Deliverable report

D3.1 An inventory of relevant applications where lignin or lignin derivatives can replace fossil-based compounds

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Verified (WP leader)	05/03/2023	Karolien Vanbroekhoven
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Working Group 3

1 Introduction - Description of broad field op lignin applications

Lignin is an abundant natural aromatic heteropolymer, it can be obtained from a variety of natural sources, including woody biomass, agricultural residues, and energy crops and thus much research has been spent on the isolation and valorizing lignin. Regardless of the biological origin or isolation methods of lignin, there are typically two approaches for lignin valorization: (1) One pathway uses the lignin as a macro-polymer to produce valuable materials and (2) another approach involves the depolymerization of lignin into low-molecular weight fractions including oligomers, dimers and monomers. The world annually produces around 100 million metric tons of lignin, worth approximately 732.7 million USD [1]. In recent decades, perspectives on lignin have changed from a waste product used as a low-grade fuel to valuable products such as polymers, adhesives, and others. More recently, lignin valorization has received interest in other upcoming sectors, like the medical and electrochemical energy materials sectors. The scope of this deliverable is an inventory for relevant applications using all different types of lignin resources available (technical lignins, hydrolyses lignins and lignin oils).

Different quotes exist like 'you can make anything out of lignin except money' which has been true for many years. However, a shift in the potential use of lignin for industrial relevant applications is observed, driving by the increased drive of consumers and big brands to include biobased content in the application as well as the search for more safer and more functional performant compounds.

2 Approach and taskforces

- Matrix of applications

  A brainstorm within the LignoCOST WG3 network resulted after the WUR meeting in Wageningen, March 2019, in a matrix defining the potential applications of lignin based on its different fractions/molecular structure.

Table 1: Matrix of fractions/applications using categorization of lignin based on molecular weight.

Application	monomers	dimers	oligomers	polymeric
carbon fiber for energy storage	0	0	0	x
carbon fiber for composites	0	0	0	x
activated carbon powder	0	0	0	x
activated carbon fiber	0	0	0	x
carbon for catalyses	0	0	0	x
reinforcement	0	0	0	x

ink additives	0	0	0	x
fillers	0	0	0	x
composites/blends	0	0	0	x
3D Printing	0	0	0	x
Polymer Blends	0	0	0	x
Lubricants	0	0	0	x
dispersants	0	0	0	x
carbon black	0	0	0	x
pellets	0	0	0	x
flameretardant additives	0	0	x	x
Nano particles	0	0	x	x
polyol	0	0	x	x
flocculant	0	0	x	x
microspheres	0	0	x	x
extender	0	0	x	x
coatings	0	0	x	x
UV resistance	0	x	x	x
surfactants	0	x	x	x
wastewater purification (microspheres, cativated carbon)	0	0	x	x
bio/catalyst support	0	0	(x)	x
drug delivery carriers	0	0	x	x
coatings	0	0	x	x
smart food packanging	0	0	x	x
dispersant (sulfonated)	0	0	(x)	x
paper additives (hydrophobization)	0	0	0	x
animal feed	0	0	0	x
Additives in packaging films	0	x	x	x
BTX	0	0	0	x
DMSO production	0	0	0	x
Lignin nanoparticles	0	0	0	x
Fillers (e.g Asphalt)	0	0	0	x
Hybrid (organic-inorganic materials)	0	0	0	x
Pharmaceuticals	x	(x)	(x)	x
Emulsifier	0	0	x	x
Feed	0	0	x	x
Fillers	0	0	0	x
Conductive Polymer	0	0	0	x
PUR Foam	0	0	0	x
Sorbants (e.g. for water treatment)	0	0	0	x
Adsorbent	0	0	0	x
absorbent	0	0	0	x
Antimicrobial	0	0	x	x
Solvents	x	0	0	x

Binder for the carbon industry	0	x	x	0
Chemicals	x	0	0	0
Fuel	x	(x)	(x)	0
Antioxydant (creams, cosmetics)	x	0	0	0
flavours	x	0	0	0
fragrances	x	0	0	0
octane buster	x	0	0	0
liquid fuel	x	0	0	0
plasticizer	x	x	x	0
Antioxidant	x	x	x	0
marine fuels	x	x	x	x
Antioxidative	x	x	x	x
antioxidants	x	x	x	x
antibacterial	x	x	x	x
adhesives	x	x	x	x
additive for fertilizers/biostimulant	x	x	x	x
fertilizer (soil improvement)	x	x	x	x
PF resins	x	x	x	x
PUR films, foams, and coatings	x	x	x	x
epoxy resins	x	x	x	x
Absorbent	x	x	x	x
Bulk chemicals (BTX, phenol)	x	x	x	x
Functional food	x	x	x	x

As can be derived from the table, there is a wealth of applications potentially possible. However, there are completely opposite interpretations of what type of lignin is possible for what type of application. The case of antioxidants and antimicrobial/antibacterial shows this.

Based on the know-how, interest of the team members and the link with WG4 to look for high TRL applications more close to industrial implementation the coming years a down selection to 7 applications and taskforces was made.

- Down selection to 7 applications and taskforces

Specific taskforces with defined taskforce leaders were initiated and organized as indicated in table below. Different members of LignoCOST were involved to contribute to the work to build specific info for each application.

Table 2: Defined taskforces for 7 applications.

		monomers	dimers	oligomers	polymeric	Taskforce leader	Taskforce coleader
TF1	Resins					Filomena Barreiro	Patrik Borenius
TF2	(Marine) Liquid Fuels					Panos Kouris	Kostas
TF3	fine chemicals (flavours, fragrances,...)					Elias Feghali	Pablo ortiz
TF4	Polymeric blends					Marleny Caceres	Patrik Eklund
TF5	Asphalt					Ted Slaghek	Richard Gosselink
TF6	Adsorbents					Jelena Rusmirovic	?
TF7	carbon fibers					Per Tomani	?

- Detailed info for each of the 7 applications: Specific information was gathered for each of the 7 applications in a standardized way:
  - Factsheets compiling info per application (template send by Karolien, completed for most of them)

3 TF1 – Resins

The incorporation of lignin into resins, directly or after chemical modification, is recognized as one of the most viable approaches to accomplish its valorization and properly exploit its unique intrinsic properties (e.g., fire retardancy). In a general way, the first option results in the incorporation of modest lignin contents, whereas the second one can improve this drawback, increasing the biobased content of the final materials. In fact, processes like lignin fractionation, functionalization, liquefaction (e.g., by oxypropylation), and depolymerization are being increasingly exploited with notorious advantages in the field of resins from lignin. Apart from lignin-based polyols, an intermediate product (co-monomer that can be used, e.g., for polyurethane synthesis), most studied lignin-based resins, which explore the polyphenolic structure and high hydroxyl functionality of lignin, include phenol resins, epoxy resins, and polyurethanes, which are high volume applications requesting biobased solutions. Phenol resins find application in the wood panel industry as adhesives, e.g., plywood, medium density fibreboard, and particle boards. Epoxy resins are mainly used as reinforcements in composite materials, coatings, adhesives, and additives e.g., in lubricating oils. Polyurethanes, one of the most versatile polymeric materials, have structural, insulation, adhesive, and medical applications. Among them, the most studied application for lignin-based polyurethanes is rigid polyurethane foams (RPU), which have high potential as fire retardancy insulation materials.

4 TF2 – Lignin fuels

Burning of plant biomass instead of fossil based fuel is one the most recognized pathways to decrease the greenhouse emissions. Lignin content in lignocellulosic cells varies in the range of 20-30% and can be characterized as the most suitable renewable solid fuel. This is explained by its aromatic structure resulting in lower O/C ratio, resulting in higher calorific values in comparison with whole plant biomass. The higher calorific value of technical lignins strongly depends on carbohydrate mixtures presented in them and can be varied in the range 22-26 MJ/kg on dry matter in comparison with 15-20 MJ/kg on dry matter of whole plant biomass. Taking into account the Van Krekelen diagram (O/C atomic ratio versus the H/C ratio) lignin occupies the position in between lignocellulosic plant and fossil based coal. It was shown that direct combustion of lignin as a by-product in the processing of lignocellulosic hydrolyses in amount is sufficient as heat and energy source for the major technological processes. Moreover about 1/3 of the lignin can be sold as high calorific biofuel pellets for outside use. The direct combustion of lignin is the oldest method for energetic valorization. Nevertheless it remains as a comparatively cheap and effective method for lignin as a fuel. Another method of lignin utilization as a biofuel is based on depolymerization of lignin and include mainly: (1) hydrothermal depolymerization and elimination of oxygen excess; (2) slow or fast pyrolyses to partial depolymerization of lignin to produce lignin liquid biooils and solid residues enriched with carbons, (3) gasification followed by biomass to liquid (BTL) or fisher tropsch process for production of different fuel fractions, and (4) solubilization in fuels/solvents already used in the transport sector like methanol or ethanol.

5 TF3 – fine chemicals

Fine chemicals are high added value products e.g. eugenol and propyl guaiacol that are usually made from high purity lignins. Based on the preliminary research done in the framework of the LignoCOST action, when it comes to fine and commodity chemicals made from lignin, the technology of production is not yet mature. Most technologies are still running at low TRL level except for Vanilin production (Borregaard 2019). 9 products were chosen based on the research interest and market relevance.

1. **BTX:** is a commodity product produced in relatively high volumes (>100 MT/y , with B and T > 90%). This product finds its use in applications such as detergent industry, pharmaceuticals, plastics, polymer, building and construction, automotive, oil and gas, textile, packaging and consumer appliances. The main sources used to produce BTX are wood, Kraft lignin and ligno-sulfonate. The production of BTX using the current technologies is expected to be economic viable when the price of crude oil is around 200 $/bbl.
2. **Catechol:** is a fine chemical with a production of 40.000 metric tons in 2017. It is used in the agrochemical industry, in cosmetics, perfumery, food industry, pharmaceutical industry and polymer industry. The main renewable sources used to produce catechol are wood, Kraft lignin and ligno-sulfonate. The expected economic viability using the current technology is estimated to be medium to high in a few years since the prices of phenol have risen in the USA, China and India, and the demand for catechol is increasing (CAGR=3.23 %).
3. **DMSO:** is a commodity chemical for which China is the market leader (45.66%) followed by the USA (28.63%). The global market was valued at 190 M US$ in 2017. The current industrial process to produce DMSO is based on the oxidation of dimethyl sulfide, a by-product of the Kraft process.
4. **Eugenol:** is a colorless to pale yellow, aromatic oily liquid extracted typically from cloves/clove oil (up to 89%). 35000 Tons were produced in 2017 and mostly used in the food sector. The main types of lignins used to produce eugenol are of high β -O-4 content (e.g. organosolv lignin).
5. **Guaiacol:** is a yellowish aromatic oil usually derived from guaiacum or wood creosote. 50.000 to 100.000 tons were produced in 2019. Guaicol is mainly used in the pharmaceutical industry, food industry, agriculture sector, flavors, fragrances. Current production processes use mainly the methylation of catechol, the dimethylation of catechol followed by selective mono-demethylation or diazotization and hydrolysis of anthranium anisole. The expected economic viability with the current technology is low since the price of guaiacol is very low and the cost of processing is high.
6. **Homovanillic acid:** is a white to light brown crystalline solid which is currently produced at a lab scale from Kraft lignin using hydrothermal or chemical processes. The technology is still at very low TRL level and the economic viability of the current technologies is still very low.
7. **Phenol:** is a commodity product that has a distinct odor that is sickeningly sweet and tarry. The capacity of production of phenol was 13 million tons in 2014. Phenol is used in the chemical, polymer and pharmaceutical industries. The main technologies used to produce phenol from lignin are: hydrogenolysis, catalytic depolymerization and pyrolysis. The expected economic viability with the current technology is low since the phenol price is very low and the cost processing is high (Annex 3).
8. **Propylguaicol:** is currently produced from the hydrogenation of eugenol and is used in fragrances & flavors. The price is around 70 USD/Kg. The raw material used to produce propylguaiacol is lignins

exhibiting high β-O-4 content (e.g. organosolv, lignin first) and the processes used is mainly hydrogenolysis through ether bond cleavage.

9. **Vanillin:** is a white to light yellow powder or crystals and is the only monomer industrially produced from lignin. Lignosulfonates, a byproduct from the manufacture of cellulose via the sulfite process, is the main raw material used (Annex 3)

6 TF4 – Polymeric blends

A polymeric blend is a material that is a macroscopically homogeneous mixture of at least two different macromolecules (polymers or copolymers) without covalent bonds between them to ensure a strong interaction. The expected forces between components are only van der Waals forces, dipole interactions or hydrogen bonds. Lignin is a biopolymer that is used to produce polymer blends. It has polar functional groups that can interact with the polymer chain of the other component of the blend. An important characteristic determining the use of lignin in the production of blends is its solubility. This is closely dependent on the molecular weight of the lignin. The lower the molecular weight, the better the solubility of the lignin and the quality of the blends obtained. The optimum characteristics of the blends are achieved by selecting appropriate proportions of the component polymers and modifying additives. Polymer blends with lignin can improve properties such as better processability, better resistance to deformation at elevated temperatures, better resistance to physicochemical agents, greater biocompatibility, lower prices.

Remark: Lignin included in polymer chain – is part of resins (phenolic, PU, epoxy, TF 1) = not part of this TF 4.

7 TF5 – Asphalt binder

Bitumen is currently used as asphalt binder (usually 5wt% in the total asphalt mix), derived from fossil resources for road construction. The bitumen market is very locally organized and specified. The main driver to substitute bitumen is the search for a sustainable alternative, that's where lignin has a big potential. A second driver is the availability of bitumen that is under pressure – because some oil refineries stopped their production, and in refineries more other products are produced what impacted the quality of the fossil derived residual bitumen. Current research shows that substitution up to 50 wt% of bitumen by lignin is possible, resulting in good performance; the application is not depending on a specific lignin resource – but big volumes will be needed to it introduced in the market; the global market of bitumen is 90 million tonnes per year (11 million tonnes per year for Europe). Specifics for lignin to get it successful in this application are: (1) dried, powdered lignin is a prerequisite, small particles (< 200 µm preferably), (2) max 10 wt% moisture content, (3) purity of minimum 60 wt% and (4) a range of MW up to 5000 g/mol. The certification is ongoing (lignin is defined as a wood component), but the long term performance (> 5 years) is still to be proven. With the trend of circularity and recycling of products at their end of life, the behavior of the 'lignin based bitumen' will need to be studied.

8 TF6 – Adsorbents

Using adsorption phenomenon is very practical, easy and common method to remove pollutants from water. Owing to the significant properties of lignin such as high surface area, porosity and availability in huge amounts, it was chosen to be used as an adsorbent surface of various pollutants. The research work done so far indicates that lignin is probably the component of lignocellulosic precursors primarily responsible for the microporosity of activated carbons. It is possible to obtain materials with specific surface properties like SBET (specific surface area, m^2/g) and Vtot (nanopore volume, mm^3/g) approaching 2000 m^2/g and 1 cm^3/g, respectively. These materials have capacities for the aqueous phase adsorption of metallic pollutants and dyes that are comparable to those of commercial activated carbons. Adsorbents derived from lignin can confer high environmental benefits due to its stability, biocompatibility and abundance in the plant kingdom.

9 TF7 – Carbon fibers

Carbon fibers (CF) is the highest strength fiber for manufacturing lightweight materials, and are quite expensive (30 USD/kg). Currently CF is being made mostly from PAN (polyacrylonitrile), which is derived from fossil resources. Typical applications where it is used is automotive industry for lighter cars, to reduce fuel consumption; also in aerospace and wind energy; next to sport goods. There is a need to make low cost CF with medium range properties for automotive industry, since there is the drive to reduce the dependency of petroleum to make these materials. PAN based carbon fibers have a CO_2 footprint 19 $kgCO_2$/kg CF; the lignin based derived one gives a lower footprint of around 6 $kgCO_2$/kg CF. Lignin has been of interest as a precursor for CF because of its high carbon content, low cost since the 60's. To make a successful CF, the type of the lignin, specifically its properties – mainly high purity lignin is required - is important. Next to this, also the processing type (solution spinning or melt spinning) is critical and also depends on the lignin characteristics. For the solution spinning, fully soluble lignin is needed with relatively high MW (> 3000 g/mol). For the melt spinning, a fully fusable lignin is needed (Tg < 150) and typically with a lower MW (< 2000 g/mol). The spun fibers are subsequently converted to carbonized/carbon fibers at different temperatures. Properties of the lignin are also important here for efficient conversion in a reasonable time (< 4 hours). In relation to the lignin properties, higher MW and higher Tg are more suitable for faster conversion. To conclude, a balance is needed between the spinning performance and conversion process with regard to the lignin properties (MW, Tg). The market is developing, and companies show a lot of interest. Stora Enso made a big investment for cellulose/lignin based carbon fiber.

10 Conclusions and outlook

Lignin has a broad potential to be used, from a technical perspective, for a wide range of applications. The different uses can be allocated based on different features, that were made based on a patent technology analyses (Figure 1).

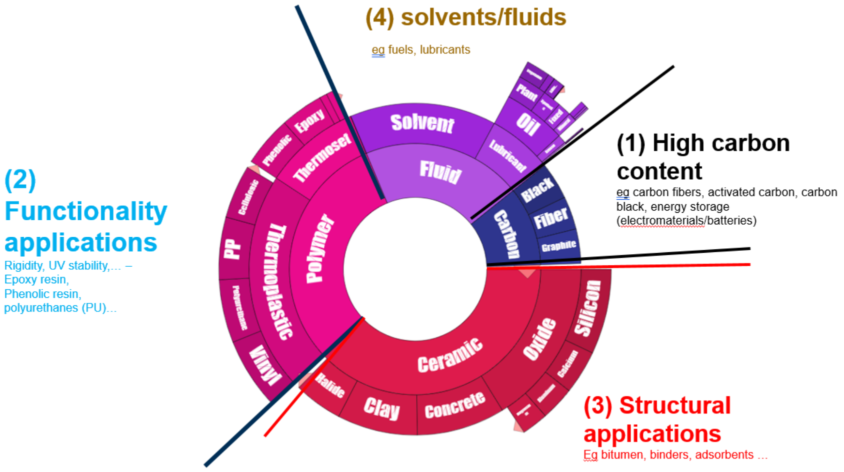

Figure 1: Features for classification of potential lignin applications (presented at renewable materials conference, 2021)

The technical potential should be linked to value chain development (WG4), sustainability assessments (WG5), price/cost estimates and potential for upscaling to decide how fast a certain market entry is feasible. The technical properties of the available resources and its potential use in applications will be further elaborated in D3.2.

11 References

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12 Annexes

TF1 - Resins : Annex 1_PU
TF2 – Fuels: Annex 2 – not present
TF3 – Fine chemicals: Annex 3_phenol and vanillin
TF4 – Polymeric blends: Annex 4
TF5 – Adsorbents: Annex 5
TF6 – Bitumen: Annex 6
TF7 – Carbon fiber: Annex 7 - not present