate an electricity surplus, which is often sold back to the local electrical grid. Considering the scale at which the Kraft process is operated, incineration of lignin can generate ca. 700 million tonnes of high-pressure steam per year). Kraft lignin thus actually constitutes one of the world's most important biofuels. Based on energy prices, moisture content, logistics cost and possible contaminants (e.g. inorganics such as chloride salts) the lignin price for energy generation can vary between \$70 and \$150 per tonne.

Products from lignin can be drop-ins (molecularly-identical bio-based equivalent of fossil based product), bio-based alternatives (e.g. dispersants), or new products for new markets (e.g. carbon fibres).

This section provides an overview of current and possible lignin applications. Most applications have not left laboratory or pilot scale. The assumption is that applications have been developed in a pragmatic rather than scientific way. A proper analysis of the perfect fit between lignin characteristics and application requirements provides room for further improvements: what changes in the lignin structure could be made to enhance performance? And how could fit for purpose lignin be achieved?

4.1 CURRENT APPLICATIONS

Current commercial non-energy applications of lignin [ref.19]:

4.1.1 Dispersants - e.g. in construction industry (lignosulfonates). Even Kraft lignins are sulfonated to obtain suitable dispersants:

- The lignin produced in Mead-Westvaco, Charleston, USA (former Borregaard LignoTech's kraft lignosulfonate) is used as dispersant and as matrix for controlled release of agrochemicals. Annual production volume is about 30.000 tonnes.
- Dye dispersant is prepared from sulfate/sulfite pulping liquors, cross-linked with sulphite/formaldehyde, products exhibits good dispersion, property, heat-resistant stability, high temperature dispersion property, fibre staining property and azo dye reducing property.
- Chemically modified lignin has been used as a dispersing agents, complexing agent, flocculent, thickener or auxiliary agents for coatings, paints or adhesives.
- Oil Well Drilling Muds.
- Coal-water slurry dispersant.
- A lignin-derived material has been reported to be a good dispersant for soils and applications shown for cleaning and/or laundry detergent compounds.
- A mixture including poly-carboxylic acid, and lignin sulfonic acid has been used for cleaning aluminium plates to prevent calcium scaling.
- Lignin sulfonates have been used as biodegradable and nontoxic emulsifiers or dispersants.
- Lignin is used either directly or chemically modified, as a binder, dispersant agent for pesticides/herbicides, emulsifier, and as a heavy metal sequesterant.
- Jet printing ink was prepared including sulfonated lignin.

4.1.2 Emulsifiers

Applied in asphalt to prepare temperature-stable asphalt emulsions

4.1.3 Foams – Plastics/Polymers

- (partial) replacement for phenol in phenol-formaldehyde resins (soda lignin).
- Lignin based rigid poly-urethane (excellent in flame retardance).
- Epoxy resin comprises an epoxy resin and a curing agent, wherein the curing agent is a lignin-derived acid anhydride.
- S-free lignin has been used for automotive brakes and epoxy resins for printed circuit boards.

4.1.4 Aromatics

Until now only vanillin is being produced on a commercial scale as a lignin-derived aromatic chemical by *Borregaard* in Särpsborg, Sweden.

4.1.5 Stiffness enhancer in board products

Lignosulfonates are applied in paper for corrugated board applications when additional stiffness is needed in comparison to starch.

Kraft lignin from the Lignoboost process is also used in dispersants and in addition finds its application in the building, construction and automotive sectors. MAST Carbon [ref.20] uses organosolv lignin (of Canadian and Russian origin) as binder material for making carbon monoliths for adsorption and filtration.

4.2 POSSIBLE NEW APPLICATIONS

At present lignin is mainly a by-product of the paper and biofuels production, resulting in suboptimal properties for many potential applications. When lignin is the primary target of fractionation, or at least considered as equally important as the polysaccharides, the process could be operated in such a way that the lignin might be recovered in a form and quality that it is needed for its purpose.

Especially when a biorefining model is envisaged, where lignin is isolated as valuable fraction next to cellulose and hemicellulose. If such an approach of maximizing the value of all three components is adopted, pretreatment or fractionation processes could be geared such that the native lignin structure is preserved more, allowing for more selective chemical depolymerisation processes. Higher value compounds (e.g. fine chemicals, building blocks for pharmaceuticals, flavouring agents and fragrances) can then be obtained first with limited yields, warranting the milder and more costly lignin separation process; in consecutive steps, the remaining lignin (which is by definition more recalcitrant), can then be valorised by successively more severe (catalytic) chemical conversion to give bulk chemicals or fuel additives, with the final remainder being used for the generation of heat and power. Such a cascade approach would allow for the maximization of the entire lignin fraction.

At the short-to-medium term, the technical lignins available will still be obtained from processes geared to maximization of the carbohydrate rather than the lignin content of biomass, however. Such processes, as those listed above, will thus generate technical lignins that are highly condensed and recalcitrant, i.e. difficult to process chemically, and only to a limited extent decorated with functional, providing limited handles for macromolecular/materials application. The production of chemicals from such lignins would then require harsher conditions to break the many c-c bonds contained in the lignin structure, providing lignin oils that can be upgraded to bulk chemicals or fuel components. Materials application will often require a further functionalization step to achieve the desired balance in physical properties and functional group density.

The main possible future applications can be broken down in different groups: carbon-based materials, macromolecular applications, fine- and specialty chemicals, bulk chemicals (e.g., aromatics and acids), higher value fuel additives and finally, as source of energy/heat.

4.2.1 Carbon-based materials

This group is made up of applications from polymeric lignin.

- Carbon Fibres.

A report summarizing the results of a public workshop sponsored by DOE/EERE in Detroit (MI, USA), on June 4–5, 2013 [ref.21] describes the potential of carbon fibre reinforced plastics as lightweight and strong replacements for steel panels in for instance the car industry. They can contribute to significantly reduce vehicle weight and improve fuel economy.

A requirement for producing lignin carbon fibres is that lignin should be melt spun at high rates. The technical barriers include the isolation of suitable quality lignin from black liquor or other lignin containing residues, and a low-cost purification of lignin to remove bound short lengths of polysaccharides, salts, particulate contaminants, water and other volatiles. Another technical challenge is dealing with lignin molecular weight poly-dispersity. A final barrier is the development of practical new methods to process, stabilize and derivatize lignin and thus optimize its thermal T_g, melt flow and melting point properties, so as to develop fibres with mechanical, chemical and functional properties that match or exceed the properties of existing carbon fibres. Another goal is to make lignin from different sources acceptable as a raw material for high-rate melt spinning and simultaneously capable of delivering high-carbon weight yields when the melt spun lignin fibre is thermally converted to carbon fibre.

- Activated carbon
- Polyurethanes (utilizing lignin as polyol component)
- Adhesives (replacing phenol in the phenol-formaldehyde resins and other phenol based resins in the manufacturing of particleboard, plywood and fibreboard)
- Complexing agents (for sorption of (heavy) metal ions in contaminated water streams)

4.2.2 Chemicals

Aromatics will be derived from monomeric C₆ fragments from depolymerized lignin.

BTX (Benzene, Toluene, Xylene): the maximum theoretical obtainable yield of BTX (benzene, toluene and xylene) from lignin is about 36-42 wt% as lignin contains 60-65% carbon of which 60-65% in C₆ aromatic rings. The main challenge in producing BTX from lignin is to selectively deoxygenate and de-alkylate the C₆ aromatic structures (typically with hydrogen), without hydrogenating the C₆ aromatic ring. BTX is the source of approximately 60% of all aromatics in volume. It represents a 100-billion-dollar market and was produced from petroleum with the following volumes in 2010: benzene: 40.2 million tonnes per year, toluene: 19.8 million tonnes per year, and xylene: 42.5 million tonnes per year. BTX represents almost 24% of the global petrochemical market in value. The average price for BTX is around \$1,200 per tonne. The BTX market is forecasted to grow at a 4.4% CAGR from 2010 to 2020. Phenols: In organic chemistry, phenols, sometimes called phenolics, are a class of chemical compounds consisting of a hydroxyl group (—OH) bonded directly to an aromatic hydrocarbon group. The simplest of the class is phenol, which is also called carbolic acid. Phenols are important raw materials and additives for industrial applications. Some natural phenols can be used as bio-pesticides or insecticides. Tannins are important elements in the flavour of wine. Some phenols are sold as dietary supplements or as drugs. Phenol was first extracted from coal tar, but today is produced on a large scale (about 7 million tonnes/year) from petroleum. It is an important industrial commodity as a precursor to many materials and useful compounds. Its major uses involve its conversion to plastics or related materials such as polycarbonates, epoxies, bakelite, nylons, detergents, herbicides such as phenoxy herbicides, and numerous pharmaceutical drugs. It should be noted that the phenols typically obtained from lignin depolymerisation processes consist of a mixture of alkylated phenols, rather than pure phenol. Dealkylation is then required or, alternatively, applications should be found that can accommodate such mixtures. For the BTX strategy, it remains to be seen if attractive price premiums can be

realised. With benzene prices around \$1.50 kg⁻¹ (Oct. 2012) and maximum theoretical gravimetric yields of BTX between 40-50%, depending on the lignin type, much will depend on the lignin price if viable cost-efficient valorisation processes can be developed. With prices estimated at \$0.25-0.50 kg⁻¹ for high purity lignin, this might leave little margin to allow for capital and operating costs as well as profit.

4.2.3 Power/fuel

In biofuel pellets, Kraft lignins have been used as additive as they increase the mechanical properties of wood pellets to a greater degree than starch. Also in these applications, the procedure used to produce the lignin has a major impact on the feasibility of using the lignin as an additive. Lignin-based slurry fuels are a potential alternative to fossil fuels in kraft pulp mills. Lignogels are mixtures of lignin, fuel oil, water and surfactant.

5. LIGNIN VALORISATION ROUTES

Lignin is a complex cross-linked polymer present in every tree or plant. Depending on the raw material selected, lignin structures vary significantly. However, lignin isolation technologies might even have a stronger effect on its characteristics. Indeed, depending on the severity of the pretreatment/isolation method employed, the technical lignins obtained will differ greatly in terms of structure, requiring dedicated valorisation strategies. In short, all current pretreatment methods that aim at biomass valorisation (i.e. excluding all those milder pretreatment methods that are applied to separate the fractions of lignocellulosic biomass primarily for analytical purposes) will lead to technical lignins of which the molecular structure is significantly altered with respect to native lignin and which will be chemically more recalcitrant to depolymerisation and valorisation. The degree of functionalization, molecular weight, connectivity, and level of impurities will vary from technical lignin to lignin. It is then imperative to match any efforts towards lignin valorisation with the lignin which structure is best suited or most amenable towards chemical conversion to the targeted product, be it chemicals, fuel components or materials.

The structural complexity and general recalcitrance of lignin could then be addressed by the cascade approach to lignin valorisation, entailing a depolymerisation process that consists of several stages. A first, highly selective step could extract targeted and isolatable high-value chemicals out of the lignin. Even if the yields and efficiency are low for this step, the high value of the products would still make such a process economically feasible. The lignin left after extraction/isolation of these high-value compounds would be more condensed than the starting material, and can be subjected to subsequent harsher cleavage steps, which focus on cleaving more recalcitrant bonds. Any heavy residues left after such a severe treatment could then in turn for example be cracked for use as fuel, used for the applications the asphaltene fraction of crude oil is used for today or still burnt for the generation of heat and power, making full use of the complete lignin input for various process streams.

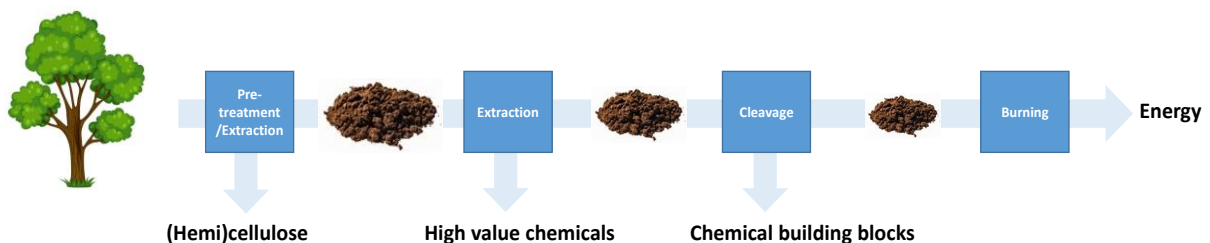


Figure 4. A cascade based lignin valorisation strategy.

6. CONCLUSIONS AND RECOMMENDATIONS

Lignin is a complex macromolecule found in nature as main component of lignocellulosic biomass. Lignins can have distinctly different molecular structures and very different structural and chemical properties. Although Lignin makes up about 20-35% of the mass of every tree or plant and the total lignin present in the biosphere exceeds 300 billion tonnes, isolated lignin is today only available in limited quantities as an industrial by-product.

The transition to a bio-based economy is expected to result in more processes that will produce a wide variety of lignins. In theory, these lignins can be used for multiple purposes: from energy generation, materials and macromolecules to chemicals, such as aromatics. However, in the form lignin is currently available, the potential for higher added value applications is limited.

In the ideal situation the lignin isolation process would be adapted to the best lignin structure required for its application. In order to develop a sound combination of isolation and valorisation strategies research is needed into the relation between lignin structure, properties and applications.

Until today, there is not enough knowledge about the detailed structure of the many types of (technical) lignins and their physical and chemical properties (e.g., functionality and solubility). Without that knowledge, it is difficult if not impossible to develop sound and economically viable valorisation strategies. Therefore, there is a need for a databank containing fingerprints of all kind of lignins, including:

- Lignins from different kind of origin;
- The effect of external conditions (e.g. season, position in the field, weather conditions) on the structure of lignin in nature; and
- The effect of specific pre-treatment processes (e.g., processing conditions and type of depolymerisation route) on the structure of lignin to be further processed.

Within this context, it is important to mention that The International Lignin Institute (ILI) is already working on protocols for information gathering.

On the short term, business opportunities will become economically attractive for lignin applications for materials and macromolecules production, as well as in the isolation of specific target molecules (e.g. similar to but other than vanillin). On the longer term, chemicals, including aromatics, will become more important.

Other partnerships are necessary in the development of lignin applications with a prominent role for the forestry and agro sector along with innovative frontrunners in chemistry.

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