Sustainable lignin valorization

Technical lignin, processes and market development

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Authors: S. Mastrolitti[a], E. Borsella[a], A. Giuliano[a], M.T. Petrone[a], I. De Bari[a,*],

R. Gosselink[b], G. van Erven[b], E. Annevelink[b], K.S. Triantafyllidis[c], H. Stichnothe[d]

Affiliations: a- ENEA (IT), b-Wageningen Food & Biobased Research (NL), c- Aristotle University of Thessaloniki (GR),
d-Thünen-Institute of Agricultural Technology (DE)

With inputs from: H. Storz[d], H. Lange[e], G. Bell[f]

Affiliations: d-Thünen-Institute of Agricultural Technology (DE), e- University of Milano-Bicocca (IT),
f- MicroBiogen – Innovative Yeast Technology Solutions (AU)

*contact: isabella.debari@enea.it

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Abstract

Lignin is the second most abundant biopolymer of land-based biomass, with great potential as a source of many aromatic chemicals and building block chemicals. Its full exploitation can increase the profitability of many lignocellulosic biorefineries and produce biobased products that can contribute to reducing GHG emissions from those of equivalent fossil-based processes. Despite the great potential for biobased materials in several industrial sectors, one main obstacle to full exploitation is the complex structural variations of isolated lignins due to the natural variability among the different biomass feedstocks and differences in biorefinery layout technologies: molecular weight distributions, functional group contents and their distributions as well as the residual impurities are specifically affected.

Large volume and low specific value applications of lignin include the production of energy and biofuels. In contrast, small volume and higher value-added applications include the production of chemicals through lignin depolymerization and specific functionalization.

While the most common kraft lignin from the pulp paper industry currently accounts for 170 kton/year, additional important current lignins include lignosulfonates, alkali lignin, acid hydrolysis lignin, steam explosion lignin and organosolv lignin. Recently, the development of novel pretreatment technologies at industrial scale, such as steam-assisted pretreatment or solvent-assisted biomass fractionation, has led to novel lignins from novel feedstocks with characteristics that are suitable for more targeted potential applications.

The present review includes the analysis of the available technical lignins with a special focus on novel lignins stemming from new technologies and producers, including market volumes at the global level. The report will detail the chemical features of the available technical lignins and provide an overview of the main processes to achieve final products. These will include polymeric materials (phenolic resins, polyurethane), carbon fibres, BTX, fuels, aromatic lignin monomers and many others. A market overview is provided to assess specific trends of penetrations and current limits.

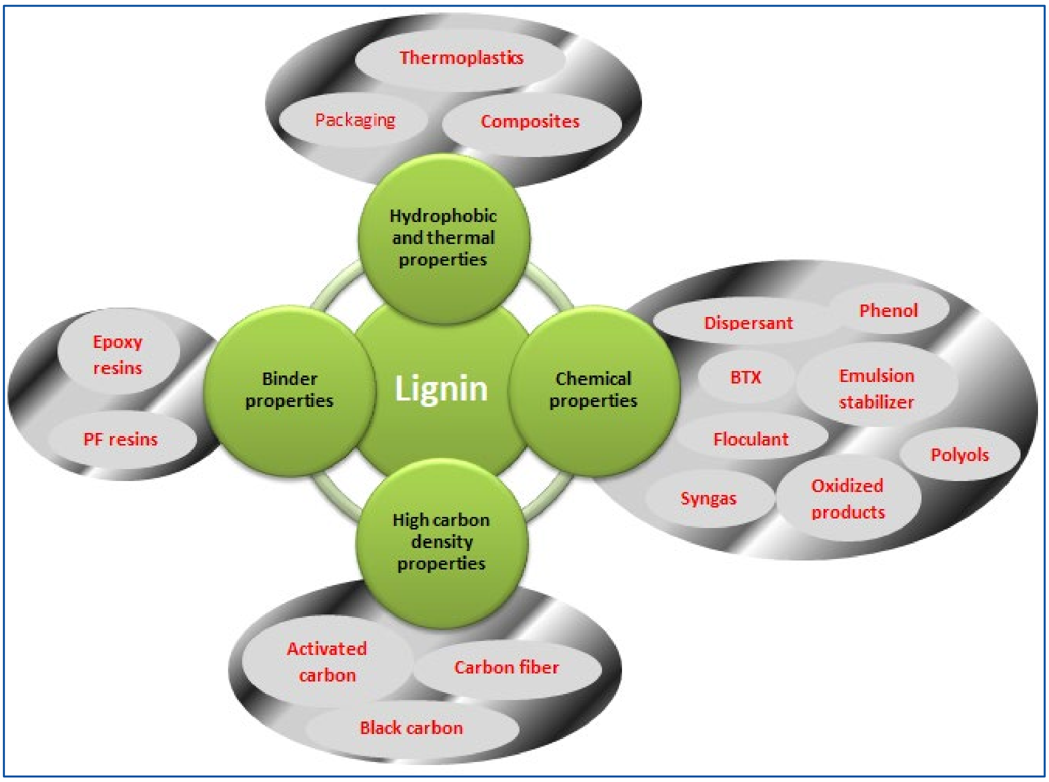
At the European level, many R&D projects have been funded in the last 10 years for the conversion of lignins to final products. The report includes an overview of the most recently funded lignin exploitation projects.

Future trends and research recommendations are finally drawn on the basis of the accumulated facts.

1. Lignin description and current global interest

1.1 INTRODUCTION

Lignin, which makes up approximately 20–35% of the plant biomass, is the most abundant natural resource of bioaromatics. The total lignin amount present in the biosphere exceeds 300 billion tons and increases by approximately 7% every year [1]. Lignin, whose structure is still not completely known, has an aromatic nature and compared to cellulose and hemicellulose, it has a lower percentage of oxygen in its structure, a property that makes this biopolymer **theoretically more easily convertible into high energy density chemicals and fuels** (Figure 1.1). Additionally, so-called technical lignins have undergone different rearrangements of the lignin structure and properties, during processing and extraction. However, these properties are accompanied by recalcitrance, and therefore, the controlled depolymerization of lignin to monomeric aromatic chemicals is generally more difficult to achieve than that of plant polysaccharides [2]. The techno-economical potential of lignin depends on its availability, extraction technology, and technical requirements of the target applications. **In the immediate future, biorefineries that treat lignocellulosic materials should use the lignin fraction by a type of "cascade" approach that leads to its best valorization to maximize the economic feasibility of the biorefinery.**



1.2 LIGNIN CHEMISTRY

Lignin is an amorphous aromatic polymer whose main functions in the plant are to provide physical strength, to form water-conducting vascular networks and to protect against microorganisms and insects. Chemically, lignin is composed of a random network of phenylpropane groups formed from the three basic structural monomeric precursors coumaryl, coniferyl and sinapyl alcohol (Figure 1.2), which respectively form *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units upon incorporation in the polymer [4]. Lignin biosynthesis can be referred to as a dehydration polymerization process, in which the precursors are oxidized to phenoxy radicals via an enzymatic route (by laccases and/or peroxidases) and then undergo radical coupling to various C-O-C and C-C linkages to form a complex three-dimensional polymer (Figure 1.3). In addition to canonical monolignols, *p*-coumarate, ferulate acetate and the flavonoid tricin are covalently incorporated into grass lignins, whereas hardwoods incorporate *p*-hydroxybenzoate moieties [5]. As a consequence, native lignin contains various types of functionalities. Common functional groups in lignin include methoxyl, phenolic, aliphatic, hydroxyl and other carbonyl groups in different percentages. Indeed, lignin can occur in a multiplicity of structures characterized both **by a different percentage values of the three characteristic phenolic units (in terms of H/G/S composition) and by the types of bonds in which these units are connected.** This difference is due to the plant family and species, part of the plant, age, and climate, and they are heavily dependent on the pretreatment to which plant biomass is subjected ("technical lignins").

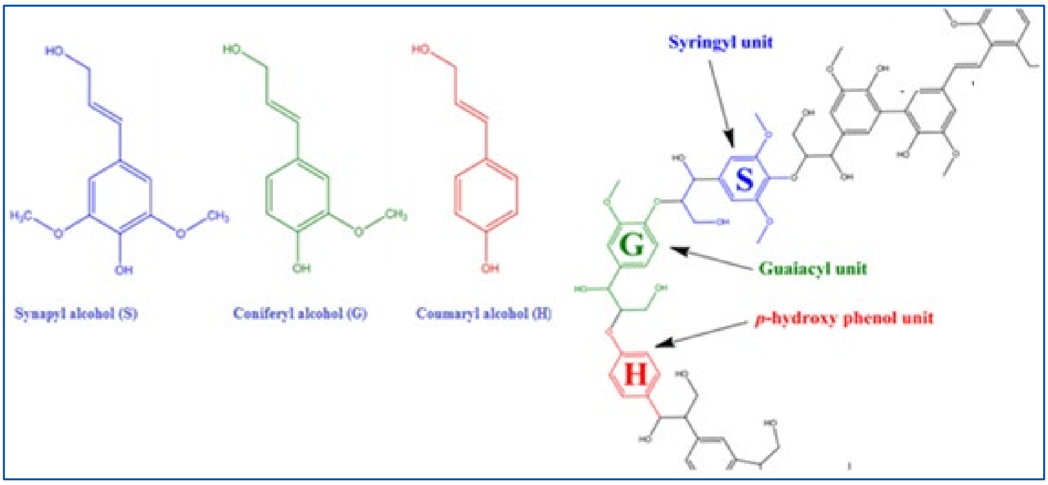


Figure 1. 2 Molecular structure of lignin with its characteristic monomers (S, G and H)

Consequently, the technical lignins resulting from such pretreatment processes have different characteristics in terms of molecular weight, solubility in water, degree of purity (e.g., the remaining covalently bound sugar residues or incorporation of nonnative elements, such as sulfur), degree of condensation and abundance of functional groups, e.g., -OH groups (phenolic, aliphatic), methoxyl groups and carboxylic acid groups.

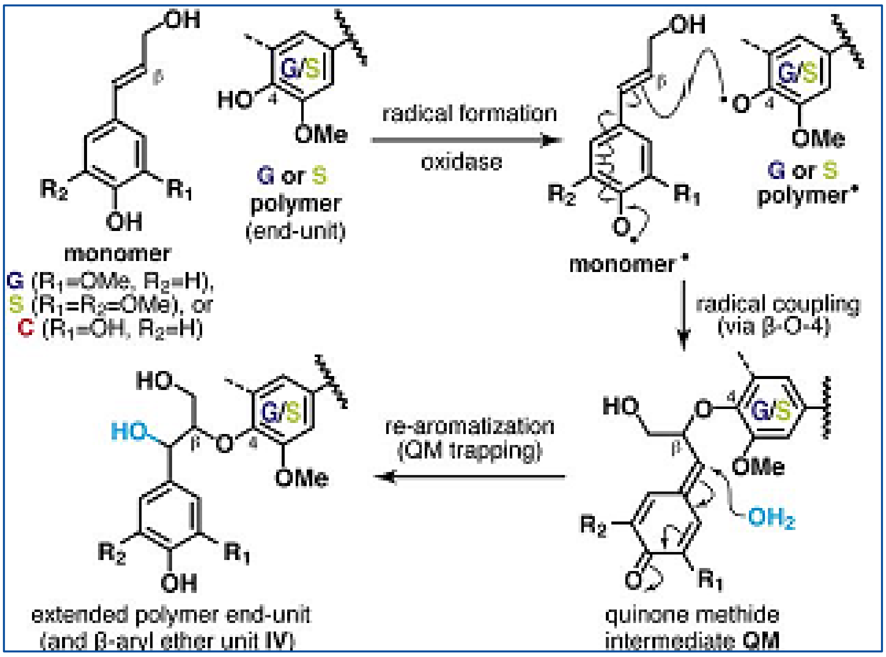


Figure 1. 3 Generation of Major Lignin Units by β-O-4-Type End-Wise Radical Coupling Reactions. Conventional pathway for β-aryl ethers via cross-coupling of a hydroxycinnamyl alcohol monomer to guaiacyl (G) or syringyl (S) polymer end units adapted from [6].

Table 1.1 presents the most common technical lignins, their properties and their main and potential applications.

Table 1. 1 Technical lignins and their properties (*)

Lignin description	**Sulfur %**	**Ash %**	**Sugars %**	**OH phenolic %**	**Acids %**	**Methoxy %**	**Purity**	**M_w ($gmol^{-1}$)**	**Ð**	**Ref.**
Lignosulfonate	5.0-8	4-8	n.a.	2.0-2.5	4-6	~9	Moderate Low	1000-50000	2.5-7.0	[7], [8], [11],[13], [15],[17], [18], [20], [24]
Kraft Lignin	1-1.7	2-6	1.4-1.6	2.6-4.5	4.1-6	11-14	High	1000-5000	2-8	[7], [13], [16], [19], [10], [12], [22]
Alkali Lignin	0-1	2-5	2-4	2.9-5.1	5.4-13.6	10-19	Moderate high	2000-10000	2.0-5.2	[7], [8], [11], [13], [17], [18], [20], [25]
Enzymatic/Acid Hydrolysis Lignin	0-1	1-3	0-2	3-9	6-10	~19	Moderate Low	2000-4500	1.5-3.2	[7], [8]
Organosolv	0	0-0.5	0.5-2	3.7-3.4	7-8	~15	High	1000-6000	1.5-4-4	[7], [8], [9] [11], [14], [17], [18], [20], [23]
Steam Explosion Lignin	0-0.5	5-8	2.5-4.0	4.7-7.0	1.0-5.0	~13	Moderate Low	3500-15000	1.4-7.0	[7], [14], [19], [21], [10]

(*) Of course, the ranges of values depend on the type of initial biomass and the severity of the pretreatment methods used.

1.3 TECHNICAL LIGNINS

In this chapter, an overview of the different technical lignins is presented **in terms of production technology as well as their structural (e.g., molecular weight and morphology) and compositional (e.g., the number and nature of functional groups) features**. In addition to its availability and cost, the specific lignin characteristics are important in determining its effective exploitation.

Several processes are available to produce lignins. In addition to pulp and paper processes, many pretreatment technologies have been developed to separate lignins from polysaccharides in the various lignocellulosic matrices. These processes mainly act on ether bonds, which are far more easy to cleavage than the relatively conversion-resistant (native) C-C linkages. In fact, such C-C bonds are often formed through recondensation/repolymerization reactions during the severe process conditions required for the separation of lignin from holocellulose. **Each method influences the distribution of the functional groups and the average molecular weight values of the isolated structures.** The final technical lignin can contain some impurities due to, for instance, the additives used during the process (e.g., sulfite groups in sulfite pulping). Finally, side recombination reactions often cause an increase in the structure complexity.

1.3.1 Kraft Lignin

Kraft pulping is the most dominant pulping process and constitutes approximately 630 kt/y (85%) of total lignin production. Kraft lignin is considered a byproduct in the paper/pulp industry and is currently often burned for internal energy demand and pulping chemical regeneration [8, 26].

Na_2S and NaOH (white liquor) are used at high temperature (150–180 °C) for several hours to depolymerize lignin into **smaller alkali soluble fragments** (Figure 1.4).

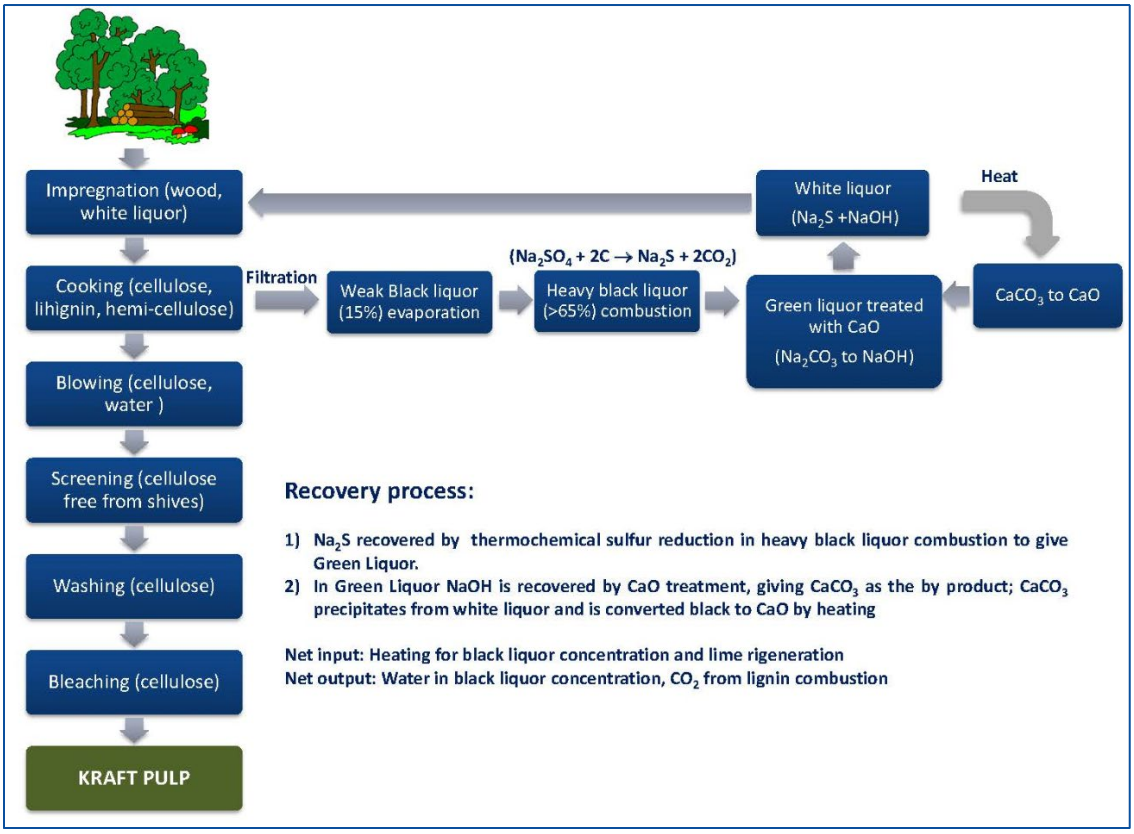
The cellulose is separated by filtration, while the lignin and hemicellulose remain in the liquid phase (black liquor). After precipitation and isolation, the resulting Kraft lignin is therefore contaminated with carbohydrates from (hemi)cellulose and a small amount of sulfur.

The basis of the success of the Kraft process is the recovery of the various chemical substances: sulfur and chlorine are essentially completely recycled (Figure 1.4). The black liquor is burned to convert the sulfate into sulfide (this is a thermochemical reaction in which part of the lignin plays a role). Figure 1.4 summarizes the main process steps.

The lignin downstream treatment provides energy in the form of steam and the byproduct sodium carbonate. Lime (CaO) is finally added to the liquor, and upon reacting with sodium carbonate, it forms a precipitate containing sodium hydroxide and calcium carbonate. The NaOH is regenerated by removing the $CaCO_3$, which is converted into lime by heating.

In principle, only a fraction of the lignin in the black liquor would be needed for sulfate reduction and energy production for the pulping process. In fact, the recovery boiler is the most expensive unit and represents the limiting step in the Kraft process; this means that lignin extraction would open up possibilities to expand the pulping capacity while the recovery boiler remains the same. Elements that do not take part in the process, such as silicon, iron, calcium, aluminium and chloride, are responsible for deposit formation on the boiler wall, compromising the process from the point of view of its energy efficiency.

The presence of residual lignin in the Kraft pulp is a function of the quantity of phenolic hydroxyl groups present in the lignin. Recent studies have shown that in this residual lignin, up to 27 phenolic hydroxy groups can be present on 100 C9 units [27]. This increase in phenolic hydroxyl moieties can be ascribed to the main depolymerization mechanism: the initial formation of quinone methide intermediates, which are subsequently attacked by the anion sulfide hydroxide to result in the cleavage of the linkage (Figure 1.5).



Recovery process:

1) Na_2S recovered by thermochemical sulfur reduction in heavy black liquor combustion to give Green Liquor.
2) In Green Liquor NaOH is recovered by CaO treatment, giving $CaCO_3$ as the by product; $CaCO_3$ precipitates from white liquor and is converted black to CaO by heating

Net input: Heating for black liquor concentration and lime rigeneration
Net output: Water in black liquor concentration, CO_2 from lignin combustion

Figure 1. 4 Kraft pulping with recovery process (adapted from [26])

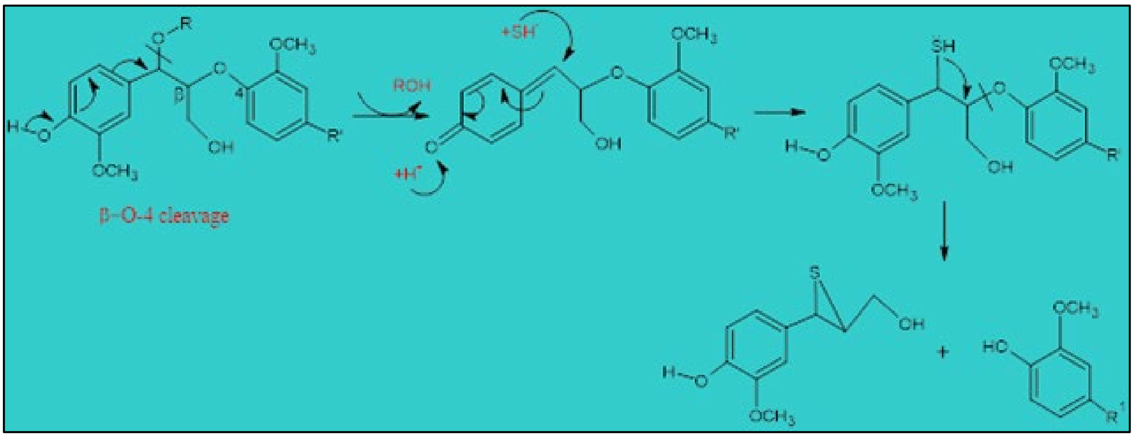


Figure 1. 5 Lignin ether cleavage and a-O-ether and β-O-4 cleavage in the Kraft process (adapted from [28])

1.3.1.1 Technologies for Kraft Lignin isolation

Partial lignin removal (~15%) before thermochemical conversion (i.e., incineration) of black liquor makes lignin available for value-added applications and simultaneously allows a size reduction of the boiler, which is especially beneficial for larger scale facilities. Indulin AT lignin has been the only commercially available technical lignin from Kraft processing for many years. Indulin AT is the technical lignin byproduct from Kraft black liquor linerboard pulp production. It was marketed by the West Virginia Pulp and Paper Company (Now Ingevity) in the 1950s, with applications in asphalt emulsifiers, rubber reinforcement, etc. In the last two decades, efforts have been made to improve the economic and environmental performance of Kraft pulp mills. However, most of the Kraft lignin produced by Ingevity is sulfonated to supply the markets in which lignosulfonates are typically used.

Lignin is precipitated from black liquor by acidification. When the pH begins to drop and reaches the pKa of the phenolic groups, protonation of the phenolates occurs, and flocculation of the lignin begins. The solubility of lignin is also influenced by ionic strength and temperature [29-30].

The LignoBoost process

In 1997, Inventia (formerly STFI-Packforsk and currently called **RISE, Sweden**) and Chalmers Technical University contributed to the development of a separation process of lignin by its precipitation in a highly acidic environment followed by its removal through filtration. As a result, the LignoBoost process was invented in 2002 (Figure 1.6). The process is based on adjusting the pH of the black liquor to approximately 9.5 with carbon dioxide, after which lignin flocculates and is separated by filtration. In the second step, salts are efficiently removed by lowering the pH to approximately 2 by H2SO4. As a consequence, the ash content of the final Kraft lignin product is very low.

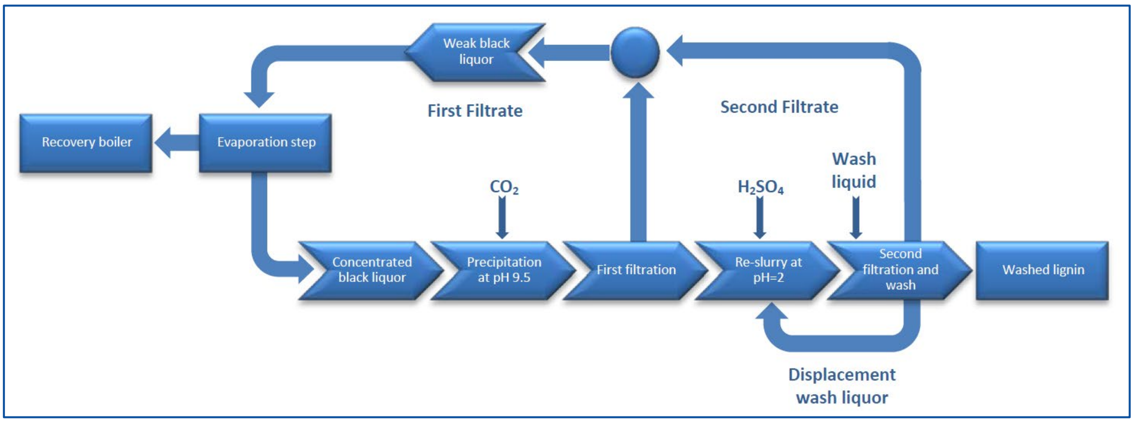


Figure 1. 6 LignoBoost Process to isolate Kraft Lignin

The LignoBoost process was first scaled up in Nordic Paper Bäckhammer (Sweden) for demonstration in 2007 and then further scaled up in other facilities. In 2013, **Domtar** installed this process for the production of Kraft lignin with a capacity of 25,000 tons per year. In 2015, **Stora Enso** installed a facility at Sunila Mill (Finland) that is able to produce LignoBoost lignin at 50,000 tons per year, considerably contributing to lignin production from LignoBoost facilities (Figure 1.7). Currently, several other LignoBoost pilot plants have been installed to contribute to the further expansion of Kraft lignin production (Table 3.1.2).

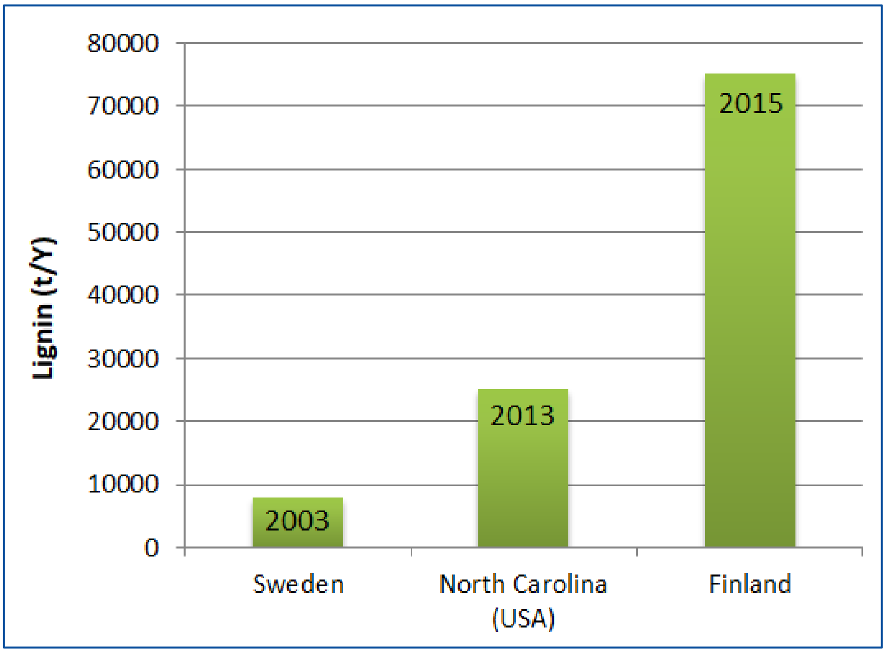


Figure 1. 7 Increasing lignin production from LignoBoost facilities from 2007 to 2015.

The LignoForce process

The LignoForce process was invented by the FPinnovations group in 2008. The main scope of the process was to improve the quality of the lignin by removing the incorporated totally reduced sulfur. The lignin produced in the process was to be used for specific applications; in particular, it had to replace the phenol in the phenol-formaldehyde resins.

The process consists of sparging oxygen into a black liquor containing 30-40% solids. To **reduce the sulfide concentration to the desired level, the oxidation process** is performed at 75 °C. Subsequently, the solution is acidified by CO_2 to a pH of approximately 10, at which point the lignin coagulates (performed at 65-70 °C). Diluted sulfuric acid is then used for product washing (Figure 1.8), after which high-purity lignin is produced by a single filtration process. Lignin forms larger particles in the coagulation step, thus facilitating the filtration process. The totally reduced sulfur (TRS) compounds are converted into more acidic compounds (sulfate, sulfonate and sulfone), which reduced the need for CO_2 to adjust the pH in the precipitation step. The oxidation eliminates a TRS hazard in the filtration and washing steps. In 2015, **West Fraser** built a lignin plant based on LignoForce technology in **Canada**. The scale is 30 tons per day, with a removal rate of 0.15 ton of lignin per ton of pulp. The production capacity equals approximately 10,000 tons per annum.

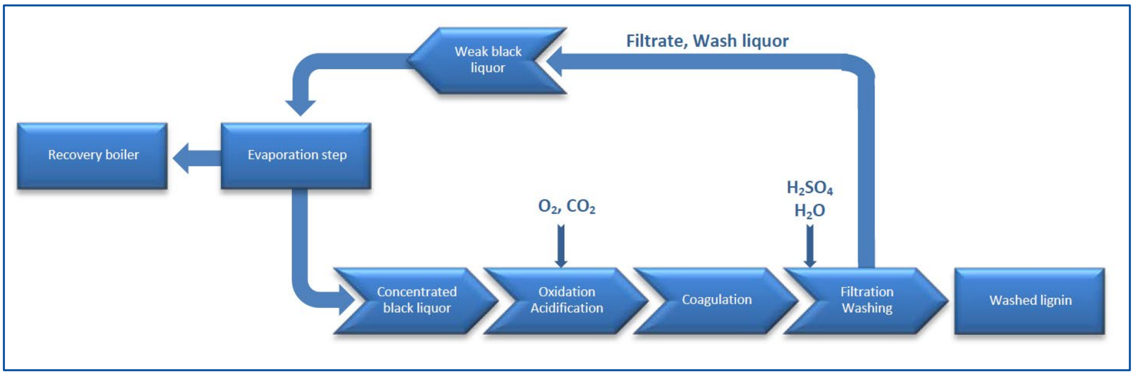


Figure 1. 8 LignoForce Process to isolate Kraft Lignin

Main chemical characteristics of the Kraft Lignin

Even though the exact chemical structure of Kraft lignin heavily depends on the processing and isolation conditions and the feedstock, some common features can be mentioned. In general, Kraft lignin achieved through the acid precipitation process of the black liquor and drying has a dry matter content up to 98%, its sulfur content is in the range of 1–2%; it presents a high purity (>90% based on Klason lignin content), a M_w in the range of 1000–5000 (g mol-1), residual ash of 2–6%, and a [OH] phenolic value in the range of 2.6–4.5% (Table 1.1); sulfonate groups are absent and, consequently, these lignins are only soluble in an alkaline aqueous solution (pH> 10). Kraft lignin is heavily condensed, i.e., rich in C-C linked substructures, and devoid of initial native linkages, which extensively obstructs its (controlled) depolymerization. The most abundant functional groups are methoxy groups with percentage values in the range of 11–14%. Non-hindered methoxy groups are responsible for its great potential use for the synthesis of phenolic resins based on lignin.

1.3.1.2 Producers of Kraft Lignin

Table 1. 2 Kraft Lignin resource availability

Suppliers	Short description	Scale of operation	Market sector	Biomass source	Lignin volume (Kt/year)	Purity	Sulfur presence (%)	Target products from lignin	Reference
Ingevity (ex Westrock/MeadWestvaco) (US)	Paper and packaging company. (1967)	Commercial	Pulp and paper industry	Softwood Hardwood	60 Purified Kraft lignin (Indulin AT) production is limited. Most of the lignin is sulfonated	high	1-2	Fertilizers and Pesticides Polymers/Plastics Binders and Resins Phenol and Derivatives Activated carbon Carbon fibres Other Applications	ingevity.com
Stora Enso (FI)	Pulp and paper producer. (1998)	Commercial	Pulp and paper industry	Softwood	50	High	1-2	Bio-asphalt, batteries, PF resins, composites, carbon fibres, other applications	www.storaenso.com
Domtar (US)	Pulp and paper producer. (1848)	Commercial	Pulp and paper industry	Softwood	25	High	1-2	Applications under evaluation	www.domtar.com
Westfraser (CAN)	Pulp and paper producer. (1955)	Commercial	Pulp and paper industry	Softwood	10	high	1-2	Plywood, other applications	

UPM (FI)	global leader of the bio-based forest industry. (1996)	Pilot; + selling Kraft lignin from Domtar in Europe	Pulp and paper industry	Softwood Hardwood	1	High	<2	Wood-based chemicals and materials (Resins, adhesives, bioplastics and polyurethanes, functional fillers); Biofuels.	upmbiochemicals.com
Suzano (BR)	Pulp and paper producer. (1924)	Demo	Pulp & paper industry	Hardwood (Eucalyptus)	20	high	<2	Resins, rubber, thermoplastics	www.suzanoecolig.com.br
Klabin (BR)	Pulp and paper producer. (1899)	Pilot	Pulp & paper industry	Hardwood and softwood	1	high	<2	Resins, other applications	www.klabin.com

1.3.2 Lignosulfonate Lignin

The sulfite process is the **oldest pulping method**. It is characterized by the flexibility to operate over a wide pH range and temperatures between 140 °C and 160 °C. At the base of the process, the formation of the pulp liquor is the **combustion of sulfur in a controlled oxygen atmosphere**. The second step is the reaction of the obtained **sulfur dioxide with water**, resulting in the formation of sulfuric acid. The counterion source is added to the solution as the corresponding carbonate or hydroxide salt (Ca^{2+}, Mg^{2+}, Na^{+} and NH_4^{+}). The **spent sulfite liquor (SSL) is largely composed of lignosulfonate**, acetic acid, sugars from hemicellulose, inorganics, and small quantities of derivatives from sugar dehydration.

The resulting isolated polymer contains up to 5% sulfur in the form of sulfonate groups, is water soluble, highly cross-linked and includes substantial carbohydrate fractions as impurities. The reaction mechanism favours the cleavage of the ß-O-4 linkages. However, the occurrence of condensation events through reaction of the intermediate carbocation leads to a lignosulfonate with a high molecular weight (M_w close to to 50,000 g mol-1) and a dispersity (Đ) value of between 4 and 9.

This method of pulping requires a **sophisticated procedure to isolate** the water-soluble **lignosulfonate**: first, complexation with a long-chain alkyl amine to form a water insoluble product, subsequent organic solvent extraction of the complex formed, and finally regeneration of lignosulfonate by the addition of a base.

Main chemical characteristics of the Lignosulfonate Lignin

The property of lignosulfonates also dependent on biomass feedstock. Hardwood lignosulfonate has a weighted average molecular weight (M_w with UV detection) of 7200–11000 gmol-1 with dispersity values of 3.0–5.3, while the softwood lignosulfonate has a M_w of 35–50 kDa with dispersity values of 8.2–12.3 [23]. The degrees of sulfonation of hardwood and softwood are similar but are inversely correlated to the molecular weight.

1.3.2.1 Producers of Lignosulfonate Lignin

Table 1. 3 Lignosulfonate Lignin resource availability

Suppliers	Short description	Scale of operation	Market sector	Biomass type	Lignin volume (Kt/year)	Purity	Sulfur presence	Target products from lignin	Reference
BORREGAARD LIGNOTECH (NO, worldwide)	one of the world's most advanced and sustainable biorefineries. (1889)	Commercial	Construction, agrochemical, batteries, food an beverage industry.	Softwood Hardwood	1000	Low-Medium	Yes	Biopolymers used as binding and dispersing agents; **Biovanillin is supplied** to flavour and fragrance companies.	borregard.com
RAYONIER advanced materials (FR, US, CA)	world’s leading producer of high-yield hardwood pulp. (1926)	Commercial	Paper, Food, Health, Biotech and Construction industry.	Softwood Hardwood	150	Low-Medium	Yes	High-purity performance fibres, Biopolymers.	rayonieram.com
DOMSJO FABRIKER (SE)	Industrial company for production of cellulose, lignin and bioethanol. (2020)	Commercial	Pulp, food, textile, medical, ceramic, tires, paint, construction and energy industry.	Softwood Hardwood	120	Low-Medium	Yes	Dispersing agents, water reducing agents and binders in animal food.	domsjo.adityabirla.com
LA ROCHETTE VENIZEL (FR) NOW SAICA (ES)	Industrial company leader of packaging, paper, waste management (1943)	Commercial	Paper industry, pharmaceuticals, food industry, retail and automotive industry	Softwood Hardwood	~100	Low-Medium	Yes	Biofuels, chemicals, adhesives, resins for construction industry.	saica.com

CARTIER BURGO (IT)	one of the European's leading producers of coated and specialty papers . (1905)	Commercial	Pulp and paper industry, paper product distribution, engineering and energy.	Softwood (spruce)	38	Low-Medium	Yes	Cement mixtures, surface-active agents, carbon black, emulsions colourants, bonders and resins, soil stabilization, tanning, ceramics and firebricks, industrial detergents, anti-parasite products, slurry conditioning, water treatment and mineral flotation.	burgo.com
NIPPON PAPER CHEMICALS (JPN)	Consists of approximately 160 affiliates and related companies, headed by Nippon Paper Industries Co., Ltd., (1949)	Commercial	Pulp & Paper, Liquid Packaging Cartons, DP & Chemical Products, Functional Film, Energy Business	Softwood and hardwood	100	Low-medium	Yes	Binders, wood adhesives, promoters for paint, coating, ink and adhesives, bumpers, interior parts, packaging films, adhesive and printing inks.	nipponpapergroup.com

1.3.3 Soda and Alkali Lignin

The soda isolation process is generally applied to nonwoody biomass (e.g., straw, sugarcane, bagasse). In this method, lignocellulose is treated with a **highly concentrated (13-16%)** aqueous NaOH solution at approximately 140–170 °C, yielding low molecular weight lignin (M_w between 1000–6000 g mol^{-1}) with a dispersity (Đ) comparable to that of lignin obtained by the Kraft pulping method. In addition to the use of sodium hydroxide, additional bases include $Ca(OH)_2$ and $Ba(OH)_2$. Delignification is a consequence of the **saponification of the ester bonds** between lignin and hemicellulose in grasses generally present as lignin-diferulate-hemicellulose complexes. Partial lignin deconstruction is primarily caused by the cleavage of the ß-ether linkages [31]. Soda lignin, recovered as a precipitate after acidification of the black liquor, is free of any additive such as sulfur. This feature offers distinct advantages for applications in the field of material chemistry (bioplastic and composites), as well as in the area of catalytic deconstruction to obtain interesting aromatic building blocks.

Main chemical characteristics of the Soda and Alkali Lignin

Like Kraft lignins, soda/alkali lignins are heavily condensed and devoid of native linkages. This technical lignin presents a moderate purity, a M_w in the range of 2000-10000 (g mol-1), a residual ash value of 2-6%, and a [OH] phenolic value in the range of 2.0–5.0% (Table 1.1); sulfur is absent and the most abundant functional groups are methoxy groups with percentages in the range of 10–19% which are responsible for its great use for the synthesis of phenolic resins (in particular methoxy resins) and other different types of bioplastic and biocomposites.

1.3.3.1 Producers of Soda and Alkali Lignin

Table 1. 4 Soda Lignin resource availability

Suppliers	Short description	Scale of operation	Market sector	Biomass type	Lignin volume (Kt/year)	Purity	Sulfur presence	Target products from lignin	Reference
GREENVALUE SA (CH/production in India)	Company in the producing, developing, and commercializing sustainable, value-added products from lignocellulosic biomass (2003)	Commercial	Lignin	Wheat straw, wood, bagasse, flax	6000	Medium-High	No	Wood adhesives, HP laminate resins, sand binders and refractory binders, novolacs and moulding compounds.	suprabio.eu/suprabioconsortium/greenvalue-sa/
Northway Lignin Chemical (CA)	A leading technology company in the advanced biproducts in chemical sector. (2010)	Pilot/RTD	Na-carbonate lignin (polybind300).	Softwood and Hardwood	0.5	Medium-High	No	Plant nutrition, product binders, emulsifiers, stabilizers, dispersants.	n.a.

1.3.4 Organosolv Lignin

The organosolv extraction methods are based on the hydrothermal treatment of biomass with a mixture of water, an organic solvent, and additional additives (often acids) to give rise to a high-quality sulfur-free lignin. **The outcome is steered by the severity of the process, but in general, the ß-O-4 ethers are targeted [18].** For this reason, mildly produced OS-lignin could be a good candidate for the preparation of polymers, such as biobased phenol formaldehyde resins, polyurethanes and polyesters. **Commonly used organic solvents are methanol, ethanol, acetone or a mixture thereof.** After the treatment, cellulose pulp is separated from the black liquor by filtration. **Water and strong acid are then added to the black liquor to precipitate lignin that is subsequently isolated, while digested hemicellulose and smaller lignin fragments remain in the liquid.** In the next step, the organic solvent is stripped from the liquid phase by flash distillation, leaving saccharides from digested hemicellulose in the remaining syrup. Xylose can be recovered from syrup as a byproduct. An acid catalyst can be added both to improve the cleavage of ether-linkages and also to result in **intramolecular condensation reactions**, giving rise to a more complex lignin structure. For this reason, **while more homogeneous in overall structure**, i.e., of lower molecular weight and dispersity, organosolv lignins can be as **chemically recalcitrant** as soda or Kraft lignins. Organosolv lignins are being produced at both the pilot and demonstration plant scales from hard and softwoods.

Beyond the use of classical acid catalysts such as HCl, H_2SO_4, acetic and formic acid, the influence of different Lewis acids (e.g., FeCl2, $ZrOCl_2$) on the lignin structure has been explored by other groups. An interesting application of a heterogeneous-acid catalysed OS process is the treatment of biomass with a mixture of 2-MeTHF (methyltetrahydrofuran) and a solution of oxalic acid in water [32]. The main advantages of this method are the recovery of lignin by simple concentration of the organic phase and the use of a biomass-derived solvent (2-MeTHF).

1.3.4.1 ALCELL Process

In 1989, **Repap Enterprise** Inc. built a commercial-scale mill based on the Alcell process in New Brunswick, Canada. The process uses a recovered EtOH/water mixture from later steps as the solvent for the prior steps to minimize the amount of net ethanol used. The pulp from the process is easily bleached and exhibits properties similar to those of Kraft pulp. Lignin is an important byproduct (Figure 1.9).

Repap Enterprises Inc. produces lightweight, coated groundwood paper that is used in magazines, catalogues, inserts, and other commercial printing applications. The company operates a paper complex in New Brunswick, Canada that includes a number of pulp and paper mills as well lumber operations. The company was acquired by UPM-Kymmene OYJ. The organosolv process is currently not in operation.

The **ALCELL process**, a proprietary organosolv pulping process, produces a novel lignin as a byproduct. Its physical and chemical properties are different from those of kraft and lignosulfonate lignins. It has a low molecular weight (Mn ~ 1000 g mol^{-1}), is highly hydrophobic and insoluble in neutral or acidic aqueous media, and is soluble in moderate to strong alkaline solutions and some organic solvents. It has a Tg value of approximately 130 °C. This material has many potential applications. It can be used as a partial replacement on an equal weight basis for phenol-formaldehyde resins in waferboard, urea-formaldehyde (OSB type 1, nonstructural, nonwaterproof) and other wood composites. **The ALCELL process was acquired by Lignol and recently taken over by Fibria (BR). A pilot plant is available in Vancouver Canada.**

Main chemical characteristics of the OS Lignin

Organosolv lignin has a low molecular weight (1000–5000 g mol-1) with relatively low dispersity, no sulfur, and low ash content (<1%).

Compared to kraft lignin and lignosulfonate, this lignin is more hydrophobic and has a lower glass transition temperature. It is used for high value biochemical products, such as elastomers, carbon fibres, polyurethanes, polyesters, coating resins and binders.

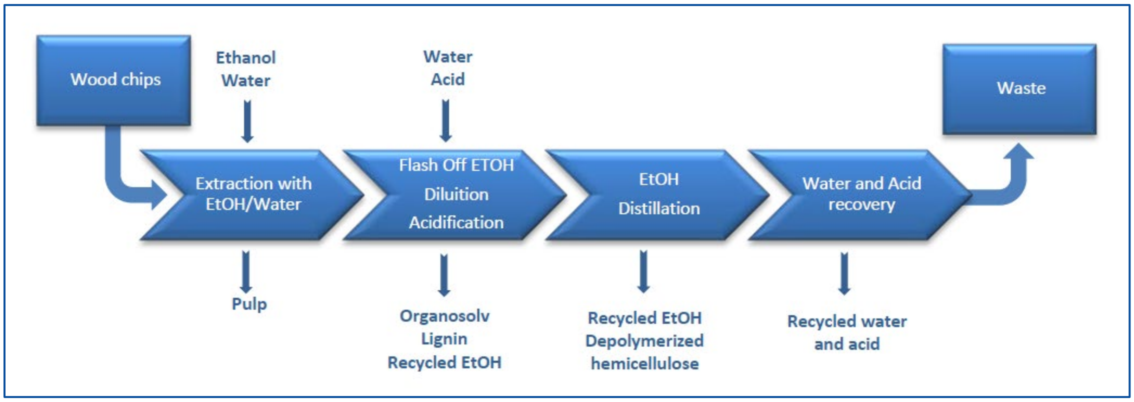


Figure 1. 9 Organosolv lignin from Alcell process

1.3.4.2 Producers of Organosolv Lignin

Table 1. 5 Organosolv Lignin resource availability

Suppliers	Short description	Scale of operation	Solvent	Market sector	Biomass type	Lignin volume (Kt/year)	Purity	Sulfur presence	Target products from lignin	Reference
CIMV (FR)	Biomass Industrial Company (2006)	Pilot	Formic acid/Acetic acid	Biolignin (low PM), cellulose,C5 sugars, silica.	Wheat straw, wood, bagasse	1	High	No	Glues and adhesives, elastomers, carbon fibres, polyurethanes and polyesters.	cimv.fr
Fibria/Lignol (CA)	A leading technology company in the advanced biofuels and renewable chemicals sector. (2010)	Pilot	Ethanol	Ethanol and lignin.	Softwood and Hardwood wood	1	High	No	High-purity lignin to use for coatings, resins, binder and thermoplastic production.	lignol.ca

Fortum/Chempolis (FI)	A renowned provider of ground breaking biorefining technologies for energy, biofuel, oil, paper and chemical industries and companies. (2009)	Pilot/Demo	Formic acid	Ethanol, pulp, lignin, xylose and biochemical	Hardwood and softwood, straw, grasses, bagasse, and many other residues	1	High	No	High-purity lignin for high-value end products.	chempolis.com
Fraunhofer/LEUNA park(DE)	Process centre for the use of renewable raw materials.	Pilot	Ethanol	Ethanol, lignin, xylose	hardwood	0.5	High	No	PF resins, carbon fibres, other applications	n.a.

1.3.5 Steam Explosion Lignin

Steam explosion biomass pretreatment was patented in 1926 by Mason et al. (1926). Steam at high temperature and high pressure, followed by a rapid pressure release, promotes the breaking of the chemical bonds between lignin, cellulose and hemicellulose. In the original process, the temperature was set at 285 °C, pressure at 3.5 MPa for approximately 2 min and then increased rapidly to approximately 7 MPa for approximately 5 s. Currently, the temperature and pressure range can also be different depending on the type of biomass to be processed. After this steam treatment, the biomass is discharged through a narrow orifice (Figure 1.10); at this stage, at atmospheric pressure, intercellular liquids evaporate instantaneously, thus bringing about extensive biomass fibre destruction (explosion).

The effects of chemical hydrolysis and mechanical stress on lignocellulosic material are determined by the process severity parameter, nominally Ro, which is quantified by a semiempirical relationship that is a function of the retention time and saturated steam temperature, as shown below [33]:

R0 = t*exp[(T-100)/14.75], T is the temperature in °C, t is the time in minutes

Steam explosion processes can be operated in continuous or batch modes. A batch reactor is usually used for lab-scale pretreatment, while continuous systems are commonly used for industrial processes.

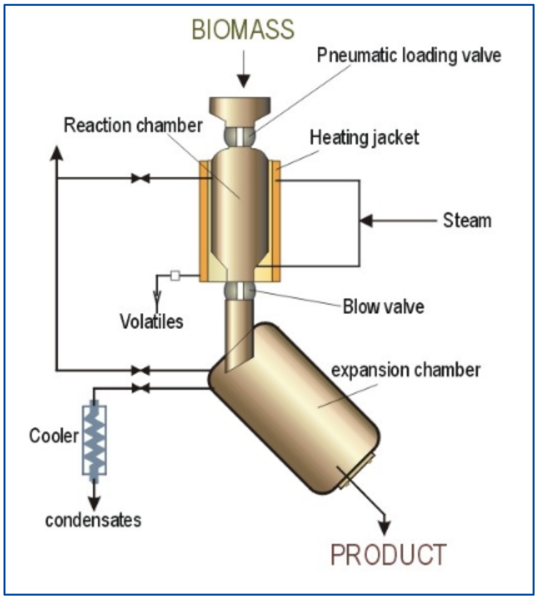


Figure 1. 10 Scheme of steam explosion pretreatment (ENEA)

In this process, (autocatalytically) acid-hydrolysed lignin can be extracted from cellulose, to a large extent, by alkali or organic solvents [33-34]. Steam explosion processes present many advantages: no use of chemicals (except water), good yield of hemicelluloses and lignin with low degraded byproducts, and the mild reaction media pH (when compared to acid hydrolysis processes), which minimizes equipment corrosion. However, the process is rather energy intensive.

Most of the steam explosion pretreatments have been carried out in small-size batch reactors. However, continuous processing is of major interest for industrial applications. In particular, the disruption and hydrolysis of cellulose fibres is more effective in continuous reactors. On the other hand, mechanical compression causes a reduction in fibre exposure to the enzyme at high pretreatment severity, and lignin can recondense on the biomass pores. Figure 1.11 shows the conceptual design of a continuous steam explosion device.

Main chemical characteristics of the Steam Explosion Lignin

Steam explosion lignin resembles the native lignin more than the other produced technical lignins, despite still being structurally very different, due the fact that chemical structural changes are fewer due to the milder applied process conditions. It contains a sugar content in the range of 2.4–4%, moderate/low extractive impurities, a very low sulfur quantity (~0), which makes it able to be processed in a catalytic reaction without catalyst poisoning, and a reasonable quantity of methoxy groups ~13% and OH phenolic groups in the range of 4.7–7% (Table 1.1), which allows it to be used in the synthesis of different phenolic resins.

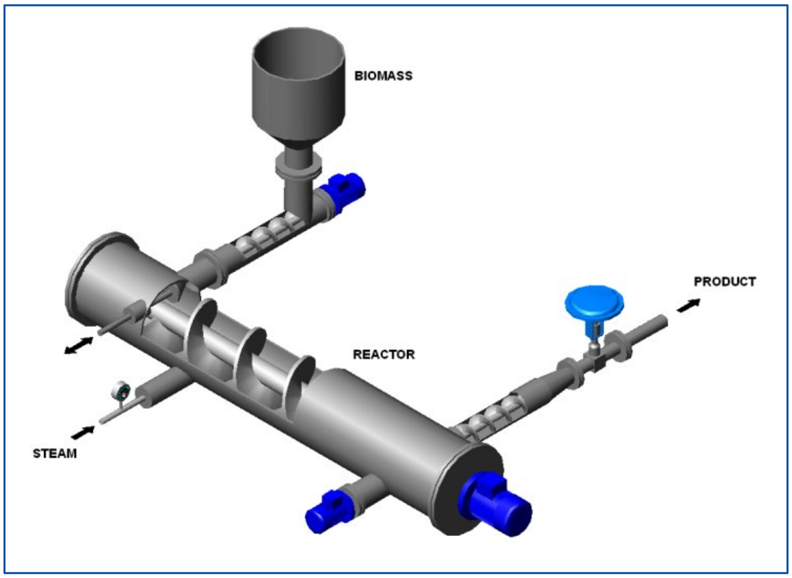


Figure 1. 11 Conceptual design of a continuous steam explosion device

1.3.5.1 Producers of steam explosion lignin

Table 1. 6 Steam Explosion Lignin resource availability

Suppliers	Short description	Scale of operation	Market sector	Biomass type	Lignin volume (Kt/year)	Purity	Sulfur presence	Target products from lignin	Reference
ZEACHEM (US)	Company for the creation of bio-chemical platform for producing ethanol, fuel, and chemicals. (2002)	Commercial	Renewable energy and chemicals	Forestry residue, agricultural residue and/or dedicated energy crops	11	Medium	No	Advanced bio-fuels Chemicals: Vinyl Acetate Monomer, Ethylene Vinyl Acetate, Ethylene, Propylene, Acrylics, etc.	http://zea2llc.com/
ENEA (IT)	Agency for New Technologies, Energy and Sustainable Economic Development public research institution. (1960)	RTD-Pilot	Renewable energy and chemicals	Hardwoods, softwoods, corn stover, wheat straw, sugarcane bagasse	<0.5	Medium	No	Biofuels and Chemical	enea.it
DuPont (US)	Chemical company world leader in biotech industries, Communication Technologies, Performance Materials, Coatings and Colour tech., Safety and Protection, and Agriculture and Nutrition Food. (1802)	Commercial, not in operation	Food, Health, Biotech industries	Corn stover	110	Medium	No	Adhesive, Fibres, Packaging materials	dupont.com

Versalis/Biochemtex (IT)	Global leader company in the development and engineering of technologies and bio-chemical processes based on the exclusive use of non-food biomass. (1958)	Demo	Energy	Agricultural residues, wood	n.a.	medium	No	Different applications, currently energy	www.biochemtex.com
Granul Invest (EST)	Operates in the field of bioenergy and renewable energy production, forestry and biomaterials development. (2003)	Demo building phase	Biochemicals	Hardwood	n.a.	medium	No	Different applications	www.graanulinvest.com/
Clariant (DE)	Biochemical company; the company is focused on four business areas: care chemicals, catalysis, natural resources and plastics & coatings. (1995)	Pre-commercial building phase (RO)	Biochemicals, energy	Agricultural residues	n.a.	medium	No	Different applications	www.clariant.com

1.3.6 Acid Hydrolysis Lignin

This hydrolysis process is a direct method for the separation of carbohydrates and lignin in biomass using a dilute or concentrated acid, such as sulfuric acid and hydrochloric acid, as catalysts that have a stronger effect on hemicellulose and lignin than on cellulose, making cellulose more accessible to enzymes. Sometimes, other organic and inorganic acids, including nitric (HNO_3), phosphoric (H_3PO_4), acetic, and maleic acids, can be used. While concentrated acid methods can be performed at moderate temperatures, dilute acid methods are usually applied together with high temperatures to be effective enough. 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, lignin is condensed into a highly insoluble polymeric material.

Main chemical characteristics of the Acid Hydrolysis Lignin

Acid hydrolysis lignin can have a wide molecular weight range (2000–5000 g mol-1) depending on the type of pretreatment with low Đ (1.5-3) to high Đ (4–8) values, a percentage of sulfur in a wide range (0–1%), and a moderate-low purity. With respect to others technical lignins it has a greater quantity of methoxy groups (near 19%), which makes it particularly suitable for the synthesis of various types of polymers.

1.3.6.1 Producers of Acid Hydrolysis Lignin

Table 1. 7 Acid Hydrolysis Lignin resource availability

Suppliers	Short description	Scale of operation	Market sector	Biomass type	Lignin volume (Kt/year)	Purity	Sulfur presence	Target products from lignin	Reference
Avantium (NL)	Pioneer in the emerging industry of renewable and sustainable chemistry. (2000)	Pilot	Packaging, textiles and film sectors, Na-carbonate lignin (polybind300).	Softwood and Hardwood wood	0.001	Medium-High	No	Bio-asphalt, chemical and aviation fuels.	www.avantium.com
ST1 (FI)	Renewable energy production company and pioneer in the production of ethanol fuel. (1995)	Demo	Energy field.,	Softwood and Hardwood wood	15	Medium-High	No	Renewable diesel and jet fuels.	www.st1.com
SEKAB (CH)	Company for the production of biofuel and various chemicals. (1985)	Demo	Energy field.,	Softwood and Hardwood wood	0.5	Medium-High	No	Bio-based products and advanced biofuels.	www.sekab.com

1.4 ANALYTICAL METHODS TO ASSESS LIGNIN

Lignin is a very complex polymer. To elucidate its chemical structure, different analytical techniques are required and used in concert. The large number of available characterization techniques allows us to determine the chemical structure differences of lignins obtained from different plants, as well as different methods of biomass pretreatment and fractionation. Yet various characterization challenges remain, in particular the determination of the condensed substructures that are often encountered in extensively processed, technical lignins. Lignin is also routinely modified for various reasons. Structural characterization can help identify appropriate lignin modifications and to investigate the efficacy of the modification.

The major and commonly used techniques are presented in Table 1.8.

Table 1. 8 Analytical techniques for the characterization of lignin

Technique	Measures	Restrictions
TGA	Evaluation of the thermal decomposition process	Mass and heat transfer.
DSC	Evaluation of the softening/glass transition temperature (Ts/Tg)	Mass and heat transfer and complexity of the structure
GPC/SEC	Molecular weight distribution	Measurements of the molecular are highly weight dependent on the system and standards used; no real lignin standards are available; molecular weight can be severely underestimated if lignin is cross-linked.
Pyrolysis-GC-MS	subunit composition, structural fingerprint	Care should be taken with assignment of pyrolysis products to structures in the polymer
FTIR	Rapid, economical, easy, and non-destructive technique widely used in polymer investigations functional groups	Sample preparation and solvent type have effects on the analytical results.
RAMAN	In situ determination on the cell walls of plants even with no sample preparation. Functional groups	Presence of fluorescence phenomena, generated by the excitation of the laser; alteration of the sample, due to thermal or photochemical effects as a consequence of the heating by the laser radiation
^{31}P NMR	subunit composition	Limited to determination of phenolic end groups.
^{13}C NMR	Cα-oxidized moieties, ratio of phenolic/etherified units, 'degree of condensation'	Severely impacted by signal overlap
2D HSQC NMR	Subunit composition, interunit linkages, non-canonical constituents (e.g., ferulate, coumarate, tricin)	Limited to linkages containing C-H bonds; spectral crowding in some regions; assignments for non-native, technical lignin structures are less developed.

1.4.1 Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)

TGA and DSC are routinely applied techniques to determine the thermal behaviour of lignin. Due to its complex structure, the decomposition of lignin strongly depends on its nature, reaction temperature, heating rate and atmosphere in which the process takes place, and these are also responsible for both the conversion and product yields. The glass transition temperature (Tg) of lignins is strongly influenced by the water content, and for this reason, samples must be well dried (i.e., at a minimum temperature of 60 °C for 24 h and then dried in a vacuum oven to release all of the water). Moreover, Tg is often too indiscernible to be calculated with reliability, and its value is different for lignins from different pretreatment methods (Table 1.9). TGA curves reveal the percentage of weight loss of the polymer as a function of the increase in temperature to which it is subjected. To determine the corresponding rate of weight loss, derivative TG curves are used, providing a measure of the polymer thermal decomposition and allowing the comparison of the thermal stability characteristics of different polymers. TGA and DSC analyses of lignin from different sources and/or from different pretreatment methods show that the degradation processes and the breakdown of the structure depend on the specific treated lignin (Figure 1.12). **Typically, lignin thermograms show a wide range of degradation temperatures from 100 °C to 900 °C [35] due to the complex branched structures of these molecules.**

Table 1. 9 Glass transition temperatures of different technical lignins determined by differential scanning calorimetry [36]

Type of lignin	Glass transition temperature (°C)
Softwood Kraft lignin	162
	141
	153
Hardwood Kraft lignin	108
Kraft lignin	165
Alcell® (organosolv) lignin	97
Hardwood organosolv lignin	95
Rice straw soda lignin	155
Wheat straw soda lignin	150
Softwood sodium-lignosulfonate	138
Hardwood sodium-lignosulfonate	127

The thermograms present three characteristic steps: the first is due to water evaporation and occurs in the range of 40–120 °C, the second is ascribed to volatile gases (CO, CH_4, CO_2) formed from the presence of impurities of carbohydrates in the lignin and appears in the temperature range of 200–350 °C and, finally, the polymer degradation at temperatures higher than 350 °C. During this final step, phenolic species, alcohols, and aldehyde acids are formed and easily removed as gaseous species. When performed under an inert gas atmosphere at temperatures higher than 320 °C, a pyrolytic process occurs (DTGmax) involving the fragmentation of lignin interunit linkages and release of monomeric species and derivatives of phenols into the vapour phase. At higher temperatures (> 500 °C), the breaking and therefore the decomposition of heavier aromatic rings takes place.

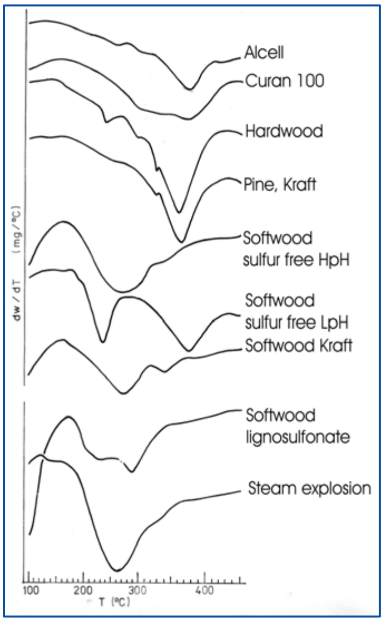


Figure 1. 12 DTG curves of different technical lignins from woody plants [35]

1.4.2 Pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS)

Pyrolysis in combination with gas chromatography and mass spectrometry (Py-GC/MS) is among the most frequently used techniques for lignin characterization due to its ability to provide details of the molecular structure of this polymer, without the need for extensive sample preparation or lignin isolation [37-43]. During pyrolysis, polymers are decomposed by heat in the absence of oxygen. The stable, volatile degradation fragments thus formed can provide useful information about the structure of the polymer. More detailed information is obtained when fewer undesirable secondary reactions occur and when fragment yields are higher (Figure 1.13). When lignin is pyrolyzed, the degradation products can be separated by gas chromatography and identified by mass spectrometry; the identification of mass spectra peaks is usually achieved by reference to a scientific database library.

Under appropriate analytical conditions, the pyrolysis of lignin, even in the presence of impurities, **gives rise to a characteristic product pattern that is, in other words, a ‘structural fingerprint’, of substituted phenols derived from the characteristic phenyl propane subunits usually labelled H, G and S (Table 1.10).** Lignin-derived pyrolysis products can be relatively easily distinguished because of the abundance of molecular ions relating to the characteristic fragmentation spectrum. Note, however, that *p*-hydroxyphenol products can originate from proteins (aromatic amino acids) and other residual phenolics in addition to lignin. Likewise, care should be taken with the annotation of vinylic pyrolysis products in grass lignins, as these products are derived both from lignin and hydroxycinnamic acids, which are not *per se* part of the lignin macromolecule [44].

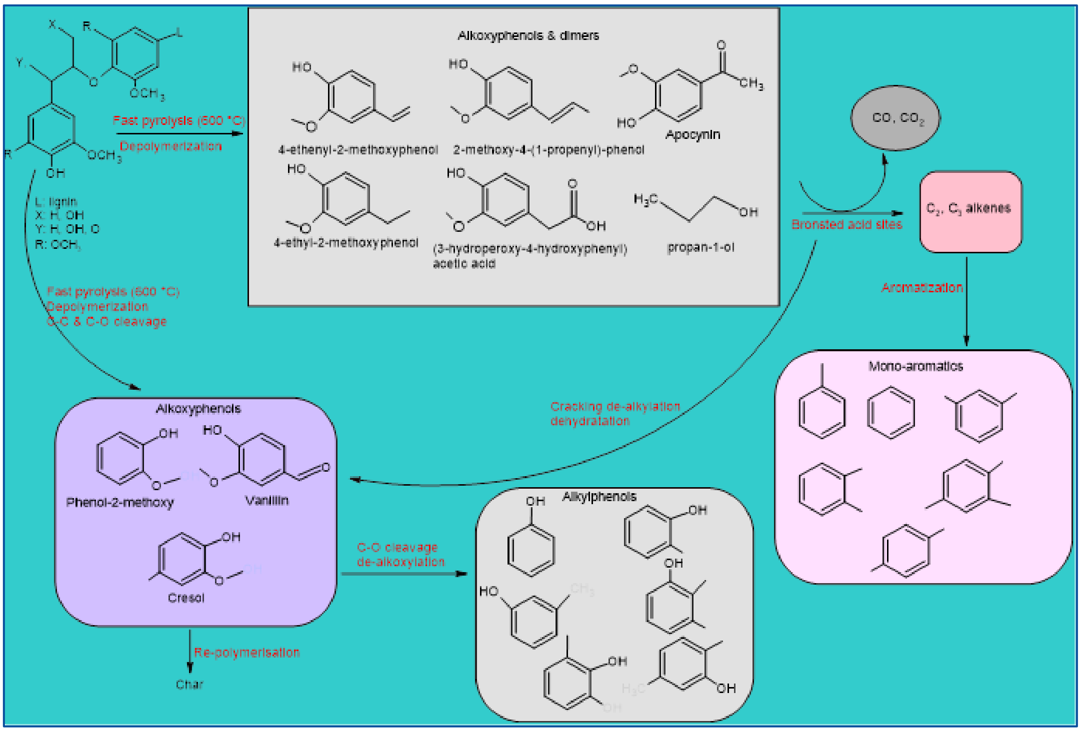


Figure 1. 13 Possible pathways in the noncatalytic and catalytic fast pyrolysis of kraft lignin (adapted from [39])

Depending upon the quantities of the S and G monomers and therefore on their ratio, it is possible to predict whether one lignin has a greater reactivity than another. Indeed, lignin with a higher percentage of G units generally has more condensed structures because of the availability of the aromatic C5 position for coupling, which is at the origin of the formation of very resistant types of C-C bonds (β-5 and 5-5). The S-units are mainly linked by more labile ether bonds (mainly at the C4 positions of the aromatic rings), as described in various lignin structural models.

Table 1. 10 Identification of pyrolysis products from different lignins at different extraction methods (600 °C and 20 s) using GC/MS [45]

Peak no.	Type	Pyrolytic compound	Relative concentration (compound area/I.S area)			
			ML	OL	IL	KL
1	-	Acetic acid	235	005	029	010
2	-	Dimethyl Sulfoxide (DMSO)	-	-	-	294
3	-	2-Furancarboxaldehyde	011	021	-	-
4	-	1-Methyl-1H-Imidazole	-	-	006	-
5	H	Phenol	281	053	125	095
6	-	4-Hydroxy-5,6-dihydro-(2H)-pyran-2-one	013	-	018	-
7	G	2-Methylphenol	-	009	004	018
8	H	3-Methylphenol	017	012	-	-
9	G	Guaiacol	149	213	207	030
10	S	6-Methylguaiacol	018	021	011	006
11	S	1,2-Benzenediol	027	027	011	-
12	G	4-Methylguaiacol	251	251	079	023
13	S	3-Methyl-1,2-benzenediol	032	015	-	004
14	S	3-Methoxy-1,2-benzenediol	169	179	260	047
15	G	4-Ethylguaiacol	083	116	036	011
16	G	4-Methyl-1,2-benzenediol	021	019	-	-
17	G	4-Vinylguaiacol	110	108	127	-
18	-	Unknown	019	016	010	-
19	G	2,4-Dimethoxyphenol	-	014	005	010
20	S	Syringol	429	738	758	092
21	G	Eugenol	041	030	022	-
22	G	4-Propylguaiacol	022	031	017	-
23	G	Vanillin	135	111	052	-
24	G	Isoeugenol (cis)	036	029	031	-
25	S	4-Methylsyringol	645	721	260	060
26	G	Isoeugenol (trans)	194	131	227	-
27	G	Homovanillin	051	027	012	-
28	G	Acetoguaiacon	101	039	025	023
29	-	Levoglucosan	-	-	-	012
30	H	4-Hydroxy-benzoic acid	157	-	-	-
31	S	4-Ethylsyringol	128	238	088	-
32	G	Guaiacylacetone	-	030	121	-
33	S	4-Vinylsyringol	219	223	349	007
34	G	4-(oxo-allyl)-guaiacol	065	-	-	-
35	S	2,6-dimethoxy-4-(1-propenyl)-phenol (cis)	109	099	091	-
36	S	4-propylsyringol	036	077	040	-
37	S	2,6-dimethoxy-4-(1-propenyl)-phenol (trans)	097	103	110	-
38	S	Syringaldehyde	421	314	173	015
39	S	Methoxyeugenol	511	445	480	010
40	S	Acetosyringone	232	131	089	025
41	G	Coniferaldehyde	153	028	038	-
42	G	Coniferyl alcohol (trans)	084	018	135	-
43	S	Syringyl acetone	061	100	231	008
44	S	Propiosyringone	025	074	034	007
45	S	4-(oxo-allyl)-syringol	062	-	-	-
46	S	Dihydrosinapyl alcohol	025	051	046	-
47	S	Sinapaldehyde	258	075	081	-
48	S	Sinapyl alcohol (trans)	054	032	222	-

1.4.3 Gel permeation chromatography (GPC) or size exclusion chromatography (SEC)

Gel permeation chromatography (GPC) is a type of high-performance liquid chromatography (LC) used to understand and characterize the whole molecular weight distribution of lignins through the separation of their major oligomers on the basis of their size. The molecular weight of a lignin is a very important property that affects biomass recalcitrance and lignin valorization. Indeed, the determination of the distribution of molecular weights of a lignin favours knowledge of its chemical-physical properties, providing and determining several important parameters (Table 1.11 left) that affect many of the characteristics of this polymer (adhesive strength, tensile strength, impact strength, toughness, drawability, adhesive tack, cure time, melt viscosity, hardness, softening temperature, stress crack resisting, coefficient of friction, and melt viscosity).

GPC of a lignin is often performed under alkaline conditions (called SEC) or by using organic solvents, usually THF, after derivatization through acetylation. GPC by using neutral solvents without the need for derivatization, e.g., through the use of DMSO containing LiBr, is gaining popularity [46]. Different types of detectors can be used for the investigation of a lignin; the main are a UV absorbance detector and an evaporative light scattering detector (ELSD). GPC analysis of lignins obtained from different pretreatment and separation processes shows, once again, how much these procedures can influence the properties of the polymer, leading to very different values of the distribution of molecular weights and average molecular weight of the technical lignins examined (Table 1.11 right).

Table 1. 11 left) Parameters of a polymer obtained by means of GPC/SEC; right) The average molecular weights (Mw) and dispersity indices (Đ, Mw/Mn) of different technical lignins [Table 1.1]

Parameter	Formula
Number-average molecular weight (Mn)	Mn= ΣiNiMi/ΣiNi where Ni is the number of polymers chain, Mi is the molecular weight of a chain
The weight average molecular weight (M_w)	M_w= ΣiNiMi ^{2}/ ΣiNiMi
Dispersity (Đ)	Đ = Mw/Mn
The Z-average molecular weight	MZ= ΣiNiMi^{3}/ ΣiNiMi ^{2}

Type of lignin	M_w (g mol^{-1})	Đ
Kraft Lignin	1000-5000	2.0-8.0
Enzymatic/Acid Hydrolysis Lignin	2000-4500	1.5-3.2
Alkali Lignin	2000-10000	2.0-5.2
Organosolv Lignin	1100-5700	1.5-4.4
Lignosulfonate	1000-50000	2.5-7.0
Steam Explosion Lignin	3500-15000	1.4-7.0

1.4.4 Spectroscopy methods

1.4.4.1 FTIR Spectroscopy

FTIR spectroscopy is a rapid, economical and nondestructive technique that is very often used in polymer studies. This is one of the most commonly used techniques for the determination of the functional groups of a lignin based on the selective absorption of radiation of specific wavelengths, which causes a change in the dipole moment of sample molecules. In the Table 4.6 FTIR assignments of the hydroxyl, carbonyl, methoxyl, carboxyl, aromatic and aliphatic C-H groups present in this polymer are reported. It is possible to obtain FTIR spectra by using several techniques. Attenuated total reflectance (ATR) is a method that directly analyses a sample, and no sample preparation is needed. It is often used for the evaluation of kraft lignin in acylation [47-48]. Another technique is diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, which is useful for characterizing powders. Both of these techniques are usually employed for the characterization of a lignin because the rapid analysis of samples does not require any preparation besides milling and only small amounts of the polymer. However, many structures overlap; therefore, multivariate analyses are often required to distinguish (and group) spectra and spectral features.

Table 1. 12 Assignment of Bands in FTIR Spectra of softwood and hardwood Milled and Wood Lignins[9]

Softwood[a](cm^{-1})		Hardwood[b](cm^{-1})		Assignment
3430	vs	3440	Vs	O-H stretch, H-bonded
2938	m	2942	M	C-H stretch methyl and methylene groups
2885	sh	2882	Sh	C-H stretch in methyl and methylene groups
2849	sh	2848	Sh	C-H stretch O-CH3 group
1717	sh	1737	Vs	C]O stretch, unconjugated ketone, carboxyl, and ester groups
1667	sh	1670	Sh	Ring-conjugated C]O stretch of coniferaldehyde/sinapaldehyde
1645	sh	1643	Sh	Ring-conjugated C]C stretch of coniferyl/sinapyl alcohol
1600	s	1596	S	Aryl ring stretching, symmetric
1513	vs	1506	Vs	Aryl ring stretch, asymmetric
1466	s	1464	S	C-H deformation, asymmetric
1458	sh	1425	M	O-CH3 C-H deformation, asymmetric
1428	m	1379	M	Aromatic skeletal vibration combined with C-H in plane deformation
1375	w	1367	Sh	O-CH3 C-H deformation symmetric
1331	sh	1330	M	Aryl ring breathing with C-O stretch
1270	vs	1252	Vs	Aryl ring breathing with C]O stretch
1226	m			C-C, C-O, and C]O stretches
1142	s	1159	Sh	Aromatic C-H in plane deformation
		1127	Vs	Aromatic C-H in plane deformation
1085	w	1082	Sh	C-O deformation, secondary alcohol, and aliphatic ether
1035	s	1050	Vs	Aromatic C-H in plane deformation
914	vw	905	W	C-H deformation of out of plane, aromatic ring
878	sh			C-H deformation of out of plane, aromatic ring
863	w			C-H deformation of out of plane, aromatic ring
823	w			C-H deformation of out of plane, aromatic ring
748	vw			CCH wag
742	vw			Skeletal deformation of aromatic rings, substituent side groups, side chains

[a] *Black spruce milled wood lignin, guaiacyl lignin.*

[b] *Aspen milled wood lignin, guaiacyl and syringyl lignin.*

[C] *vs very strong; s strong; m medium; w weak; vw very weak; sh shoulder; relative to other peaks in the spectrum.*

1.4.4.2 Raman Spectroscopy

Raman spectroscopy, as the sister spectroscopic technique of FTIR, can provide complementary information and, rather than reporting the absorption of the photons as a specific frequency, the photon frequency shift is reported. Raman spectroscopy, which is most often conducted using visible lasers, is suitable for the investigation of the chemical structure of a lignin for analysis; however, near-IR laser-based Raman spectroscopy is particularly useful (Table 1.13). Moreover, Raman microscopy is a particularly useful technique to investigate the structural changes of lignocellulosic cell walls during different pretreatments of biomass because it can provide in situ determination of the cell wall of plants even with no sample preparation. In particular, the environmental effects of the solvents in which a lignin is dissolved must be considered [49].

Table 1. 13 Assignment of Bands in FT-Raman Spectra of Softwood and Hardwood Milled Wood Lignins (MWLs) [9]

Softwooda,c (cm-1)		Hardwoodb,(cm-1)		Assignment
3071	M	3068	M	Aromatic C–H stretch
3008	Sh	3003	Sh	C–H stretch in OCH3, asymmetric
2940	M	2939	S	C–H stretch in O–CH3, asymmetric
2890	Sh	2893	Sh	C–H stretch in R3C–H
2845	M	2847	Sh	C–H stretch in OCH3, symmetric
1662	S	1661	S	Ring-conjugated C]C stretch of coniferyl/sinypl alcohol; C]O stretch of coniferaldehyde/sinapaldehyde
1621	Sh	1620	Sh	Ring-conjugated C]C stretch of coniferaldehyde/sinapaldehyde
1597	Vs	1595	Vs	Aryl ring stretching, symmetric
1508	Vw	1501	Vw	Aryl ring stretch, asymmetric
1453	M	1455	S	O-CH3 deformation; CH2 scissoring; guaiacyl/syringyl ring vibration
1430	W	1426	W	O-CH3 deformation; CH2 scissoring; guaiacyl/syringyl ring vibration
1392	Sh	1395	Sh	Phenolic O–H bend
1363	Sh	1367	Sh	C–H bend in R3C–H
1334	M	1331	S	Aliphatic O–H bend
1298	Sh			Aryl–O of aryl–OH and aryl–O–CH3; C]C stretch of coniferyl alcohol
1272	M	1272	M	Aryl–O of aryl–OH and aryl–O–CH3; guaiacyl/syringyl ring mode
1226	Vw	1224	W	Aryl–O of aryl–OH and aryl–O–CH3; guaiacyl/syringyl ring mode
1192	W	1190	W	A phenol mode
1136	M	1130	M	A mode of coniferaldehyde/sinapaldehyde
1089	W	1088	W	Out of phase C–C–O stretch of phenol
1033	W	1037	M	C–O of aryl–O–CH3 and aryl–OH
975	Vw	984	Sh	CCH and –HC]CH– deformation
928	Vw	918	Sh	CCH wag
895	Vw	899	W	Skeletal deform. of aromatic rings, substituent side groups, side chains
787	W	797	W	Skeletal deform. of aromatic rings, substituent side groups, side chains
731	W	727	W	Skeletal deform. of aromatic rings, substituent side groups, side chains
637	Vw	638	W	Skeletal deform. of aromatic rings, substituent side groups, side chains
		597	M	Skeletal deform. of aromatic rings, substituent side groups, side chains

588	Vw	588	W	Skeletal deform. of aromatic rings, substituent side groups, side chains
557	Vw			Skeletal deform. of aromatic rings, substituent side groups, side chains
534	Vw	531	M	Skeletal deform. of aromatic rings, substituent side groups, side chains
		522	Sh	Skeletal deform. of aromatic rings, substituent side groups, side chains
		503	Vw	Skeletal deform. of aromatic rings, substituent side groups, side chains
491	Vw	490	Vw	Skeletal deform. of aromatic rings, substituent side groups, side chains
		472	Vw	Skeletal deform. of aromatic rings, substituent side groups, side chains
457	Vw	461	Vw	Skeletal deform. of aromatic rings, substituent side groups, side chains
		447	Vw	Skeletal deform. of aromatic rings, substituent side groups, side chains
		431	Vw	Skeletal deform. of aromatic rings, substituent side groups, side chains

[a]*:Black spruce milled wood lignin, guaiacyl lignin.*

[b]*Aspen milled wood lignin, guaiacyl and syringyl lignin.*

[c]*vs very strong; s strong; m medium; w weak; vw very weak; sh shoulder; relative to other peaks in the spectrum.*

1.4.4.3 NMR spectroscopy

Solid-state NMR is a nondegradative technique used for the characterization of lignocellulosic biomass. However, due to the higher molecular weight, greater viscosity, and lower solubility of polymers as a consequence of short relaxation times and broadening of signals, solid-state NMR cannot currently provide sufficiently detailed information about a lignin's structure. By using particular precautions, such as an appropriate lignin isolation methodology, an appropriate instrument sensitivity and appropriate acquisition parameters, solution-state lignin NMR analysis can provide interesting information [50]. Moreover, novel techniques, which allow nondegradative dissolution of a woody material in opportune solvents such as DMSO and N-methylimidazole (NMI) followed by in situ acetylation, have been developed to eliminate degradative pretreatment, while fractionation and isolation methods of each component are accomplished (procedures responsible for the alterations in native cell wall chemistry, e.g., deacylation, oxidation, or other degradative processes) so that a lignin, as well as thepolysaccharides, can be characterized in their most native state possible without the need to separate the three fractions of biomass, i.e., whole cell wall gel-state analysis [51–52]. One-dimensional (1D) NMR methods, including ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR, the latter two only after derivatization, now become important techniques for the characterization of a lignin, providing a detailed analysis of the distribution of the functional groups and the amounts of linkages and H/G/S units as well as other components, and characteristic bonds in lignin can be qualitatively and quantitatively determined [53–54]. The chemical shifts of functional groups in a lignin in the ^{1}H, ^{13}C, and ^{31}P NMR spectra have been well established (Table 1.14). Nevertheless, 1D NMR is not exempt from drawbacks, and excessive spectral overlap deserves especially to be mentioned here. 2D NMR provides additional signal dispersion and is therefore far more versatile in terms of unambiguous signal assignment. ^{1}H-^{13}C HSQC NMR is most commonly applied for lignin characterization. Limitations of the latter technique in comparison to the former 1D methods mainly lie in the quantitiveness, which is often semiquantitative (relative) at best [52].

Table 1. 14 Assignments of signals in NMR spectrum

a: Assignments of signals in 1H NMR spectrum to typical functional groups in lignin in CD_3Cl[55].		b: Assignments of signals in ^{13}C NMR spectrum to functional groups in lignin [55].		c: Assignments of signals in ^{31}P NMR spectrum to hydroxyl groups in lignin [55].	
Chemical shift/ppm	Assignments	Chemical shift/ppm	Assignments	Chemical shift/ppm	Assignments
9.7-9.9	Cinamaldehydes and benzaldehydes	167-178	Unconjugated -COOH	145.5-150.0	Aliphatic -OH
6.7-7.1	Aromatic-H in guaiacyl	162-168	Conjugated -COOH	136.5-144.7	Phenols
6.2-6.7	Aromatic-H in syringyl	140-155	C3, C4 aromatic ether or hydroxyl	140.0-144.5	C5 substituted
5.8-6.2	Benzylic OH in β-O-4 and β-1	127-140	C1, aromatic C-C	143.5	β-5
4.9-5.1	Carbohydrates	123-127	C5, aromatic C-C	142.7	Syringyl
3.3-4.0	Methoxyl	117-123	C6, aromatic C-H	142.3	4-O-5
3.0-3.1	Hβ in β-1	114-117	C5, aromatic C-H	141.2	5-5
2.2-2.4	Phenolic OH	106-114	C2, aromatic C-H	139.0-140.0	Guaiacyl
1.6-2.2	Aliphatic OH	78-90	Aliphatic Cβ-O	138.2-139.0	Catechol
		67-78	Aliphatic Cα-O	137.3-138.2	p-Hydroxyphenyl
		54-57.5	Methoxyl	133.6-136.6	Carboxylic acid -OH

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2. Mapping and description of European networks and projects on lignin

Sustainable lignin valorization represents an important challenge for the future development of biorefineries. To meet this challenge, it is essential to promote **interdisciplinary research** and to establish a sound network of experts at the international and European levels able to share and enhance knowledge, skills and infrastructures.

In recent years, various networks and a significant number of research projects have been carried out with the aim of creating suitable exchange platforms between the various players involved in the transformation of **lignin into products with high added value.**

It is the objective of this chapter to identify new networks and research projects on lignin valorization for the industrial production of lignin-derived chemicals and compounds. The most important of these are described below.

2.1 LIGNIN NETWORKS

One of the ways to unlock the potential of lignin and to create the basis for its industrial application is networking groups of scientists and experts who have been dealing with its valorization for years.

In our journey through lignin, the existence of **a fair number of networks** emerged, the descriptions of which are provided in the paragraphs below.

ILI

The International Lignin Institute

Description, challenges & vision

The **INTERNATIONAL LIGNIN INSTITUTE (ILI)** is an international professional association, created in 1991, that has its headquarter in Lausanne, Switzerland. ILI primarily functions as a networking organization, supporting its members and the cause of lignin. The ILI is guided by the vision of a future technology for the multi-product conversion of alternative lignocellulosic plants in environmentally proper cyclic processes in which lignin is a major product, and it is used at its highest possible value. The ILI attempts to complement existing wood chemistry and chemistry institutions and promote modern R&D management concepts in terms of teamwork, partnerships and interactive, focused communications.

The ILI vision is translated into a COMMON ACTION of stakeholders in the lignin field for the efficient promotion of lignin research and introduction of lignin into markets.

Network objectives & actions

The **ILI main activities** are:

- ILI Umbrella Programme
- Norms and Standards
- Continuation of Round Robins
- Publications
- Conference and Workshops
- Eurolignin Database

Working groups and members

It is possible to become a ILI member by paying an annual membership fee that gives access to a series of membership benefits.

The basic membership in ILI gives access to the non-confidential information available to the ILI. It also gives access to the network of members and to the ILI communication system as well as to the project information reserved to ILI members. When the profile of interests for a member is known ILI might also transfer relevant information and contacts. The members can inform the ILI about developments and competencies to facilitate the role of the ILI as a clearing house for information and in specific cases as a technology transfer agent. The ILI can also function as a "matchmaker" in establishing partnerships. The **Online Newsletter** is accessible to members and is open to inputs from members in the form of articles, advertisements and announcements. ILI publications and conference proceedings are available to members at reduced cost.

Web site

https://www.ili-lignin.com

LIGNIN CLUB ECOSYSTEM

PAN-European Network on the Sustainable Valorisation of Lignin

Description, challenges & vision

The **LIGNIN CLUB ECOSYSTEM brings international industry players together to co-create a globally unique lignin ecosystem that connects technology suppliers, existing and potential producers and refiners into a single network**. It features potential end-user companies worldwide, representing sectors such as chemical, forestry, mechanical engineering, coating, biofuels and aircraft industries.

In addition to lignosulfonates and kraft lignin, there are other processes from which lignin can be extracted. For instance, second-generation ethanol production yields significant volumes of hydrolysis lignin. There are considerable opportunities in refining lignin into more value added products. The commercialization has however been a long time challenge**. One of the key points of the LIGNIN CLUB ECOSYSTEM is to accelerate lignin market development.**

Network objectives & actions

The LIGNIN CLUB ECOSYSTEM accelerates lignin market creation and empowers the success of end-user applications.

The LIGNIN CLUB ECOSYSTEM main objective is:

- **to accelerate lignin market development** by bringing together potential and existing lignin producers, end-users and technology developers.

The **LIGNIN CLUB ECOSYSTEM main actions** are:

- **to promote credible supply chains;**
- **to organize workshops and meetings;**
- **to catalyse development projects;**
- **to create application know-how to overcome the barriers of lignin commercialization.**

Working groups and members

LIGNIN CLUB ECOSYSTEM members are:

1) ANDRITZ
2) Borealis
3) CH-Bioforce
4) Chempolis Ltd
5) CMPC
6) Finnair
7) Fortum
8) Futurity
9) Graanul Biotech
10) Hexion
11) Ingenio La Unión
12) LignoPure
13) LXP Group GmbH
14) A.P. Moller Maersk
15) MetGen
16) Metsä Fibre
17) Montisera
18) Omya
19) Pöyry
20) Sappi Limited
21) SciTech-Service
22) The SILOX
23) Stora Enso
24) St1
25) synergyCom SOOO
26) Tikkurila
27) UPM
28) VTT
29) Valmet

Keywords

Lignin market development
Novel end-user lignin application

Web site

https://www.ligninclub.fi

Network details

LIGNIN CLUB ECOSYSTEM is coordinated by Pöyry Management Consulting OY and funded by participating companies and organizations

Network coordinator

AFRY Management Consulting
(former Pöyry)

Main contacts

Petri Vasara
petri.vasara@poyry.com

Hannele Lehtinen
Hannele.lehtinen@poyry.com

LignoCOST

PAN-European Network on the Sustainable Valorisation of Lignin

Description, challenges & vision

The LignoCOST is a networking Action, supported by COST. It is a PAN-European Network on the Suitable Valorization of Lignin coordinated by Wageningen Food & Biobased Research (a research institute of the Wageningen University & Research).

Lignin is a largely underexploited side stream of the pulp & paper and lignocellulosic biorefinery industry. It is a very valuable raw material for industrial applications as it contains aromatic molecules, polymer properties UV stabilization and antimicrobial activities. LignoCOST challenge concerns the creation of added value applications for lignin that lead to extra revenues for industries to make them more economical viable and sustainable.

The LignoCOST vision focuses on sharing and creating knowledge that stimulates lignin valorization towards industrial applications.

Network objectives & actions

The **LignoCOST main objective** is:

- **to establish a sound network of experts to tackle and overcome together the challenge faced in lignin industrial valorization, joining force to stimulate the commercial use of lignin in sustainable products.**

The **LignoCOST main actions** are:

- **to organize 1) Short Term Scientific Missions (STSM) between partner institutions, 2) conference grants, 3) networking events, 4) workshops and 5) training schools.**

No support is available to perform Research & Development (R&D) activities.

Working groups and members

LIGNOCOST is organized in **5 different Working Groups (WG)**:

- **WG1** is developing a **database** containing lignin literature over the last 50 years (WikiLignin);
- **WG2** is working on gathering information on **technologies** for lignocellulosic processing and lignin isolation;
- **WG3** is focusing on relevant **applications** where lignin can replace fossil-based compounds;
- **WG4** is creating **value chains for lignin valorization**;
- **WG5** is centred on technical and full **sustainability** aspects, LCA, market deployment, potential and implementation of lignin-derived end-products.

LignoCOST brings together partners with outstanding and complementary expertise and is active over the whole lignin value chain from production to applications. Currently, it has 260 participants from 36 European countries, 4 Near Neighbour_Countries and 4 International Partner Countries.

Keywords

Collaboration network on lignin uses
Lignin valorization
Novel economic lignin application
Sustainable lignin value chain
WikiLignin

Web site

https://www.lignocost.eu

Network details

Type of action	COST
Start date	04 October 2018
End date	03/10/2022
State	OPEN
EU contribution	€

Network coordinator

Wageningen Food & Biobased Research

Main contacts

Dr. Richard GOSSELINK
richard.gosselink@wur.nl

Dr. Ted SLAGHEK
ted.slaghek@wur.nl

Dr. Olena SEVASTYANOVA
olena@kth.se

Prof. Konstantinos TRIANTAFYLLIDIS
ktrianta@chem.auth.gr

LIGNOVAL

Valorization of lignocellulosic biomass side streams for sustainable production of chemicals, materials & fuels using low environmental impact technologies

Description, challenges & vision

The **LIGNOVAL is a networking Action, supported by COST**. It is a European network for the valorization of lignocellulosic biomass side streams for sustainable production of chemicals, materials and fuels using low environmental impact technologies.

The LIGNOVAL challenge lies on developing low impact environmentally sound and cost-effective lignocellulose valorization technologies to be exploited in the production of industrially relevant bio-derived chemicals, materials and fuels.

The LIGNOVAL vision is to generate a long-term effect on the transformation of the European industry towards bio-based products as a basis for a European Bioeconomy.

Network objectives & actions

The **LIGNOVAL main objective** is:

- to develop a solid European multidisciplinary network able to provide a range of innovative alternatives to the valorization of lignocellulosic residues into chemicals, fuels and materials making use of environmentally sound protocols from pretreatment/fractionation to conversion to valuable end products.

The **LIGNOVAL measurable actions** include:

- **Short Scientific Missions** (exchanges for young researchers);
- **Workshops**;
- **Training Schools..**

Working groups and members

LIGNOVAL is organized into **4 different Working Groups (WG):**

- **WG1** is concerned with pretreatment/fractionation of lignocellulosic biomass;
- **WG2** focuses on the valorization of hemicellulose derived streams (xylan/xylose);
- **WG3** concerns valorization of lignin derived streams;
- **WG4** presents LCA analysis and techno-economical perspectives.

Keywords

Lignocellulosic biomass valorization
Lignin-reach side streams

Web site

https://www.lignocost.eu

Network details

Type of action	COST
Start date	15 May 2014
End date	14 May 2018
State	CLOSED

Network coordinator

Universidad de Cordoba

Main contacts

Prof. Rafael LUQUE
q62alsor@uco.es

Prof. Konstantinos TRIANTAFYLLIDIS
ktrianta@chem.auth.gr

WAGENINGEN UR LIGNIN PLATFORM

A platform for the lignin valorization of the Wageningen University & Research (UR)

Description, challenges & vision

WAGENINGEN UR LIGNIN PLATFORM brings together unique competences covering the whole lignin value chain from lignocellulosic biomass to aromatics and other bio-based products.

Lignin is a complex natural polymer, which normally provides firmness to plant tissues. Currently, the scientific and commercial interests for aromatics and other lignin-derived products is rapidly increasing as part of the integral Biorefinery concept. In this context, **the WAGENINGEN UR LIGNIN PLATFORM aims to promote interdisciplinary research and to create a network for industrial lignin valorization aimed at the production of lignin-derived chemicals and compounds.**

Network objectives & actions

The WAGENINGEN UR LIGNIN PLATFORM main objective is:

- to promote interdisciplinary research and to create a network on the valorization of lignin for the industrial production of lignin-derived chemicals and compounds.

The WAGENINGEN UR LIGNIN PLATFORM actions are:

- to promote lignin-related research;

to implement lignin-based production processes.

Working groups and members

The WAGENINGEN UR LIGNIN PLATFORM was initiated and is coordinated by the Wageningen UR research institute Food & Biobased Research.

Currently, it is composed of a large number of outstanding scientists from quite different disciplines and a number of industrial sponsors.

Among the Wageningen UR members there are:

1) Food & Biobased Research (Wageningen UR)
2) Wageningen University
3) Plant Breeding
4) Plant Research International
5) Alterra

The WAGENINGEN UR LIGNIN PLATFORM has a number of industrial sponsors and supporters. It is sponsored by:

1) GENENCOR
2) DSM
3) ONTARIO BIOAUTO COUNCIL

and supported by:

1) StartLife
2) University of Eindhoven
3) University of Utrecht

Keywords

Lignin-related research
Industrial lignin valorization
Lignin-derived chemicals and compounds

Web site

https://www.wur.nl

Network coordinator

Wageningen UR research institute Food & Biobased Research

Main contacts

Dr. Richard GOSSELINK
richard.gosselink@wur.nl

Dr. Ted SLAGHEK
ted.slaghek@wur.nl

2.2 BBI-JU PROJETCS ON LIGNIN

Most EU-funded research and innovation projects fall within the funding provided by the Bio-Based Industries Joint Undertaking (BBI JU). The BBI JU initiative is a 3.7 billion-euro public-private partnership between the EU Commission and the Bio-based Industries Consortium (BIC). Three types of actions characterize it:

- RIA (Research and Innovation Actions)
- IA-DEMO (Innovation Actions - Demonstration)
- IA-FLAG (Innovation Actions - Flagship)

The difference consists of the different technology readiness levels (TRLs) of the developed technology. RIA projects are concerned with the development and validation of the technology (TRL3-TRL5). DEMO projects are concerned with the construction of a demo-scale production facility in Europe (TRL6-TRL7). The FLAG projects are concerned with the “first-of-a kind” application (large-scale production facility) in Europe (TRL8-TRL9).

A separate group of actions falling under the BBI-JU concerns the so-called CSA actions (Coordination and Support Actions). Any TRL may characterize these types of actions.

In all, 15 BBI-JU projects on lignin valorization were identified as follows.

The following table shows the list of projects related to the development of lignin-related technologies funded under the BBI JU initiative as RIA actions (TRL 3–TRL 5).

Project name	Feedstock type	Target products	Action (TRL)	Coordinator	Project times (duration)
BIOFOREVER	Lignosulfonate lignin	Carbon binders, FDCA, acid resins	DEMO (6-7)	API Europe (Greece)	01.09.2016 31.12.2019
EUCALIVA	Kraft lignin	Carbon fibres	DEMO (6-7)	Contactica (Spain)	01.09.2017 31.07.2021
GreenLight	Kraft lignin	Carbon fibres	RIA (3-5)	Innventia (Sweden)	01.07.2015 30.06.2019
LIBRE	Kraft lignin	Carbon fibres	RIA (3-5)	University of Limerick (Ireland)	01.11.2016 31.10.2020
LigniOx	Kraft lignin, organosolv lignin, hydrolysis lignin	Dispersants, plasticizers	DEMO (6-7)	VTT (Finland)	01.05.2017 28.02.2022
Provides	Kraft lignin	Value-added fibres	RIA (3-5)	Stichting S-ISPT, PPP (The Netherlands)	01.07.2015 30.12.2018
SMARTBOX	Kraft lignin	Aromatic lignin momomers, FDCA, polycarbonates	RIA (3-5)	Bio Base Europe Pilot Plant (Belgium)	01.05.2019 30.04.2023
SmartLi	Kraft lignin	Phenolic resins	RIA (3-5)	CLIC Innovation (Finland)	01.07.2015 30.06.2018
SSUCHY	Kraft lignin	Phenolic resins	RIA (3-5)	Université de France-Comté (France)	01.09.2017 31.08.2021
SWEETWOODS	Soda-/alkali-lignin	Polyurethanes, biochemicals	FLAGSHIP (8)	Graanul Biotech (Estonia)	01.06.2018 31.05.2023
UNRAVEL	Soda-/alkali-lignin	Lignin-based polyols for polyurethane (PUR) and polyisocyanurate (PIR) foams; sugar-based bitumen additives and chemical building blocks as malic or xylonic acid	RIA (3-5)	Fraunhofer (Germany)	01.06.2018 31.05.2022
US4GREENCHEM	Kraft lignin	Lignin-derived poliphenols	RIA (3-5)	TTZ (Germany)	01.07.2015 30.06.2019
ValChem	Kraft lignin	Glycol monopropylene, lignin-based chemicals	DEMO (6-7)	UPM (Finland)	01.07.2015 30.06.2018
WoodZymes	Kraft lignin	Phenolic resins	RIA (3-5)	CSIC (Spain)	01.06.2018 30.11.2021
Zelcor	Industrial lignin (?)	Fine chemicals (functional biopolymers, lignin oligomers. phenolic monomers)	RIA (3-5)	INRA (France)	01.10.2016 30.09.2020

SWEETWOODS

Production and deploying of high purity lignin and affordable platform chemicals through wood-based sugars

Project overview

The SWEETWOODS project aims at developing a first-of-a-kind biofractionation flagship plant in Estonia using sustainable hardwood biomass. The process combines innovative pretreatment technology with enzymatic solutions to provide recovery of sugars at levels of over 90% with exceptionally high-quality lignin. Sugars and lignin are further processed and converted into high-value biomaterials capable of replacing fossil-based chemicals in a wide range of products. In particular, dried solid lignin and depolymerized lignin are demonstrated in novel applications, namely, in elastomer foams for tube insulation, rigid polyurethane foam panels for insulation, and polymer compounds intended for injection moulding. In addition, demonstration of the conversion of high purity sugars into the production of bio-IBN, xylitol, and lactic acid production are made.

SWEETWOODS

Project objectives & expected impacts

SWEETWOODS has six core objectives. It targets to:

- develop a new technology for industrial scale production of high-purity lignin along with C5 and C6 sugars from hardwood (e.g., birch);
- use 90% of wood feedstock;
- produce high-purity lignin for a range of novel applications;
- produce high-purity sugars for novel end-uses;
- establish markets for lignin and sugar-based platform chemicals;
- develop an LCA analysis.

SWEETWOODS impacts consists in:

- **5 new bio-based value chains;**
- **4 novel bio-based materials in the areas of insulation and elastomeric foams, injection moulding, biofuels and biochemicals;**
- **80% less waste from the biorefining process.**

Flagship plant in Estonia, Imavere

Project concept

Feedstock origin	Forest-based (e.g. birch)
Feedstock type	Lignin & wood sugars
Target products	Biochemicals, insulation foams, cushions, panels etc.
Plant scale/TRL	Industrial/TRL 9 (at the end of the project)

Web site

https://sweetwoods.eu/

Project details

Type of action	IA-Flagship
Start date	01 June 2018
End date	31 May 2023
State	OPEN
BBI-JU contribution	€ 20,959,745.00

Consortium

Graanul Biotech OÜ (Estonia)
Metgen OY (Finland)
Tecnaro Gesellschaft Zur Industriellen Andwendung Nachwachsender Rohstoffe MBH (Germany)
Recticel NV (Belgium)
Global Bioenergies (France)
2B srl (Italy)
Soinverse OY (Finland)

Former member

Vertech Group (France)

Project coordinator

Graanul Biotech OÜ (Estonia)

Contact

Karl Peebo
karl.peebo@graanulinvest.com

BIOFOREVER

BIO-based products from FORestry via Economically Viable European Routes

Project overview

The BIOFOREVER project aims to demonstrate the commercial feasibility of the conversion of lignocellulosic feedstocks into chemical building blocks and high added value products.

Most specifically, BIOFOREVER addresses the techno-economic demonstration of 5 different value chains from feedstock to final product. Within this framework, several conversion technologies are demonstrated, up to pre-industrial scale, using several types of feedstock while commercialization routes for the most promising value chains are explored.

Project objectives & expected impacts

BIOFOREVER's objectives are:

- to demonstrate 5 lignocellulosic value chains at pre-industrial scale including 3 new valorization routes for co-products utilizing 4 different cascading biorefinery concepts;
- to obtain high-quality fractions (e.g., cellulose, C5/C6 sugars, specialty sugars, lignin, humins);
- to establish optimal conversion routes for building blocks and end-products (i.e., butanol, resin acid, enzymes, FDCA).

BIOFOREVER's impacts are:

- **to demonstrate direct replication potential of 4 or more biorefinery concepts;**
- **to produce competitive bio-based products in terms of cost or product performance;**
- **to validate lignocellulosic value chains.**

Bioprocess pilot refinery (Delft, NL)

Project concept

Feedstock origin	Forest-based
Feedstock type	Lignin and wood residues
Target products	Carbon binders, specialty sugars (mannose and xylose), butanol and acetone, acid resins, hydrolytic enzyme cocktail, FDCA
Plant scale/TRL	Pre-industrial scale

Web site

https://www.bioforever.org

Project details

Type of action	IA - Demonstration
Start date	01 September 2016
End date	31 December 2019
State	CLOSED
BBI-JU contribution	€ 9,937,998.02

Consortium

API Europe (Greece)
Avantium Chemicals BV (The Netherlands)
Bioprocess Pilot Facility BV (The Netherlands)
Borregaard AS (Norway)
Bio Refinery Development BV (The Netherlands)
DSM (The Netherlands)
Elkem Carbon AS (Norway)
Green Biologics Ltd (United Kingdom)
MetGen OY (Finland)
Nova Institute (Germany)
Novasep Process SAS (France)
Phytowelt Green technologies GmbH (Germany)
Port of Rotterdam (The Netherlands)
SUEZ Groupe (France)

Project coordinator

API Europe (Greece)

EUCALIVA

EUCAlyptus LIgnin VAlorisation for advanced materials and carbon fibres

Project overview

The EUCALIVA project is based on extracting high-purity soluble lignin from the kraft pulping process (black liquors) and to transform it through different lines, achieving a cost-efficient alternative to today's petroleum-based carbon fibre raw materials.

New applications are reached in EUCALIVA: multifunctional conductive, piezo-resistive and piezoelectric materials (e.g., stretchable electronics and smart fabrics from functional fibres), as well as applications based on nonwoven fabrics and their carbonized derivatives (activated carbon).

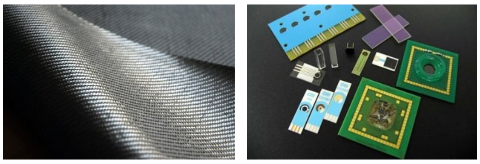
Project objectives & expected impacts

EUCALIVA's objectives are:

- to use lignin blends as a precursor material for the production of carbon-based fibres (CF), fibrous mats, stretchable films and non-wovens;
- to validate a demonstration pilot scale chain using kraft lignin for the production of precursor blends to be further processed into fibrous derivatives and to investigate new applications of the lignin fraction.
- to increase the mechanical, thermal and conductive properties of the carbon fibres derived from lignin blends to be used in structural applications such as fibre-reinforced composites (GFRP) and other derivatives, partially substituting conventional glass fibres; non-structural protective and insulating carbon-based materials, and multifunctional conductive, piezo-resistive and piezoelectric materials.
- to demonstrate the viability of the processing of lignin into carbon fibre (CF) and CF derived functional materials with customized features for the smart wearables and biosensors markets with the aim of achieving a cost-efficient alternative to today's petroleum-based carbon fibre raw material (polyacrylonitrile, PAN).
- to valorize lignin from kraft pulp mills;
- to assess via LCA the sustainability of the developed products and related processing routes.

EUCALIVA's impacts are:

- **to introduce of "lignin-to-(bio)-product" concepts at a semi-commercial scale**



Advanced products from EUCALIVA

Project concept

Feedstock origin	Forest-based
Feedstock type	Pulp & paper
Target products	Carbon fibres (CF) and CF derived functional materials
Plant scale/TRL	Demo scale

Web site

https://eucaliva.eu

Project details

Type of action	IA-Demonstration
Start date	01 September 2017
End date	31 July 2021
State	OPEN
BBI-JU contribution	€ 1,795,009.88

Consortium

Contactica SL (Spain)
Envirohemp SL (Spain)
Grado Zero Innovation srl (Italy)
Biosensor srl (Italy)
Sächsisches Textilforschunsinstitut eV (Germany)
TTY-Säätiö

Project coordinator

Contactica SL (Spain)

Contact

contactica@contactica.es

LIGNIOX

Lignin oxidation technology for versatile lignin dispersants

Project overview

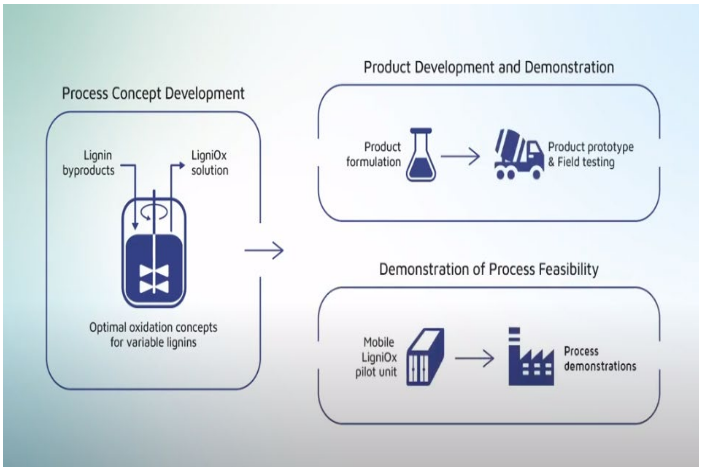
The LIGNIOX project aims to demonstrate the techno-economic viability of the unique alkali-O2 oxidation technology (LigniOx) for the conversion of several lignin-rich side-streams into versatile dispersants, and especially high-performance concrete and mortar plasticizers.

Project objectives & expected impacts

LIGNIOX's primary objective is:
- to demonstrate the techno-economic viability of the alkali-O2 oxidation process for the production of lignin-based dispersants.

LIGNIOX's overall objectives are:
- to add value to the underexploited lignin biomass side-streams;
- to provide a flexible lignin upgrading technology thus enabling lignin use in high-value products instead of energy production;
- to introduce a technology that can be readily integrated into lignocellulosic biorefineries;
- to create sustainable and cost-competitive high-performance lignin dispersants for a wide range of applications;
- to reduce GHG emissions and waste streams.

LIGNIOX's impacts are:
- **a sustainable, resource-efficient and economically feasible industrial process for the conversion of lignin-side streams to commercial bio-based products;**
- **a novel market for lignin-based high-performance plasticizers.**



LigniOx Process Concept

Project concept

Feedstock origin	Forest-based, agri-based
Feedstock type	Wood-based lignin from pulp production
Target products	Dispersants (i.e. additives that improve solutions and mixtures), plasticizers
Plant scale/TRL	Demonstration/TRL 6-7

Web site

https://www.ligniox.eu

Project details

Type of action	IA-Demonstration
Start date	01 May 2017
End date	28 February 2022
State	OPEN
BBI-JU contribution	€ 4,338,374.88

Consortium

Teknologian tutkimuskeskus VTT Oy (Finland)
Vlaamse Instelling voor Technologisch Onderzoek NV (Belgium)
Metsä Fibre Oy (Finland)
Andritz Oy (Finland)
ST1 Biofuels Oy (Finland)
Compagnie Industrielle de la Matière Végétale (France)
Dow Deutschland Anlagengesellschaft mbH (Germany)
Fortum (Finland)

Former members

Exergy Ltd (United Kingdom)
BioChemtex SpA (Italy)
Vertech Group (France)

Project coordinator

Teknologian tutkimuskeskus VTT Oy (Finland)

Contact

tiina.liitia@vtt.fi

VALCHEM

Value added chemical building blocks and lignin from wood

Project overview

The VALCHEM project aims to demonstrate at a pilot scale the techno-economic viability of producing green chemical products, such as monopropylene glycol, bio-MPG, and lignin-based performance chemicals, from wood-based raw materials. All the processes used have already been demonstrated at least at a pilot scale. The main process aims to demonstrate the valorization of over 75% of the wood-based raw material

Project objectives & expected impacts

VALCHEM has three core objectives:

- to demonstrate a sustainable and integrated process for converting wood to lignin-based performance chemicals and monopropylene glycol;
- to show that wood-based chemicals are identical to, or can perform in applications similar to fossil-based chemicals, in terms of quality and production cost;
- to perform pre-marketing for monopropylene glycol (for use in unsaturated polyester resins, paints and coatings, heat-transfer, de-icing, and personal care) and for lignin-based performance chemicals (reactive applications with a high value added).

VALCHEM's impacts consists of:

- **2-6 times higher added value of wood-based chemicals compared to traditional products;**
- **over 75% of wood raw material;**
- **increased sustainability of wood production and industrial processing.**

Demonstration plant at SEKAB in Örnsköldsvik.

Project concept

Feedstock origin	Forest-based
Feedstock type	Lignin & wood residues
Target products	Monopropylene glycol, lignin-based performance chemicals
Plant scale/TRL	Industrial/TRL 9 (at the end of the project)

Web site

https://www.valchem.eu

Project details

Type of action	IA-Demonstration
Start date	01 July 2015
End date	30 June 2018
State	CLOSED
BBI-JU contribution	€ 13,125,941.00

Consortium

UPM-Kymmene (Finland)
Sekab E-Technology AB (Sweden)
METabolic Explorer (France)
Technische Universität Dermstadt (Germany)

Project coordinator

UPM-Kymmene (Finland)

Contact

Peter Röger, UPM
peter.roger@upm.com

GREENLIGHT

Cost effective lignin-based carbon fibres for innovative light-weight applications

Project vision

The vision of GREENLIGHT project is to utilize lignin, largely available as a by-products of pulp mills, as a precursor for green and cost-efficient carbon fibres. Bio-based cost-efficient carbon fibres would enable an increased replacement of steel with carbon fibre composites in cars. This would in turn decrease the weight and fuel/electricity consumption.

Objectives & Results

GREENLIGHT's objectives are:

- to demonstrate the viability of processing lignin into carbon fibre (CF) and specific carbon fibres with structural and customized features (lightness, strength, cost-effectiveness) for the automotive industry
- to create new business opportunities and jobs in the pulp and paper industry by valorizing lignin from kraft pulp mills.

GREENLIGHT's impacts are:

- **to contribute to the increase of competitiveness of the forest-based industry in Europe;**
- **to decrease fuel consumption and GHG emissions by using lighter structural materials in the automotive sector (a 10% weight reduction means a 7% reduction in fuel consumption);**
- **to create a sustainable European industry in the production of lignin-based CF, which has applications in diverse sectors (automotive, aircraft, wind energy, etc.)**
- **to reduce the European dependence on imported CF and CF precursors;**
- **to reduce by at least 20% the greenhouse gas emissions of the production of lignin-based CF when compared to those of production of PAN-based CF.**

Project overview

Concept

Feedstock origin	Forest-based
Feedstock type	Lignin from kraft pulp mills
Target products	Carbon fibres
Action/TRL	RIA/3-5

Web site

https://greenlight-project.eu/

Project details

Type of action	Research & Innovation Action
Start date	01 July 2015
End date	30 June 2019
State	CLOSED
BBI-JU contribution	€ 1,299,163

Consortium

Innventia AB (Sweden)
Swerea SICOMP AAB (Sweden)
Sodra Skogsagarna Ekonomisk Forening (Sweden)
Faserinstitut Bremen EV (Germany)
Saechsisches Textilforschungsinstitut EV (Germany)
Fourné Machinenbau Gmbh (Germany)
Centro Ricerche Fiat SCPA (Italy)
Blatraden AB (Sweden)
Netcomposites Ltd (United Kingdom)

Project coordinator

Innventia AB (Sweden)

Contact

ewellyn.capanema@ri.se

LIBRE

Lignin based carbon fibres for composites

Project overview

The LIBRE project aims to use lignin-rich side-streams from the papermaking industry blended with a polymer precursor fibre to create a more resource-efficient and sustainable carbon fibre (CF) production process. Its ultimate aim is to create novel CF materials with a superior structure for novel potential markets. In particular, the LIBRE scope is to develop **novel precursor fibre (PF) materials from blends of modified lignin and biopolymers to be converted into carbon fibre (CF).** The obtained CF can in turn be processed into carbon fibre reinforced polymers (CFRP) for a number of industrial applications (i.e., automotive, ICT, construction).

Project objectives & expected impacts

LIBRE's main objectives are:

- to develop **novel bio-based precursor fibre (PF) from blends of modified lignin;**
- to **replace polyacrylonitrile (PAN) PF with lignin-based PF** blended with biopolymers;
- to produce biopolymers from lignin suitable for conversion to **carbon fibre (CF) that in turn** can be processed into **carbon fibre reinforced polymers (CFRP)**

LIBRE's main impacts consist of:

- **the development of new bio-based composite materials using lignin from the pulp and paper industry blended with biopolymers as a precursor;**
- **the reduction of energy consumption and GHG emissions using a novel manufacturing process based on microwave and radio frequency (MW/RF) in conjunction with novel non-metallic (MW/RF) subsectors incorporated into the PF.**

Autoclave for composite processing

Project concept

Feedstock origin	Forest-based
Feedstock type	Pulp & paper (black liquor and sidestreams)
Target products	Car parts (door and roof panels), mobile phone casing, manhole cover (construction industry)
Plant scale/TRL	

Web site

http://www.libre2020.eu

Project details

Type of action	Research & Innovation Action
Start date	01 November 2016
End date	31 October 2020
State	CLOSED
BBI-JU contribution	€ 4,566,560.00

Consortium

University of Limerick (Ireland)
C-Tech Innovation Ltd (United Kingdom)
University of Bolton (United Kingdom)
TECNARO GmbH (Germany)
Fraunhofer-Gesellschaft zur Foerderung der Angewandten Forschung eV (Germany)
Institute for Composite Materials (Germany)
Chalmers Tekniska Hoegskola (Chalmers University of Technology) (Sweden)
Centro Ricerche Fiat SCpa (Italy)
Centexbel (Belgium)
German Institutes for Textile and Fibre Research Denkendorf (DITF) (Germany)
ÈireComposites Teoranta (Ireland)
Dralon GmbH (Germany)

Project coordinator

University of Limerick (Ireland)

Contact

libre@ul.ie

PROVIDES

PROcesses for Value added fibres by Innovative Deep Eutectic Solvents

Project overview

The PROVIDES project aims to develop a radically new, sustainable and techno-economic feasible pulping technology for wood- and agro-based lignocellulose raw materials based on Deep Eutectic Solvents (DES).

The overall aim of PROVIDES is to outperform traditional pulping processes by producing the highest quality products at the lowest energy consumption and costs.

Provides
Deep Eutectic Solvents for Sustainable Paper Production

Project objectives & expected impacts

PROVIDES's objectives are:

- to develop a radically new pulping technology for wood- and agro-based lignocellulose raw materials based on DES;
- to decompose via DES lignin, hemicellulose and cellulose at low temperature and atmospheric pressure for further processing into high added-value materials and chemicals;
- to introduce novel lignin dissolving DES technology to current pulping processes.

PROVIDES's impacts consist of:

- **40% process energy intensity reduction;**
- **80% reduction in CO_2 emissions;**
- **a 50% savings in investment costs.**

Deep Eutectic Solvents (DES)

Project concept

Feedstock origin	Forest-based
Feedstock type	Cellulose lignin and wood residues
Target products	Value-added fibres
Action/TRL	RIA/3-5

Web site

http://www.providespaper.eu/

Project details

Type of action	Research & Innovation Action
Start date	01 July 2015
End date	30 December 2018
State	CLOSED
BBI-JU contribution	€ 1,079,551.00

Consortium

Stichting S-ISPT, PPP (The Netherlands)
Sappi Netherlands Services BV (The Netherlands)
WEPA Nederland BV, Van Houtum (The Netherlands)
Voith Paper GmbH & Co. KG (Germany)
Holmen Aktiebolag (Sweden)
Metsä Fibre OY (Finland)
Omya International AG (Switzerland)
Parenco BV (The Netherlands)
The navigator company SA (portugal)
Smurfit Kappa Nederland Bv (Netherlands)
Stora Enso Oyj (Finland)
Upm Kymmene Oyj (Finland)
Centre Technique De L'industrie Despapiers Cartons Et Celluloses (France)
Crown Van Gelder Nv (Netherlands)
Ds Smith Packaging Netherlands Bv (Netherlands)
Buckman Laboratories (Belgium)
Technische Univerisiteit Eindhoven (Netherlands)
Mondi Ag (Austria)
Zellstoff Poels Ag (Austria)
Mayr Melnhof Eerbeek Bv (Netherlands)
Eska Graphic Board Bv (Netherlands)
Teknologian Tutkimuskeskus Vtt Oy (Finland)
Universiteit Twente (The Netherlands)
Universidade De Aveiro (Portugal)
Celulose Beira Industrial Sa (Portugal)
Sca Tissue France (France)
Valmet Technologies Oy (Finland)

Project coordinator

Stichting S-ISPT, PPP (The Netherlands)

SELECTIVELI

Conceptual Study of Electrochemical based novel process using Lignosulfonates to produce bio-based monomers and polymers

Project vision

The SElectiveLi project aims to address the challenge of extracting high-value bio-sustainable chemicals from lignin at the lab scale, one of the most important low-cost lignosulfonate feedstocks that is largely available as a by-product of the pulp and paper industry. More specifically, using electrochemical process, it aims to produce a range of **aldehydes for potential food, adhesive, and pharmaceutical applications** as well as **intermediates for conversion into polymers**. Some, such as vanillin, can be used directly while others others are to be used to produce drugs, chemicals and plastics for everyday applications.

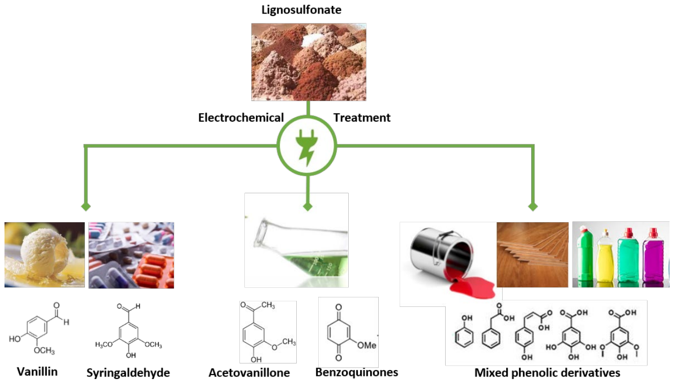
Project objectives & expected results

SElectiveLi's objectives are:

- to create and preserve jobs in Europe;
- to encourage the use of a continuous electrochemistry biorefinery system for lignosulfonate valorization;
- to develop a green and sustainable strategy opening access to basic chemicals that does not compete with food sources.

SElectiveLi impacts are:

- **to improve the efficiency of integrated biorefineries (by producing higher-value chemicals at a lower cost using less energy)**
- **to develop innovative bio-based products for identified markets (aldehydes and derivates for use in common polymers)**
- **to create and accelerate the uptake of bio-based products and applications, by supplying lignin-based products to global market.**



Project concept

Project concept

Feedstock origin	Forest-based
Feedstock type	Lignosulfonate feedstock from paper & pulp industry
Target products	Vanillin, Syringaldehyde, acetovanillone, benzoquinones, mixed phenolic derivatives
Plant scale/TRL	Laboratory scale

Web site

https://selectiveli-project.uni-mainz.de

Project details

Type of action	Research & Innovation Action
Start date	01 May 2019
End date	30 April 2023
State	OPEN
BBI-JU contribution	€ 2,497,224.00

Consortium

Johannes Gutenberg-Universitat Mainz
Sappi Papier Holding GmbH (Austria)
Vlaamse Instelling voor Technologisch Onderzoek NV (Belgium)
Optimizacion Orientada a la Sostenibilidad SL (Spain)
SINTEF AS (Norway)
Acondicionamiento Terrasense Asociacíon (Spain)
Life Cycle Engineering srl (Italy)
Chimar (Hellas) AE - Anonymi Viomichaniki Kai Emporiki Etaireia (Greece)

Project coordinator

Johannes Gutenberg-Universitat Mainz

Contact

Prof. Dr. Siegfried R. Waldvogel
+49 6131 39-26069

SMARTBOX
Selective Modifications of ARomatics Through Biocatalytic OXidations

Project overview

The **SMARTBOX** project aims to develop an advanced computational engineering platform for the simulation of **oxidative enzyme-based processes** in a biorefinery context. The platform will be applied to make a number of biorefining processes more sustainable and to create new ways of valorizing lignin and carbohydrates. More specifically, SMARTBOX aims to develop the **one-enzyme conversion of HMF into FDCA and intermediates** and **the one-enzyme conversion of lignin monomers into a potential biobased building blocks for the production of polycarbonates and vanillin.**

Project objectives & expected results

SMARTBOX's objectives are:

- to create an enhanced platform for the computationl engineering of oxidative enzymes processes;
- to scale up a new biorefinery concept that is based on <u>reductive catalytic fractionation</u> and oxidative biocatalysis to the pilot level.

SMARTBOX's impacts are:

- **to create a new cross-sectoral space using biorefineries for the flavour and fragrance industry, the polycarbonate industry and enzyme developers;**
- **to validate 3 new value chains on a pre-industrial scale: to implement a novel biorefinery approach based on <u>reductive catalytic fractionation</u> and biocatalysis, reducing the process steps by using RCF and applying only one enzyme per value chain, and to improve vanillin yields from lignin;**
- **to create a completely new value chain by creating a new biobased building block for polycarbonate production;**
- **to reduce production costs and increasing**

Bio Base Europe Pilot Plant

Project concept

Feedstock origin	Forest-based
Feedstock type	Lignin and wood residues
Target products	FDCA and intermediates, biobased building blocks for polycarbonates and vanillin
Plant scale/TRL	Pilot

Web site

http://www.smartbox-project.eu

Project details

Type of action	Research & Innovation Action
Start date	01 May 2019
End date	30 April 2023
State	OPEN
BBI-JU contribution	€ 3,924,163.00

Consortium

Bio Base Europe Pilot Plant VZW (Belgium)
Rijksuniversiteit Groningen (The Netherlands)
Zymvol Biomodeling SL (Spain)
Universidade Nova de Lisboa (Portugal)
Università degli Studi di Pavia (Italy)
Katholieke Universiteit Leuven (Belgium)
AVA Biochem BSL AG (Switzerland)
B4PLASTICS (Belgium)
Covestro Deutschland AG (Germany)
Borregaard AS (Norway)
QUANTIS (Switzerland)

Project coordinator

Bio Base Europe Pilot Plant VZW (Belgium)

Contact

Tanja Meyer, Bio Base Europe Pilot Plant
tanja.meyer@bbeu.org

SMARTLI

Smart Technologies for the Conversion of Industrial Lignins into Suitable Materials

Project overview

The SMARTLI project aims to develop valorization routes for lignin, creating materials, such as composite materials and resins, with potentials to replace fossil-based equivalents.

More specifically, the SMARTLI project adds value to underexploited technical lignin from the pulp and paper industry to replace fossil-based products in 4 product categories: thermoplastic composites, PF resins, PU foams and epoxy resins.

Project objectives & expected impacts

SMARTLI's objectives are:

- to develop and demonstrate technologies and processes to use technical lignin (kraft lignins, lignosulfonate and bleaching effluents) as raw materials to produce biomaterials, such as components with improved properties fr composites, plasticisers and different types (PU, PF, epoxy) of resins;
- to replace **25-75% of the phenol in formaldehyde resins** and at least **50-70% of the polyols in polyurethane foams;**
- to assess via LCA the economic, environmental and social sustainability of the developed products and identify a strategy for market penetration

SMARTLI impacts are:

- **to develop applications for underexploited technical lignin;**
- **to facilitate market penetration of 4 bio-based lignin-derived products: thermoplastic composites, PF resins, PU foams and epoxy resins;**
- **to reduce GHG emissions by 20%.**

SmartLi target products

Project concept

Feedstock origin	Forest-based
Feedstock type	Pulp and paper industry (black liquor)
Target products	Thermoplastic composites, PF resins, PU foams and epoxy resins
Action/TRL	RIA/3-5

Web site

https://clicinnovation.fi/activity/smartli/

Project details

Type of action	Research & Innovation Action
Start date	01 July 2015
End date	30 June 2018
State	CLOSED
BBI-JU contribution	€ 1,481,258.00

Consortium

CLIC Innovation (Finland)
Tecnaro Mbh (Germany)
Aep Polymers srl (Italy)
Fraunhofer Gesellschaft zur Forderung der Angewandten Forschung EV (Germany)
De Vlaamse Instelling Voor Technologisch Onderzoek NV (Belgium)
Metsa Fiber OY (Finland)
Teknologian Tutkimuskeskus VTT OY (Finland)
SAPPI (The Netherlands)
Foresa Industrias Quimicas del Noroeste Sa (Spain)
Kompetenzzentrum Holz Gmbh (Austria)
Prefere Resins Finland OY (Finland)
Kotkamills OY (Finland)
Andritz OY (Finland)

Project coordinator

CLIC Innovation (Finland)

Contact

Tejia Laitinen
tejia.laitinen@clicinnovation.fi

SSUCHY

Sustainable structural and multifunctional bio-composites from hybrid natural fibres abd bio-based polymers

Project overview

The SSUCHY project aims to develop of composite constituents, based on a renewable resource (i.e. biopolymers and plant fibre reinforcements) for the development of multifunctional recyclable and/or biodegradable bio-based composites with advanced functionalities for application in different sector: transportation (ground transportation and aerospace) and high value market niches such as the acoustic and electronic sectors. It is dedicated to the development of specific concepts, technologies and materials to achieve a complete value chain and prove the principle at the scale of product demonstrators.

Project objectives & expected impacts

SSUCH's objectives are:

- multifunctional bio-based composites;
- hemp-based competitive reinforcement;
- hybrid fibre reinforced composites;
- bio-based functionalized and optimized polymers for FCs;
- **tailored lignin derived monomers for high-grade polymers.**

SSUCHY's impacts are:

- **to set the basis and validate new bio-based constituents for composites;**
- **to propose new composites structures and products from these bio-based constituents and demonstrate their advanced functionalities at the demonstration scale.**

Development of bio-based composites for structural applications - prototypes:

High performance green loudspeaker system

Bio-based monocoque structure for electric scooter

Bio-based interiors for electric aircraft

Bio-based floor and trim panel structures for automotive applications

Application fields

Project concept

Feedstock origin	Forest-based, agri-based
Feedstock type	Lignin, crop residues and wood residues
Target products	Bio-based core and composite materials, polymer materials
Action/TRL	RIA/3-5

Web site

https://www.ssuchy.eu/

Project details

Type of action	Research & Innovation Action
Start date	01 September 2017
End date	31 August 2021
State	OPEN
BBI-JU contribution	€ 4,457,194.75

Consortium

Université de Franche-Comté (France)
Association Industries et Agro-resources (France)
Katholieke Universiteit Leuven (Belgium)
University of Bristol (United Kingdom)
Centre national de la recherché scientufuque CNRS (France)
Stockholms universitet (Sweden)
École nationale d'ingénieurs de Tarbes (France)
Akzo Nobel Functional Chemicals BV (The Netherlands)
Linificio e Canapificio Nazionale srl (Italy)
CERA ApS (France)
Wilson Benesch Ltd (United Kingdom)
Eadco GmbH (Germany)
NPSP BV (The Netherlands)
École nationale supérieure des arts et industries textiles (France)
University of Derby (United Kingdom)
Université Dijon Bourgogne (France)
Università Cattolica del Sacro Cuore (Italy)

Project coordinator

Université de Franche-Comté (France)

UNRAVEL

UNique Refinery Approach to Valorise European lignocellulosics

Project vision

The UNRAVEL project aims to develop advanced pretreatment, separation and conversion technologies for complex lignocellulosic biomass. The technology relies on pre-extraction, fractionation using low-temperature acetone and subsequent downstream processing to isolate and convert the lignocellulosic constituents for high-value applications. This will produce usable lignin fragments and monomeric sugars from the cellulose along with a hemicellulose fraction suitable for biochemical conversions.

Project objectives & expected results

UNRAVEL's objectives are:

- to develop a pre-extraction process optimized for mixed lignocellulosic biomass streams;
- to achieve at least 80% delignification, 90% glucan recovery, 80% yield of monomeric hemicellulose sugars and less than 1% solvent loss;
- to achieve at least 95% lignin recovery and 99% (non-condensed) solvent recovery from the liquor;
- to develop an economically viable process for purifying the hemicellulose hydrolysate to ferment the hemicellulose sugars effectively into chemical building blocks;
- to achieve over 90% sugar conversion, over 20% reduction of hydrolysis time and 20% reduction of enzyme dosage compared to cellulose alone;
- to demonstrate the low inhibitory effect of the C5 and C6 hydrolysate produced by fermentation;
- to activate and depolymerise lignin from the FABIOLA process;
- to establish a series of high-value lignin applications.
- to show a 30% reduction in operating expenses through lower overall energy consumption and cost as compared with a benchmark pretreatment process;
- to demonstrate an overall reduction of at least 15% of the carbon footprint compared with the state-of-the-art bio-based operation.

UNRAVEL's impacts are:

- **to create a new cross-sector interconnection among the forestry and/or pulp and paper industry, biotechnology industry and building and/or construction material industry;**
- **to establish a new value chain using a mixture of different lignocellulosic biomasses to produce extractives, lignin-based polyols and chemical building blocks for the sugar fractions.**

Concept

Feedstock origin	Forest-based
Feedstock type	Lignin & wood residues
Target products	Lignin-based polyols for polyurethane (PUR) and polyisocyanurate (PIR) foams; sugar-based bitumen additives and chemical building blocks as malic or xylonic acid
Plant scale/TRL	Pilot

Web site

http://unravel-bbi.eu

Project details

Type of action	Research & Innovation Action
Start date	01 June 2018
End date	31 May 2022
State	OPEN
BBI-JU contribution	€ 3,603,545

Consortium

Fraunhofer-Gesellschaft zur Förderung der Angewandten Forschung eV (Germany)
Celignis Ltd (Ireland)
MetGen OY (Finland)
Soprema (France)
Stichting Energieonderzoek Centrum Nederland (The Netherlands)
Institut fur Energieund Umweltforschung Heidelberg GmbH (Germany)
Rita Clancy EURIDA (Germany)
Centre National de la Recherche Scientifique CNRS (France)
Sappi Lanaken (Belgium)
Max-Planck-Gesellschaft zur Förderung der Wissenschaften eV (Germany)

Project coordinator

Fraunhofer-Gesellschaft zur Förderung der Angewandten Forschung eV (Germany)

US4GREENCHEM

Combined Ultrasonic and Enzyme Treatment of Lignocellulosic Feedstock as a Substrate for Sugar Based Biotechnological Applications

Project overview

The US4GREENCHEM project aims to design a biorefinery concept for the complete valorization of lignocellulosic biomass that is energy- and cost-efficient and based solely on green technologies.

More specifically, US4GREENCHEM combines mechanical pretreatment methods with ultrasound pretreatment for the disruption of the lignocellulosic matrix with reduced energy input and minimal production of inhibitory by-products.

Project objectives & expected impacts

US4GREENCHEM's objectives are:

- to design a biorefinery concept for the **complete valorization of lignocellulosic biomass**;
- to develop **ultrasound (US) pretreatment** to disrupt the lignocellulosic matrix;
- to maximize the release of **sugars**;
- to develop purification and conversion strategies for **lignin-based products**;
- to valorize the **solid residues**;
- to **reduce the cost of enzymatic hydrolysis** of cellulose fibres by 50%;
- to propose an effective integration and **upscaling to a pilot scale**.

US4GREENCHEM impacts are:

- to develop a new technology for converting lignocellulosic biomass into **high-quality sugars and lignin-derivatives** that will be further used in industrial applications.

Pilot plant, Finland

Project concept

Feedstock origin	Forest-based, agri-based
Feedstock type	Lignin, crop residues and wood residues
Target products	Sugars, lignin-derived polyphenols
Plant scale/TRL	50L, expected capacity 50kg biomass/day

Web site

http://www.us4greenchem.com/

Project details

Type of action	Research & Innovation Action
Start date	01 July 2015
End date	30 June 2019
State	CLOSED
BBI-JU contribution	€ 3,457,602.50

Consortium

TZZ (Germany)
Università degli Studi di Torino (Italy)
Weber (Germany)
Environmental Systems GmbH (Germany)
VTT (Finland)
UAB Biocentras (Lithuania)
LSIWC (Latvia)
Tecnalia (Spain)
Jowat AG (Germany)

Project coordinator

TZZ (Germany)

Contact

info@us4greenchem.eu

WOODZYMES

Extremozymes for wood based building blocks: from pulp mill to board and insulation products

Project overview

The WOODZYMES project aims to develop extremozymes (enzymes able to function under extreme environments) and extremozyme-based processes for the valorization of underutilized lignin and hemicellulose fractions of kraft pulp mills.

More specifically, WOODZYMES covers the entire **value chain** from forest biomass (hardwood and softwood) to phenolic and sugar-derived equivalents of fossil-derived chemicals for the manufacture of **medium density fibreboard (MDF), polyurethane (PU) insulation foam and bleached paper**, through the transformation of the underutilized lignin and hemicellulose fractions extracted from pulp mills with **tailor-made extremophilic enzymes**.

Project objectives & expected impacts

WOODZYMES's objectives are:

- to develop **extremozymes** adapted to industrial operation conditions (high temperature and pH) by screening and protein engineering that will be applied as biocatalysts in the wood conversion sector;
- to use the developed extremozymes for the production of **lignin-derived phenols** and **hemicellulose-derived sugars**;
- to obtain new **medium-density fibreboards** and **polyurethane materials** by using lignin-based resin precursors and phenols and to use hemicellulose-derived sugars as **papermaking additives**;
- to evaluate the **technical, environmental and socio-economic feasibility** of the previous objectives.

WOODZYMES's impacts are:

- **to illustrate the potential of extremozymes in the global bio-based economy by contributing to the sustainability and competitiveness of cellulose and board and polyurethane manufacture;**
- **to reduce the use of petro-chemical products and non-renewable materials in the building sector and furniture industry.**

Project concept

Feedstock origin	Forest-based
Feedstock type	Lignin and wood residues
Target products	Paper, fibreboards, insulation foams
Action/TRL	RIA/3-5

Web site

htpps://www.woodzymes.com/

Project details

Type of action	Research & Innovation Action
Start date	01 June 2018
End date	30 November 2021
State	OPEN
BBI-JU contribution	€ 3,253,874.00

Consortium

Agencia Estatal Consejo Superior de Investigaciones Cientificas (Spain)
MetGen OY (Finland)
Centre Technique du Papier - CTP (France)
Institut Technologique Forêt Cellulose Bois-construction Ameublement – FCBA (France)
Instituto de Investigação de Flosta e Papel – RAIZ (Portugal)
The Navigator Company SA (Portugal)
FINSA France SAS (France)
Soprema (France)
Fibre Excellence Saint-Gaudens SAS (France)

Project coordinator

Agencia Estatal Consejo Superior de Investigaciones Cientificas (Spain)

Contact

Dr. Susana Cameraro
susanacam@cib.csic.es

ZELCOR

Zero Waste Ligno-Cellulosic Biorefineries by Integrated Lignin Valorisation

Project overview

The ZELCOR project aims to demonstrate the feasibility of transforming lignocellulose recalcitrant side-streams into high added-value bio-based products, including fine chemicals. It addresses three types of recalcitrant raw materials: lignocellulosic residues from ethanol production, lignins dissolved during the pulping process and lignin-like humins formed by sugars conversion.

Its concept is to combine chemical and enzymatic catalysis with insects-based biological conversion, within a biorefinery-integrated approach.

Project objectives and expected impacts

ZELCOR's main objective is:

- to demonstrate the feasibility of transforming recalcitrant by-products, namely, lignin- and humins-rich streams, into high added-value bio-based products, including fine chemicals.

The specific driving idea is to combine chemical and enzymatic catalysis with microbial bioconversion to develop an integrated flexible biorefinery system for the conversion of these heterogeneous and variable by-products.

ZELCOR's main impacts are:

- **to optimize the economic value from agricultural residues;**
- **to valorize the lignin fraction of lignocellulosic biomass by creating valuable products, while reaching at least a 3-fold value increases compared to the current energy value;**
- **to create 3 new bio-based products from lignin;**
- **to establish 2 convergent routes for the production of valuable bio-based products from lignin**
- **to improve the overall value chain.**

Project concept

Feedstock origin	Forest-based, agri-based
Feedstock type	Lignin and wood-residues, agri-food industrial sidestreams
Target products	Functional biopolymers, lignin oligomers, and phenolic monomers
Action/TRL	RIA/3-5

Project concept

Feedstock origin	Forest-based, agri-based
Feedstock type	Lignin and wood-residues, agri-food industrial sidestreams
Target products	Functional biopolymers, lignin oligomers, and phenolic monomers
Action/TRL	RIA/3-5

Depolymerised lignin fractions

Web site

https://www.zelcor.eu

Project details

Type of action	Research & Innovation Action
Start date	01 October 2016
End date	30 September 2020
State	CLOSED
BBI-JU contribution	€ 5,256,993.00

Consortium

Institut National de la Recherche Agronomique - INRA (France)
Aalto-yliopisto (Finland)
Ardilla Technologies UK Ltd (United Kingdom)
Arterra Bioscience srl (Italy)
Avantium Chemical BV (The Netherlands)
Biome Bioplastics (United Kingdom)
Inra Transfert (France)
Institut National de l'Environnement Industriel et des risques – INERIS (France)
Nova Institut (Germany)
Quantis SARL (Switzerland)
Sabic (The Netherlands)
Food and Biobased Research – FBR (The Netherlands)
Tereos (France)
Université Paris-Est Crétel Val de Marne (France)
University of Warwick (United Kingdom)
W42 Industrial Biotechnology GmbH (Germany)
Ynsect (France)

Project coordinator

Institut National de la Recherche Agronomique - INRA (France)

Contact

stephanie.baumberger@versailles.inra.fr

OTHER PROJECTS

A significant number of lignin projects are funded at European level outside the classic funding mechanisms (H2020, BBI JU) and see the participation of cutting-edge companies, universities and research institutes that work together with the intent to create successful synergies.

Some of the most important projects on lignin are mentioned below.

ARBOREF

Refining of Wood to Aromatics

Project overview

The ARBOREF project intends to propose a bio-refinery for aromatics, describing chemical routes for the production of some essential aromatics from renewable raw materials such as wood and grasses.

Central to the project is a recently developed KU Leuven technology, which converts wood into high yields of mono-phenols (from lignin), and a fixed (hemi) cellulose pulp. Useful aromatics will be produced from both fractions in this project. On the one hand, the phenols are reduced to building blocks that can be used in the polyurethane, polyester, polyamide, polycarbonate and phenolresin industry. On the other hand, the sugar pulp is also used for the production of aromatics such as benzene, styrene, and terephthalic acid. The ultimate ambition is to set up a biorefinery, which produces aromatics from timber with 90% carbon efficiency.

Project objectives & expected impacts

The ARBOREF multidisciplinary project will work on the following issues and challenges:

- **production of both new and drop-in molecules of industrial interest, within a novel 'lignin-first' biorefinery technology;**
- **full valorization of soluble phenolic fraction and solid carbohydrate pulp.**

The overall ambition of the project is to integrate the production of aromatics, with focus on both new and drop-in molecules of industrial interest, within a novel 'lignin-first' biorefinery technology developed at KU Leuven, which is capable of converting entire lignocellulosic biomass feedstock into a soluble phenolic fraction and a solid carbohydrate pulp fraction. Hereto, the project suggests fermentative and chemical synthesis pathways to convert both fractions to the aromatic chemicals in an atomic efficient manner.

Web site

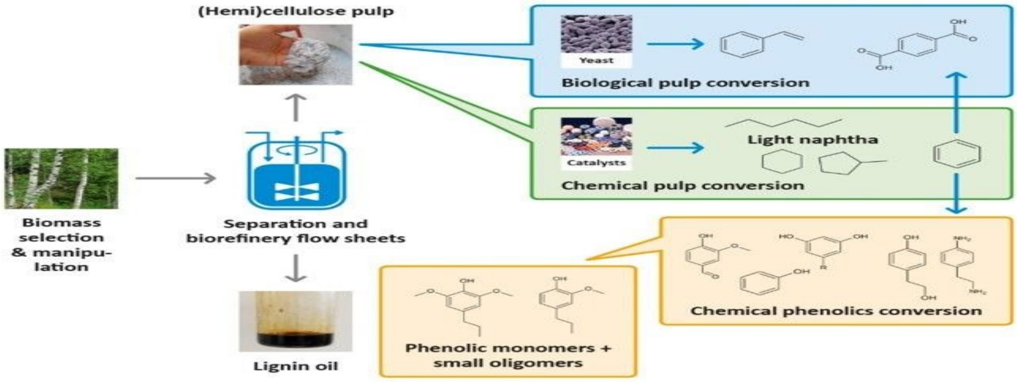
https://catalisti.be/project/arboref/

Project details

Project type	SBO
Start date	01 April 2015
End date	31 March 2019
State	CLOSED
Total budget	€ 2,999,555

Project concept

Feedstock	Wood and grasses
Lignin type	Kraft lignin
Target products	Aromatics, phenols



Project overview

BAFTA

Refining of Wood to Aromatics

Project goal

The BAFTA project seeks to initiate the first steps in closing the virtual "valley of death" between research and industrial scale, thereby focusing on the general aim of the transition towards a biobased chemical industry in Flanders using lignocellulosic feedstock. The target group of companies that will benefit from this project are found throughout the value chain of bio-aromatics (from paper, wood, and waste treatment companies as a primary/secondary source for feedstock, over producers of polymers or fine-chemicals based on phenolic compounds, to formulators in the area of adhesives, UV-stabilizers, dyes, inks, coatings).

The main goals of this project are fivefold. First, a technology mapping for the conversion of lignin and wood biomass into useful chemical building blocks will be done. Secondly, a feedstock overview will be worked out both quantitative and qualitative for three different types, being virgin wood, waste wood and lignin. Another goal is creating a clear overview of the IP landscape and freedom-to-operate for conversion technologies of lignin and wood biomass. This will lead to the selection of 2 most promising technologies per feedstock (lignin and wood) based on a decision support framework. A detailed analysis of the two selected technologies per feedstock and recommendations for future research and follow-up projects will be provided. The last goals is the sampling of 4 different technologies at kg-scale and characterization of obtained samples on both stability and reproducibility.

Web site

https://catalisti.be/project/renewable-chemicals/bafta/

Project details

Project type	SBO
Start date	01 April 2015
End date	31 March 2019
State	CLOSED

BIO-HArT

Biorizon Innovation and Upscaling of Renewable Aromatics Technology

Project overview

The cross-border project BIO-HArT, acronym in Dutch for “Biorizon Innovation and Upscaling of Renewable Aromatics Technology”, was set out in 2016 to scale up technology for the production of bio-aromatics from biomass, focusing specifically on woody biomass sources. By the end of 2018 this must result in functioning bench-scale demonstrators and optimized processes with which samples can be provided to the industry on a kilogram scale.

Interreg
Vlaanderen-Nederland

Project objectives & expected impacts

The BIO-HArT project is the next step in the industry-driven roadmap of Biorizon. **The project has three objectives:**

- **to develop optimised procedures for the chemical reactions and the conversion and separation processes.**
- **To realize of generic and multi-purpose process setups for three technologies (wood, sugars and lignin to aromatics).**
- **to manufacture of test samples of sugars, lignin, furans, alkylphenols, mono-, di- and tri-acids, functionalised phenols and other aromatic compounds. In collaboration with industry applications will be developed based on these test samples.**

The project was realized thanks to a contribution of the European program Interreg V Flanders-Netherlands that stimulates innovation, renewable energy, a healthy environment and the labor market through cross-border projects.

Web site

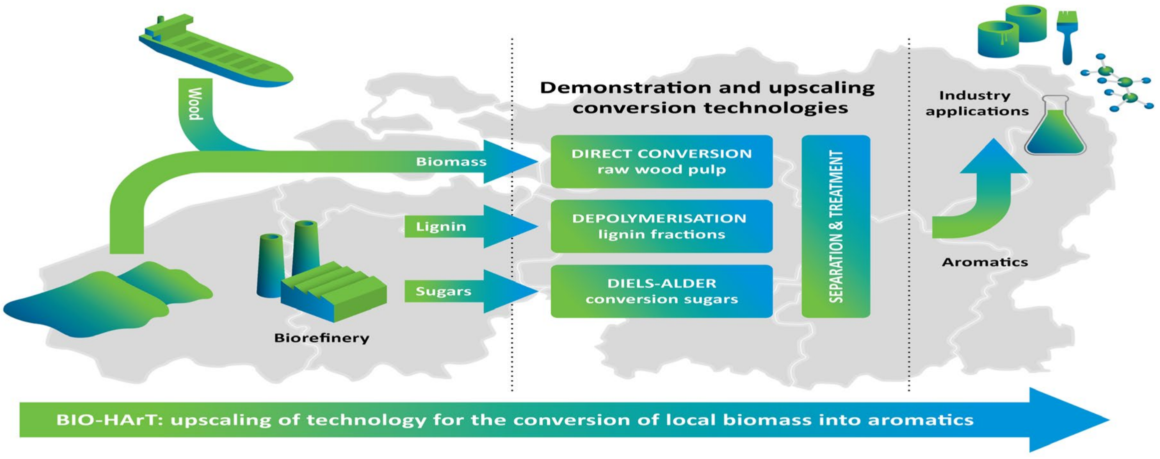
https://www.biorizon.eu/bio-hart

Project details

Project type	SBO
Start date	01 April 2015
End date	31 March 2019
State	CLOSED
Total budget	€ 6.085.445,38 I
Interreg contributes	€ 3.042.722,69

Project concept

Feedstock	Wood
Lignin type	Kraft lignin
Target products	Aromatics



A visual impression of the BIO_HArT project

Partners: TNO innovation for life, vito vision on technology, DSM, Chemelot InSciTe, Maastricht University, KU Leuven, TU/e, University of Antwerp, avantium, Bio Base Europe Pilot Plant

MAIA

Manufacturing of Advanced & Innovative Bio-Aromatics

Project goal

The overall goal of MAIA is to fully utilize the natural functionality of biomolecules by catalytically converting preferably waste wood and flax shives into solubilized proto-lignin fractions and a solid (hemi-)cellulose pulp with a main focus on the production of aromatic molecules with a maximized amount of (hydroxyl) functionalities and a (hemi-)cellulose fraction suitable for further processing into paper or functional sugars. This altered scheme for the biorefinery of wood, compared to existing paper mills, intends to maintain the reactivity of the derived molecules by producing a limited variety of bio-aromatic compounds. In this project the waste wood and flax shive refinery will be fine-tuned in function of several selected applications represented by 5 industrial partners, such as dispersion agents and emulsifiers, resins for ink, foundry, refractory and wood modification, wood adhesives, UV-stabilizers and flavours.

AGENTSCHAP INNOVEREN & ONDERNEMEN
Vlaanderen is ondernemen

Beaulieu International Group
CHEMSTREAM SUSTAINABLE CHEMISTRY
COBALIN
LAWTER
2nGs
TFC
KU LEUVEN
vito

Web site

https://catalisti.be/project/maia/

Project details

Project type	SBO
Start date	01 September 2015
End date	31 August 2017
State	CLOSED
Total budget	€ 937,901
Subsidy	€ 765,006

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8. https://bioforever.org/
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14. https://ispt.eu/projects/provides/
15. https://selectiveli-project.uni-mainz.de/
16. https://www.smartbox-project.eu/
17. https://clicinnovation.fi/project/smartli/
18. https://www.ssuchy.eu/
19. http://unravel-bbi.eu/
20. https://www.us4greenchem.com/
21. https://www.woodzymes.eu/
22. https://zelcor.eu/
23. https://catalisti.be/project/arboref/
24. https://catalisti.be/project/renewable-chemicals/bafta/
25. https://www.biorizon.eu/bio-hart
26. https://catalisti.be/project/maia/

3. Lignin-derived products

The lignin structure enables its use as a feedstock for many biobased products that can replace many corresponding fossil based products and materials.

Figure 3.1 displays the main lignins estimated market costs, market volumes and lignin-derived products. Low-cost and more abundant lignins are suitable for low-cost applications, including energy production. Lignins with higher costs are more suitable for higher value-added applications, including the production of chemical derivatives.

Table 3.1 lists the main biobased products that can be produced from lignins along with production technologies, target market sectors, lignin preferentially employed and TRL.

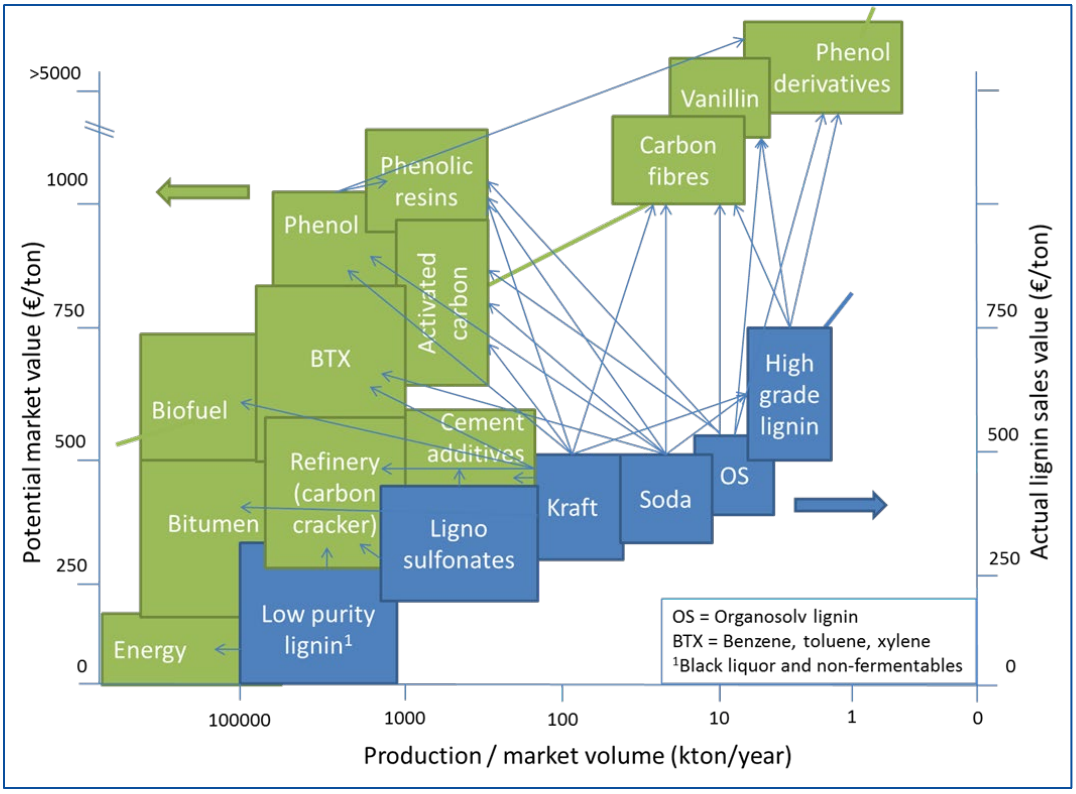


Figure 3. 1 Estimated 2016 market value for the main lignin and lignin-derived products. (Reproduced from Ref. [3]).

*Table 3. 1 Main products from **lignin platforms** ordered in macro-categories, their industrial use, technologies and processes. The products in the grey cells, which have a greater market exploitation and/or innovation perspectives, have been selected for a detailed description in the present document.*

Macro-category	Product	Sub-product/application	Sector	Preferred lignin type	Technologies	Ref.	TRL
Polymeric Materials	**Dispersants**	**Lignin-based Asphalt**	Building	Lignosulfonates and kraft (alkali-oxidated)	Blends with Asphalt	[17-28]	5
		Concrete modifier			Almost direct use	[14, 29-35]	5
		Drilling muds modifier	Oil extraction	Lignosulfonates	Almost direct use	[37-42]	5
		Agricultural chemicals	Agriculture	Lignosulfonates and kraft (alkali-oxidated)	Almost direct use of a selected molecular weight range of pure lignin	[12-16]	7
		Dyes	Textile, Cosmetic				
		Carbon black in battery electrodes	Automotive				
	Phenolic resins	Panels	Building, Furnishings	Kraft, Organosolv, Soda	Phenolic unit activation and polymerization (partial substitution of traditional resins)	[7, 43-88]	8
		Plywood, Laminates	Building, Furnishings				
		Food packaging	Packaging				
	Polyurethane	Foam	Building, Furnishings, Automotive	Kraft, Organosolv, Soda	Polyol reactivity improv. and di-isocyanate reaction (lignin polyol chains extension: hydropropylation, glycerol and glycerol deriv. grafting, etc.)	[89-138]	6
		Panels	Building				
		Coatings	Building, Electronic				
		Rubber replacing	Apparel				
	Blends with PE, PP, PET, etc.	Coatings, Plastic	Food, Animal feed, Agriculture	Kraft, Organosolv, Soda	Blends improving the existing technology	[139-156]	9
		Displays	Electronic				
Electro-chemical applications	**Energy storage applications**	Additive in electrodes, flow-batteries, supercapacitors	Building, automotive	Lignosulfonates	Lignosulfonate-functionalized graphene hydrogels, Lignosulfonate with single-walled carbon nanotubes and cellulose hydrogels	[157-165]	5
BTX (Benzene, Toluene, Xylenes)	**Chemicals**	Solvents, Monomers, Fuels	Industry (synthesis, solvents, etc.), Automotive, Transport	Kraft (biomass)	Pyrolysis, Hydrothermal treatments, Hydrodeoxygenation, Separation	[169 – 223]	4-6
Fuels	**Hydrocarbons**	Automotive fuels (light hydroc.)	Automotive, Transport	Kraft, Organosolv, Soda (biomass)	Pyr., Gasification, sequential Pyr/HDO	[224-255]	5
		Jet-fuels (Alkyl benzene related)	Aircraft, Transport				5
	Aromatic rich pyr. oil (petroleum like)		Refinery products (fuels, chemicals)				5
	Syngas (CO, H2, CH4)		Power production				9
Carbon Fibres			Automotive, Steel repl.	Kraft, Organosolv, Soda	Lignin modif. (filaments), blends (PAN, other poly.)	[256-259]	5
Activated carbon/Biochar		Agricultural amendment	Agriculture	Lignosulfonates, Kraft, Organosolv, Soda	Pyr., Gasification	[1-3, 6, 8-10, 12, 14, 29, 50, 52, 54, 73, 86, 125, 221-224, 253, 256, 258]	6-8
Aromatic lignin monomers	**Quinones**	Solvents, Polym. building block	Industry (synthesis, solvents, etc.)	Kraft, Organosolv, Soda	HTU (acid and alkali cat), HDO + Separation and Purification Technologies		3-5
	Benzylic aldehydes	Solvents, Polym. building block	Industry (synthesis, solvents, etc.)				5
	Phenols	Solvents, Polym. building block	Industry (synthesis, solvents, etc.)				5-7
	Aromatic alcohols	Solvents, Polym. building block	Industry (synthesis, solvents, etc.)				5
	Vanillin	Spice production	Food	Lignosulfonates	Lignin oxidation (Borregaard process)		9
Mixed organic acids	**Short chain acids, di-acids, -OH acids**	Solvents, Polym. building block	Industry (synthesis, solvents, etc.)	Kraft, Organosolv, Soda	Lignin oxidation process + Sep. In addition, Pur. Technol.		5

3.1 POLYMERIC MATERIALS

Lignin exploitation for polymers started after 2010. The main applications include thermoplastic polymers and asphalts, components for polyurethanes, and phenolic or epoxy resins. In 2010, a systematic study used principal component analysis (PCA) to assess the utilization and applicability of different lignins to obtain polymeric materials [4].

The main driver of lignin utilization is the need to reduce the exploitation of natural fossil resources and mitigate climate change [5, 6].

The main obstacles still hindering the development of industrial initiatives are not the absence of suitable technological innovations but the lack of promotional initiatives [7]. It is necessary to develop new business models bridging the gap between the laboratory and the market [8], perform environmental analyses that demonstrate economic feasibility and sustainability [9], and build networks and industrial organizations that cross-operate together at the regional to world scale [10].

Among the polymeric materials derived from lignin, the main categories selected for a detailed description are:

- Dispersants
- Phenolic resins
- Polyurethanes
- Blends with PE, PP, PET, etc.

A shorter description will be provided for the remaining products in Table 3.1.

3.1.1 Dispersants

The uses of lignin in dispersants are well known [11] but continue to attract scientific interest, leading to the development of novel patents and new products. Lignin-based dispersants can decrease their fossil component and can improve the viscosity and fluidity of products such as asphalt, concrete, drilling muds for oil recovery and agricultural chemicals [12]. Other applications requiring **high lignin purity are dyes for textiles** [13] **and carbon black in battery electrodes** [14]. Some additional applications require fine tuning of the molecular weights (ranging from 10000 to 30000 g/mol), as reported for some inkjet [15] and coal-water-slurry (CWS) formulations [16].

A focus will be provided for **asphalt, concrete** and **drilling muds that are** closely related to the oil market.

3.1.1.1 Lignin-based asphalt

The practical uses of lignin/bitumen mixtures for road paving were probably suggested due to their structural similarities and started at least forty years ago [17]. The final aim was the production of new asphalts in which bitumen is partially replaced by renewable resources with improved properties against thermal, UV and mechanical stresses and higher durability than commercial products [18–21]. In addition to the need to reduce the carbon footprint associated with human activities and products, the development of this application can be supported by the expected scarcity of bitumen in the future due, for instance, to the limited availability of fossil resources, closure of oil refineries and to the more attractive alternative use of bitumen for the production of lower hydrocarbon chains.

In the Netherlands (NL), the first experimental trials paving roads with lignin-based asphalt were carried out in mid-2015 [19]. More recently, asphalt improvement was also part of a national TKI project [22], coordinated by Wageningen Food & Biobased Research (NL) and called "CHAPLIN" (Collaboration in asphalt applications with LIgniN). As part of the CHAPLIN work programme, some roads and cycling paths (see Fig. 3.2) **have been paved with bioasphalt, where 50% of conventional bitumen has been replaced with three types of technical lignin** (Soda, Kraft, Hydrolysis). This asphalt, according to patent WO2019/092278 [23], is produced in commercial asphalt plants. This technology has been demonstrated at TRL of 6-7.

Figure 3. 2 Cycling path paved with lignin-based asphalt at Wageningen campus in 2017

The first project data, referred to as the "kraft lignin trials", showed a bioasphalt that is more resistant to environmental stresses and has better characteristics than fossil asphalt in terms of noise reduction, rolling resistance and brake deceleration [24]. The estimated CO_2 emissions reduction percentage with respect to fossil asphalt is more than 20%.

3.1.1.1.1 Market (Lignin-based asphalt)

Global bitumen demand is expected to increase by 2.8 percent per year to 122.5 million tons [25]. In Europe, the estimated bitumen consumption in 2018 was less than 15 Mton [26].

Figure 3.3 presents an analysis of the data made available by the United Nations (UN) [27] on bitumen consumption in Europe from 1990 to 2018. The data show an oscillating trend until 2010 followed by a decrease in the following years.

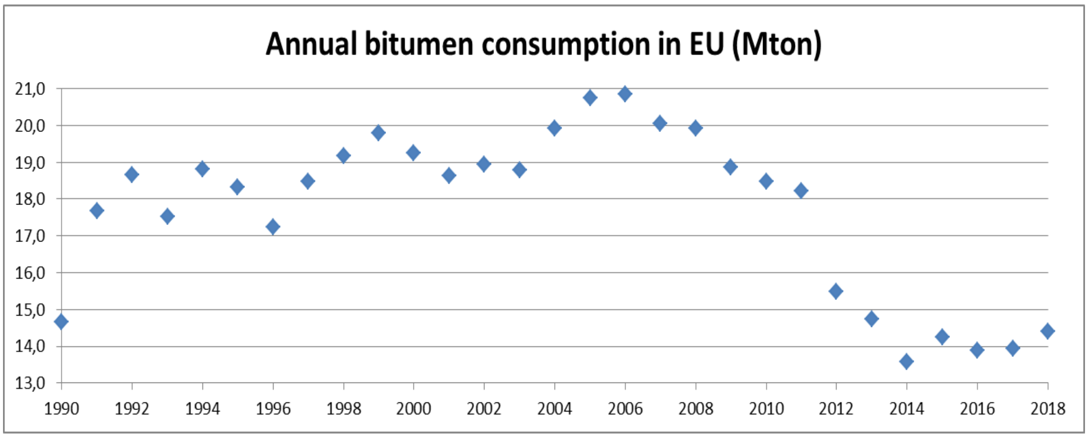


Figure 3. 3 Bitumen consumption in Europe from 1990 to 2018 (data collected from an online UN database [27])

This trend is presumably at least partially explained by periodic maintenance (every 6 years) of roads combined with a decrease in road construction. Between 2010 and 2014, the consumption of bitumen decreased, perhaps due to the diminished need to build new roads. The trend over the past 6–8 years shows a new flatter oscillating trend.

The COVID crisis has led to an increase in home work and cycle mobility. In the coming years, this effect could further decrease bitumen consumption. On the other hand, driving in your own car gives safety perceptions, and this will probably increase future road traffic. Figure 3.4 shows the FCD-Floating Car Data (collected by traffic satellites) in Rome from February to June 2020 [28]. The traffic seems to rapidly return to the pre-crisis levels.

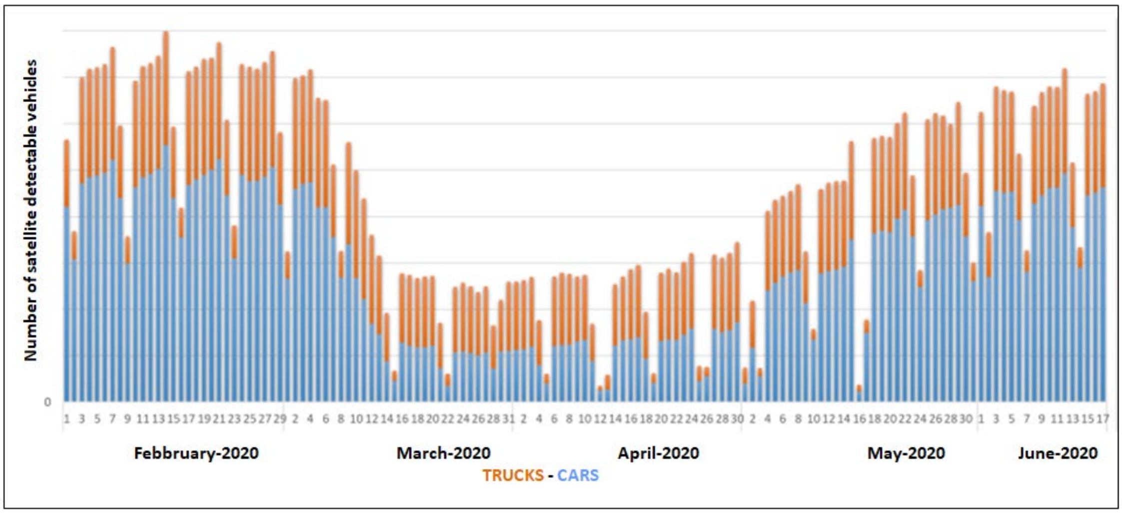


Figure 3. 4 Satellite detected road traffic data in Rome from February to June 2020

3.1.1.1.2 Patents (Lignin-based asphalt)

Table 3.2 shows the 30 main patents issued in the last 5 years sorted by publication date related to the applications of lignin for asphalt mixtures. The WIPO patent, shown in bold, proposes the replacement of up to 50% bitumen with lignin. Clusters of patents are reported on a coloured background.

Table 3. 2 Patents, selected by keywords on the ORBIT Patents DataBase [36], concerning the lignin applications for asphalt published in the last 5 years (the WIPO-Patent is shown in bold, while patent-clusters are presented on coloured backgrounds) – Acronyms: L/M (Large industry/Multinational), E/C (Enterprise/Company), U/RO (University/Research Organization), I (Inventor), CHN (China), NL (The Nederlands), IT (Italy), DK (Denmark).

Title	Applicant(s)	Applicant(s) business and country (acronym)		Publication number	Publication date	Patent org.
Anti-freezing asphalt mixture and preparation method thereof	BEIJING LINGBEI ROAD BUILDING MATERIALS	E/C	CHN	CN111268944 (A)	12/06/2020	China
Lignin hydrogenated oil copolymer asphalt modifier and preparation method thereof	GUANGDONG YIHE KEJIE TECHNOLOGY	E/C	CHN	CN110872451 (A)	10/03/2020	China
Asphalt anti-stripping agent as well as preparation and application methods thereof	CHENGDU LUTAI HIGH TECHNOLOGY ENGINEERING TECHNOLOGY RESEARCH INSTITUTE SICHUAN KELUTAI TRAFFIC TECHNOLOGY	U/RO	CHN	CN110734649 (A)	31/01/2020	China
Lignin asphalt modifier	GUANGDONG YIHE KEJIE TECHNOLOGY	E/C	CHN	CN110511574 (A)	29/11/2019	China
Additive composition for bituminous conglomerates with high mechanical performances	ITERCHIMICA S R L	E/C	IT	TW201922900 (A)	16/06/2019	Taiwan
Lignin-based bio-asphalt	**ASFALT KENNIS CENTRUM** **STICHTING WAGENINGEN RESEARCH**	**U/RO**	**NL**	**WO2019/092278 (A1)**	**16/05/2019**	**WIPO**
High-strength asphalt concrete and preparation process thereof	SHANGHAI SHISHEN INDUSTRY & TRADE	L/M	CHN	CN109574552 (A)	05/04/2019	China
Bio-based asphalt road ice suppressing agent and preparation method thereof	SHENZHEN PROSPEROUS NEW MATERIAL SCIENCE & TECHNOLOGY	E/C	CHN	CN108753255 (A)	06/11/2018	China
Asphalt improving material with anti-coagulation and cold resistant function	BEIJING OUMEIZHONG SCIENCE & TECHNOLOGY RESEARCH INSTITUTE	U/RO	CHN	CN108410189 (A)	17/08/2018	China
Anti-aging wear-resistant cement-emulsified asphalt mixture	BEIJING OUMEIZHONG SCIENCE & TECHNOLOGY RESEARCH INSTITUTE	U/RO	CHN	CN108395726 (A)	14/08/2018	China
Root-resistant waterproof lignin-modified asphalt sheet and production method thereof	GUANGXI WUXUAN JINPAI WATERPROOF MATERIAL TECHNOLOGY	E/C	CHN	CN108099320 (A)	01/06/2018	China
Flame-resistant waterproof lignin-modified asphalt roll and production method thereof	GUANGXI WUXUAN JINPAI WATERPROOF MATERIAL TECHNOLOGY	E/C	CHN	CN108099314 (A)	01/06/2018	China

Lignin modified asphalt waterproof coiled material and preparation method thereof	GUANGXI WUXUAN JINPAI WATERPROOF MATERIAL TECHNOLOGY	E/C	CHN	CN108068419 (A)	25/05/2018	China
Asphalt waterproof coating and production method thereof	GUANGXI WUXUAN JINPAI WATERPROOF MATERIAL TECHNOLOGY	E/C	CHN	CN108003791 (A)	08/05/2018	China
Waterproof coating of bridge deck and preparation method thereof	GUANGXI WUXUAN JINPAI WATERPROOF MATERIAL TECHNOLOGY	E/C	CHN	CN107987725 (A)	04/05/2018	China
Lignin and coupling agent synergistic type modified asphalt waterproof coil and preparation method thereof	GUANGXI WUXUAN JINPAI WATERPROOF MATERIAL TECHNOLOGY	E/C	CHN	CN107984853 (A)	04/05/2018	China
Bitumen compositions comprising lignin	INBICON	E/C	DK	US2018346658 (A1)	06/12/2018	USA
Carbon products derived from lignin/carbon residue	GRAFTECH INTERNATIONAL HOLDINGS	L/M	USA	US20180282166 (A1)	04/10/2018	USA
Novel polymer mixture for road and preparation method thereof	BEIJING UNIVERSITY OF CIVIL ENGINEERING & ARCHITECTURE	U/RO	CHN	CN108083699 (A)	29/05/2018	China
Biological asphalt and preparation method thereof	BEIJING ZHONGLU GAOKEHIGHWAY TECHNOLOGY RESEARCH INSTITUTE OF HIGHWAY MINISTRY OF TRANSPORT	U/RO	CHN	CN107916122 (A)	17/04/2018	China
High-performance asphalt additive	LIUZHOU BOZE TECHNOLOGY	E/C	CHN	CN106995613 (A)	01/08/2017	China
Asphalt modifier and preparation method thereof	LIUZHOU BOZE TECHNOLOGY	E/C	CHN	CN106977967 (A)	25/07/2017	China
Sodium lignosulfonate grafted magnesium-aluminum-based LDH (layered double hydroxide) modifier, ultraviolet-aging-resistant SBR (styrene-butadiene rubber) modified asphalt and preparation method of ultraviolet-aging-resistant SBR modified asphalt	WUHAN UNIVERSITY OF TECHNOLOGY	U/RO	CHN	CN106832973 (B)	28/06/2019	China
Alkali lignin-grafted magnesium aluminum-based layered double hydroxide modifying agent, anti-ultraviolet anti-ageing SBS modified asphalt and preparation method thereof	WUHAN UNIVERSITY OF TECHNOLOGY	U/RO	CHN	CN106800673 (B)	05/02/2019	China
Lignin grafted magnesium aluminum-based layered double hydroxide modifier, anti-ultraviolet ageing asphalt and preparation method thereof	WUHAN UNIVERSITY OF TECHNOLOGY	U/RO	CHN	CN106700579 (B)	12/07/2019	China

Lignin polyamine cation rapid-cracking type asphalt emulsifier and preparation method thereof	SHANDONG UNIVERSITY	U/RO	CHN	CN105968382 (B)	20/03/2018	China
Lignin polyamine quaternary ammonium salt cationic asphalt emulsifier and preparation method thereof	SHANDONG UNIVERSITY	U/RO	CHN	CN105885060 (B)	20/03/2018	China
Lignin diamine cationic asphalt emulsifier and preparation method thereof	SHANDONG UNIVERSITY	U/RO	CHN	CN105860092 (B)	16/03/2018	China
Bitumen composition	TNO	U/RO	NL	WO2015137813 (A1)	17/09/2016	WIPO
Asphalt insect-proof and water-proof roll	BENGBU NANZI INSTRUMENT	E/C	CHN	CN105038271 (A)	11/11/2015	China

The patents from China are quite numerous with a limited extension in China. These patents include clusters of patents reporting few modifications of the same invention proposed by the same applicant. With the exception of both WIPO patents proposing at least 25% to 50% bitumen replacement with lignin, the other patents mainly concern asphalt additives or modifiers employing limited amounts of lignin-derived products (lignin pyrolysis oil, black liquor salts resulting after lignin separation) or lignin (or lignosulfonates). Often, to obtain these modifiers, lignin was chemically upgraded and then mixed with other components. Rarely, there is a real direct lignin effect on asphalt. Its effect is deduced or is a minor effect with respect to the other bulk components.

The only cluster of patents reporting a 50% lignin replacement was proposed by "GUANGXI WUXUAN JINPAI WATERPROOF MATERIAL TECHNOLOGY" (six patents related to the same asphalt in which different properties or uses are recognized). The paving described in one of these six patents has a "…five-layer structure and comprises, from top to bottom, a top isolating layer, an upper root-resistant lignin-modified asphalt layer, a padding layer, a lower root-resistant lignin-modified asphalt layer and a bottom isolating layer". The lignin-modified layers contain 50% phenolated lignin. Among the older patents (2015) reported in the table, one deals with an asphalt roll containing 10–20% of components that are almost fossil-free in which a maximum of 2% is epoxidized alkali-lignin. This roll is "insect-proof" thanks to the minimal content of "sodium sulfaquinoxaline" (antimicrobial) and chili powder, which "…can effectively prevent insect damage".

3.1.1.2 Concrete modifiers

Plasticizers are often added into concrete mixtures to disperse cement particles and enhance flow properties to use low water contents and obtain stronger concrete. In the case of lignin-derived plasticizers, the functional sulfonic and carboxylic groups interact with cement, determining particle repulsion.

To date, the largest utilization of lignosulfonates [14] is in concrete mixtures, with an estimated volume of 700,000 tons annually [29].

Unmodified alkali lignins [30] have shown good performance as plasticizers, but lignin treatments enhancing their superplasticizer properties have also been reported. One of the most promising treatments proposes oxidation with oxygen (5–40 bar) under alkaline conditions (pH range of 12.7–13.4), which introduces carboxylic acid groups and depolymerizes lignin into lower molecular weight products.

Detailed descriptions of the laboratory processes are available in [31].

3.1.1.2.1 Market (Concrete modifiers)

The global production of plasticizers had a market size of approximately USD 5 billion in 2019 and is forecast to be USD 10 billion within the next 5 years. The key market players operating in concrete conventional superplasticizers are listed in Table 3.3. Their most frequently employed technology is based on polycarboxylate superplasticizers in ready-mix concrete [32–33].

Table 3. 3 Key players operating in the concrete conventional superplasticizer market

Market main players on conventional superplasticizers	***Country***
Arkema	France
Sika	Switzerland
BASF	Germany
GCP Applied Technologies	US
Mapei	Italy
Kao Corporation	Japan
Enaspol	Czech Republic
Concrete Additives and Chemicals	India
Rhein-Chemotechnik	Germany
Rain Carbon	US

New lignin-based plasticizers and biobased polycarboxylate superplasticizers are ready for the market [34]. Table 3.4 contains the world's leading suppliers of lignin-based products to the Concrete Admixture Industry [35].

Table 3. 4 Worldwide leading suppliers of lignin-based products to the Concrete Admixture Industry

Market main players of bio-based plasticizers	***Country***
Borregaard LignoTech	US
Sika	Switzerland
Ingevity	US
KMT lignin	UK

3.1.1.2.2 Patents (Concrete modifiers)

Strong scientific and industrial interest in this field can be inferred from Table 3.5, displaying 22 recent patents concerning lignin applications for concrete preparation. Figure 3.5 includes images of the application described in patent N° WO2015/049424 (A1). This lignin-based superplasticizer was obtained by the consortium of the EU project "LignOX" and was also registered at the end of 2018 in China (CN105705475).

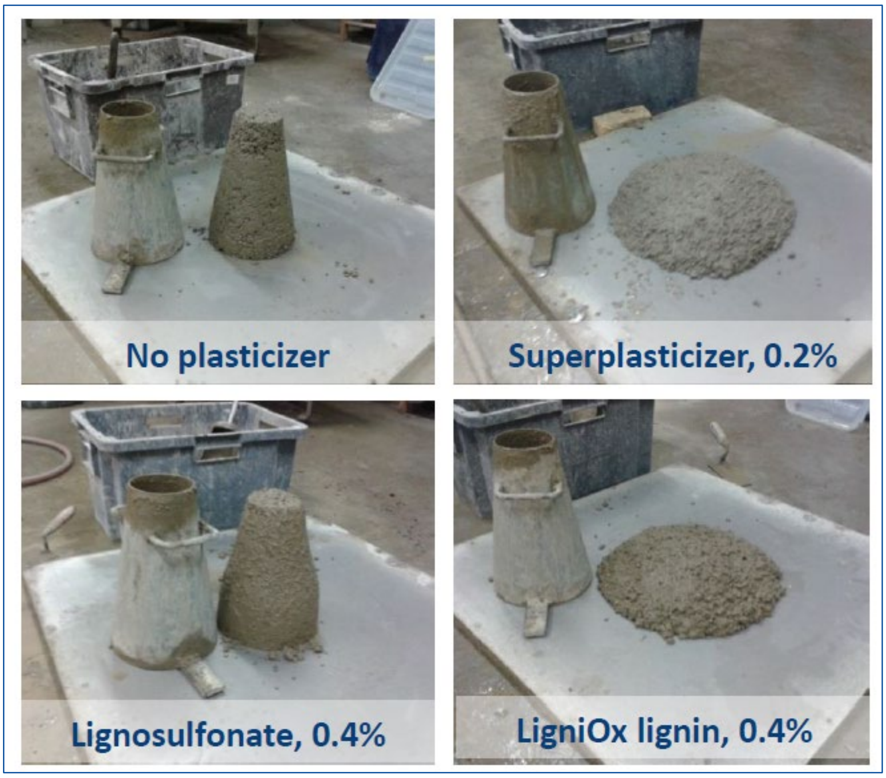


Figure 3. 5 Performance of the lignin-based superplasticizer LignOX

Table 3. 5 Patents selected by keyword on the ORBIT Patents DataBase [36], concerning the lignin applications on concrete technology published in the last 5 years (some patents belonging to the main bioplasticizers producers are shown in bold) – Acronyms: L/M (Large industry/Multinational), E/C (Enterprise/Company), U/RO (University/Research Organization), I (Inventor), WIPO (World Intellectual Property Organization)

Title	**Applicant(s)**	**Applicant(s) business and country**		**Publication number**	**Publication date**	**Patent org.**
Lignocellulose type cement grinding aid and preparation method thereof	HUIZHOU SANHUA NEW TECH CO LTD	E/C	China	CN109320129 (A)	12/02/2019	China
Method for producing lignocellulose mixture for reinforcing cement material	SUMITOMO FORESTRY	L/M	Japan	JP2019014620 (A)	31/01/2019	Japan
Method for preparing superplasticizer from lignin	ZUNYI GUKUANGBA BUILDING MAT CO LTD	E/C	China	CN109180046 (A)	11/01/2019	China
Lignin-based foam concrete foaming agent	GAO ZHIMING	I	China	CN108947311 (A)	07/12/2018	China
Polycarboxylic acid superplasticizer based on lignin based polyether monomer as well as preparation method thereof and application thereof to concrete	UNIV SOUTH CHINA TECH	U/RO	China	CN107964073 (B)	27/04/2018	China
High-strength cellulose/lignin composite material with reinforced concrete structure and preparation method thereof	UNIV SOUTH CHINA TECH	U/RO	China	CN107042559 (B)	15/08/2017	China
Alkali-O2 oxidized lignin as dispersant	TEKNOLOGIAN TUTKIMUSKESKUS VTT OY	U/RO	Finland	WO2017077198 (A1)	11/05/2017	WIPO
Lignin foam concrete foaming agent and preparation method thereof	ANHUI GEYI CYCLIC ECONOMY IND PARK CO LTD	E/C	China	CN106542764 (A)	29/03/2017	China
Lignin mud-resistant sacrificial agent, preparation method thereof, and application thereof in concrete	UNIV SOUTH CHINA TECH	U/RO	China	CN106279705 (B)	04/01/2017	China
Method for preparing cement water reducer from lignin	ANYANG HUASEN PAPER CO LTD	E/C	China	CN106046392 (A)	26/10/2016	China

Method for preparing biologically-modified composite lignin cement grinding aid	LEI CHUNSHENG	I	China	CN105481284 (A)	13/04/2016	China
Modified lignosulfonate superplasticizer and preparation method thereof	JIANGSU MINGHE GROUP CO LTD	E/C	China	CN105271886 (A)	27/01/2016	China
Milling aid for cement clinker based on polycarboxylate ethers and/or lignosulphonates	**SIKA TECHNOLOGY AG**	**L/M**	Switzerland	**MX2015005614 (A)**	**06/11/2015**	**Mexico**
Research on synthetic condition of lignosulfonate modified polycarboxylate superplasticizer	QINGDAO HUICHENG PETROCHEMICAL - TECHNOLOGY CO LTD	E/C	China	CN104672409 (A)	03/06/2015	China
Novel lignin concrete modifier	QINGDAO DESHENGTAI CONSTRUCTION AND INSTALLATION ENGINEERING CO LTD	E/C	China	CN104609762 (A)	13/05/2015	China
Lignin concrete modifier	QINGDAO DESHENGTAI BUILDING INSTALLATION ENGINEERING CO LTD	E/C	China	CN104556792 (A)	29/04/2015	China
Use of oxidized lignin as a dispersant	**TEKNOLOGIAN TUTKIMUSKESKUS VTT**	**U/RO**	**Finland**	**WO2015/049424 (A1)**	**09/04/2015**	**WIPO**
Ammoxidized lignosulfonate cement dispersant	**LIGNOTECH USA INC**	**L/M**	**US**	**US6238475 (B1)**	**29/05/2001**	**USA**
Low retarding, high fluidity producing lignin dispersant for concrete	**LIGNOTECH USA INC**	**L/M**	**US**	**WO0136344 (A3)**	**25/05/2001**	**WIPO**
Cement compositions and biodegradable dispersants therefor	**HALLIBURTON ENERGY SERV INC - LIGNOTECH U S A INC**	**L/M**	**US**	**US6019835 (A)**	**01/02/2000**	**USA**
Improved lignosulfonate concrete additive	**SIKA AG**	**L/M**	Switzerland	**JPH10167788 (A)**	**23/06/1998**	**Japan**
Lignin-based cement fluid loss control additive	**WESTVACO CORP**	**L/M**	**US**	**US4926944 (A)**	**22/05/1990**	**USA**

3.1.1.3 Drilling mud modifiers

Drilling muds are well-known technological solution that are able to improve the effectiveness of oil well perforation and extraction operations. Their composition usually contains polymeric compounds and surfactants acting on the viscosity and on the oil droplet entrapment [37].

Due to the presence of charged groups in their complex polymeric matrix**, lignosulfonates have been a resource for the oil drilling industry since the 1980s** [38]. It was found that 50% of commercial drilling muds could be replaced by lignosulfonates without compromising the surfactant performance [39].

Among the lignosulfonates, those containing divalent cations (principally Ca^{2+}) in mixed petroleum sulfonate/lignosulfonate systems could remarkably improve the interfacial tension and the specific conductivity, changing the coalescence behaviour of oil droplets [40, 41].

3.1.1.3.1 Market (Drilling mud modifiers)

The growing demand for crude oil and natural gas in various energy-intensive industries has urged exploration companies to increase their investments in drilling activities [42]. The global drilling fluid market size was valued at USD 8.0 billion in 2019, with an expected growth rate of 4.2% from 2020 to 2027. Figure 3.6 presents the U.S. market size projection.

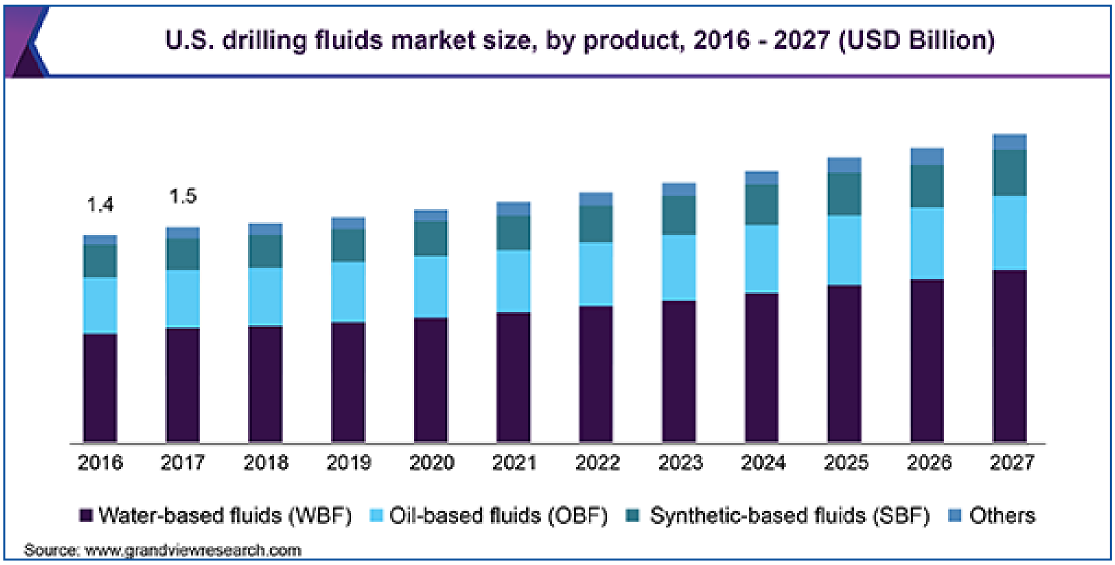


Figure 3. 6 U.S. drilling fluid market size (2016-2027 expressed in USD Billion)

However, growing concerns about the limitations of fossil resources and the environmental impact of drilling fluids have prompted regulatory bodies in various regions to issue strict regulations regarding the use, disposal and treatment of waste. Furthermore, the consequences of COVID-19 on the global economy and on the drilling fluid market have not yet been studied extensively, but it will likely reduce global mobility and the oil industry market. These problems could change the economic forecasts presented above.

Bio-based drilling fluids derived from biomass have been used since the 1980s. Their use covers approximately 10% of the size of the global market for this product. In addition, biobased solutions applied to the drilling fluid market represent the smallest part (approximately 10%) of the size of the global market for biobased dispersants.

3.1.1.3.2 Patents (Drilling mud modifiers)

Due to the maturity of the technology related to the use of lignin in the production of drilling muds, combined with a decreasing interest for applications in the oil extraction sector, patents published in this field in recent years are few and have limited geographical coverage. There were 11 main patents in the last 5 years, among which only one was published in 2019, the WIPO patent by “NIPPON PAPER INDUSTRIES” [36]. This patent, WO201939609 “Lignin derivative compound and use thereof”, addresses a new lignin derivative compound (obtained by the reaction between a lignosulfonate compound and a water-soluble aromatic compound) that can act as a dispersant of various substances (cements, dyes, oil drilling muds, etc.).

3.1.2 Phenolic resins

Lignin has a phenolic structure that can be exploited for the production of phenol-formaldehyde (PF) resins that are mainly used as wood adhesives. Inclusion of lignin within the binder components not only replaces part of the fossil-derived phenols but can also reduce formaldehyde emissions in some applications during manufacturing and also during the life of wood panels [43].

However, compared to pure phenols, lignin has a lower reactivity towards formaldehyde due to its high molecular weight and steric hindering. To overcome this limitation, lignin currently only replaces part of the PF-resin phenol content, and it is typically treated to increase the phenol functionalities.

Among the available biomass feedstocks, softwoods are more suitable than hardwoods to produce lignin-based phenol-formaldehyde (LPF) resins due to their specific structure, which has a higher number of nonhindered reactive phenolic units [44, 45]. In the case of LPF resin, the total released heat is lower than that of the commercial PF resin, reflecting both the **lower reactivity and homogeneity** of the LPF system [46, 47].

Lignin reactivity in condensation reactions can be increased through chemical (methylolation [48] and phenolation [49]), enzymatic (through the use of laccase and oxidase enzymes [50]) and thermochemical (i.e., mild hydrogenolysis [51] and pyrolysis [52, 53]) approaches. Improvements in reactivity can also be achieved through the thermal dehydration of residual sugars in lignin to form reactive furan aldehydes derivatives [54, 55].

Among the lignin activation processes, the enzymatic processes overall require low energy inputs and are solvent free [1]. Batog and Przepiera [50] tested this approach on technical lignins exploiting laccase with electron exchange mediators (see Figure 3.7).

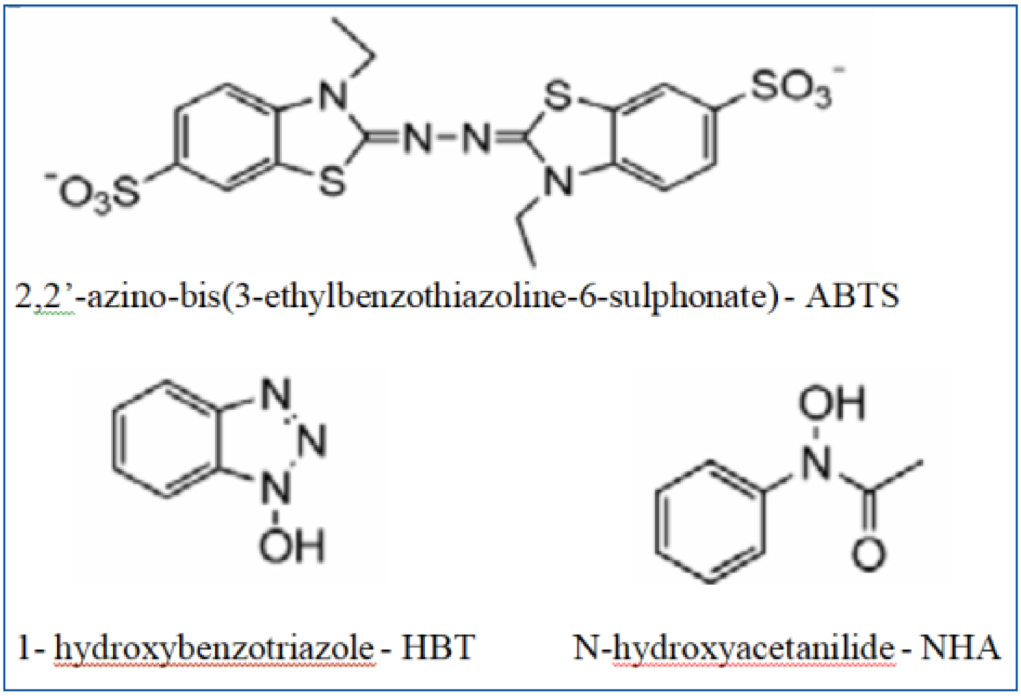


Figure 3. 7 Laccase mediators

A wood board was produced with bonding strength in the range of 10–20 MPa, almost without fossil-based resins (a petroleum-based binder was present up to 6%). However, the cost and nonrecyclability of enzymes can be limiting factors.

Table 3.6 lists the main technical features of the main lignin-based PF resins obtained from various sources of lignins.

Table 3. 6 Main technical features of PF resins classified on lignin employed as the starting material.

Lignin	Advantage	Disadvantage	Phenols replacement threshold and process	Technical feature	Main applications	Ref.
Lignosulfonates	• Low market price • High molecular weight increases the bonding properties	Less water resistant than fossil based products (up to 30%)	• Typical replacement: 30%- 50%. • Typical reaction conditions includes alkaline condensation with formaldehyde	Bonding strength (ply wood): 0.8-1.2 MPa; 30% substitution already ensures improved workability and thermal resistance.	Plywood	[46, 47, 56-61]
Kraft lignin	• Medium market price • High molecular weight increases the bonding properties	Activation or depolymer. process needed	Typical repl. up to 50% Two steps process: (1) depolymerized lignin Mw 800-1700 g/mol, phenol, NaOH sol., and methanol at 60 °C; (2) formalin addition (37 vol.% formaldehyde water sol.) 80 °C	Higher water resistance than the commercial resins OSB panels: elasticity and rupture limits, comparable with fossil products.	Plywood, OSB panels, high pressure laminates	[45, 58, 62-64]
Organosolv Lignin	High number of free phenolic units,	• Low ramifications and low molecular weight. • Lignin is not a side stream product; high lignin cost	Typical replacement up to 30%; following an activation process the replacement grow to 75%	LPF resins with high replacement (50%-75%) have adhesive prop. and thermal stability comparable to fossil products	Wood panels	[48, 49, 51, 65, 66]

Hydrolysis Lignin	Side stream product in existing plants, low market price	Low percentage of phenolic units available for condensation	Replacement up to 50% (Formaldehyde/Phenolic-units molar ratio of 1.5), needed activation (phenolation)	LPF resins up to 50% show adhesive strength higher than commercial resins.	Plywood	[67, 68]
Soda Lignin	Exploitation of non woody biomass	High molecular weight requiring chemical hydrolysis	Typical replacement: 30%- 50%. Activation through oxidation, and or reduction, and or acid hydrolysis (HCl 35%)	Shorter gel time and a lower curing temperature.	Not specified wood adhesive	[69-71]
Steam Exploded Lignin	Self-binding properties due to free phenol-like and furfural-like molecules following the thermal activation, low market price	Few exposed phenolic units available on lignin structure because of the phenomena of inter and intra –lignin condensation due to the heating	Self condensation enhanced by the sugars impurities	Products achieved through self-adhesion processes do not fulfil the minimum requirements for any board type of the EU standard	Hot-pressed boards	[72, 55]

In addition to the most abundant lignin obtained through pulp and paper operations, novel sources of lignin exploitable as feedstocks for resin production can be achieved through **biorefineries** based on sugar platforms [1, 63, 64].

Technical data on biomass pretreatment by steam explosion and enzymatic approaches are provided in Tables 3.7 and 3.8.

Table 3. 7 Steam explosion pretreatments were applied to some biomass feedstreams to activate lignin as a binder for the production of fossil resin-free wood panels.

Feedstock	Process notes	Set-up for the production of panels (explored ranges or optimized values)			Ref.
		T (°C)	Time (min)	P (MPa)	
Miscantus	Steam temperature explored range: 196–236 °C, in the time range: 1-8 min.	130-230	1,6-18	12	[75]
Miscantus	The optimal pretreatment condition was 203 °C for 7,35 min (achieved in [75]). The mechanical properties of the panels at a pressing temperature of 130 °C were improved by adding commercial Kraft lignin in the range of 13,2–46,8% (w/w on dry biomass)	120-170	3-8	12	[76]
Wheat straw	Acid impregnation of biomass with sulfuric acid 0,75% (w/w on dry biomass) and treatment Fenton's reagent and water peroxide. Pretreatment in a 1500 rpm rotating grooved disk performing pressure (0.5 – 0.7 MPa) and heating (170–190 °C) gradients in 3 min	203	1,5	0,5	[77]
Banana bunch	Severity parameter (log R0) of the steam explosion in the range: 3.16–4.84	133-217	5+5 (two steps)	4-14	[78]
Cynara cardunculus	Steam temperature explored range:160–240 °C, in the time range: 2,5 – 12,5 min	190-230	1-9	4-20	[79]
Vitis vinifera	Steam temperature explored range:160–240 °C, for a duration of 2,5–12,5 min. Commercial alkaline lignin at 15% (w/w on dry biomass) improved the mechanical properties but reduced the water absorption and the thickness swelling	190-210	3-7	8-16	[80]
Vitis vinifera	Optimize pretreatment conditions were 218 °C for 6 min ([80]). Commercial softwood kraft lignin at 15% (w/w on dry biomass) improved all the main properties	205	4+5 (two steps)	12	[81]

Table 3. 8 Enzymatic pretreatments applied to some biomass feedstocks to activate their lignin as a binder for the production of fossil resin-free wood panels. The presented data have been collected among the most cited publications that have at least one tested experimental wood particle board that complies with the main European standards for at least one of the intended uses.

Feedstock	**Lignin enzymatic activation**	**Set-up for the production of panels (explored ranges or optimized values)**			**Ref.**
		T (°C)	**Time (min)**	**P (MPa)**	
Beecch fibres	**Preheating of fibres** at 170 °C for 4 min. **Enzymatic treatment**: Myceliophtera thermophila laccase (24 U/ml per g dry fibres) at pH 7 and temp. 60 °C (moisture controlled at 55%) in a rotary system for 30 min. The further addition during the enzymatic treatment of waxes (1% w/w) enhances the water absorbance properties of the panel but decreases the other properties.	200	3,3	0,85	[82]
Leaf sheath fibre bundles from commercial plantain plants	**Enzymatic treatment**: laccase EC 1.10.3.2 from Aspergillus oryzae in the range of 6–12–24 U/(g of fibre). Fibres suspended in aqueous solution (5%) with laccase at 30 °C, pH 5,5 for 1 h. Then fibre bundles were filtered and dried at 40 °C for 24 h and thermo-pressed.	190–210	1+7 (two steps)	8-16	[83]
Wood fibres (80% Spruce, 20% Fir)	**Enzyme**: Commercial laccase (100 U/ml per 1 g dry fibres); **Lignin added**: Calcium-Ligninsulfonate (6% referred to 1 kg dry fibres); **Mediators (for the enzymatic electron transfer)**: caffeic acid or vanillic acid (10 mM per 1 g dry fibres).These ingredients, incubated with the wood fibres at pH 6 and at room temp for 15–60 min. are then the mixture for the panel production.	190	2	n.d.	[84]

3.1.3.1 Market (Phenolic resins)

The global production of phenol-formaldehyde (PF) resins is expected to reach 10 Mt with an estimated value of approximately $13.36 billion in 2019 [85]. More than 50% of these resins are used to produce adhesives for wood-based panels. A 2018 report on biobased products [86] assesses the market for biobased resins as close to 1% of the global market share of these resins. Despite their scarce diffusion into the market, UPM, a major Finnish operator, in the organic products sector recently launched in 2018 the WISA biobond technology based on its BIOPIVA lignin. Similarly, another important Finnish player, STORA ENSO, recently announced a biobased resin for plywood binding or paper impregnation called “LINEO”. In May 2019, the Italian ARPA Industriale, as a result of 8 years of collaboration with WUR, NEMHO, TRESPA (all from The Netherlands) and other research organizations and materials technology companies, launched "BLOOM", an innovative core technology for high-pressure laminates for internal use. It contains a "technology lignin" that reduces the amount of phenol included in the resin by 50%. BLOOM won the 2019 Interzum "High Product Quality" Award. It is widely reported that these bioresins can replace many fossil-based resins [69, 87, 88] for coatings, moulding materials, adhesives for wood for the production of engineered wood, etc. The 2018 report estimates that the TRL for the production of biobased phenolic resins is 8 and that their prices could be competitive with those of fossil resins (approximately USD 2,000/t). The leading producers of biobased resins are shown in Figure 3.8.

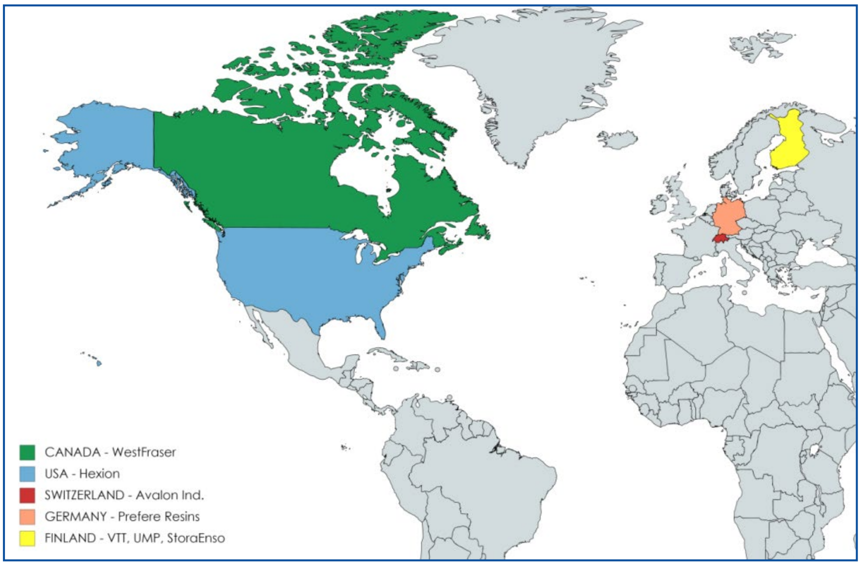


Figure 3. 8 The leading producers of bio-based phenolic resins

The main constraints affecting the market development of these types of products are the lignin feedstock, which is difficult to obtain with standardized pricing, consistent quality and large quantities. Additional constraints are the costs to switch plant equipment and processes to produce the bioresins and the resin-containing products (panels, coatings, etc.). It is important to enhance the cross-sectorial cooperation between stakeholders to enhance the economic convenience associated with lignin-based resin employment [7].

3.1.3.2 Patents (Phenolic resins)

According to the market data, the patent analysis shows a growing interest in this geographically characterized field (see the main patents reported in bold in Table 3.9) in a few European countries and in North America. Many patents have been registered in China.

Table 3. 9 Patents, selected by keyword on the ORBIT Patents DB [36], concerning the lignin applications for PF resins published in the last 5 years (patents in bold belong to the same producers) - Acronyms: I (Inventor), L/M (Large industry/Multinational), E/C (Enterprise/Company), U/RO (Univ./Research Org.), WIPO (World Intellectual Property Organization)

Title	Applicant(s)	Applicant(s) business and country		Publication number	Publication date	Patent org.
High-activity lignin phenol-formaldehyde resin adhesive and preparation method therefor	UNIV BEIJING FORESTRY	U/RO	China	CN105111394	03/03/2020	China
Method for treating lignin and for producing a binder composition	**UPM KYMMENE CORP**	**L/M**	**Finland**	**US2020040022**	**06/02/2020**	**USA**
Phenolated lignin modified expandable resorcinol-phenol-formaldehyde resin and preparation method	INST CHEM IND FOREST PROD CAF	U/RO	China	CN104892877	17/01/2020	China
Adhesive based on materials containing latex-lignin and process for producing same	CENTRO NAC DE PESQUISA EM ENERGIA E MATERIAIS	U/RO	Brazil	WO2019213730	14/11/2019	WIPO
Biobased hot-melt adhesive including lignin as a component	**TEKNOLOGIAN TUTKIMUSKESKUS VTT OY**	**U/RO**	**Finland**	**US2019338168**	**07/11/2019**	**USA**
Use of low Mw lignin together with lignin for the production of a PF binder composition	**STORA ENSO OYJ**	**E/C**	**Finland**	**WO2019202478**	**24/10/2019**	**WIPO**
Adhesive formulation comprising lignin	**UPM KYMMENE CORP**	**L/M**	**Finland**	**EP 3556796**	**23/10/2019**	**UE**
Phenol-modified lignin resin, method for producing resin composition, rubber composition, and cured product	SUMITOMO BAKELITE CO	L/M	Japan	CN105873970	10/09/2019	China
Demethylated lignin phenolic resin adhesive	UNIV NANJING FORESTRY	U/RO	China	CN110041481	23/07/2019	China

modif. by halogen acid						
Preparation method of lignin-based resorcinol-phenol-formaldehyde resin adhesive	UNIV NANJING TECH	U/RO	China	CN107099010	02/07/2019	China
Lignin modified urea-formald. resin adhesive and preparation method and application thereof	GUANGXI GAOLIN FORESTRY CO LTD	E/C	China	CN109868101	11/06/2019	China
Preparation method and application of lignin-based biomass aldehyde-free adhesive	GUANGXI JINGXI CHEMICAL TECH CO LTD - JIAMU YUANJING BEIJING TECH CO	E/C	China	CN109868100	11/06/2019	China
Method for preparing lignin-phenol-formaldehyde resin adhesive	HUANG YU	I	China	WO2019104815	06/06/2019	WIPO
Demethylated lignin-based resorcinol-phenol-formaldehyde resin adhesive and preparation method thereof	UNIV NANJING TECH	U/RO	China	CN107177026	05/03/2019	China
Phenolic resin obtained by polycondensation of formaldehyde, phenol and lignin	COMPAGNIE IND DE LA MATIERE VEGETALE CIMV	E/C	France	AU2018203118	17/01/2019	Australia
Lignin-based formaldehyde-free adhesive, and preparation method	HUNAN LVDA NEW MAT CO LTD	E/C	China	CN109181585	11/01/2019	China
Lignin-based phenol-formaldehyde resin adhesive for improving pavement performance and application thereof	JINING MINGSHENG NEW MAT CO LTD	E/C	China	CN108948755	07/12/2018	China
A method for preparing an activated lignin	**TRESPA**	**E/C**	**NL**	**WO 2018190720**	**18/10/2018**	**WIPO**

composition						

Preparation method of modified lignin and starch composite material for phenolic resin adhesive	SUQIAN BOGU TECH CO LTD	E/C	China	CN107840935	27/03/2018	China
Calcium salt precipitated lignin-based phenol formal. resin preparation method	UNIV NORTHEAST FORESTRY	U/RO	China	CN107629180	26/01/2018	China
Method of producing aldehyde-free lignin-based wood adhesive by using lignin	UNIV NORTHEAST FORESTRY	U/RO	China	CN107286905	24/10/2017	China
Method for preparing oxidized lignin phenolic resin adhesive	HUAINING COUNTY GAZEBO BUILDING MAT CO LTD	E/C	China	CN106590488	26/04/2017	China
Method for preparing oxidized lignin phenolic resin adhesive	HUAINING COUNTY GAZEBO BUILDING MAT CO LTD	E/C	China	CN106590488	26/04/2017	China
Lignin based binder and use thereof for production of particleboards, OSB boards, MDF boards, HDF boards, plywood and wood laminate	**SEMA**	**E/C**	Germany	**WO2017055464**	**06/04/2017**	**WIPO**
Binder compositions comprising lignin derivatives	**FIBRIA INNOVATIONS INC**	**E/C**	**Canada**	**US2017044409**	**16/02/2017**	**USA**
Lignin adhesive production method through steam explosion conducted on	UNIV ZHEJIANG A&F	U/RO	China	CN105505269	20/04/2016	China

gramineous plants						
Lignin-phenol-urea-formaldehyde polycondensated resin adhesive and preparation method	UNIV BEIJING FORESTRY	U/RO	China	CN103804619	20/01/2016	China
Lignin rock wool phenolic resin binder and its preparation method and use method	HEBEI JINYUAN BUILDING MATERIALS TECHNOLOGY CO LTD	E/C	China	CN103911104	23/09/2015	China
Lignin adhesive	**GEORGIA PACIFIC CHEMICALS LLC**	**L/M**	**USA**	**WO2015116612**	**06/08/2015**	**WIPO**
Preparation method of lignin-modified phenol aldehyde resin adhesive	NINGBO ZHONGJIA LOW CARBON NEW TECHNOLOGY RES INST CO LTD	E/C	China	CN103613727	22/07/2015	China

3.1.3 Polyurethane

Polyurethane (PU) production typically involves the reaction between polyol hydroxyl groups and a diisocyanate (often 2,4 toluene-diisocyanate).

In principle, the aliphatic and aromatic hydroxyl groups derived from several biobased sources, such as vegetable oils [89, 90], starch [91], wheat straw [92], and modified and unmodified lignins [93-96], could replace those available in the polyols used in PU synthesis. Additionally, the isocyanates could be “biobased” [97–99].

The sugar fractions are one of the main polyol sources obtained from biomass and exploited in the bio-PU synthesis path [100]. Seed oils are another primary natural oil polyols (NOPs) precursor.

Lignin exploitation in this field is well known and has often reached TRL 5/6 at pilot-scale activities. In particular, due to the rigid lignin structure, technical lignins are evaluated mostly for their use in rigid foams for insulation and construction panels. It is widely reported that the best results can be achieved by improving lignin reactivity via oxypropylation (mainly by alkali reaction with propylene oxide), etherification reactions, and depolymerization processes [101-106]. A simpler approach uses lignin pretreatment with bromidic acid (HBr), which raises the number of hydroxyl groups by more than 20% [107]. **The main strategy of these modifications aims to extend the lignin chains by increasing the number of available aliphatic hydroxyl**

groups. Therefore, many papers include lignin grafting with glycerol and glycerol-like molecules and macromolecules [108, 109], with cardanol (extracted from cashew nut shells) [110], with polycaprolactone chains [111-114], or with formaldehyde to crosslink lignin units into macromolecules rich in hydroxyl groups ready for reaction with diisocyanate [115–117].

Another proposed lignin modification is lignin **prefunctionalization with isocyanates** (briefly, small amounts of lignin are prepolymerized to improve further reaction steps) **[118-120].**

The direct reaction of technical lignin with isocyanates without modifications has also been reported [121, 122]. Some of these applications of unmodified lignins generated PU foams are exploitable in the automotive industry [123, 124], in which the polyol reagent is partially replaced (up to 30%, w/w).

The lignin type can influence the specific function of lignin in the synthesis [125]. As an example, the low molecular weight and high number of exposed hydroxyl units of organosolv lignin (see par. 1), can be exploited as a chain extender. **On the other hand, Kraft lignin, with few hydroxyl-exposed groups and a higher molecular weight, could mainly act as a crosslinker.** Organosolv lignin can be used for a wide variety of PU materials, unlike Kraft lignin, which can only be used for a few types of PU materials (often brittle materials optimally used for coatings [118–120]). Furthermore, **organosolv lignin, sometimes modified with simple reactions (for example, with catalysed propylene oxide KOH [132]), can replace almost all the polyol components of PU especially to obtain foams; otherwise, Kraft lignin can replace a part of the polyol component and often has to be pre-modified by the introduction of aliphatic OH functionalities.**

Despite Kraft lignin is less expensive and more readily available than organosolv lignin, its employment is limited as ite requires a significant lignin treatment to ensure the target properties. **From an economic point of view, this problem does not have a unique solution and always requires a case to case evaluation.**

Table 3.10 summarizes the main information regarding the possible uses of the various lignins and the characteristics of the PU materials obtainable. The table also includes the processes and the main PU material characteristics.

Table 3. 10 Possible uses of the various lignins to obtain some obtainable PU materials. The processes and the main PU material characteristics are reported.

Main appl.	Lignin	Advantage	Disadvantage	Polyol replacement threshold and process	Technical feature	Ref
Elastomers	kraft	• Low lignin market price • High lignin molecular weight favours reticulated structures	Pre-modification by reaction with polycaprolactone is necessary	Typical replacement up to 25%; polymerized with Toluene diisocyanate (TDI)	Improvement of thermic and elastic properties with respect to the commercial material	[116]
	Organosolv Lignin	Lignin containing a high number of free phenolic units.	High lignin cost	Typical replacement up to 40%; polymerized with TDI	PU material doesn't lose its properties till -40 °C. The PU production yields are near the 80%	[117]
	Soda Lignin	High lignin moleculae weight	Few hydroxyl units available	Typical replacement: 5%- 10%; polymerized with TDI	Lower elastic properties and lower transition temperature than the commercial PU	[93]
Coatings and adhesives	Kraft (from black liquor)	• Low lignin market price • High lignin molecular weight increases the crosslinks	Necessary the pre-dissolution in poly ethylene glycol (PEG)	Typical repl. up to 50%, the best results are available with PEGs of low Mw (equal to 200 g/mol); polymerized with TDI	Good coating material. Shear strength (SS) higher than 3 N/mm^2 on various materials on several materials (commercial PU coatings are in the range 2 to 4,5 N/mm^2)	[118]
	Kraft	Low lignin market price	Necessary partial pre-polymerization (via esterification or etherification) of lignin to extend the lignin chains thereby increasing the available hydroxyl groups	Possible full replacement. Acceptable results in reactions of modif. lignin with various diisocyanate types (DI) methylene, diphenyl (MDI), hexamethylene (HDI), and toluene (TDI).	Shear strength (SS) better or comparable with one referred to commercial adhesives and the other to bio-based adhesives	[119]
	Kraft (extracted with 2 methyl tetrahydrofuran)	• Low lignin market price • The extraction solvent is bio-based	• Expensive lignin pretreatment • Despite its bio-base origin, the solvent use is not sustainable	Typical replacement: up to 90%; polymerized with TDI	For use as a coating material, the comparison with the oil based (polyol-TDI) PU coatings shows that for some properties (thermal behaviour, film formation, hydrophobicity) equal performance characteristics when applied on glass, or wood.	[120]

Flexible and rigid foams	Soda Lignin	Side stream product of industrial processes	Pre-dissolution in PEG 400 (i.e., in a microwave) and glycerol, chain extension reaction with poly propylene glycol (PPG) triol or castor oil	Typical replacement up to 13%. The PU foam through polymerization with TDI is 45% bio-based.	The comparison with the commercial FLEXIBLE PU foams shows a competitive material as filling-packaging material. In this bio-based co-polymer, the lignin acts as hard block and the PEG acts as a soft block. The PU foam has a medium density in the range of 110–170 kg/m^3, and medium compressibility in the range of 4,5*10^{-2} - 2,1*10^{-2}MPa.	[100,111,112]
	Lignosulfonates	Low market price	Low polyol replacement level, it is necessary to dissolve in PEG.	Maximum replacement with lignin 16%; polymerized with TDI	Obtained a RIGID PU foam (the reaction time decreases as the lignin percentage increases). The comparison with the homologous rigid PU foam shows better compression performances.	[126, 127]
	Kraft	Low market price	Lignin oxypropylation is necessary	Maximum repl. 20% (used TDI for the polymerization)	The modified lignin contributes to the formation of a furan polyol-based RIGID PU foam fire resistant of class I.	[128]
	Kraft	Low market price	Lignin modification by liquefaction is necessary in a bio-based polyol (sucrose or glycerol)	Replaced up to 100% (used MDI for the polymerization)	The RIGID PU foam achieved has uniform closed cells whose diameter is 650 µm. This property gives the polymer a low density but compression behaviour comparable with commercial foams.	[129]
	Kraft (softwood)	Low market price	Lignin modification by enzymatic reaction with fungi is necessary followed by its liquefaction in a biobased soybean oil	Total bio-replacement (soy based polyol, lignin and cellulosic micro-nanofibre) up to 40% (used MDI for the polymerization)	The RIGID PU foam has mechanical and thermal properties comparable with commercial foams and achieves the EU standards as a thermal insulating material.	[130]
	Kraft and lignosulfonates	Industrial secondary stream materials	Lignin pre-dissolution in polyols is necessary	Total lignin replacement up to 20% (polymerized. with MDI)	Obtained RIGID PU foam thermally stable till 300 °C.	[131]
	Organosolv (ethanol)	organosolv lignin, can replace almost all of the fossil-polyol	Expensive starting material, on which a modification is necessary. Lignin was reacted with propylene oxide (KOH catalysed)	Total lignin replacement up to 100% (polymerization with MDI)	RIGID PU foams were synthesized directly by reaction of the “lignin polyol” with MDI (catalysed by dimethylcyclohexaneamine). Pentane was used as the blowing agent. The foam significantly improved mechanical and thermal properties due to the optimal lignin structure (OH content and crosslinks generated) and it was further improved by adding cellulose nanowiskers	[132]
	Depolymerized kraft lignin in alkaline solution	• Solvent free treatment • Low market price	Lignin oxypropylation is necessary	Bio-replacement up to 50%, polymerization with MDI	A RIGID PU foam whose compression behaviour was comparable to the one of the commercial foams was obtained	[91]

3.1.4.1 Market (Polyurethane)

The global polyurethane market was valued at $65 billion in 2019 and is expected to reach $80 billion in 2023 [133]. The current global demand of PU is almost 20 Mtons [27].

Most of the PU is consumed in the production of rigid and flexible foams, and a large part of the PU is destined for protective and decorative coatings of a wide variety of substrates, such as wood, metal, plastic, leather and fabrics. The rest of the PU is consumed as elastomers, adhesives, sealants and other uses [134–136]. Rigid polyurethane foams are widely used as insulating and structural materials for construction, transportation and decoration. These foams represent almost one third of the polyurethane market. Out of the 1.3 million tons of the North American polyol market annually, approximately 50% is used for the production of rigid polyurethane foams [137].

A market analysis focused on bio-PUs is contained in reference [138]. It appears that their market share is less than 1%, which also contains the small part related to lignin-based PU.

Forecasts for the future of bio-PU over the next 5 years [133] show that due to the growing interest in environmental issues, new policies will be activated that promote the manufacture of bio-based products. Among the bio-PU producers, the German multinational BASF, whose plants produce bio-PU foams using succinic acid and castor oil, both of biological origin, appears to be the most important player [138].

3.1.4.2 Patents (Polyurethane)

The number of main patents concerning bio-PUs in the **last 5 years** is 26 (see Table 3.11). Patents from China are the majority, but these inventions do not appear close to market exploitation. In the majority of applications, lignin was directly added in various percentages to the reaction pot. Three patents in the table (WO2019/193142-Germany, WO2016/085145-Korea and WO2015/083092-Finland) show a more systematic approach to the lignin mixing strategy.

The other most commonly used strategy to obtain an effective lignin-based polyol involves passing lignin through a modification and/or co-reaction with other reagents, which is able to produce a polyurethane with specific characteristics and properties. **Epoxidation (alkoxylation**) and **hydroxylation** are among the most commonly used lignin modification reactions (Pat. Num.: WO2020/109460, CN111171264, CN111171264, CN110982057, WO2019/099405). **Cyclic alkyl carbonates** are also cited as effective reagents for lignin modification (Pat. Num,: WO2020/109460, WO2019/241607). Additionally, lignin **phosphorylation** is used to enhance the mechanical and flame-resistance properties of polyurethane (Pat. Num.: CN103910850).

A specifically patented lignin depolymerization through hydrogenolysis can generate more reactive polyols (Pt. Num.: CN109206589). Finally, a recent patent, Pat. Num.: WO2017/067769, uses nano-lignins to obtain PU.

Table 3. 11 Patents selected by keyword on the ORBIT Patents DB [36], concerning lignin applications for polyurethanes in the last five years (patent-clusters have a grey background, the WIPO-Patents are in bold) - Acronyms: L/M (Large industry/Multinational), E/C (Enterprise/Company), U/RO (Univ./Research Org.), B (Belgium), CHN (China), D (Germany), E (Spain), FIN (Finland), KOR (South Korea), TW (Taiwan), WIPO (World Intellectual Property Organization)

Title	Applicant(s)	Applicant(s) business and country (acronym)		Pub. Number (type code A)	Pub. date	Patent org.
Lignin-based polyurethane film and synthetic method thereof	CHINA PETROLEUM & CHEMICAL SINOPEC DALIAN RESEARCH INSTITUTE OF PETROLEUM & PETROCHEMICALS	U/RO	CHN	CN111349208	30/06/2020	CHN
Lignin-based polyols	**FUNDACION TECNALIA RESEARCH & INNOVATION**	**U/RO**	**E**	**WO2020/109460**	**04/06/2020**	**WIPO**
Hydroxyl-enriched lignin acetate polyurethane adhesive and preparation method thereof	SOUTH CHINA UNIVERSITY OF TECHNOLOGY	U/RO	CHN	CN111205807	29/05/2020	CHN
Lignin-based polyol, modified lignin-based polyurethane material, modified lignin-based polyurethane film, and preparation method and application thereof	SOUTH CHINA AGRICULTURAL UNIVERSITY	U/RO	CHN	CN111187428	22/05/2020	CHN
Preparation method of lignin polyurethane	TIANJIN JIAMEITE BICYCLE	E/C	CHN	CN111171264	19/05/2020	CHN

Preparation method of lignin-based polyol	TIANJIN JIAMEITE BICYCLE	E/C	CHN	CN111171263	19/05/2020	CHN
Preparation method of modified lignin polyurethane	TIANJIN JIAMEITE BICYCLE	E/C	CHN	CN111171262	19/05/2020	CHN
Polysiloxane-based polyurethane/lignin elastomer and preparation method and application thereof	CAS GUANGZHOU CHEMISTRY GUOKE GUANGHUA NANXIONG NEW MATERIALS RESEARCH INSTITUTE NANXIONG CAS INCUBATOR OPERATION	U/RO	CHN	CN111171258	19/05/2020	CHN
Polyether polyol derived from solvent-free liquefied lignin and preparation method thereof	SHANGHAI DONGDA POLYURETHANE	L/M	CHN	CN110982057	10/04/2020	CHN
Lignin-based polyurethane prepolymers, polymers, related compositions, and related methods	**MICHIGAN STATE UNIVERSITY**	**U/RO**	**USA**	**WO2019/241607**	**19/12/2019**	**WIPO**
Phosphated lignin-based flame-retardant and reinforced rigid polyurethane foam and preparation method thereof	HEFEI GENIUS NEW MATERIALS	L/M	CHN	CN103910850	01/11/2019	CHN
Lignin-containing polyurethanes	**RAMPF HOLDING**	**L/M**	**D**	**WO2019/193142**	**10/10/2019**	**WIPO**

Lignin-containing environmentally friendly polyurethane elastomer and preparation method thereof	NORTHEAST FORESTRY UNIVERSITY	U/RO	CHN	CN110183615	30/08/2019	CHN
Modified acetic acid lignin polyurethane adhesive and preparation method thereof	SOUTH CHINA UNIVERSITY OF TECHNOLOGY	U/RO	CHN	CN110055025	26/07/2019	CHN
Biomass thermoplastic polyurethane	INDUSTRIAL TECHNOLOGY RESEARCH INSTITUTE	U/RO	TW	US20190202971	04/07/2019	USA
Alkoxylation of lignins	**HEXION HEXION RESEARCH BELGIUM**	**L/M**	**B**	**WO2019/099405**	**23/05/2019**	**WIPO**
Lignin-based polyurethane and preparation and application thereof	JIANGNAN UNIVERSITY	U/RO	CHN	CN109734864	10/05/2019	CHN
Lignin-based polyurethane foam and preparation method thereof	CHINA PETROLEUM & CHEMICAL SINOPEC DALIAN RESEARCH INSTITUTE OF PETROLEUM & PETROCHEMICALS	U/RO	CHN	CN109575351	05/04/2019	CHN
Thermosetting lignin-based polyurethane elastomer suitable for cyclic processing and preparation method thereof	SOUTH CHINA UNIVERSITY OF TECHNOLOGY	U/RO	CHN	CN109485824	19/03/2019	CHN

Preparation method of alkali lignin-based waterborne polyurethane	SHAANXI UNIVERSITY OF SCIENCE AND TECHNOLOGY	U/RO	CHN	CN104628982	22/01/2019	CHN
Preparation method of polyurethane film	BEIJING UNIVERSITY OF CHEMICAL TECHNOLOGY	U/RO	CHN	CN109206579	15/01/2019	CHN
Cracked lignin and preparation method of lignin based polyurethane rigid foam	BEIJING UNIVERSITY OF CHEMICAL TECHNOLOGY	U/RO	CHN	CN109206589	15/01/2019	CHN
Aromatic polyester polyol compositions	**INVISTA INVISTA TEXTILES**	**L/M**	**USA**	**WO2017/127224**	**27/07/2017**	**WIPO**
Incorporation of lignin in polyurethane products	**HUNTSMAN INTERNATIONAL**	**L/M**	**USA**	**WO2017/067769**	**27/04/2017**	**WIPO**
Rigid polyurethane foam and preparation method therefor	**CJ CHEILJEDANG CORPORATON**	**L/M**	**KOR**	**WO2016/085145**	**02/06/2016**	**WIPO**
A composition in the form of a lignin polyol, a method for the production thereof and use thereof	**STORA ENSO**	**L/M**	**FIN**	**WO2015/083092**	**11/06/2015**	**WIPO**

3.1.4 Blends

The employment of lignin as a component of a polymer blend, mostly with thermoplastic polymers, can reduce their fossil component, infer new properties and improve their known properties. In polymer/lignin blends, the mutual diffusion of the components, regulated by their mutual miscibility and interactions, can lead to products that are homogeneous (with no observable particles and interphases) or heterogeneous. Obviously, homogeneous blends as assessed by the glass transition temperature" Tg and microscopic techniques are preferred [139]. A homogeneous mix, at most containing small, <50 μm particles, has only a single Tg and shows at most small particles (almost less than 50 μm).

The Tg of lignin generally does not exceed the temperature range of 100–170 °C, which is usually lower than the normal processing temperatures of thermoplastic materials [139].

Table 3.12 shows the main results obtained by mixing lignins with some thermoplastic matrices, focusing on the effects of the lignin/thermopolymer interactions.

Mixtures of lignin with **polyolefins** such as polyethylene (PE) or polypropylene (PP) are reported in the literature [140–142]. It is not easy to mix "polar" lignin with an "apolar" polyolefin (only weak dispersion forces can influence the blends). Consequently, to obtain acceptable results, only small quantities of lignin can be added to polymer matrices. Modification of lignin, for example, by esterification, could increase the amount of lignin that can be incorporated in the blends.

Lignin stabilizes polyolefins against oxidation (usually associated with UV or thermal stress) [140]. Increasing lignin percentages improves their elastic modulus [141], but on the contrary, their tensile strength and deformability often decrease [142]. The best performances were observed with lignin contents in the range of 10–25% [141, 142].

Theoretically, when the **polymeric component contains aromatic rings**, π interactions can also be obtained with consequent improvement of the mixing conditions and transfer of the properties of the lignin to the mixtures. Polystyrene (PS) blends could exemplify the combination of the effects of weak dispersion forces and π interactions. Unfortunately, the results did not confirm the theoretical expectations, and the mechanical properties of PS deteriorated with the addition of lignin [140, 143]. A clear explanation needs further study.

However, focusing on the mechanical properties, "aromatic" polymers also containing polar groups or regions, such as poly(ethylene terephthalate) (PET) and poly(ethylene oxide) (PEO), seem to give good results, but it is still difficult to extrapolate and generalize these observations. G. Szabó et al. [144] tried to predict the strength of the interaction (and therefore the mechanical properties) in blends containing lignin in combination with four polymers PP, (polycarbonate) PC, PS and PET. PET showed the best results, which were attributed to its ability to form at least three types of interactions with lignin (dispersion, π interactions, and H bonding). In the same work, it was also demonstrated that the blends showed the best properties when the lignin content did not exceed 20–25% w/w.

Table 3. 12 Lignin blends with some thermoplastic matrices (focus on lignin/polymer interactions)

Thermoplastic polymer matrices		**Lignin blended**	**Optimal lignin contents (w/w)**	**Expected lignin-polymer interactions**	**Improved properties with respect to the original polymer**	**Ref.**
Polyolefin	PE	Kraft Lignin	10%-25%	Weak Diffusion Forces	Against oxidative stresses (UV and Thermic), Modulus	[140-142]
	PP	Kraft Lignin, lignosulfonates	10%-25%	Weak Diffusion Forces		
Aromatic polymers	PS	Organosolv	10%-20%	Weak Diffusion Forces + π interactions	Tensile strength	[140, 143]
	PET	Lignosulfonates	20%-25%	Weak Diffusion Forces + π interactions	Tensile strength	
Aromatic polar (H-Bond)	PEO	Organosolv	20%-25%	Weak Diffusion Forces + π interactions + H-Bond	Elongation	[144-148]
	PVC	Organosolv	10%-20%	Weak Diffusion Forces + π interactions + H-Bond	Modulus, Tensile strength, Elongation	
Bio-polymer	PLA	CEL	20%-30%	Weak Diffusion Forces + π interactions + H-Bond	Shore hardness, Impact strength	[149-151
	PHB	Soda	10%-30%	Weak Diffusion Forces + π interactions + H-Bond	Thermo-mechanical properties	

Blends of PEO with lignin were extensively studied by Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC) [145, 146], demonstrating the presence of many H-bonds and uniform blends with good mechanical properties. The optimal lignin percentages were in the range of 20–25%

Poly(vinyl chloride) (PVC)/lignin blends have also been widely studied [147,148]. The PVC/lignin miscibility is mainly due to interactions between the α hydrogen of PVC and the hydroxyl groups of lignin. Optimized blends can contain almost 10% lignin.

Hydrogen bonds were also observed in lignin blends with **biobased polymers such as polylactic acid (PLA) and polyhydroxybutyrate (PHB)**. PLA formed a homogeneous single-phase structure in blends containing up to 40% lignin [149]. The best performances were registered for lignin contents in the range of 20–30%. PHB/lignin miscibility was remarkably high, where up to 40% lignin content could be achieved [150, 151]. Most likely, the quite surprising PHB miscibility with lignin (compared to PLA) is due to its less polar structure. Good thermomechanical properties were found for lignin contents in the range of 10-30%.

To increase lignin miscibility, the effects of **plasticizers** on regulating polymer/lignin interactions were also investigated. Among these, glycerol increased the suitability of unmodified kraft and alkali lignins [152, 153] for blend applications. The use of diethylene glycol dibenzoate as a plasticizer for PVC/lignin blends enabled the incorporation of organosolv lignin up to 23% and enhanced the mechanical properties when compared to PVC alone [147].

Lignin copolymerization with two or more polymeric matrices can help to overcome the partial immiscibility of lignin in polymeric matrices and can add new properties to the copolymer system. In the case of the binary system PLA/PEO [154], the introduction of lignin gave a good balance of stiffness and strength. In fact, lignin provided strength, while PEO increased deformability.

Copolymerization of lignin with PE and PP in the presence of polar components can increase the performance of the final blends. Ten percent (w/w) ethylene-vinyl acetate (EVAc) in LDPE/lignin blends doubled their tensile strength and increased their elongation-at-break more than tenfold [155]. In PP/lignosulfonate blends, the addition of maleic anhydride-grafted polypropylene (MAPP) increased the tensile strength until 40% lignin was present [156].

3.1.4.1 Market (Blends)

Thermoplastic polymer blends containing lignin have not yet reached the market. The direct use of natural fibres such as in the hemp**-based Trifilon BioLite®** as reinforcement in PP matrices is preferred [86]. Nevertheless, recent patents confirm growing scientific and industrial interest and expectations.

3.1.4.2 Patents (Blends)

The most recent patents in this field number 15 (see Table 3.13). Only a small number of these patents are from China. The other patents are mostly WIPO patents recorded by European or North American multinationals or research organizations. The patented blends often contain polyacrylonitrile and they are intended to be used for biobased carbon fibres. Polyolefin blends are reported along with their melt extrusion techniques.

Table 3. 13 Patents, selected by keyword on the ORBIT Patents DB [36], concerning the lignin applications for Blends published in the last 5 years (patent-cluster have a grey background, WIPO-Patents are shown in bold) – Acronyms: I (Inventor), L/M (Large industry/Multinational), E/C (Enterprise/Company), U/RO (Univ./Research Org.), BR (Brazil), CHN (China), D (Germany), EU (Europe), JAP (Japan), WIPO (World Intellectual Property Organization)

Title	**Applicant(s)**	**Applicant(s) business and country (acronym)**		**Pub. Number**	**Type code**	**Pub. date**	**Patent org.**
Preparation method of lignin and polyacrylonitrile blend fiber and carbon fiber thereof	NINGBO INSTITUTE OF INDUSTRIAL TECHNOLOGY CHINESE ACADEMY OF SCIENCES	U/RO	CHN	CN108624985	B	14/07/2020	China
Producing polyolefin products	UNIVATION TECHNOLOGIES	L/M	USA	EP3677605	A1	08/07/2020	EU
Acrylonitrile butadiene styrene copolymer/lignin blends	PRISMA RECYCLED COMPOSITE	E/C	USA	US20200131359	A1	30/04/2020	USA
Compositions including lignin and methods for making the same	CHEN SARKANEN YI RU	I	USA	WO2019/183350	A1	26/09/2019	WIPO
Functional lignin, and its use in producing blends, copolymers, and self-healing elastomers	**UT BATTELLE**	**L/M**	**USA**	**WO2019/161180**	A1	**22/08/2019**	**WIPO**
Lignin-based polymers with enhanced melt extrusion ability	**UT BATTELLE**	**L/M**	**USA**	**WO2019/147896**	A1	**01/08/2019**	**WIPO**
Lignin-based polymers with enhanced melt	**UT BATTELLE**	**L/M**	**USA**	**WO2019/147895**	A1	**01/08/2019**	**WIPO**

extrusion ability							
Thermoplastic polymer compounds with low-molecular-weight lignins, a method for producing same, mouldings and uses	FRAUNHOFER	U/RO	D	EP2954008	B1	05/06/2019	EU
Dust suppressant and soil stabilization composition comprising lignocellulosic byproducts	SUSTAINABLE FIBER TECHNOLOGIES	E/C	USA	US20190161678	A1	30/05/2019	USA
Composition of polyacrylonitrile/lignin blend and use thereof in melt spinning carbon fibre precursors	LABORATORIOS QUIM E METROLOGICOS QUIMLAB	E/C	BR	EP3366723	A4	24/10/2018	EU
High performance lignin-acrylonitrile polymer blend materials	**UT BATTELLE**	**L/M**	**USA**	**WO2017/011494**	A1	**19/01/2017**	**WIPO**
PP (polypropylene)-PBT (polybutylene terephthalate) blend plastic composite	TONGCHENG ZHONGHUI PLASTIC INDUSTRY	E/C	CHN	CN106280316	A	04/01/2017	China
Blending lignin with thermoplastics and a coupling agent or compatibilizer	CYCLE WOOD SOLUTIONS	U/RO	JAP	EP2914666	A4	08/06/2016	EU

Polylactide-graft-lignin blends and copolymers	DORGAN JOHN R EYSER MICHAEL PAUL PERBIX CLAY	I	USA	US8993705	B2	31/03/2015	USA
Preparation of alkali lignin/PVA light insulation blend membrane	NORTHEAST FORESTRY UNIVERSITY	U/RO	CHN	CN104292483	A	21/01/2015	China

3.2 ELECTROCHEMICAL APPLICATIONS

Lignin shows redox functionalities that play a role in a variety of electrochemical reactions. In plants, the redox functions of lignin are used in energy conversion processes such as respiration and photosynthesis, where energy conversion and storage are achieved through a series of reversible reduction and oxidation reaction cascades.

These reactions are similar to the electrochemical reactions that occur when electrical storage devices are charged and discharged. Therefore, the potential use of lignin in energy storage applications is increasingly being investigated [157]. In addition to applications in which lignin is only used in small quantities, e.g., as an additive in the electrodes of lead-acid cells, flow batteries and supercapacitors are applications in which lignin can be used as the main components [157].

Among the various lignin variants, lignosulfonates (LS) are the most commonly used starting materials in these applications. LS can relatively easily be extracted from black liquor by ultrafiltration [158]. LS are hydrophilic biopolymers with electroactive methoxyphenol groups that are soluble in water and acidic solutions [159]. These properties render lignosulfonates interesting for redox flow batteries. In this type of battery, the electrolyte is stored externally, generally in tanks, and is pumped through a reactor where electrochemical reactions take place.

The main difference from conventional batteries is that the energy and power of the redox-flow battery are fully independent. The capacity of such a battery thus depends on the electrolyte volume, whereas the power depends on the reactor size [160].

Mukhopadhyay et al. developed a flow battery electrolyte based on ultrafiltrated lignosulfonates [161]. The material successfully passed several reduction/oxidation cycles without a noticeable decrease in activity. In contrast to many redox-flow batteries that are being used today, LS batteries are inexpensive and do not rely on metal catalysts with limited availability.

For mid- and short-term energy storage of larger amounts of energy, supercapacitors are an alternative to batteries because they can provide substantially higher energy densities. Li et al. developed a supercapacitor based on lignosulfonate-functionalized graphene hydrogels that showed a very high specific capacitance (432 F/g), nearly twice as high as that of graphene-based supercapacitors alone [162]. Peng et al. developed a flexible supercapacitor based on lignosulfonate, single-walled carbon nanotubes and a cellulose hydrogel. It also showed very high specific capacitance (292 F/g) and extraordinarily high electrochemical stability with 98% capacitance retention in 1000 bend cycles with a bend angle of 90° [163]. Clearly, lignin-based electrolytes are successful nature-inspired materials that can furthermore be sourced regionally. The necessary conversion of lignin not only supports development in rural areas but also reduces the demand for social and/or environmental conflict-carrying metals such as cobalt and vanadium. Both are mentioned in the recently published fourth list of critical raw materials published by the European Commission [164].

Scientific research in the field of electrochemical applications of lignin is far from complete, with the heterogeneity of lignin and long-term stability of batteries remaining major challenges. However, the examples shown here demonstrate the great potential of the use of lignin in future energy storage technologies, both for stationary applications and backup systems in hospitals, IT systems, military bases, etc. as well as for flexible and portable devices.

The increasing number of patent publications (Table 3.14) indicates a new trend in the use of lignin in high-value applications; however, more intensive studies on large-scale synthesis and production together with an optimization of (chemical) structures are essential for further progress in this field.

Table 3. 14 Patents related to the application of lignin in redox-flow batteries and supercapacitors published in the last 3 years [165]. Acronyms: E/C (Enterprise/Company), U/RO (University/Research Organization). CHN (China), D (Germany), WIPO (World Intellectual Property Organization)

Title	**Applicant(s)**	**Applicant(s) business and country (acronym)**		**Publication number**	**Publication date**	**Patent org.**
Lignin-based electrolytes and flow battery cells and systems	Northeastern University (Boston, USA)	U/RO	USA	US10818952 (B2)	27/10/2019	USA
Sulfonated aromatic compounds	CMBLUPROJEKTAG (Alzenau, D)	E/C	D	WO2017174206 (A1)	02/05/2019	WIPO
Process for the production of lignin derived low molecular products	CMBLUPROJEKTAG (Alzenau, D)	E/C	D	WO2018146343 (A1)	16/08/2018	WIPO
Process for the production of sulphonated low molecular weight derivatives from lignin	CMBLUPROJEKTAG (Alzenau, D)	E/C	D	WO2018146344(A1)	16/08/2018	WIPO

A kind of preparation of ultracapacitor lignin nano carbon fiber	Tianjin University (Tianjin, CHN)	U/RO	CHN	CN107956001 (A)	24/04/2018	CHN
Novel methods for processing lignocellulosic material	CMBLUPROJEKTAG (Alzenau, D)	E/C	D	WO2019072386 (A1)	18/04/2018	WIPO

In the near future, lignin-based redox-flow batteries can become an important component of future renewable-based energy systems by providing urgently required energy storage capacity and simultaneously supporting grid stability at competitive costs. The development and implementation of lignin-based redox-flow batteries have the potential to support a sustainable, circular economy and are in line with a number of European goals and strategies, such as the Green New Deal, the Bioeconomy Strategy, the EU Forest Strategy, and the Action plan for “Nature, people and the economy”, among others.

3.3 BTX (BENZENE, TOLUENE, XYLENE)

The use of lignin for the production of BTX began in the early 1970s and continues to this day (Figure 3.9). Over the years, the advent and application of technological and scientific innovations has caused a sharp increase in the number of publications and patents.

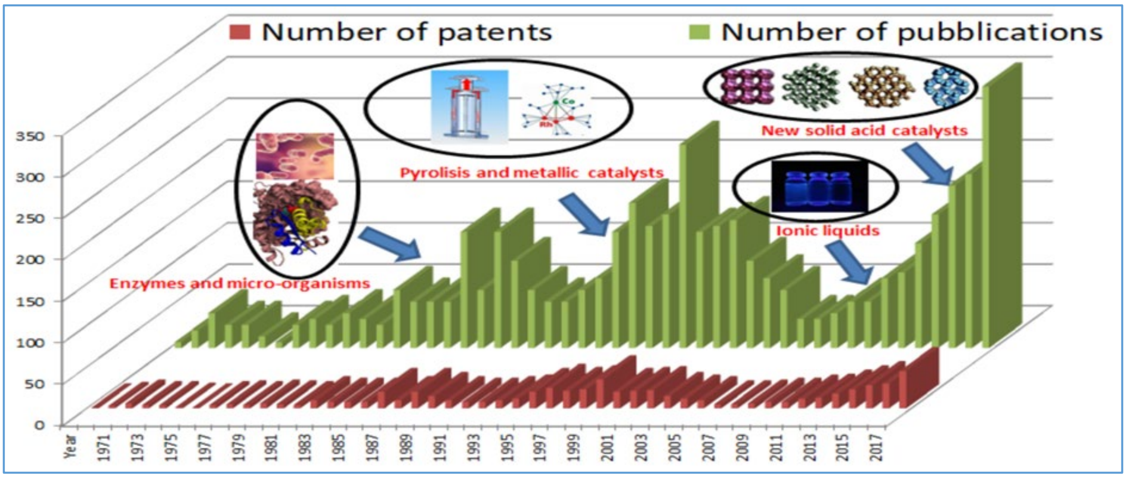


Figure 3.9 - Chronological study of fuels and BTX production by lignin depolymerisation (adapted from [166])

BTXs, obtained from lignin, are usually coproducts of complex biorefinery processes leading to other products [167–169].

The complexity of the process and the relevant costs limit the choice of the type of lignin to convert. Only some low-cost technical lignins with low sulfur contents have been proposed so far to develop economically feasible processes.

The main processes to obtain lignin-BTX include the following approaches:

HTL – Hydrothermal liquefaction and similar treatments using systems operating close to critical water conditions, NCW – Near critical water;

FP - Fast pyrolysis – thermal process at higher temperature ranges (typically up to 600 °C) in the absence of oxygen and a short residence time in the gas phase during the process;

CFP - Catalytic fast pyrolysis (for the in situ or ex situ deoxygenation and aromatization of lignin pyrolysis oils);

RCF – reductive catalytic fractionation [170–178], whose direct application to biomass belongs to the “Lignin First” approaches [179, 180] aimed at the production of oxygenated phenolic monomers during the initial pretreatment/fractionation step of lignocellulosic biomass.

All the above pretreatment/depolymerization technologies generate phenolic fractions that require a further specific hydro-deoxygenation (HDO) step for BTX production.

The strengths and weaknesses of the four technologies cited above are summarized in Table 3.15.

Table 3. 15 Strengths and weaknesses of the four main technologies applicable to lignin-BTX production (rif. [167-169])

	Conversion technology (two steps)	**Feedstock**	**BTX yield* ($w_{BTX}/w_{dry\ feed}$)**	**Total Initial investment**	**Annual operational costs**	**Catalyst for the production of MOAMON**	**TRL**
				Feed stream - 25 ton/h (estimated costs in million $)			
1	HTL + HDO	Wet biomass (black liquor)	< 15%	< 200	90	Alkaline pretreatment	6–7
2	FP + HDO	Dry lignin (biomass)	< 10%	~ 135 (pretreatment) + 40 (HDO)§	70	No catalysts	6–7
3	CFP + HDO	Dry lignin (biomass)	< 25%	> 135 (pretreatment)# + 40 (HDO)§	> 70#	High amounts of zeolites (ZSM-5)	3–4
4	RCF + HDO	Dry biomass	< 30%	> 135 (pretreatment)# + 30 (RCF-HydMan@) + 40 (HDO)§	> 70# + 5 (RCF-HydMan@)	Low amounts of precious catalysts (Ru, Pd, etc.)	3–4
*Overall yield (BTX/raw materials)							
§ HDO cost for the conversion step of phenols to BTX							
# The catalysts overall management costs were not included							
@RCF-Hyd-Man: Reductive Catalytic Fractionation (Hydrogen Management)							

FP of biomass feedstocks is an industrial technology employed in Finland and the Netherlands to produce liquid pyrolysis oil. Despite iths maturity, it is not yet competitive with fossil-based BTX production technologies. Installation and management costs are currently too high.

HTL can also work with wet feedstocks. It is not necessary to bring biomass or a biorefinery plant stream to dryness before the treatment and usually gives high phenolic yields, but only the water soluble phenolic fraction can generally be readily converted to BTX. The water-insoluble bio-oil fraction has to be further managed. Moreover, the final phenolic-to-BTX HDO conversion step requires a further expensive solvent extraction step and subsequent distillation step. All steps considered, plant installation and management, involve huge costs.

FP works only with dry feedstocks. The feedstock drying cost is conterbalances by lower plant installation and management costs with respect to HTL. Usually, the bio-oil yields are low (a large part of the feedstock is turned into char), and the BTX fraction is usually separated after the HDO conversion of the whole produced bio-oil.

CFP is still far from industrial employment. It is based on dried feedstocks, proposing an interesting alternative that reduces/avoids the use of hydrogen (and the related high cost of the HDO processes). Its weaknesses are principally due to the catalysts management costs (amounts, manufacture costs, recovery, etc.) and to the low yields. However, recent developments in the tailoring of zeolitic or aluminosilicate catalysts used in petroleum refining (thus being produced in huge amounts with optimized/reduced costs) may offer further perspectives on this technology.

Despite the huge potential identified, RCF is still not ready for industrial applications. The process turns dried biomasses into phenolic monomers and oligomers along with a charbohydrates residue using usually expensive catalysts and high amounts of hydrogen. It needs a further HDO step to convert the monomeric phenolics into BTX.

L. T. Funkenbusch [168] and I. V. Gursel [169], a few years ago, simulated the conversion processes based on two more mature technological approaches (HTL-like and FP) and provided tools for comprehension of the current gaps in industrial applications.

Figure 3.10 presents a schematic of a refinery process based on HTL technology that uses an NCW reactor as proposed by L. T. Funkenbusch.

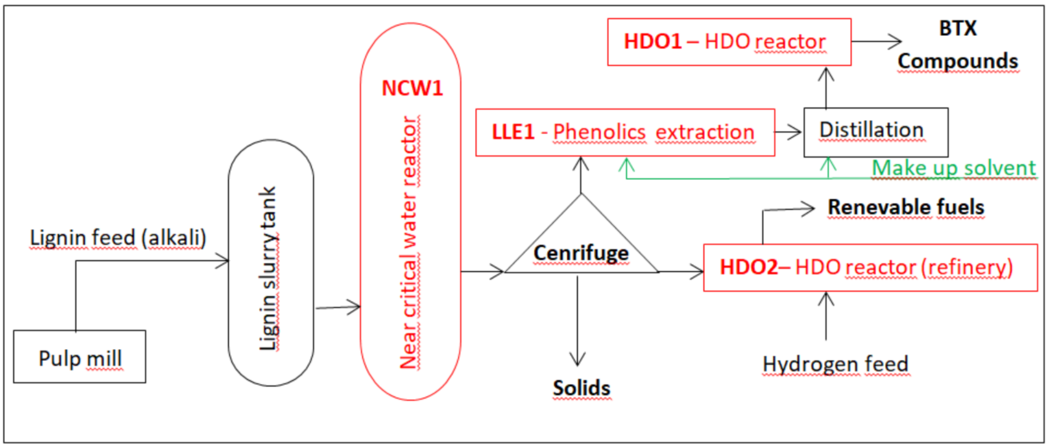


Figure 3. 10 Integrated pulp mill to refinery process with modelled processes shown in red. (BTX = benzene, toluene, xylenes; HDO = hydrodeoxygenation; LLE = liquid-liquid extraction; NCW = near-critical water). (Adapted from [168])

The simulation evaluates the process using a feedstock from a pulp mill with a capacity of 20000 kg/h dry lignin coproducing BTX and fuel-type hydrocarbons.

The technical assumptions of the simulation are:

NCW1 (Near Critical Water reactor): running at 350 °C and 25 MPa alkali catalysed optimized to increase the C/O ratio (oxygen removal) and decrease the C/H ratio (increases the aromatic content) from the biomass to bio-oil.

NCW technology is effective for direct applications on wet lignin-rich streams (it is not necessary to remove the water), but this treatment has to be improved with an end-capping reagent to prevent the recombination of the lignin deconstruction products.

Centrifuge: a three-phase centrifuge able to separate solids (char-like), bio-oil (the not water miscible fraction) and the aqueous phase (containing the phenolic fraction).

LLE1 (Liquid-Liquid, Extraction): optimized for water removal and recycle, and for phenolic fraction specific extraction, purification and concentration, to feed a proper HDO reactor with this phenolic fraction for the production of the BTX stream.

HDO1 (Hydro-DeOxygenation) for BTX production: a specific reactor containing specific catalysts for the hydro-deoxygenation of the phenolic fraction to remove the oxygen without compromising the aromatic rings.

HDO2 for renewable fuels: a reactor optimized for the bio-oil treatment to yield two final hydrocarbon products, a fully deoxygenated aromatic hydrocarbon and a fully saturated aliphatic compound in a 0.45 to 0.55 ratio. A more feasible conversion for bio-oil could involve a partner refinery in which the bio-oil would be blended with crude oil (in this case, to preserve the catalyst performance, the bi-oil oxygen content must be under 10%).

The final economics are summarized in Table 3.16. Bio-BTX coproduction resulted economically still not competitive. Both the final coproducts achieved through HDO processes cost approximately \$1/gallon more than the market price of the corresponding fossil products.

Table 3. 16 Main economic data referring to the two main products obtained by HTL-HDO technology

	Bio-fuel (\$/gallon)	**BTX (\$/L)**
Minimum selling price (MSP) - HTL technology	3.52–3.86	1.65–2.00
Average market price	2.88	1.00
HTL (NCW) product overprice	~1.00	~1.00

To lower the bio-BTX price, the critical step is phenol extraction in LLE1 and, more specifically, the operating costs of this module.

I. V. Gursel et al. [169] compared the performance characteristics of a simulated pyrolysis plant fed 25000 kg/h dry Kraft lignin with a hydrothermal upgrade plant (HyThUp), which is an HTL technology. The target product for the two plants was the phenolic fraction called "mixed oxygenated aromatic monomers" (MOAMON), which is considered the platform stream for the HDO step in BTX production.

The technical data inputs of the simulation were:

In the first case study lignin was converted to MOAMON through a pyrolytic treatment in a circulating fluid bed reactor at 500 °C. Light organics, heavy organics, and char were obtained. To achieve the MOAMON fraction, three distillation steps were necessary: the first separates the light organics (methanol-like), the second separates the water, and the third separates MOAMON from the high-boiling heavy organics.

In the second process, the resulting slurry after the hydrothermal reaction was sent to a filter to separate the solid char from the liquid, then the product of the several separation steps was a mix of MOAMON and light and heavy organics. Finally, methyl isobutyl ketone (MIBK) solvent is used to Liquid-Liquid Extract (LLE) phenols from the liquid stream (separation of MIBK from phenols is achieved by distillation).

Table 3.17 summarizes the economics of MOAMON production in the two case studies. The HTL-like process achieved a higher production of phenols than the pyrolysis-based process.

Table 3. 17 FP and HTL simulations: Main input and output data (extrapolated from [169])

		Pyrolysis (FP) (ton/h)	**HTL (HyThUp) (ton/h)**
Raw Materials (ton/h)	Lignin	25,0	25,0
	Aq. NaOH	-	125,0
	Air	13,0	0,8
Products (ton/h)	MOAMON	2,5	6,0
	Light organics	0,8	1,9
	Heavy organics	3,8	4,7
	Char	8,8	1,2
	Flue gas	17,1	2,0

On the other hand, the pyrolysis plant had low capital and operating costs (Table 3.18), while the other plant guarantees better revenues.

Table 3. 18 Comparison HTL - FP: main economic data (data collected from [169])

	Total capital investment (M€)	Operating costs (M€/year)	Total revenues (M€/year)	MOAMON revenues (M€/year)
HTL (HyThUp)	182	95	109	70
Pyrolysis (FP)	135	72	83	29

Pyrolytic treatments (whose benefits are their low initial investment and operational costs) could be further optimized, by tuning the reaction conditions and using more appropriate catalysts to increase MOAMON and BTX production in one step, i.e., by direct deoxygenation and aromatization of the thermally produced lignin pyrolysis vapours. Moreover, wet technologies (HTL-like) should also be further optimized. The annual operating costs of the liquid-liquid extraction (LLE) step significantly affect the lignin-BTX minimum selling price, and this is the first significant technological challenge to be addressed [168]. In both of the above technologies, especially in FP, additional revenues may be derived from the valorization of the produced (bio) char via the increasing interest in this bio-derived side product in applications ranging from agriculture to polymer composites, and others.

Table 3.24 summarizes the main elements of the four technologies to demonstrate that the first two are almost ready for the market and the second two are still not ready but are truly promising for these applications.

Among these latter applications, catalytic fast pyrolysis (CFP) offers a suitable approach for the direct production of BTX. Table 3.19 summarizes some of the details of some recent promising lab catalytic conversion reactions tested to convert some types of lignin into BTX.

Table 3. 19 Details of some recent promising lab catalytic conversion reactions tested to turn some types of lignin in BTX by the catalytic fast pyrolysis (CFP) approach

Feedstock (Lignin)	Catalyst	CFP (Catalysed Fast Pyrolysis) Reaction Conditions				Yield (BTX)	Ref.
		Reactor /reaction	Cat/Lignin (wt ratio)	T (°C)	Time (s)	wt %	
Softwood kraft	ZSM-5 (nano-sized, mesoporous)	Fixed-bed	4	600	12	less than 25% with respect to lignin	[181]
Birch - Spruce	ZSM-5 (nano-sized, mesoporous)	Fixed-bed	4	600	12		[182]
Masson pine###	HZSM-5 (Zn modified)	Shape Selective (SS)*	3	700	20		[183]
Alkaline	Zr/MCM-48	Fixed-bed	2	600			[184]
Black liquors (Eucalyptus hardwood paper mills)##	Ga-modified H-ZSM-5	In situ CFP**	20	600	30		[185]
## Black Liquor containing almost 30% water, 40% organics (32%lignin 8% Carbohydrates) and 30% inorganics							
### Milled Wood Lignin (MWL) purified and partially deoxygenated at 300 °C Torrefaction Deoxygenation Pretreatment (TDP)							
*Lignin and catalyst were separately placed between two layers of quartz wool in a quartz tube (reactor)							
** Black liquor and catalyst mixed in a reactor (from 40 to 600 °C, 20 °C/s)							

The CFP process could easily be scaled up from lab to pilot plant and rearranged for the use of less expensive technical lignins, but further techno-economic assessments are necessary. Engineering and reactor design issues related to the possible clogging effects of lignin need to be considered.

The last promising technology reported in Table 3.3.1 is reductive catalytic fractionation (RCF). It belongs to the "lignin-first" approaches whose first objective is the recovery of lignin or lignin-derived phenolics from biomass, in contrast to conventional processes where the carbohydrates are the prime target and lignin is basically considered a process waste.

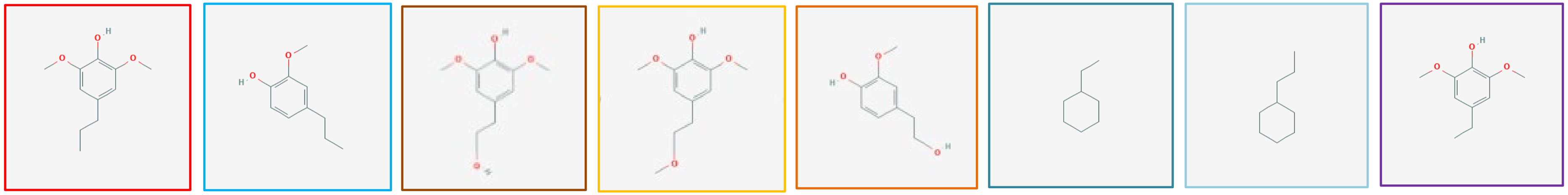
Table 3.20 presents the details of the most promising (in terms of yield) RCF treatments published in the last 5 years for obtaining MOAMON.

Table 3.21 presents the details of representative catalytic HDO reactions/processes to obtain lignin-BTX from the MOAMON fraction.

Table 3. 20(adapted from [179]) - The most promising (in terms of yield) Reductive Catalytic Fractionation (RCF) catalytic conversion reactions with a lignin-first approach performed directly on the biomass for the lignin monomers (MOAMON) published in the last 5 years.

Feedstock	**Catalyst**	**Solvent**	**Reaction Conditions**			**Main aromatic products**	**Lignin Monomers - Total Yield (wt %)**	**Ref.**
			T(°C)	H_2 (bar)	t(h)			
miscanthus	Ni/C	MeOH	200–225	60	12	**propylsyringol**, **propylguaiacol**	68	[187]
beech				60	5		51	[188]
poplar				30	1		48	[189]
poplar				35	12		90	[190]
birch	Pd/C	MeOH	250	30	3	**propylsyringol**, **propanolguaiacol**	49	[191]
birch		Ethylene Glycol					50	[192]
eucalyptus		MeOH					50	[193]
birch	Pd/C + $Al(OTf)_3$	MeOH	180	30	2	**methoxypropylsyringol**	55	[194]
oak							46	[195]
birch	Pd/C + $Yb(OTf)_3$	MeOH	200	30	2	**propanolsyringol**, **propanolguaiacol**	48	[196]
birch			250	20	20	**lignin-oil**	83	[197]
birch sawdust	Ru/C	MeOH	200–250	30	6	**propylsyringol**, **propylguaiacol**	52	[198]
poplar		MeOH			15	**propylsyringol**, **propanolsyringol**	78	[199]
cornstalk		H_2O			8	**ethylcyclohexane**, **propylcyclohexane**	97	[200]
eucalyptus		BuOH/H2O (1:1)			2	**propanolsyringol**, **propanolguaiacol**	49	[201]
eucalyptus		BuOH/H_2O (1:1)			2	**propanol-substituted phenolics**	49	[202]

sawdust								
apple wood	Ru/SiC	MeOH	250	10	3	**propylsyringol**, **ethylsyringol**	48	[203]
poplar	Zn-Pd/C	MeOH	225	35	12	**propylsyringol**, **propylguaiacol**	54	[204]



propylsyringol **propylguaiacol** **propanolsyringol** **methoxypropylsyringol** **propanolguaiacol** **ethylcyclohexane** **propylcyclohexane** **ethylsyringol**

Table 3. 21(adapted from [186]) The main catalytic HDO conversion reactions to obtain lignin-BTX from the MOAMON fraction

Lignin derived oxycompound	**Catalyst (Reaction time - RT)***	**T (°C)**	**P (bar)**	**Reductive reaction gas**	**Aromatics Yield %**	**Main target products (BTX)**	**Ref.**
Phenol	MoO_3-NiO-Al2O_3	500	30–60	H2	64–78	Benzene	[205]
p-Cresol						Toluene	
Guaiacol						Benzene + Toluene	
Syringol						Benzene + Toluene	
Phenols (-CH_3 and or OCH_3 substituted)						Toluene + Xylene	
Anisole	Pt/Hbeta	400	1	H2 (H2/anisole=50)	70–90	Benzene + Toluene	[206]
	Pt/SiO2					Benzene	

Guaiacol	Fe/SiO_2 (RT=20 min)	400	1	50% H_2, 40% N_2, 10% (CO_2, CO, H_2O)	75	Benzene + Toluene	[207]
Anisole	Ni/C	310	3	H_2	65	Benzene	[208]
Anisole	Pt-Sn/CNF(Carbon Nano-Fibre)/Inconel (Ni-Cr Alloy) (RT=45 min for Anisole and RT=5 min for Guaiacol)	400	1	H_2	64–66	Benzene	[209]
Guaiacol							
Phenol	Ni/HZSM-5	240	4	H_2	59	Benzene	[210]
Guaiacol	Ni2P/SiO_2	300	1	80% H_2/N_2	72	Benzene	[211]
Benzaldehyde	HZSM-5	550	1	H_2	89–95	Benzene	[212]
	Ga/HZSM-5					Toluene	
Benzaldehyde	Pd/SiO_2-Al_2O_3	60	1	H_2	93–100	Ethylbenzene	[213]
		140	Conversion without gas			Toluene	
	Pt/Al_2O3 (RT=15 min)	200				Benzene	
m-Cresol	Ga/Hbeta	550	1	H_2	78	Toluene	[214]
m-Cresol	Rh/Fe_2O_3	300	1	40 vol% H_2, N_2	87	BTX	[215]
Benzaldehyde	Pt-Pd/ZrO_2	160	6	H_2	50	Ethylbenzene	[216]
Guaiacol	Pd-Fe/C	450	0.4	H_2	83	Benzene	[217]
4 Propylphenol	Re-Ni/ZrO_2 (RT=60 min)	300	40	H_2	54	n-Propyl-benzene	[218]
Anisole	FeReOx/ZrO_2	350	1	H_2	48–62	Benzene	[219]
m-Cresol						Toluene	

3.3.1 Market (BTX)

BTX-based polymers and chemicals are primarily used as starting materials for a wide range of products in different industries:

- Health care and pharmaceuticals
- Automotive industry (car parts)
- Packaging
- Electronics (DVDs, keyboards, mobile phones, etc.),
- Textiles (e.g., fibres),
- Sports equipment construction industry (e.g., insulation, piping materials and window frames)

Among the BTXs, due to its versatile chemical structure, benzene is the most requested. It is widely used as an intermediate for the production of many industrial polymers, the largest of which is polystyrene.

Toluene production exceeds market needs, so excess production is often converted back to benzene or xylene. It is mainly used for the production of polyurethane and as an additive to increase the octane value of gasoline.

The uses of para-xylene in the industrial production of polymers, as a precursor of polyethylene terephthalate (PET) or for aromatic polyamides resistant to heat and mechanical stress (e.g., Kevlar, Nomex and Twaron), classify this isomer of xylene as the most requested by the market. The other two isomers are rarely used and often isomerized to the para isomer or hydrodealkylated to form benzene (or toluene).

The results of the analysis of the most requested compounds among the BTX, are presented in Table 3.22, which reports the 2018 traded quantity and the average prices on the EU 28 market.

Table 3. 22 BTX compound 2018 EU 28 market data (collected from [27])

EU 28 (2018)		TRADE (Million USD)		Quantity (Million kg)		Average price ($/kg)
		Import	Export	Import	Export	
Benzene		8450	910	9670	1060	0,9
Toluene		140	2100	180	2810	0,8
Xylene	Ortho	1140	180	1200	200	0,9
	Meta	1230	4	800	3	1,4
	Para	3330	3160	3020	3010	1,1
TOTAL		14290	6354	14870	7083	0,9

The market demand for BTX over the next 10 years will increase by approximately 50%, reaching 220 million tons (280 billion USD) in 2030 [86].

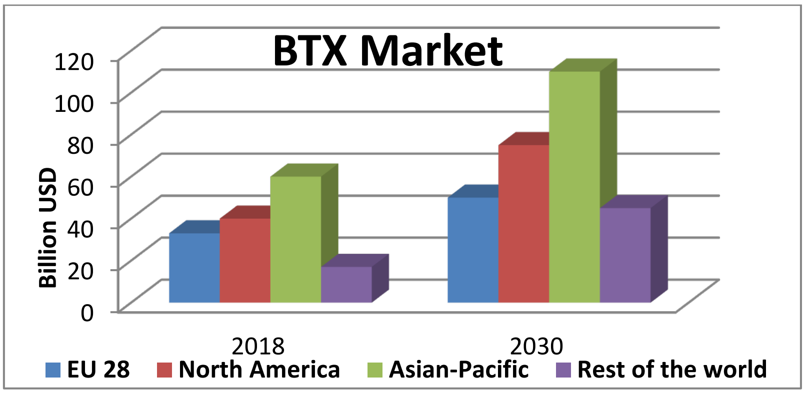


Figure 3. 11 BTX Market dimensions

The market shares in Figure 3.11 indicate 20% for the EU 28, 30% for North America and 40% for the Asian-Pacific countries.

Bio-BTX could easily enter this market if cost competitiveness is achieved. This could be facilitated by a regular supply of biomass, technological improvements, rising fossil energy and oil prices, and the benefits of new environmental regulation. However, by 2030, **the estimated production of bio-BTX will be 450 kilotons, which is less than 1% of the total production [86].**

One event that may play a role in the spread of Bio-BTX is the expected growing shortage of aromatics from the petrochemical industry. Therefore, the demand for chemicals from renewable sources is expected to increase rapidly and generate an urgent need for alternative raw materials and sustainable technologies to produce drop-in biobased alternatives [221]. Currently, all lignin-based BTX aromatics are still in the R&D phase, and commercial-scale production could begin after 2025. **The actual TRL associated with lignin-based BTX production is 4-6, and its estimated actual selling price is 1,4 €/L, while the fossil-based BTX selling price is less than 1 €/L [86].**

Among the R&D initiatives that obtained interesting results, there are [86, 222, 223]:

- ICCP (Integrated Cascading Catalytic Pyrolysis) by BioBTX project (The Netherlands), which uses catalytic pyrolysis. However, the whole process is based on a new two-step pyrolysis aimed at protecting the zeolite catalyst from minerals in the feedstock and enhancing the BTX yields (to petrochemical grade). One of the main patents associated with this technology is reported below in the patents section.
- BIORIZON (EU research project) based on tailored separation technology (nanofiltration and/or pervaporation) applied to a specific lignin hydrolysis system. The final stream containing phenolics and polymers can be processed to BTX (approximately 60%) and other products.
- The biome bioplastics (UK) process is based on novel lignin-degrading bacteria/enzymes that can lead to aromatics.

Other R&D initiatives on lignin-BTX are carried out by multinationals and research consortia, mostly in North America and Europe. Figure 3.12 presents the main R&D efforts at the global scale.

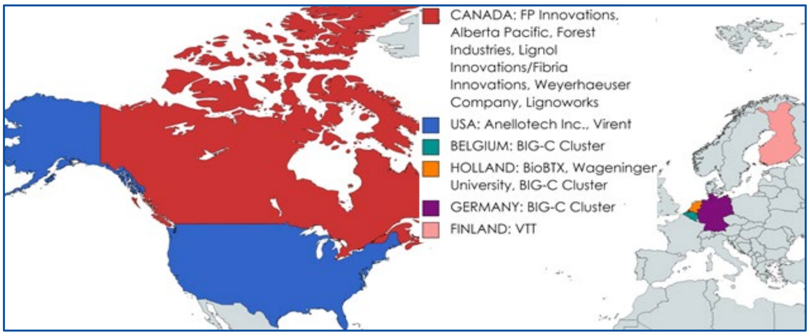


Figure 3. 12 The leading actors in lignin- based BTX [86]

3.3.2 Patents (BTX)

Table 3. 23 Patents selected by keyword on the ORBIT Patents DB [36]. Patents related to lignin-based BTX production in the last 5 years (patent clusters have a grey background, the main patents are shown in bold. Among these, the University of Seoul patent data were partially prepublished [217-219] and are reported in Table 3.3.7). Acronyms: L/M (Large industry/Multinational), E/C (Enterprise/Company), U/RO (University/Research Organization). CHN (China), NL (The Netherlands), WIPO (World Intellectual Property Organization)

Title	Applicant(s)	Applicant(s) business and country (acronym)		Pub. Number	Pub. date	Patent org.
Method for preparing aromatic hydrocarbons from biomass pyrolysis liquid hydrodeoxygenation oil	HENAN BUF BIOENERGY	E/C	CHN	CN110028983	2019–04–26	CHN
BTX Catalyst for Increasing production of BTX aromatics by mild-condition hydrodeoxygenation of lignin pyrolysis-derived phenolics and selective production method of BTX aromatic using thereby	**UNIVERSITY OF SEOUL**	**U/RO**	**Korea**	**KR10–2020–0107413**	**2019–03–07**	**Korea**

Method for selectively producing btx aromatics from phenols, which are generated through lignin pyrolysis, by mild condition hydrodeoxygenation reaction using fereo_x/zro_2 catalyst	**UNIVERSITY OF SEOUL**	**U/RO**	**USA**	**WO2019/045150**	**2017–08–31**	**WIPO**
Method for microwave pyrolysis of biomass	CHINA PETROLEUM & CHEMICAL	L/M	CHN	CN111099943	2018–10–29	CHN
Efficient recovery of valuable components from biomass catalytic pyrolysis effluent	ANELLOTECH	L/M	USA	WO2019/022743	2017–07–27	WIPO
Improved catalytic fast pyrolysis process with impurity removal		L/M	USA	US20200290896	2016–06–22	WIPO
Process for producing BTX by catalytic pyrolysis from biomass without recycling oxygenated compounds	IFPEN - IFP ENERGIES NOUVELLES	U/RO	France	EP3464511	2016–05–31	EU
Process for producing BTX and alcohols by catalytic pyrolysis of biomass and fermentation of the gaseous pyrolysis effluent	IFPEN - IFP ENERGIES NOUVELLES	U/RO	France	WO2017/207200	2016–05–31	WIPO
Process for producing BTX by catalytic pyrolysis from biomass with injection of oxygenated compounds	IFPEN - IFP ENERGIES NOUVELLES	U/RO	France	US20200255743	2016–05–31	USA

Method for preparing BTX through catalytic cracking of biomass pyrolysis gas	NORTH CHINA ELECTRIC POWER UNIVERSITY	U/RO	CHN	CN106244184	2016–08–22	CHN
Method for preparing BTX through catalytic pyrolysis of biomass		U/RO	CHN	CN106244185	2016–08–22	CHN
Process for the preparation of low molecular weight aromatics (btx) and biofuels from biomass	**BIOBTX**	**E/C**	**NL**	**US20200181498**	**2016–06–24**	**USA**
Synergistic co-pyrolysis of biomass and methane for hydrocarbon fuels and chemicals production	OKLAHOMA STATE UNIVERSITY	U/RO	USA	WO2016/196517	2016–05–31	WIPO

The most recent patents include 14 inventions. The main conversion technology used is catalytic pyrolysis of biomass.

In patent CN110028983, BTX production is achieved from bio-oil through thermal cracking and hydrodeoxygenation of the biomass. This process is followed by fractionation, extraction, disproportionation, isomerization and separation steps aimed at purifying the final product.

The University of Seoul is the applicant of two patents proposing the production of BTX from lignin by means of a reaction catalysed by XReO.x/YO_2 (X can be Fe, Pd, Ni, Ru, Cu and Y can be ZrO_2, CeO_2, $ZrCeO_2$). The maximum BTX yield (77,2%) was achieved with Pd at 350 °C. The major component of the BTX composition (71,3%) was toluene.

The patent from IFPEN - CHINA PETROLEUM & CHEMICAL deals with a microwave-assisted method for the pyrolysis of biomass mediated by a porous composite material. According to the method, the porous composite material can generate electric arcs in microwaves so that high temperature is rapidly generated and the biomass is cracked into chemical raw materials.

The two patents by ANELLOTECH-USA regard an improved catalytic fast pyrolysis process for producing mainly aromatic compounds (benzene, toluene and xylenes) from biomass feedstock containing impurities (alkali and alkaline earth metals, sulfur and nitrogen components) and a separation process for the pyrolysis effluent containing a naphthalene-rich oil phase, a phenolic-oil phase and a vapour phase containing off gas, water and BTX. The vapour phase can be condensed to separate liquid water, liquid hydrocarbons and BTX.

The cluster of 3 patents from IFPEN - IFP ENERGIES NOUVELLES (a French public R&D institution) describes a process for the production of BTX and alcohol from biomass. The process includes a biomass catalytic pyrolysis treatment in fluidized-bed reactors and a subsequent separation leading to BTX. The residual gaseous and liquid streams are bioconverted to achieve at least one oxidized compound (usually alcohols, diols, acid alcohols, carboxylic acids, aldehydes, ketones and esters with 2 to 6 carbon atoms).

The cluster of 2 patents from NORTH CHINA ELECTRIC POWER UNIVERSITY (a public R&D institution) reported a new method for preparing BTX (benzene-toluene-xylol) by catalytic pyrolysis of biomass. A zeolite carrying metal nitride serves as a catalyst, and biomass is mechanically mixed during catalytic pyrolysis at 450–850 °C. The condensed pyrolysis gas is rich of BTX.

BIOBTX (The Netherlands) is a company that patented an interesting process (ICCP technology described above) for the preparation of aromatic compounds from biomass. The biomass is converted in a catalytic reaction (called "catalytic aromatization"), producing a higher molecular weight fraction comprising polyaromatic hydrocarbons (PAHs) and a lower molecular weight fraction (BTX). These fractions are separated by distillation. The PAH fraction is catalytically hydrogenated to obtain (and separate) polycyclic alkanes and a residue that is recycled in the initial biomass feed stream.

Oklahoma State University developed novel catalytic approaches for producing BTX from biomass using MoAg/HZSM-5 and MoZn/HZSM-5 catalysts in a methane atmosphere. This approach follows a patent based on the use of a microwave-assisted pyrolysis reactor for the production of a bio-oil from a carbonaceous material. The raw bio-oil contains oxidized aromatic hydrocarbons that can be catalytically reduced to produce an upgraded bio-oil with reduced aromatic hydrocarbons.

3.4 FUELS

The latest IEA Report "Energy Technology Perspectives 2020" [224] reports desirable future technical developments and social choices aimed at reducing greenhouse gas (GHG) emissions over the next 30 years influencing the trend in CO_2 emissions (see Figure 3.13). Among the major contributors to CO_2 emissions, the transport sector is expected to achieve a rapid reduction of its emissions in the future.

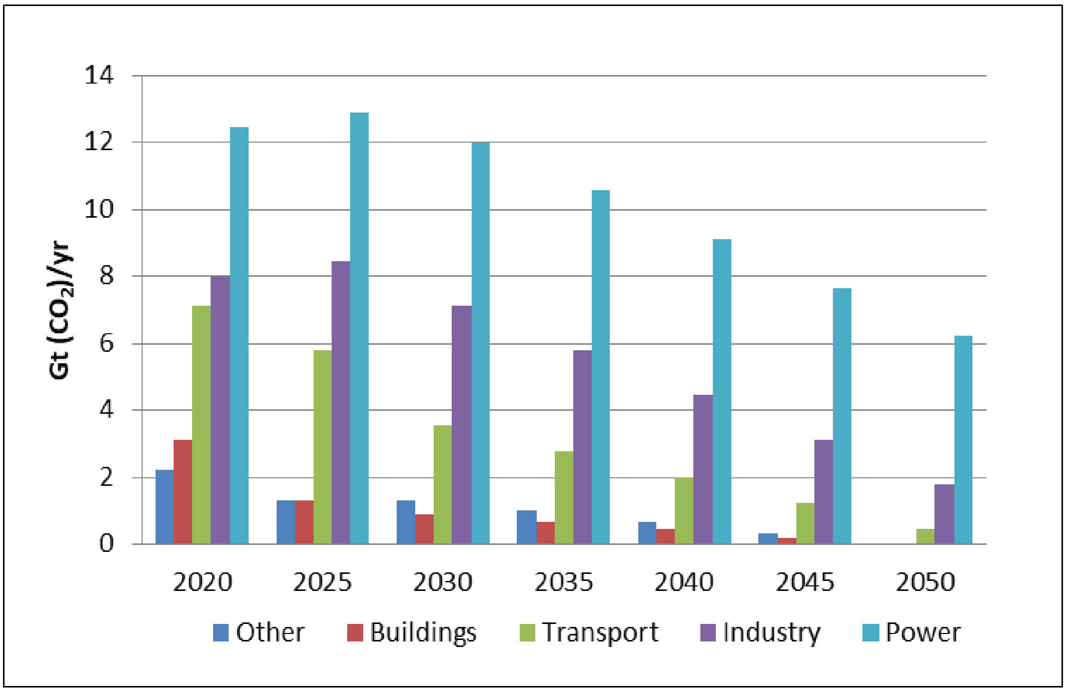


Figure 3. 13 CO_2 emission trends expected (data collected from [224])

The introduction of new sustainable transportation strategies, technological evolutions and the sustainable use of energy sources and fuels obtained from renewable sources will contribute significantly to achieving this goal.

The development of bio-oil or biocrude intermediates compatible with existing petrochemical plants derived from renewable sources is of capital importance. The use of existing petrochemical technologies, and the full compatibility with existing engines for cars, boats and airplanes, could ensure the rapid replacement of fossil fuels with biomass-derived fuels. These fuels could be added to fossil fuels as "drop-in" fuels.

The different bio-oils can rarely be blended with crude oil as a feedstock for the refinery process (see Fig. 3.14). They are preliminarily sent to hydrotreating sections or, especially for feedstocks with an initial boiling point higher than 340 °C, to the fluid catalytic cracking (FCC) section [225].

The treatment conditions (e.g., relative percentages, temperature, pressure and flows of crude oil and biopetroleum) must be set after a thorough evaluation of the biocrude characteristics and the plant layout. The goal is to improve yields and prevent the palnts damage (e.g., against corrosion, deactivation of the catalyst, clogging of the system).

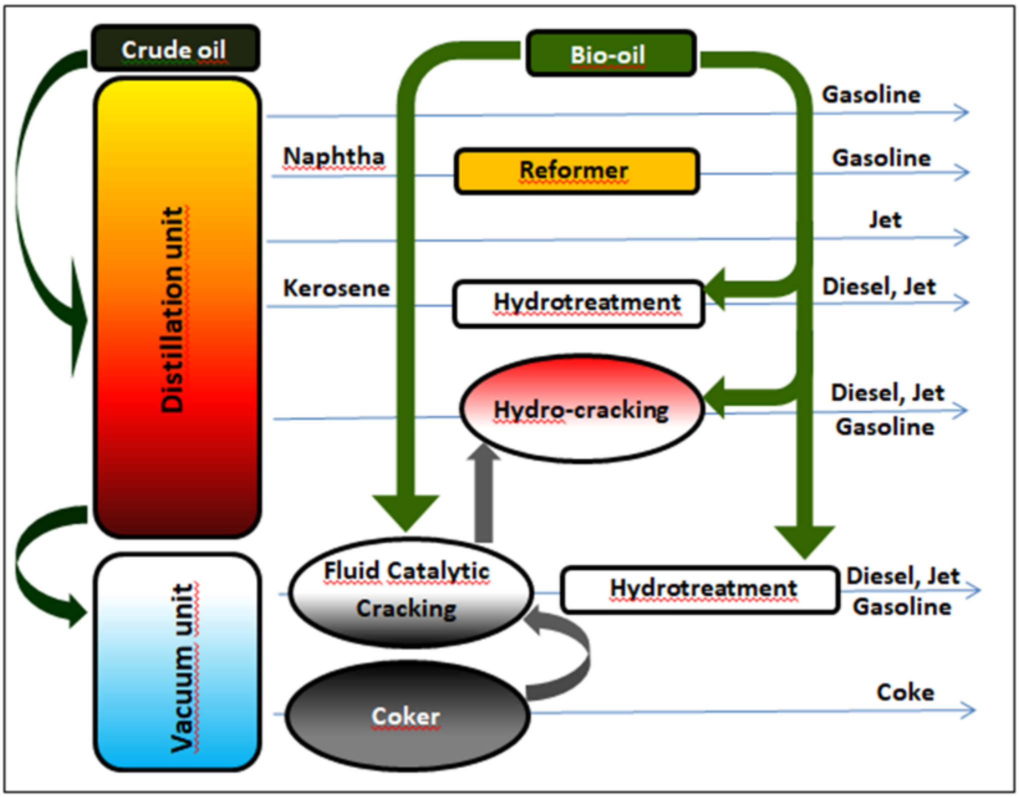


Figure 3. 14 Bio-oil preferential insertion points in a typical petrochemical refinery scheme (adapted from [225])

The main parameters of bio-oil that influence the quality and quantity of refined products are:

- residual oxygen content (which mainly affects the yield and quality of products)
- acidity (increases corrosion)
- miscibility and viscosity (make plant management more complicated)

Some IEA-Task 39 publications [225, 226] recommend insertion at the FCC instead of at the hydrotreating section.

In the FCC section of a classic petrochemical plant, the heavy crude oil (with an initial boiling point above 340 °C) are converted into lighter molecules at approximately 500 °C in a fluid system containing zeolites as catalysts. Then, these streams are separated in other refinery sections, and the catalyst is regenerated in the FCC section at approximately 700 °C. Table 3.24 presents the pros and cons of bio-oil insertion in the FCC section.

Table 3. 24 Pros and cons of bio-oil insertion in the FCC section

FCC (Fluid Catalytic Cracking) bio-oil insertion in a typical petrochemical plant	
Pros	**Cons**
Few risks of catalyst inactivation	Suitable for bio-oils containing heavy molecules and having high boiling point temperatures
No additional hydrogen required	The main product is gasoline (low amounts of the other fuels can be obtained)

During hydrotreatment, catalytic hydrogenations are aimed at converting low value products products (usually generated in other plant sections) into more valuable fuels such as jet fuel. The hydrogenations must be efficient and complete (the aromatic components must be quite completely hydrogenated).

Table 3.25 shows the pros and cons of bio-oil insertion at hydrotreatment.

Table 3. 25 Pros and cons of bio-oil insertion at hydrotreatment

Hydrotreatment bio-oil insertion in a typical petrochemical plant	
Pros	**Cons**
Conversions aimed at the production high value fuel fractions (jet fuel, diesel, gasoline)	Probable and often irreversible catalyst deactivation (possible negative effects on some plant sections, on the yields and on the products quality)
Efficient catalysts (high yields of the target products)	Necessary brittle and expensive catalysts (containing noble metals such as Ru, Pd, Pt) and strong pressure/temperature conditions with large hydrogen requirements

Among the conversion pathways from biomass to drop-in biofuels, many approaches are still reported at the lab-level [167]. Often, the whole biomass is employed and is converted by means of different technological solutions (or combinations of them). A few interesting niche applications regard the conversion of the residual lignin to jet fuels [167, 186, 203].

An description of biomass- and biomass-derived lignin to fuel is reported, with a specific focus on the “sustainable aviation fuels” (SAFs) contributing to the production of jet fuels.

3.4.1 Lignocellulosic feedstock derived SAF

"Sustainable Aviation Fuel" (SAF) comprises fuels derived from renewable sources that can be used in the production of jet fuel. SAFs are certified to be safe to use, usually mixed (as “drop-in fuels”) with fossil based jet fuels to varying degrees and supplied by the same infrastructure without requiring any adaptation of aircraft or engines.

As reported in the final publication (September 2020) of the Air Transport Action Group (ATAG)[1] project called "WAYPOINT 2050[2]" [227], "*…by 2015, the first regular supply of SAF was being delivered to airports, and since then, a number of new production facilities have been in development or construction. Despite this progress, it is estimated that by 2025, only approximately 2% of total jet fuel use will be with sustainable aviation fuels.*"

The same publication, whose data consider the effects of COVID-19, reports in 2021 a mean "number of kilometres travelled by paying passengers (RPK)" decrement from 8 to 3 trillion. This gap is expected to remain until 2050, when the RPK will be 20 trillion (instead of 25 expected before the COVID era). The future RPK increment, decelerated by the pandemic, will still be important and will need to be managed to limit CO_2 emissions.

According to the ATAG [227], for the 2050 aviation industry goal (in the SAF-based scenario), it is possible to increase the RPK ten times and halve the CO_2 emissions (grey bars in figure 3.15). The overall CO2 emissions foreseen at 2050 can be significantly reduced up to 60% through the replacement of fossil fuels (Figure 3.15).

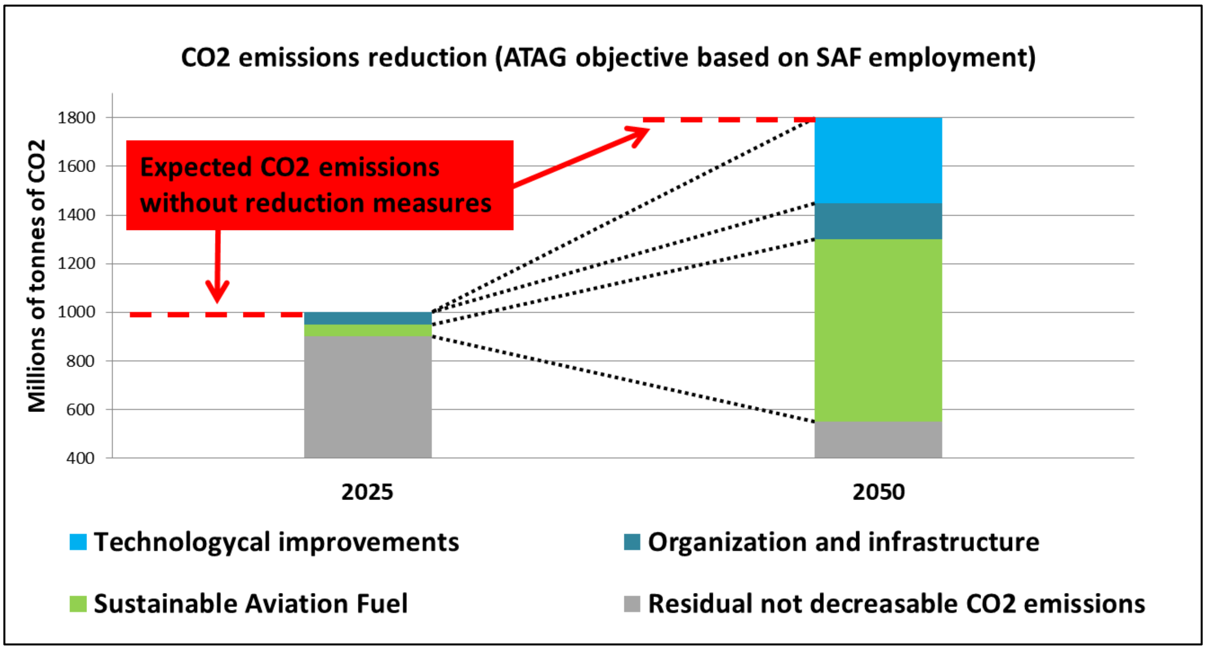


Figure 3. 14 CO_2 emissions reduction objectives from 2025 to 2050 (data extrapolated from [227])

It is possible to hypothesize several scenarios targeted on the same 2050 objective [227]. These additional scenarios are mainly based on faster technological evolution. The most ambitious

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[1] The Air Transport Action Group (ATAG) is an highly respected not-for-profit association that represents all sectors of the air transport industry. The ATAG provides a platform for the commercial aviation sector to work together on long-term sustainability issues. It is funded by its members. These include airports, airlines, airframe and engine manufacturers, air navigation service providers, leasing companies, airline pilot and air traffic controller unions, aviation associations, chambers of commerce, tourism and trade partners, ground transportation and communications providers. The membership, which is spread across the aviation value chain, provides a robust basis to speak with international decision-makers and represent a broad industry view. The ATAG has 40 members worldwide. Its funding members play a driving role within the ATAG and devote substantive time and resources to the association. They include: Airports Council International (ACI), Airbus, ATR, Boeing, the Civil Air Navigation Services Organisation (CANSO), CFM International, GE, the International Air Transport Association (IATA), Pratt & Whitney, Rolls-Royce and Safran.

[2] WAYPOINT 2050 is a collaboration of experts from across the aviation sector, looking at how industry can accelerate working together to contribute to the world's climate action mission.

scenarios depict the exclusive use of 100–200 seat aircraft flying with electric and/or hydrogen engines.

Among the potential sources of SAF, lignocellulosically derived fuels and lipids from oil crops are the greatest contributors [167]. Municipal solid waste, industrial off-gases (containing CO and CO_2) and atmospheric CO_2 capture/oligomerization technologies complete the list of sources.

The technology for the conversion of lipids to fuels consists of catalytic hydrodeoxygenation, which can generate a certifiable SAF (the ASTM D1655 standard on the co-processing of lipids to produce biojet fuel was recently approved). The conversion pathways referring to the other renewable sources need further evolution to be regularly co-processed in petrochemical facilities. Currently, ASTM D7566 (created for alternative jet fuels) specifies the blend limit, and ASTM D4054 standard describes the tests and properties necessary for the evaluation and approval of a new fuel from nonconventional sources.

Conversion of lignocellulosic biomass into fuel include thermal conversion by catalytic pyrolysis or by hydrothermal liquefaction (HTL) (both obtain a bio-oil whose characteristics must be improved to comply with the ASTM standards) and gasification followed by Fisher-Tropsch (FT) processes.

Lignin can be a feedstock for the production of SAF. A few applications (presented in Section 3.4.2) are available for the specific conversion of lignin by the thermal treatments already described. A technical focus on the atm project regarding the use of forest biomasses in order to obtain SAF was included in the box below. Even if the project described used the entire biomass, the achieved results provide a reference scenario regarding the production of SAF from lignocellulosics through thermal processes.

TECHNICAL FOCUS ON THE ATM PROJECT REGARDING THE USE OF FOREST BIOMASSES IN ORDER TO OBTAIN SAF

An interesting assessment regarding the use of forest biomasses to obtain SAF, is reported in the publications of the ATM project. The final report of this project (published in March 2019) is hosted on the IEA task 39 website [227]. The main funders of the ATM project were the Canadian consortium GARDN (Green Aviation R&D Network) and BOEING. The forest biomass to bio-crude conversion processes tested in the ATM project are:

- FP - Fast Pyrolysis (BTG-Bioliquid - Empyro Hengelo, NL)
- CP - Catalytic Pyrolysis (VTT – Catalytic Pyrolysis plant, FIN)
- HTL - HydroThermal Liquefaction (Aarus University plant, DK)

Table 3.26 compares three bio-crudes with a typical crude oil.

Table 3. 26 Comparison of three bio-crudes and crude oil (data collected and adapted from [227])

Parameters	FP (BTG)	CP (VTT)	HTL (Aarhus)	Crude oil
Heating Value, MJ/Litre (HHV)	In the range of 20 – 35 (sharply less than the crude oil value)			44
Density (g/l)	~ 1,2 (management risks due to the density ranking: Bio-crude > H_2O > Crude-oil)			0.86–0.94
Oxygen %	> 40	~ 15		< 1
H/C	0,17	0,08	0,09	0,15
Aromaticity %	42.9	63.9	60.9	5–30
pH	2,5 – 4,5 (all the bio-crudes show an acidic pH)			---
Water, wt %	> 20	< 10		0.1
Biocrude yield, wt%	64	18	37	---

Compared to crude oil, bio-crude oils from biomass show a high oxygen (mainly FP bio-crude characterized by an oxygen content above 40%) and a high aromatic compound contents.

The high oxygen contents of bio-crude oils increase their reactivity and lower their energy density. Aromatics[3], water[4] and other biomass components (mainly belonging to the cellulose and hemicellulose fractions of the biomass) content also negatively affect the use of bio-crude in the normal jet fuel production path.

To better comply with the standards, it is necessary to upgrade the bio-crude oils. To use bio crude oils in the usual jet fuel production path, the ATM project evaluated the experimental upgrade tests on the three bio-crudes, by simulating their feeding into specific petrochemical refining phases.

The three bio-crudes upgrading trials were conducted through two technological approaches and were carried out at pilot scale to obtain distillation products:

- Mix of bio-crudes (reported in Table 3.27) with furnace fuel oil (fossil-based) and a single-stage hydrotreatment (parameters and description in Table 3.4.5) in presence of MoS_2 as the catalyst (**Canmet ENERGY-Ottawa technology**).
- Two stage hydrotreatment of the bio-crudes (**Pacific Northwest National Laboratory-Washington technology**).
- **Canmet ENERGY-Ottawa's (CE-O)** upgrading approach involves oil blends of bio-crude and furnace fuel oil (fossil-based) optimized for a petrochemical-like hydrotreatment. Table 3.28 reports the average composition of the oil-blends.

Table 3. 27 Feedstock oil blends composition (data from [227])

Oil blends average composition	
Bio-crude	**18%**
Furnace fuel oil	**70%**
Surfactant	**4%**
Methanol	**1%**
Diluent (viscosity agent)	**4%**
Other minor components	**3%**

The catalyst proposed (MoS_2) is typically used in refinery processes (hydrogenation, hydrocracking and hydrodesulfuration) and it can also promote the hydrodeoxygenation of the bio-crude.

Canmet ENERGY – Ottawa (pilot scale plant parameters and description)

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[3] The presence of aromatics in transport fuel blends (e.g., in gasoline up to 40%) is tolerated. Their concentration in jet fuels has to be sharply lowered (mainly because of their low H/C ratio). A high aromatics concentration accelerates coke formation. Moreover, their upgrade to cycloalkanes by hydrogenation is challenging and requires high temperatures, high hydrogen pressures and highly active catalysts containing precious metals.

[4] Water is present in the biomass feedstock and is formed in the dehydration reactions (mainly during pyrolysis). The water affects the combustion efficiency and promotes phase separation during fuel storage. Moreover, the water can directly and indirectly (by favouring the creation of acidic conditions thus accelerating the polymerizations and the coke formation) deactivate the catalysts.

Table 3. 28 Canmet ENERGY pilot scale plant parameters and description (Ottawa)

Feed	Reactor	Streams	Oil phase distillation fractions
1) Oil-blend microemulsion catalyst (MoS_2) 2) Sulfiding solution (catalyst in situ regeneration) 3) Hydrogen	Bubble column reactor	1) Gas 2) Aqueous phase 3) Solids (catalyst, organic) 4) Oil phase	1) Naphtha (155 °C) 2) Jet fuel (155–250 °C) 3) Heavy middle distillates (250–345 °C) 4) Heavy gas oils (+345 °C)

The fate of the renewable carbon fraction initially present in the 18% of bio-crude added in the starting mix, can be determined using ^{14}C analyses (radiocarbon method). More than 75% of the renewable carbon is distilled into one of the product fractions. More than 30% of this carbon contributes to the heavy middle distillates fraction (250–345 °C) and almost another 30% is converted to jet-fuel (155–250 °C) [227].

The **Pacific Northwest National Laboratory (PNNL), Richland Washington, USA,** approach is based on an initial hydrotreatment at low temperature in a Ru-catalyst bed reactor, aimed at separating a hydrophobic phase containing stabilized bio-crude (effective especially for the FP bio-crude) and a second hydrotreatment, characterized by more drastic reaction conditions (higher temperature and H_2 pressure), in a down-flow packed-bed reactor loaded with a commercial Ni-Mo sulfide catalyst. The PNLL upgrade test addressed only bio-crude oils (no mixtures with fossil-derived oils were prepared).

After the PNLL upgrade, the distilled jet-fuel fraction yield is not far from 30% and the diesel fraction is higher than 40%.

The final part of the ATM project report includes a techno-economic comparison of the six tested refined bio oils (RBO).

Table 3.29 presents the main results of this comparison.

Table 3. 29 Techno-economic analysis: Main results of the six tested refined bio oils (RBO) (adapted

from [227]).

	FP (CE-O)	FP (PNNL)	CP (CE-O)	CP (PNNL)	HTL (CE-O)	HTL (PNNL)
Total (bio-crude+upgrade) RBO yield(wt%)	~ 20		~ 10		~ 25	
Heating Value (HV) - RBO/HV - Crude-oil	0,80 – 0,90 (fossil based oil Heating Value considered as reference is 44 MJ/l)					
Minimum Selling Price (MSP)/jet fuel (SP)[5]	**4**	**5**	**5**	**6**	**3**	**3**
CAPEX (M€)	100 – 130 (mostly due to the bio-crude production facility: HTL > CP > FP)					
Jet fraction (%)	20.8	24.7	32.8	36.6	29.8	22.9
Cost sensitivities in consumable furniture	H_2 > Biomass	Biomass > H_2	Biomass	Biomass	Biomass > H_2	Biomass > H_2

The data in Table 3.29 show a large gap between the bio-jet and the conventional fossibil based products. The co-processing of bio-crudes in existing petrochemical facilities is a fundamental requirement and has to be further improved for the short- to mid-term partial replacement of fossil fuels.

For the mid-to-long term situation feeding the plant with lignin can represent a valuable options also considering that they could be more easily convertible into cycloalkanes for jet fuels, as described in the following paragraph.

3.4.2 From lignin to biofuel (lab-research overview)

Hydrocarbons for fuels require intense hydrodeoxygenation (deep HDO) to reduce the oxygen content and obtain (cyclo)alkanes and (alkyl)aromatic fractions [167, 186].

The lignin-derived liquid fuels targeted are usually:

- Aliphatic (iso)alkanes or cyclo-alkanes for jet fuels, gasoline and diesel [186]
- Aromatics, mainly in the form of alkyl benzenes [170–178] that offer specific properties to fuels (i.e., octane boosters in gasoline or for improving the quality and properties of jet fuel, such as elastomeric swelling and lubricity characteristics)
- Heavy fractions (low sulfur) of phenolic/aromatic lignin oils (oligomers) that can be blended with heavy marine (bunker) fuels [230–237]

The integrated lignin conversion technologies may include [170–185, 240–250]:

- Lignin depolymerization processes, as described in 3.3, namely:
    - Fast pyrolysis (FP)
    - Liquid Phase Solvolysis (with organic solvents, noncatalytic)
    - Liquid phase oxidative/reductive depolymerization (mainly using organic solvents), including the “lignin-first” approach, which applies directly to biomass
    - HydroThermal Liquefaction (HTL)

- Gasification to syngas (followed by Fischer Tropsch synthesis of methanol, olephines or by syngas fermentation to bio-alcohols)

- Deoxygenation processes, as described in 3.3, include the following:

    - Deep HDO of lighter phenolic bio-oil fractions for direct production of

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[5] IATA (International Air transport Association) observatory on Jet-Fuel selling price estimated mean price aat 0,36€/l

(cyclo)alkane fuels [245–247]

- Mild hydrodeoxygenation (HDO) to produce marine heavy fuels or biocrude for coprocessing with gas oil [244]
- Catalytic fast pyrolysis (CFP) for direct deoxygenation and aromatization of phenolics to BTX aromatics and naphthalenes [181–185]
- Alkylation of BTX aromatics (if needed) to meet the specifications for jet fuels [206, 210–212]

With regard to the liquid phase depolymerization processes leading to oxygenated phenolic bio-oil, significant R&D advances have been reported and several pilot-scale demonstrations have been realized coupled with techno-economic evaluation [167–169, 224–239]. The main challenge of this step is to decrease H_2 use (in the hydrogenolysis processes) and improve the effective and energy efficient solvent recovery and separation/extraction of the light and heavier phenolic fractions for downstream upgrading.

In the deep hydrodeoxygenation processes that aim to directly produce drop-in (cyclo)alkanes, effective and **stable bifunctional catalysts** (or dual catalyst systems comprising of an acid and a hydrogenation-supported metal) need to be developed.

With regard to the CFP, as discussed in Section 3.3, there are catalysts available (mainly zeolitic) and FP technology that can offer bio-oils with high (>80%) concentrations in aromatic hydrocarbons of the BTX family and (methyl)naphthalenes [181–185].

When milder “reactive/aromatization” parameters (catalyst, temperature) are applied, which lead to the coproduction of BTX/naphthalenes and alkyl-phenols, the **cost of** aromatic/phenol separation also needs to be considered.

When the aromatics or cyclo-alkanes (present in the first intermediate products still not separated) are intended for jet fuels, selective **downstream alkylation processes**, i.e., with zeolites at moderate temperatures and with appropriate alkylation agents such as bio-alcohols, are needed to obtain the appropriate composition typically containing C12-C18 paraffins (~5%), dicycloparaffins (~60%), cyclo-olefins (~10%), and cyclohexanone and cyclohexanol derivatives (~10%) [224].

The utilization of low-sulfur heavy lignin oils as marine/bunker fuels (blends with heavy petroleum fuels), derived by low-cost **solvolysis of technical lignins** (moderate temperature, no catalyst, no external H_2) with the use of eco-friendly and recoverable solvents, such as methanol and ethanol, has been regarded as a promising application. Recently, a spin-off company, Vertoro (The Netherlands), has produced CLO (**crude lignin oil**) with the trade name GEM® (GOLDILOCKS® enriched methanol), which can be derived either from isolated lignins or from the parent biomass, based on previous work developed at the Eindhoven University of Technology.

The project, IDEALFUEL H2020 [235], in collaboration with other important partners (CSIC-ITQ, OWI, Bloom Biorenevables, Uniresearch, Winterthur Gas & Diesel, GoodFuels, GmbH and Varo Energy), aims to convert lignin into a biogenic heavy fuel oil (Bio-HFO) usable as a drop in fuel in the maritime fleet. The core technology of this project is focused on the catalytic mild HDO also applied to lignin-containing sugar impurities. The current technological readiness level in this field is 3, and IDEALFUEL has to reach at least TRL 5. This type of CLO can be considered a promising candidate for marine fuel blends, as well as lignin-derived biocrudes for downstream HDO towards alkane or aromatic transportation fuels [231–237].

Gasification of lignin generally produces syngas with a composition ($CO + H_2 + CO_2 + CH_4$) similar to those obtained from several lignocellulosic biomass feedstocks [170]. In addition, ash and H_2S can also be produced due to the presence of sulfur and inorganics in many technical lignins, such as kraft lignin. The composition of syngas can vary depending on the gasification temperature and pressure, presence of steam and oxygen, heating rate, and composition of feed lignin [249]. Downstream gas cleaning and alcohol/hydrocarbon production via fermentation [250] or FT synthesis (coupled with hydrocracking in the case of wax production) utilizes the same technologies and processes as those used with the more conventional coal/biomass gas-to-liquid (GTL) processes. However, the need for gas cleaning makes this technology less mature than GTL processes.

3.4.3 Market (Fuels)

Many IEA initiatives (Tasks, Special Projects and Inter-Task Projects), in the “IEA Bioenergy Work Programme 2019-2021 Triennium” [251], were dedicated to biofuels. Report published include informations on market data and ongoing research [224–226, 237, 251–253]. This section summarizes some highlights of these publications with a particular focus on lignocellulosic biomass (especially the lignin fraction)-and more in details, jet fuels.

To meet GHG emissions targets [224], established conventional biofuels, such as ethanol, fatty acid methyl ester (FAME) and hydrotreated vegetable oils (HVOs), must be quickly complemented by **new advanced biofuels** produced from abundant and sustainable feedstocks.

In the policies framework, the IEA WEO 2018 suggests the introduction of a “Carbon Price” (measured in EUR/tonne CO_2eq), for the emissions due to the use of fossil fuels. The effect at 2040 could be boost the diffusion of advanced biofuels, lowering the fossil fuel demand and stabilizing the current crude oil prices.

In the IEA 2020 publication “Advanced Biofuels – Potential for cost reduction” [252], a comprensive analysis of advances biofuels was reported. In particular, Figure 3.16 compares the cost of some advanced biofuels compared to 1 L of gasoline.

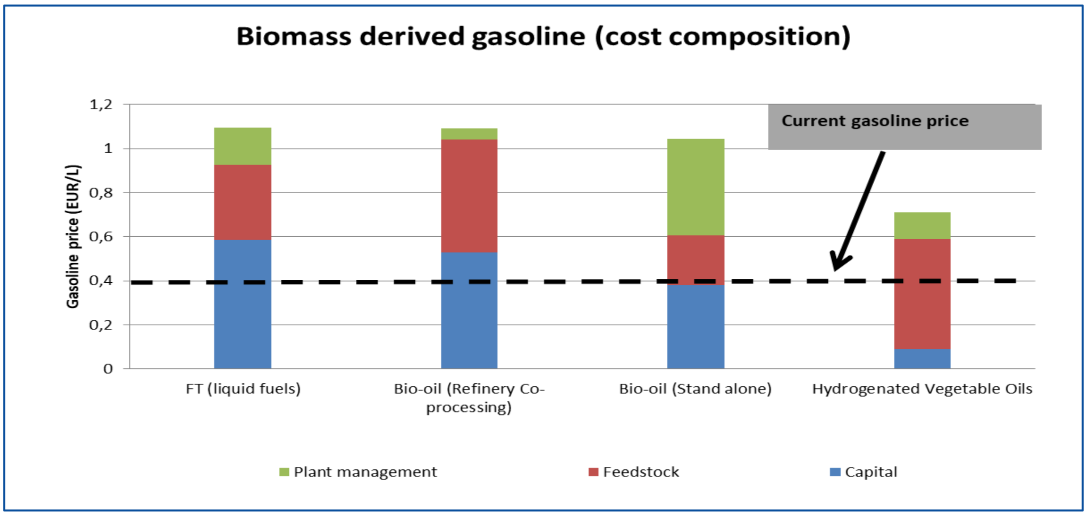
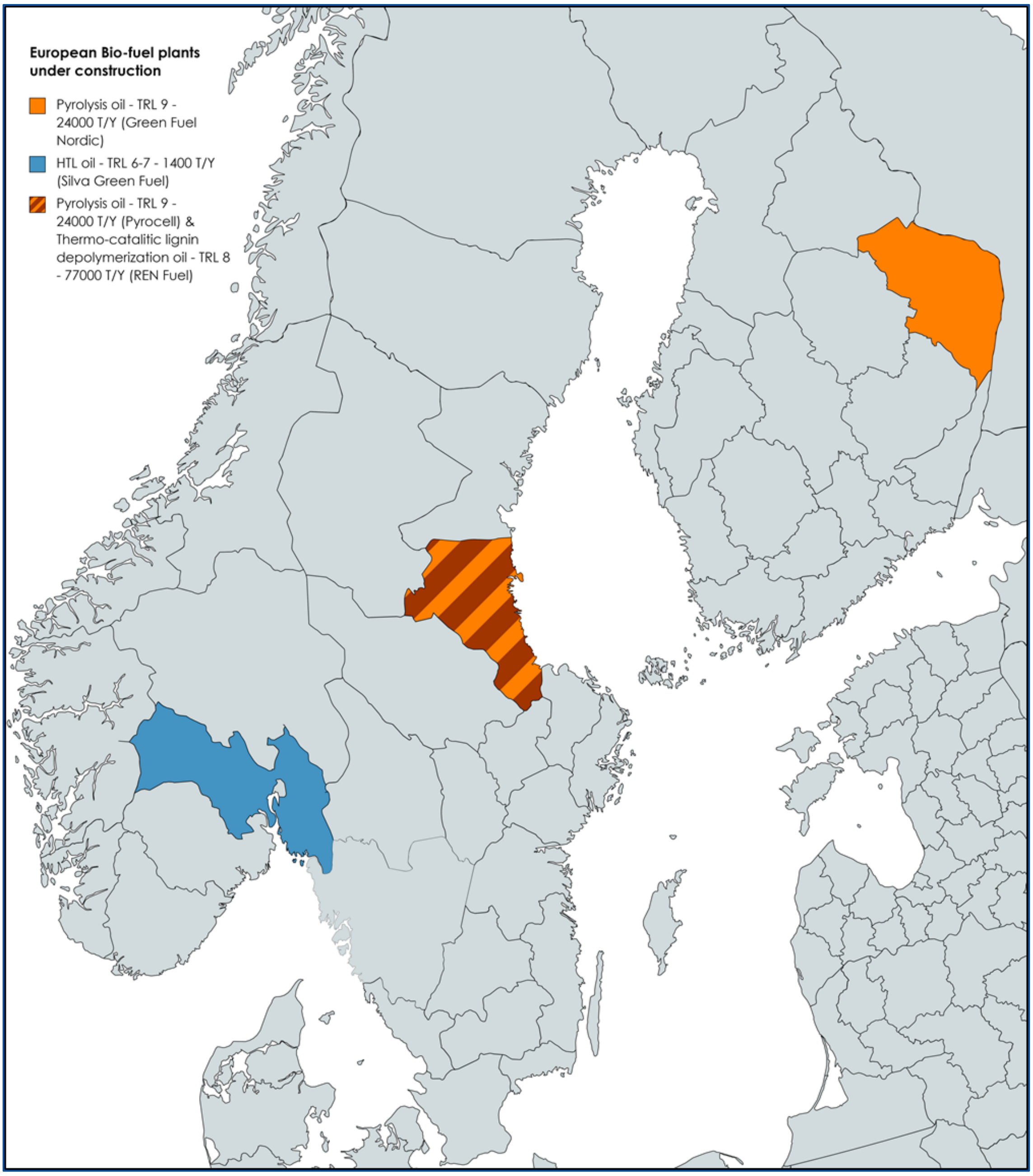


Figure 3. 15 Composition of gasoline prices (€/L) linked to invested capital, management costs and feedstock costs related to 4 hypothesized technologies (data collected from [252])

The ETIP[6] Bioenergy working Group 2 (conversion processes) in 2020 published “Current status of advanced biofuel demonstrations in Europe” [254]. In Figure 3.17, the main characteristics of the latest European bio-oil plants under construction in Scandinavian countries are presented.



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[6] European Technology and Innovation Platforms (ETIPs) are industry-led stakeholder fora recognized by the European Commission as key actors in driving innovation, knowledge transfer and European competitiveness in the energy sector. The mission of ETIP Bioenergy is to contribute to the development of cost-competitive, innovative world-class bioenergy and biofuels value chains, to the creation and strengthening of a healthy European bioenergy industry and to accelerate the sustainable deployment of bioenergy in the European Union through a process of guidance, prioritization and promotion of research, technology development and demonstration. EITP Bioenergy is organized in Working groups and is currently supported by an Horizon2020 funded project ETIP Bioenergy-SABS (Support of Advanced Bioenergy Stakeholders)

Figure 3. 16 European bio-oil plants under construction in Scandinavian countries

Other plants producing pyrolysis oil were already available in The Netherlands, Finland and Germany (built and managed by Twence, Fortum and Karlshrue Institute of Technology, respectively). REN Fuel in Sweden has operated a lignin-oil pilot plant for 5 years. Close to this facility, a larger plant has been projected (TRL 8), whose production capacity is 77000 t/y. The commercial product was commercialized as LIGNOL®

Other similar plants in the world are located in the USA (built and managed by Avello Bioenergy, Battelle Memorial Institute and UOP Honeywell), Canada (built and managed by Ensyn and ABRI-Tech CanmetENERGY), Brazil and Malaysia [86]. The estimated 2018 world production of pyrolysis oil was 500000 T with a market volume of 114 million [255]. The estimated 2014 cost for Canadian pyrolytic oil is 228 USD/T [86].

3.4.4 Patents (jet-fuels)

Almost 1000 biomass (lignin)-to-fuel patents have been published in the last five years. Approximately 400 were published in the last 2 years, and more than 250 were published in the last year.

Focusing the survey on lignin-to-jet fuel conversions, there are seven main patents, among which BIOBTX, already cited in Table 3.30.

Table 3. 30 Patents selected by keyword on the ORBIT Patents DB [36] that are related to the application of lignin based jet-fuel production over the last year. Acronyms: L/M (Large industry/Multinational) E/C (Enterprise/Company), U/RO (University/Research Organization). CHN (China), FIN (Finland), GB-D (Great Britain - Germany)

Title	**Applicant(s)**	**Applicant(s) business and country (acronym)**		**Pub. Number**	**Pub. date**	**Patent org.**
A process for converting biomass	SHELL	L/M	GB-D	EP2750795	17/02/2021	EU
System and method for converting biomass raw material into jet fuel component	CHINA PETROLEUM & CHEMICAL SINOPEC RESEARCH INSTITUTE OF PETROLEUM PROCESSING	L/M	CHN	CN108003939	13/11/2020	CHN

Co-processing for control of hydropyrolysis processes and products thereof	GAS TECHNOLOGY INSTITUTE	U/RO	USA	EP3289048	07/03/2018	EU
System for making renewable fuels including gasoline, diesel, and jet fuel	COOL PLANET BIOFUELS (acquired by NATIONAL CARBON TECHNOL.)	L/M	USA	EP2888339	20/07/2016	EU
Process for the preparation of low molecular weight aromatics (btx) and biofuels from biomass	BIOBTX	E/C	NL	US20200181498	24/06/2016	USA
Process and apparatus for producing hydrocarbons from feedstocks comprising tall oil and terpene-compounds	UPM KYMMENE	L/M	FIN	US9382483	22/06/2016	USA
Fractional catalytic pyrolysis of biomass	VIRGINIA POLYTECHNIC INSTITUTE & STATE UNIVERSITY	U/RO	USA	US8202332	17/03/2015	USA

The first (more recent) patent, owned by SHELL, regards both "*an eggshell-type catalyst having the active metal component located in the outer portion of the support*" and its hydropyrolysis process, which runs in a fluidized bed containing the catalyst (temperature: 270 C - 450 C; pressure: 1 MPa - 7.5 MPa)

The CN108003939 patent report a process for converting a biomass into a jet fuel component. A system containing all the main conversion technologies (gasification unit, synthetic gas purification unit, Fischer-Tropsch reaction unit, hydrofinishing and a hydroisomerization cracking unit) is described, which claims its unique simplicity, integration and efficiency.

The EP3289048 patent shows a versatile hydropyrolysis process able to convert "*differing types of feedstocks, including at least one biorenewable feedstock*" and process downstream to make the products to meet the "*customer requirements and/or overall market demands*". The process conditions are tuned by co-processing a precursor (aliphatic or aromatic) similar to the target product.

COOL PLANET BIOFUELS (acquired by NATIONAL CARBON TECHNOLOGIES) patented "Multiple catalytic processing stations coupled with a system which produces volatile gas streams from biomass decomposition at discrete increasing temperatures or constant temperature". The process is tuneable to maximize the jet fuel components.

The Finnish multinational firm UPM proposes (4th patent) an invention for the conversion of biomass (mainly the resinous tall oil and terpene-based compounds recoverable from the coniferous biomasses usually employed in the pulp mills) to "hydrocarbon components including n-paraffins, and subjecting the hydrocarbon components to isomerisation in the presence of a dewaxing catalyst to form a mixture of hydrocarbon components". Both the hydroprocess and its catalyst (NiW catalyst on a support selected from Al_2O_3, zeolite, zeolite-Al_2O_3, and Al_2O_3-SiO_2) are patented.

The US8202332 patent reported in Table 3.4.7 proposes a "fractional catalytic pyrolysis that allows for the conversion of biomass into target products without the need for post-pyrolysis separation". Biomass contacts a fluid catalytic pyrolysis bed that generates "the desired products in vapour and gas forms, allowing the desired products to be easily separated".

3.5 CARBON FIBRES

Carbon fibres have structures similar to those of graphite with a composition of pure carbon structures sheets arranged in a regular pattern. They have high performance characteristics in terms of heat tolerance, high stiffness, great tensile strength, low thermal expansion, light weight, high flexibility, and high fatigue resistance. Thanks to these properties, carbon fibres are employed in several sectors, including aerospace, civil engineering, automotive, and wind power [256]. Commercial processes to produce carbon fibre precursors are too costly to be applied to large markets, such as the automotive market. Currently, carbon fibres are produced from polyacrylonitrile (PAN). This feedstock is a copolymer made by condensation of acrylonitrile, methyl methacrylate, and itaconic acid that has a high molecular weights (70 000-260 000 g mol−1) and a polydispersity index values in the range of 1.5–3.5 [256]. Lignin from cellulosic biorefining operations could become an ideal precursor for carbon fibre synthesis. The understanding of the fundamental chemistry involved in this process is still limited. Furthermore, a low environmental impact is associated with carbon fibres from lignin. Lignin can result in a high carbon yield and the elimination of the toxic substances involved in carbon fibre preparation from PAN. According to the Oak Ridge National Laboratory [256], lignin feedstock has to be highly purified ensuring ash content of less than 0.1%, low sulfur, and free of particulate matter. Overcoming heterogeneity remains a critical challenge when using lignin in carbon fibre manufacturing.

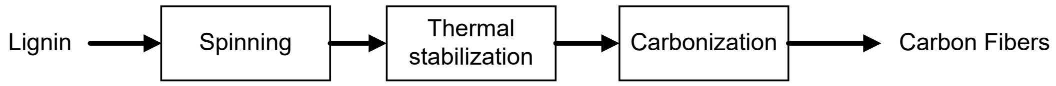

Figure 3. 17 Block flow diagram for the production of carbon fibres from lignin

To obtain lignin-derived carbon fibres, isolated lignin is first processed into fibres by extruding filaments from a melt or solvent swollen gel [1]. In particular, Figure 3.18 shows the block flow diagram of carbon fibre production from lignin. This preparation follows three main process steps:

- spinning;
- thermal stabilization;
- carbonization.

Table 3.31 shows the main differences and process conditions of the main process options to obtain lignin-based carbon fibres [257-259].

Table 3. 31 Summary of the processes to obtain carbon fibres from lignin

Process	Advantages	Disadvantages	Process conditions
Melt Spinning	Simple Low environmental impact	Need to reach the melting temperature	100 – 200 °C
Dry Spinning	Low temperature	Residual solvent Needs final drying	Solvent acetone
Wet spinning	Easy control of the diameter	Needs final drying	Solvent dimethyl sulfoxide
Electrospinning	Possibility to produce nano fibres	High costs	12 KV voltage
Thermostabilization	Maintains a stable fibre morphology	Needs pure oxygen Complex heat treatm-ent	200 – 300 °C
Carbonization	Graphitic structure obtainable	Very high temperature	1100 – 1600 °C

Spinning, in particular, can be conducted using several conditions, and these conditions have an impact on the final product and on the strenght, diameter, and morphology of the precursor fibres. As the source of lignin has a huge impact on lignin properties, the spinning temperature of various lignins varies with the type of lignin. **Depending on the nature of the lignin,**

different spinning methods can be used, such as melt spinning, dry spinning, wet spinning, or electrospinning. Melt spinning consists of rapid heating to high temperature to melt lignin. The spinning temperature is related to the lignin Tg (glass transition temperature) value, Ts (softening temperature), and molten viscosity [259] and it is typically between 100 and 230 °C. Low lignin softening temperatures allow the melt to flow [258]. Inert gases (N_2 or argon) are used to create an inert atmosphere and minimize lignin fibre oxidation.

In the dry spinning method, a suitable solvent is used to dissolve the lignin. The lignin solution is then extruded and subsequently heat dried to obtain the fibres [259].

A solvent or mix of solvents is used in the wet-spinning process. The temperature for lignin solution extrusion can be variable (with or without heating), but then partial drying is necessary to obtain lignin fibre precipitation. This precipitate is then further dried to obtain lignin fibres.

Electrospinning is the most emerging and potentially convenient spinning process. The lignin solution is spun using an electrical voltage-driven method [257]. While passing through the spinneret, the lignin solution becomes electrically charged due to the potential difference between the spinneret and the collector. The combined effect of the electrical charge on the liquid surface and the surface tension of the liquid allows the formation of a drop on the tip of the spinneret needle. Then, the repulsions between surface charges exceed the surface tension of the liquid drop, creating a lignin solution stream from the spinneret to the collector. Thanks to the evaporation of the solvent, lignin fibres are obtained. One major advantage of the electrospinning method is that it can produce nanodiameter fibre mats potentially from any source of lignin.

In general, depending on the application, carbon fibres are then either graphitized or activated to produce structural or functionalized carbon fibres. The process requires highly pure lignin to produce good-quality carbon fibres. Additionally, lignin should have a narrow molecular weight distribution. In some cases, lignin is washed and dried under vacuum and thermally pretreated under vacuum for approximately 1 h to remove any volatile compounds before spinning.

The thermostabilization process consists of a series of reactions, such as rearranging the ether bonds to C–C bonds through radical coupling, dehydration, elimination of CO or CO_2, and additional crosslinking, which raises the T_g of lignin [256]. High temperatures (200 – 300 °C) are necessary. The conversion of thermoplastic lignin into a thermoset material helps lignin fibres maintain the fibre form at higher temperatures. Thermostabilization prevents fibre-fibre fusion and the deformation of lignin fibres during carbonization. The main process parameter (together with temperature) is the heating rate until the final temperature is reached.

Finally, the stabilized fibre is carbonized. In **carbonization**, the temperature is ramped up to approximately 2000 °C to eliminate all elements other than carbon [256]. Almost all oxygen, hydrogen, and nitrogen atoms are rejected as HCN, H_2O, O_2, H_2, CO, NH_3, and CH_4. Due to the release of vapours and gases from the fibre, imperfections and defects form in the fibre, which, in turn, changes the surface and porosity of the fibre. Thus, by changing the rate of heating, the morphology and brittleness of lignin-derived carbon fibres can be controlled. Carbonization is conducted in an inert gas atmosphere that prevents the combustion of lignin fibres.

The final carbon fibres are composed of > 98% graphene carbon in a highly ordered turbostratic structure. The carbon fibres from PAN have tensile strengths of up to 7 GPa and moduli up to 900 GPa. However, PAN-based carbon fibres are expensive, so they are only used in high-value applications. Lignin-based carbon fibre has become an attractive objective, as the need for low-cost carbon fibre has emerged for making major products such as automotive components and wind turbines. In addition to low cost and renewability, lignin is expected to offer additional benefits, including high carbon yield and the elimination of the toxic substances involved in carbon fibre preparation with PAN. The best lignin carbon fibre has only reached a tensile strength of 1.07 GPa and Modulus 82.7 GPa [256]. The tensile strength of lignin-based carbon fibres is usually between 350 and 550 MPa. Nanometric lignin-based carbon fibres, prepared by electrostatic spinning, display smaller the diameters corresponding to greater mechanical strengths. Currently, the mechanical strength of lignin-based carbon fibres is still low due to material impurities and the low molecular weight of lignin.

Among many types of industrial lignin, Kraft lignin has been mostly used with respect to lignosulfonates because has higher purities.

Carbon fibres present a final morphology depending on the carbon precursor chemistry and on the processing methodology. Consequently, most lignin-based carbon fibres derived from the Kraft process have not yet resulted in good mechanical properties due to their different fibre porosities and lack of oriented graphitic structures [260].

3.5.1 Market (Carbon fibers)

In recent years, new technologies that require materials that are light, rigid and resistant to mechanical, thermal and chemical stresses are replacing those based on steel (whose main flaw is the weight) and other light materials having lower performances (see table 3.32).

Table 3. 32 - Comparison, based on density and other mechanical stress resistance characteristics, of carbon fibre with other materials (data collected from [260])

Material	Density (g/cm^3)	Tensile strenght (GPa)	Tensile modulus (GPa)
Carbon fibre	1,75	3,5	230
High-tensile steel	7,87	1,3	210
Alluminium	2,7	0,4	70
Glass fibre	2,60	3,4	22

Among the main lightweight materials that can be used for these purposes, there are those containig aluminum and magnesium but in recent years (as shown in Figure 3. 19) the demand for Carbon Fiber (CF) is growing. In the course of 2022, double demand is estimated compared to 2017.

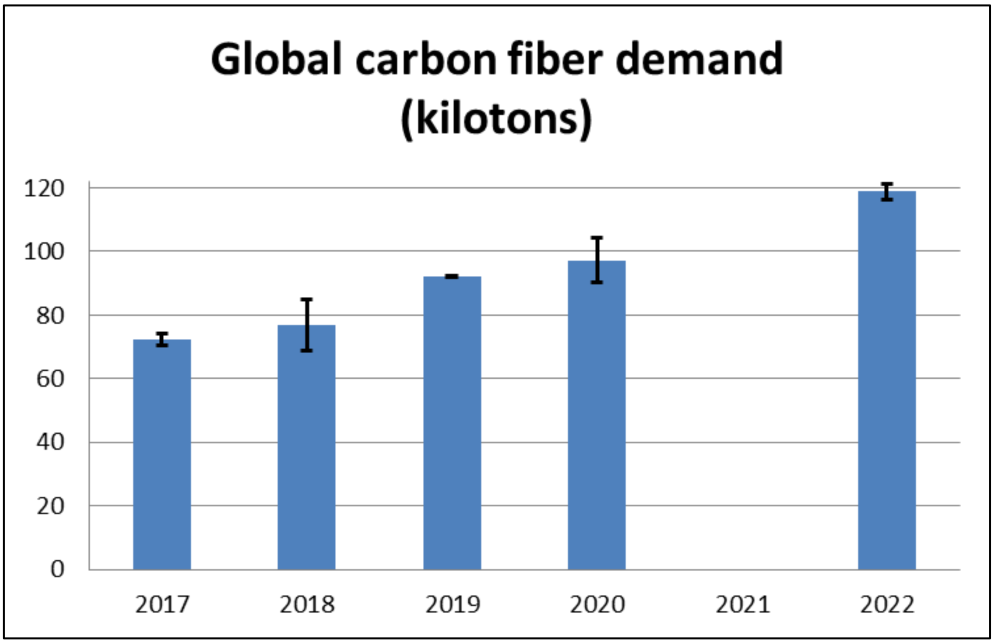

Figure 3. 19 - Estimated Global Carbon Fiber demand in the recent years. Reported also the STD calculated on the data collected from the publications [260, 262-264, 278].

The main applications for CF are reported in Figure 3. 20. All the applications are sharply growing but a faster increment is attended in the automotive and in the engineering applications.

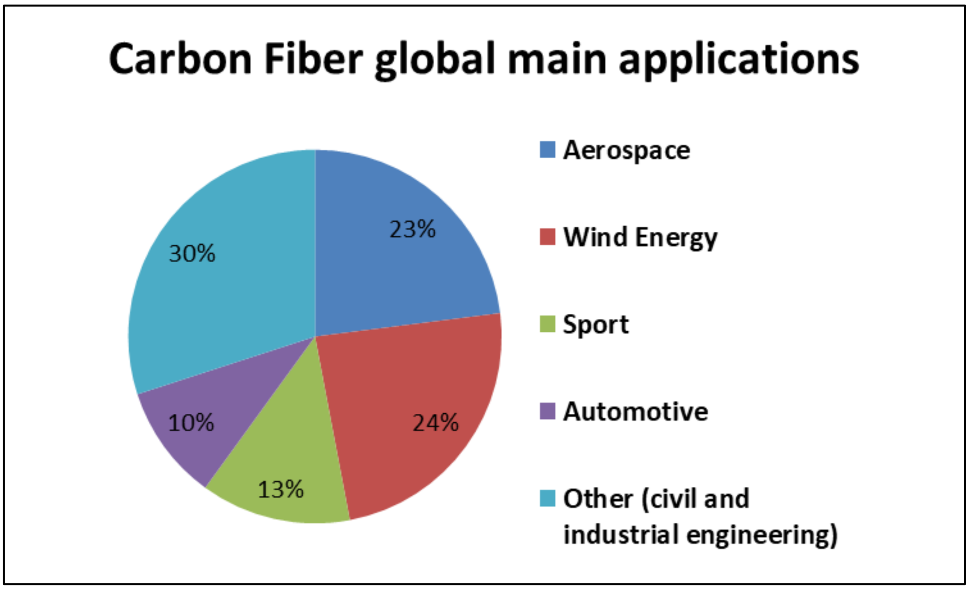

Figure 3. 20 - Main Carbon fibre global applications (data collected from [265])

One of the main boosts to the CF application in automotive industry is the current need to reduce carbon dioxide emissions and improve fuel efficiency (most of all in order to enable the electric cars to cover greater distances) approaching the carbon neutrality within few decades [260]. CHINA too has a vehicles weight reduction program approaching, within 15 years, a 35% vehicle weight loss with respect to the 2015 medium weight. This program suggests the use of lightweight materials as CF (especially as component of the Carbon Fiber Reinforced Polymers - CFRP), aluminum and magnesium, and foresees in 2035 a CFRP cost reduction till the 25% of the 2015 cost [261].

The industrial engineering applications CF can play a key role for example exploiting the weight reduction for the construction of larger components (i.e. wind turbine rotor blades) or transportable components. The civil engineering applications could potentially substitute (most of all in the earthquake risky lands) the corrodible steel concrete reinforcements. However, currently CF is ten times more expensive than conventional reinforcing materials and this overcharge is mainly due either to the CF raw material cost and to the production speed (minutes for steel, hours for CF) [278].

A simplified classification of various CF types (based on the modulus of elasticity ranges) with the relative prices and main possible applications is reported in Table 3. 33.

Carbon Fiber classification, prices, main applications					
Classification	Low	Standard	Intermediate	High	Ultra-high
Tensile modulus ranges (GPa)	40–200	200–275	275–345	345–600	600–965
Price ranges ($/kg)	15-20	20-55	55-65	65-90	>2000
Applications	Non-structure usage, CFRP production	Automotive, sport, wind turbine, pressure tanks, CFRP production	Pressure tanks, wind turbine	Aviation, military	Aerospace

Table 3. 33 - Classification of various CF types (based on the modulus of elasticity ranges) with the relative prices and main possible applications (data collected from [262])

The CF production shares by nations and the main CF suppliers are shown respectively in Figures 3.21 and 3.22.

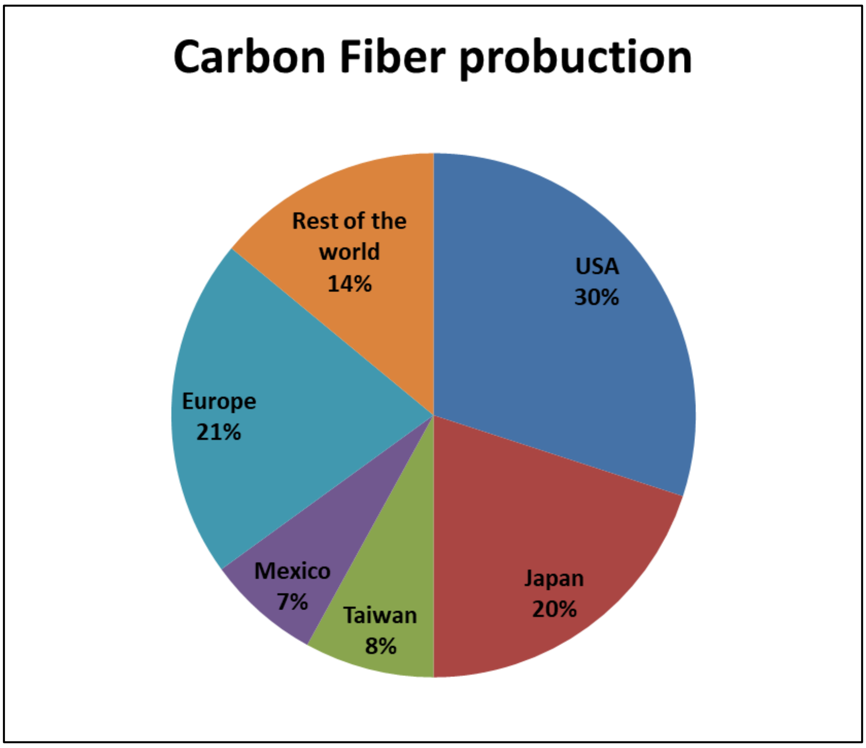

Figure 3. 21- Carbon Fiber production by nations (data collected from [264])

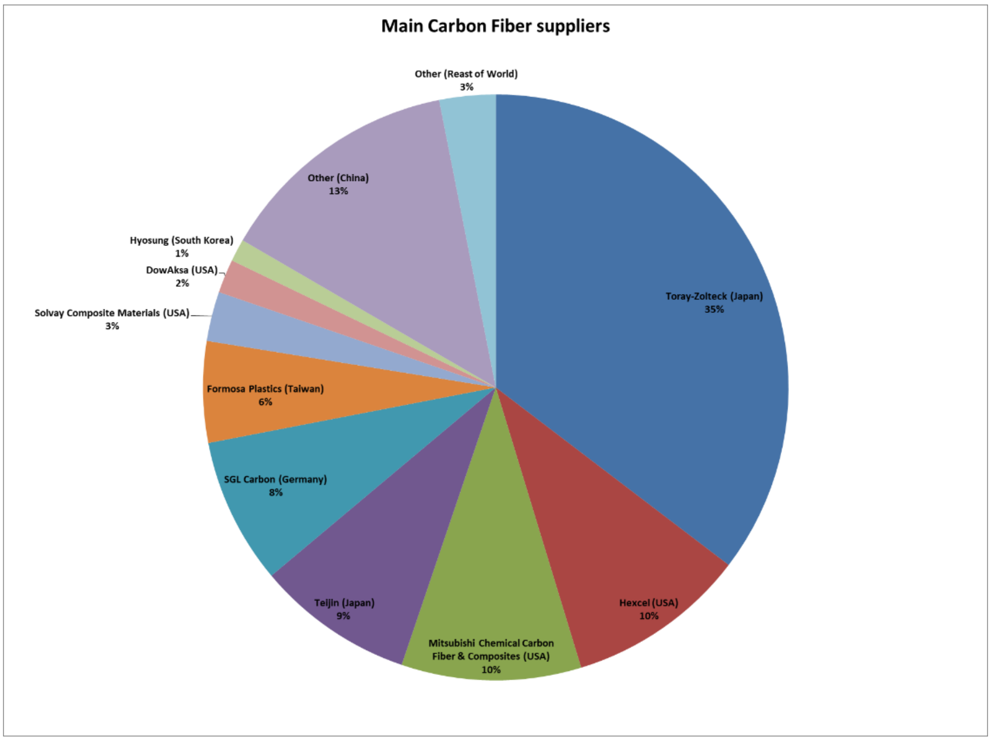

Figure 3. 22 – Main Carbon Fibers Suppliers and their headquarter location [279]

90% of the CF is produced from the same precursor: PolyAcryloNitril (PAN) which grants the better yield and product characteristics performances. The production pathway can be condensed in 4 main steps: Oxidation, Carbonization, surface treatment and sizing-collection-handling [260, 263].

The impact on production costs, both considering the steps (Figure 3. 23a) and the economic cost categories (Figure 3. 23b), highlight the importance of the cost of the feedstock.

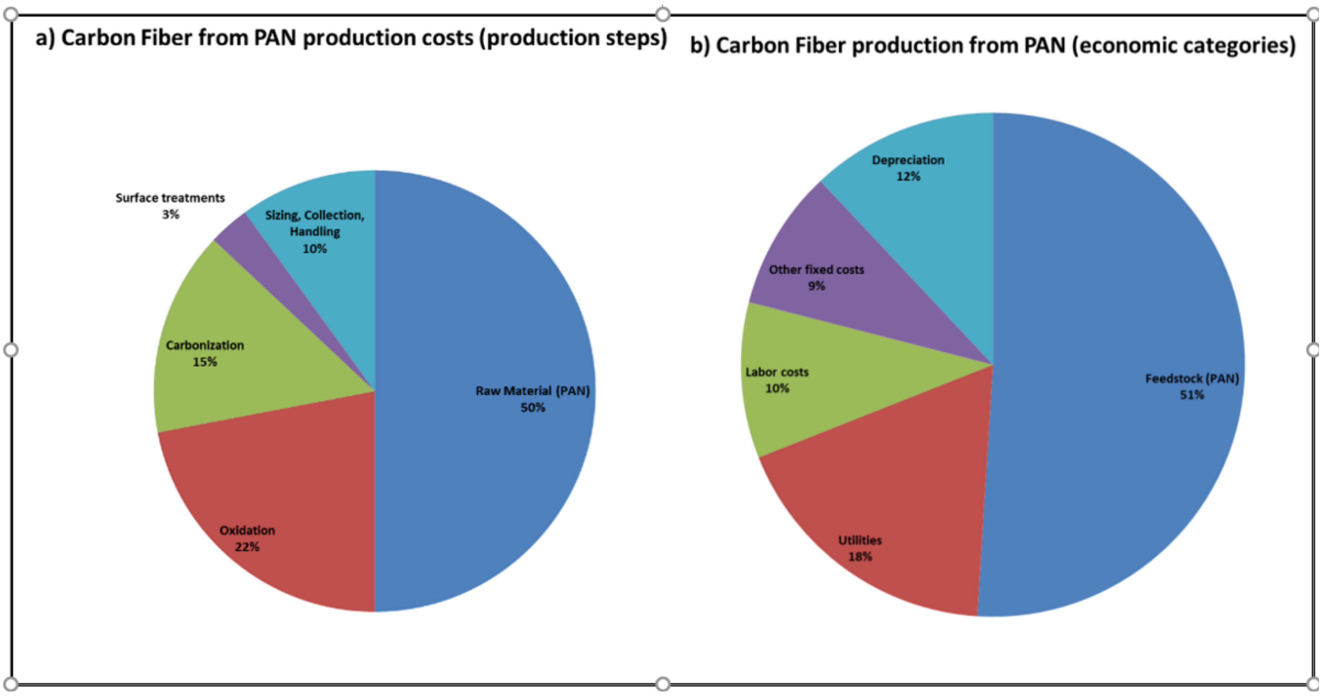

Figure 3. 23 – Costs impact on Carbon Fiber production from PAN: a) production steps costs (data collected from [260]); b) economic categories costs (data collected from [263])

The PAN is mainly produced from the petroleum. Its average cost is 7-10 USD/kg and the CF cost is 20-30 USD/kg (many parameters impact on the PAN and CF costs: oil price, PAN type, CF required properties, etc.). Moreover, in the CF production the final yield, considering all the steps, rarely reaches the 50% [260, 262, 263, 278].

The CF production costs, regarding the process and the PAN price, have been extensively investigated in order to reduce the costs. Other cheaper precursors (as pitch) and production pathways (as plasma or microwave oxidation and more efficient conversion ovens) have been experimented. Lastly also the renewable raw materials have become particularly interesting as sources of carbon fibres [262].

The cost of a lignin theoretically ready for the production of a low quality CF is 2-3 USD/kg generating a CF cost range 12-15 USD/kg [260, 262, 263]. The main problem is related to the lignin selection/preparation and the produced CF quality which could be profitable only for vehicle light-weighing applications and most of all if CF production is associated to a bio-refinery [266].

Briefly the Table 3. 34 reports the advantages and the disadvantages of lignin use as precursor.

Table 3.34-Advantages and the disadvantages of lignin use as precursor (data collected from [263, 267])

Advantages	**Disadvantages**
Inexpensive and renewable	Complex and disordered structure (not linear as the PAN one)
High carbon content	Low flexibility (due to the residual double bonds still present)
Already oxidizad	Possible cross-link generation during melt-spinning
Higher modulus (amorphous structure)	More pores in CF produced
	Lower molecular mass and higher polydispersity index Vs PAN

Moreover, the lignin can't be used as it is. The table 3.35 reports the main improvement required for an effective lignin use in order to obtain CF.

Table 3. 35 - Main improvement required for an effective lignin use in order to obtain CF (data collected from [262, 268, 269])

Chemical modification (mainly esterification) often on softwood lignin whose structure is more linear than hardwood but has a higher thermal induced intra-reactivity
Desirable pure lignin with narrow molecular weight distribution and low difference between its glass transition temperature (Tg) and softening temperature (Ts)
Increase of lignin glass transition temperature (mainly by thermal or solvent mediated treatments)
Blending with polymers as Poly Ethylene Oxide (PEO) or Terephthalate (PET), or Poly Lactic Acid (PLA)
Blending with other lignins or their fractions (often hardwood lignin becomes a plasticizer for softwood lignin)

In Table 3. 36 are reported main results regarding the CF obtained from various lignin types

Table 3. 36 - Main data regarding the CF obtained from various lignin types [262, 267, 269])

Lignin type	Fiber diameter (μm)	Tensile strength (GPa)	Tensile modulus (GPa)
Phenolated hardwood		0,5	30
Acetylated Softwood Kraft Lignin	~7	1,0	50
Pyrolytic lignin	50	0,3-0,4	35
Hardwood Alcell® lignin	40-50	0,3-0,5	25-55
HardWood	40-50	0,3-0,5	30-50
Kraft hardwood	50	0,4-0,5	~40
Lignin-PEO (3% PEO)	30-40	0,4-0,5	40-65
Lignin-PEO (5% PEO)	40-50	~0,4	30-45
Lignin-PET (25% PET)		0,5	65
Lignin-PP (25% PP)		0,1	20
Steam exploded hardwood	5-10	0,4-0,9	35-50
Organosolv hardwood	14	~0,4	25-50
Oganic purified hardwood	10	0,5-0,7	25-30
Softwood and hardwood kraft	40-80	0,2-0,4	25-30
lignosulfonate- AN copolymer	10-20		540
PAN (low modulus/quality CF)	12-50	1-3,5	40-200

As previously reported, the main CF related product is CFRP usually obtained by incorporating CF into a plastic matrix. High quality applications employ CF with epoxy resin CF significantly improves strength and stiffness in the direction of the fibers. Orthogonally to this direction, the inserted fibers cannot absorb forces. The intersection of the fiber layers during CFRP production improves these properties in other directions as well [263].

The CFRP already used for high-priced sports equipment (tennis rackets, bicycles, ski poles, etc.), is also gaining importance for other applications such as in the construction of aircraft and vehicles (e.g. the hull of the aircraft Boeing 787 "Dreamliner" and the automobiles BMW i-Series monocoque vehicles).

Figure 3.24 reports a comparison of the global demands of CFRP and CF. Usually the composition of CFRPs contain almost 50-60% (w/w) of CF [270], this means (as clearly detectable from figure 3.20) that almost all the CF is converted in CFRP.

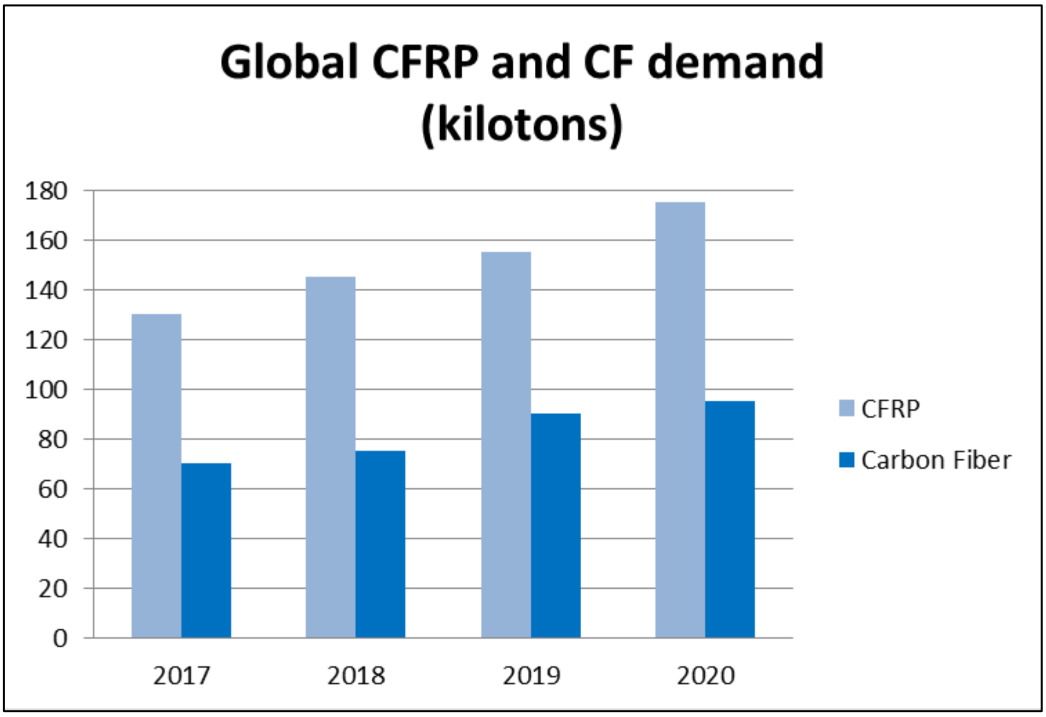

Figure 3. 24 - Global demand of CFRP [265] compared with the demand of CF (already reported in figure 3. 20)

The forecasted demand till 2050 could be stable on 180 kilotons/y [265]. This trend is mainly due to the improvement of new recycling technologies, new networks and supply chains [265, 271, 272]

In Europe, the main research player in the development of CFRP from kraft lignin is RISE (Research Institutes of Sweden) whose collaboration with other Swedish research organizations (such as Swerea SICOMP, KTH) and many industrial operators (such as Södra Skogsägarna, Scania, Volvo Cars, Fiat, Oxeon, Netcomposites, etc.) led to several projects [260].

The European main project on Lignin-Based Carbon Fibres for Composites are: “LIBRE” [277], leaded by University of Limerick in Ireland, and “GreenLight” [276] coordinated by Innventia (today RISE Bioeconomy). The first one is projecting a new bio-based composite materials utilising lignin blended with biopolymers processed by using some sustainable microwave and radio frequency (MW/RF) heating technologies, the second one aims to the production of lignin-based CFs and CFRPs using 100% lignin from a softwood kraft pulp mill; in this project RISE shares also its know-how on softening agents for melt spinning softwood Kraft lignin and on special oxidative conditions.

The USA CF and CFRP major focal research areas, mainly developed by Oak Ridge National Laboratory (ORNL) and Michigan State University, deal with alternative precursors as lignin and advanced energy-efficient processes. Among the ORNL results on lignin applications there is the successfully production of CF from melt-spun lignin and in collaboration with Volkswagen the pilot-scale (75 kg of lignin fibers in one batch) production of lignin-based CFs, with hardwood kraft lignin content till 99% [273].

The last considerable application of lignin in this field involves the production of lignin carbon nanofibre (LCNF) materials (having fibres diameter of submicron in size [260] by electrospinning [274]) whose employments include the use in batteries, supercapacitors, fuel cells, structural composites and filtration devices [275].

Electrospun LCNF, with respect to PAN originated nano-fibers, has higher production rates, lower carbonisation temperature [260].

Currently lignin-based carbon fibres production is sharply improving (TRL 4-6) The commercial scale approach still requires a few years away. A first demonstration plant with 50.000 tonnes is planned in Sweden and according to last announcement will produce CF before 2025 [260].

3.5.2 Patents (Carbon fibers)

Since 2015 649 patents were issued on the lignin-based carbon fibers. More than a half of these patents were published in the last three years with a sharp increase in the last year (as reported in Figure 3.25).

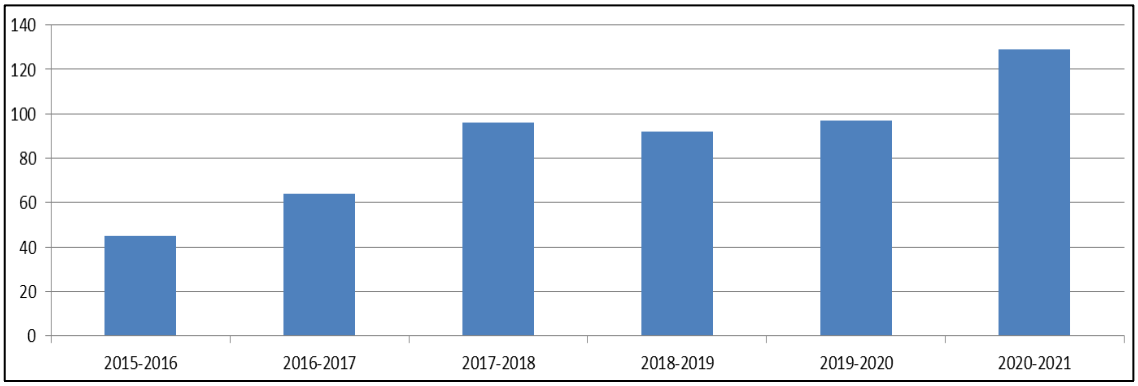

Figure 3. 25 - Annual increases, from 2015 to 2021 of the published patents on the lignin-based carbon fibres (ORBIT) [36]

Table 3. 37 – Patents, selected by keyword on ORBIT [36]. Patents related to the application of lignin based Carbon Fiber production in the last year. Acronyms: L/M (Large industry/Multinational) E/C (Enterprise/Company), U/RO (University/Research Organization). CHN (China), KOR (South Korea), F (France), FIN (Finland), S (Sweden), EU (European Union)

Title	Applicant(s)	Applicant(s) business and country (acronym)		Pub. Number	Pub. date	Patent Org.
Phenolic resin improved lignin carbon fiber and preparation method thereof	HUNAN LANKAI NEW MATERIAL TECHNOLOGY	E/C	CHN	CN113046864	18/03/21	CHN
Iron-doped lignin-based flexible carbon fiber material and preparation method and application thereof	INTERNATIONAL CENTRE FOR BAMBOO & RATTAN	U/RO	CHN	CN112981553	03/02/21	CHN
Preparation method of pore-diameter-controllable self-activated lignin-based micro-nano activated carbon fiber	DALIAN POLYTECHNIC UNIVERSITY	U/RO	CHN	CN112760751	05/01/21	CHN
Low-cost carbon fiber with excellent mechanical properties and preparation method thereof	INDUSTRY ACADEMIC COOPERATION FOUNDATION	U/RO	KOR	KR10-2202362	22/11/19	KOR
Preparation method of lignin-based carbon fiber precursor	QINGDAO UNIVERSITY	U/RO	CHN	CN109537104	29/11/18	CHN
Chain expansion modification method of lignin and preparation method of melt spun fiber	QINGDAO UNIVERSITY	U/RO	CHN	CN109518308	29/11/18	CHN
Lignin-based nanocarbon fiber, preparation method thereof, and carbon fiber electrode	GUANGDONG UNIVERSITY OF TECHNOLOGY	U/RO	CHN	CN108611704	21/05/18	CHN
Nano carbon fibers and preparation method thereof	SHANDONG SHENGQUAN NEW MATERIAL	U/RO	CHN	CN108660547	31/03/17	CHN
Method for producing carbon fibres from biosourced precursors and carbon fibres produced	ARKEMA	L/M	F	EP3532661	28/10/16	EU
A process for the manufacture of a precursor yarn	STORA ENSO	L/M	FIN	EP3359715	08/10/15	EU
Method for stabilizing lignin fiber for further conversion to carbon fiber	RISE INNVENTIA	L/M	S	EP2807294	13/12/12	EU
Lignin/polyacrylonitrile-containing dopes, fibers, and methods of making same	INTERN. PAPER	L/M	USA	US8771832	30/06/10	USA

The 12 patents reported in table 3.37 (published and yet not expired in the first half of 2021) demonstrate the growing interest of this lignin exploitation method and summarize the specific application fields. This interest is also detectable looking at the patents issued by important players as ARKEMA, STORA ENSO, RISE INNVENTIA and INTERNATIONAL PAPER.

Some of the patents regard the improvement of the lignin carbon fiber mixing them with low amounts of phenolic resins (Pat. CN11304686) or adding them with Potassium ferrate (Pat. CN112981553).

Other patents show new methods for the preparation of micro-nano lignin carbon fibers having specific surface area and better electrochemical performance (Pat. CN112760751), good in interfacial compatibility and high in mechanical strength (Pat. CN108660547), high graphene content with improved mechanical properties and the electrical conductivity (Pat. CN108611704)

Some patents propose lignin modification methods in order to obtain high quality lignin-based carbon fibers. The proposed methods suggest the blending (Pat. KR102202362) with chlorinated poly (vinyl chloride), the dissolution of lignin in an organic solvent and then the addition of diisocyanate under nitrogen gas, reaction at a temperature of 30-90 °C (Pat. CN109537104) and finally the use of specific spinning conditions in order to obtain carbon fiber with an excellent mechanical performance (Pat. CN109518308), the mix of the lignin with polyacrylonitrile or a polyacrylonitrile copolymer (Pat. US8771832).

The remaining patents are more focused on the thermo-oxidation, carbonization and stabilization conditions (Pat. EP3532661, EP3359715, EP2807294).

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4. Technoeconomic assessment of lignin valorisation to target products

Process optimization and process simulation are widely applied to innovative processes, such as biorefineries. They enable the comparison of a considerable number of alternative process layouts and conditions. These tools are useful to assess the integration of new biorefining operations in existing processes to identify the technical or economic gaps to make the selected processes feasible. In the specific case of lignin valorization, the main challenge is to develop novel processes that are capable of converting lignin in a selective, efficient and sustainable way into biobased products. For the latter issue, process optimization and integration can help to identify the most promising pathways and increase the profitability of the process. Process synthesis methods have been widely used in the conceptual design and optimization of sustainable and cost-effective bioethanol production plants [1].

The development of techno-economic analysis aims to assess and predict the limits in utilizing different lignin feeds (see Chapter 1) to produce different target products. To do this, the explored approaches consist of:

- a technical evaluation of the different process schemes for lignin valorization of several alternative products using process simulation software;
- an economic assessment of the process schemes calculating the final payback, selling price of the products or the profitability of the lignin-based biorefinery;

a mixed experimental/modelling analysis using experimental data to assess the mass and energy flows of the biorefinery.

4.1 STATE OF THE ART OF PROCESS SIMULATIONS FOR LIGNIN VALORIZATION

A systematic methodology can be developed to assess the optimal reaction routes. It includes the optimal flowsheets comprising all the unit operations and the relevant design and operating conditions to achieve a set of target value-added products and fuels, including specific flowrates, temperatures and purity values from a set of biomass-derived feedstocks with a specified composition. The final scope is minimizing costs and increasing sustainability [2].

The majority of existing biorefinery processes deal with the production of biofuels and bioethanol based on thermochemical and biochemical technologies. However, only a few studies have addressed the optimization of multiproduct biorefineries coproducing alcohols (ethanol or butanol) [3], high-value chemicals (succinic acid, BDO), electricity [4], [5], and chemicals, such as acetic acid [6], i-butene [7] and 3-butadiene [8]. Energy sustainability in the majority of biorefinery layouts is achieved through the thermal conversion of biorefinery secondary streams [9]. Luo et al. [6] identified the best design of a multiproduct lignocellulosic biorefinery producing ethanol, succinic acid, acetic acid and electricity.

Lignin valorization has been increasingly studied in the last 5 years. In particular, 3, 7, 5, 3, and 4 works were published in 2017, 2018, 2019, 2020, and 2021, respectively, with the objective of complementing the main process to valorize several types of lignin. Table 4.1 summarizes the results of the studies regarding the technical-economic evaluation of process flowsheets for the valorization of lignin. In process simulations, lignin is always considered homogeneous in composition and molecular weight. It is modelled through the use of simulation tools in which the user enters thermodynamic parameters.

The yields are highly variable and depend greatly upon the final target product. The highest yields were obtained using lignin in its macromolecular form (in phenol-formaldehyde resins and polyurethane foams); the lowest yields were obtained for monomeric compounds with high added value and lower market volume (vanillin). Phenols are the compounds most often evaluated for economic analysis. The transformation processes consist of depolymerization carried out with thermal or oxidative treatments. Biological processes are rarely considered for this type of analysis due to the scarce literature on the subject and the low yields achievable.

Table 4. 1 Main results from the techno-economic assessment of lignin valorization

Lignin source	Main lignin-based product	Main conversion processes	Yield % (kg/kg$_{LIGNIN}$)	Reference
Organosolv pretreatment of olive tree pruning	Catechol	Alkaline treatment	2.6	[15] - [16]
Dilute acid pretreatment of corn stover	Propyl guaiacol		12	[17]
Dilute acid pretreatment of corn stover	Catechol, phenol, cresol, acetic acid, formic acid, furfural, acetaldehyde	HTL	28, 8, 12, 0, 39, 0, 0	[18]
Ionic Liquid pretreatment	Eugenol and phenolics	Hydrogenolysis by Isopropanol	3, 19	[19]
Kraft lignin (Lignoboost)	Polyols/phenols	Depolymerization by glycols	56–90	[20] - [21]
Several lignins	Phenols	Depolymerization	10–50	[22]
Kraft lignin	Vanillin, Syringaldehyde	Oxidation		[23]
Kraft lignin	Vanillin	Oxidation	8	[24]
Kraft lignin (Lignoboost)	Vanillin, formic acid, acetic acid, guaiacol	Oxidation	3.2	[25]
Dilute acid pretreatment of corn stover	Jet-fuel	HDO		[26]
Kraft lignin	Aromatic monomers	Lignin pyrolysis, HDO, hydrothermal upgrading	10, 25, 24	[27]
Kraft lignin	BTEX	HTL + HDO	10	[28]
Kraft lignin	Jet-fuel/Resins	HDO	30–100	[29]
Lignin cake after fermentation	Adipic Acid	Biological conversion	6	[30] - [31]
Organosolv/Steam explosion	Formaldehyde	Gasification + synthesis	24	[32]
Kraft lignin (Lignoboost)	Colloidal Lignin Particles	Dissolution in THF	100	[33]
Kraft lignin	Carbon Fibres	Hydrothermal Base Catalysed Treatment	70	[34]

4.1.1 Phenols from lignin

Many recent studies are available for the production of phenols from lignin (Mabrouk et al. [10] [11], Han J.[12], Bbosa et al.[13], Martinez et al.[14], Dessbsell et al.[15], Ou et al. (2021) [16], Fernandez-Rodriguez et al. (2021) [17]). Higher yields were obtained for polyol and from kraft lignin by depolymerization processes (≈ 50%). Cathecol was transformed into phenolic monomers with higher yields (up to 28%) by hydrothermal liquefaction.

Mabrouk et al. [10] [11] studied the valorization of lignin obtained from the organosolv pretreatment of olive tree prunings for the production of catechol using Aspen Plus® software. Thermodynamic models such as NRTL-RK and UNIQUAC were used for the simulation; however, the physical properties and chemical characteristics were determined at the laboratory scale. Han J. [12] studied a commercial-scale integrated process for the production of cellulosic GVL using lignin-derived PG from corn stover. Bbosa et al. [13] studied the hydrothermal liquefaction process for the production of lignin-derived chemicals. Mixed laboratory and pilot-scale research was carried out to establish the conditions for the production of phenols (as the main product) and volatile acids. Martinez et al. [14] studied catalytic hydrogenolysis assisted by isopropanol (IPA) to convert biorefinery-recovered lignin to produce eugenol and phenols. SuperPro Designer was the simulation tool. Dessbsell et al. [15] evaluated the depolymerization of kraft lignin for use as a biosubstitute for polyol and phenol in the production of biobased polymers (polyurethane and phenolic resins). Ou et al. (2021) [16] studied the liquefaction of lignin to produce polyols. Fernandez-Rodriguez et al. (2021) [17] studied the polymer isolation stage before its depolymerization reaction. Four different situations were evaluated by using data inputs from previous works and compared with the assistance of a simulation software system (AspenTech®). In this work, many types of lignin (in particular, black liquors, organosolv lignin, and soda lignin) were compared and analysed [13].

Phenol production indicates favourable economics once yields are above 20–30%. Energy needs represent the greatest technical gap of these transformations, principally within the lignin pretreatment processes. When a heat integration layout was considered ([12]), over 47.4% of the total energy was saved upon considering the burning of the biomass wastes. From an economic point of view, capital costs and feedstock costs are the main cost items [13] because the chemicals and solvents used are often recovered and recycled back into the main processes.

Feedstock offers and market demand for lignin-derived biopolyols are still uncertain; thus, a supply chain model is critical for decision-making.

4.1.2 Vanillin from lignin

Rodrigues et al.[18], Wongtanyawat et al.[19], and Abdelaziz et al. [20] studied the production of vanillin from kraft lignin. The yields of this specific high-added value compound as a food flavour are less than 10%. The processes consist of oxidative depolymerization and purification systems such as distillation, extraction, and crystallization.

In particular, Rodrigues et al. [18] studied the effect of reaction conditions on the product yield, and the kinetic laws were also detailed. Wongtanyawat et al. [19] simulated kraft lignin-based vanillin production by using methanol, sulfuric acid, oxygen, ethyl acetate, and benzene as reactants, catalysts or solvents, quantifying their flow rates. The yield to vanillin was equal to 8% (vanillin/lignin). The results from the process assessments showed that processes with zeolites offered the best alternative. Abdelaziz et al. [20] presented the conceptual design by modelling, simulation, and analysis of oxidation processes in addition to using experimental data.

4.1.3 Aromatics from lignin

Shen et al.[21], Gursel et al.[22], Funkenbusch et al. [23] and Giuliano et al. [24] studied the production of aromatics/cyclic compounds for use as jet fuels from lignins. Different processes were considered in these various works. In particular, pyrolysis, HDO and hydrothermal upgrading were assessed and compared.

Shen et al. [21] studied the direct HDO process. The work indicates that the coproduction of jet fuel from the catalytic upgrading of waste lignin will dramatically improve the economic viability of an integrated process for corn-stover alcohol production. Lignin-derived jet fuel would provide the following distinctive advantages: (1) it uses low-priced raw materials while not conflicting with food or different biofuel production, (2) it has higher thermal stability, (3) it has higher energy density, (4) it is available at a low price, and (5) it reduces greenhouse emissions. Gursel et al. [22] studied the yields of mixed oxygenated aromatic monomers. Aspen Plus was used for the process simulation and method modelling from experimental information. The direct HDO method was found to be more complicated than the lignin pyrolysis method due to the utilization of H_2 and more difficult separation needs. However, it achieved a higher yield (25%). The HydroThermal Upgrading (HyThUp) method, with a yield of 24%, had the most exacting downstream process, principally thanks to the presence of a large amount of water within the system. An innovative process was studied by Funkenbusch et al. [23] that produces benzene/toluene/ethylbenzene/xylenes (BTEX) mixtures: the continuous catalytic near-critical water (NCW) reactor for the hydrothermal liquefaction (HTL) of lignin. The yield to BTX was equal to 10% (BTX/lignin). Giuliano et al. [24] built a lignin valorization process superstructure to assess the best process pathway to produce jet fuels, resins, foams or syngas from lignin. The results showed that resins for wood-based panels are the most convenient lignin-based product thanks to higher yields due to the utilization of all of the lignin as a reactant to make these polymer structures.

In terms of economics, the HyThUp process showed the highest capital cost. For the direct HDO process, due to the greater complexity of the separation tasks, it was estimated that the investment costs would be higher than those of the pyrolysis process. The direct HDO process appeared to be the most promising due to the high revenue stream (58% more than pyrolysis). Negative NPVs were calculated for the pyrolysis and HyThUp processes, suggesting economic infeasibility.

4.1.4 Biological processes using lignin as substrate

Biological processes were assessed by two groups, Corona et al. [25] and Unlu et al. (2021) [26]. The hexanedioic acid production was studied. Different lignin depolymerization processes and the development of microorganism strains that tolerate low pH values are necessary to improve the environmental profile of biobased hexanedioic acids. In particular, Unlu et al. (2021) [26] conducted a practicability analysis of a two-step method involving catalysed depolymerization to obtain monomers with low molecular mass, followed by microorganism conversion to muconic acid by genetically designed *Pseudomonas putida*. Finally, the upgrading to hexanedioic acid through chemical processes was analysed. The process synthesis methods of all the processes for hexanedioic acid production in Aspen Plus were carried out using experimental data.

4.1.5 Formaldehyde, colloidal and carbon fibres from lignin

Tey et al. [27] studied hybrid organosolv/steam explosion-pretreated lignin for formaldehyde production by methanol intermediate synthesis. This process pathway could be integrated with processes producing phenols to obtain phenol-formaldehyde resins.

Ashok et al. [28] studied Kraft lignin (LignoBoost) valorization considering colloidal lignin particles as the main product. The process involves the instantaneous formation of colloidal lignin particles (CLPs) through self-assembly when a concentrated solution of lignin in tetrahydrofuran (THF) and ethanol is introduced into water. Aspen Plus simulation software was used for the mass and energy balance calculations.

Otromke et al. (2019) [29] reported that a techno-economic analysis supported the hydrothermal base-catalysed treatment of kraft paper polymer for the manufacture of carbon fibre precursors. Analysis of the recovered oily phase indicated that catechol derivatives were stable end-products with vanillin and guaiacol as intermediates. A price of 1600 €/t was found to be achievable, the main costs are represented by the lignin supply (60%), the fixed costs (20%), and energy requirements (10%).

Figure 4.1 summarizes the main routes to the selected target products. Kraft lignin is the most commonly used raw material. The lignin-based products that are closer to the market are the aromatic monomers (also referred to as BTX or jet fuels).

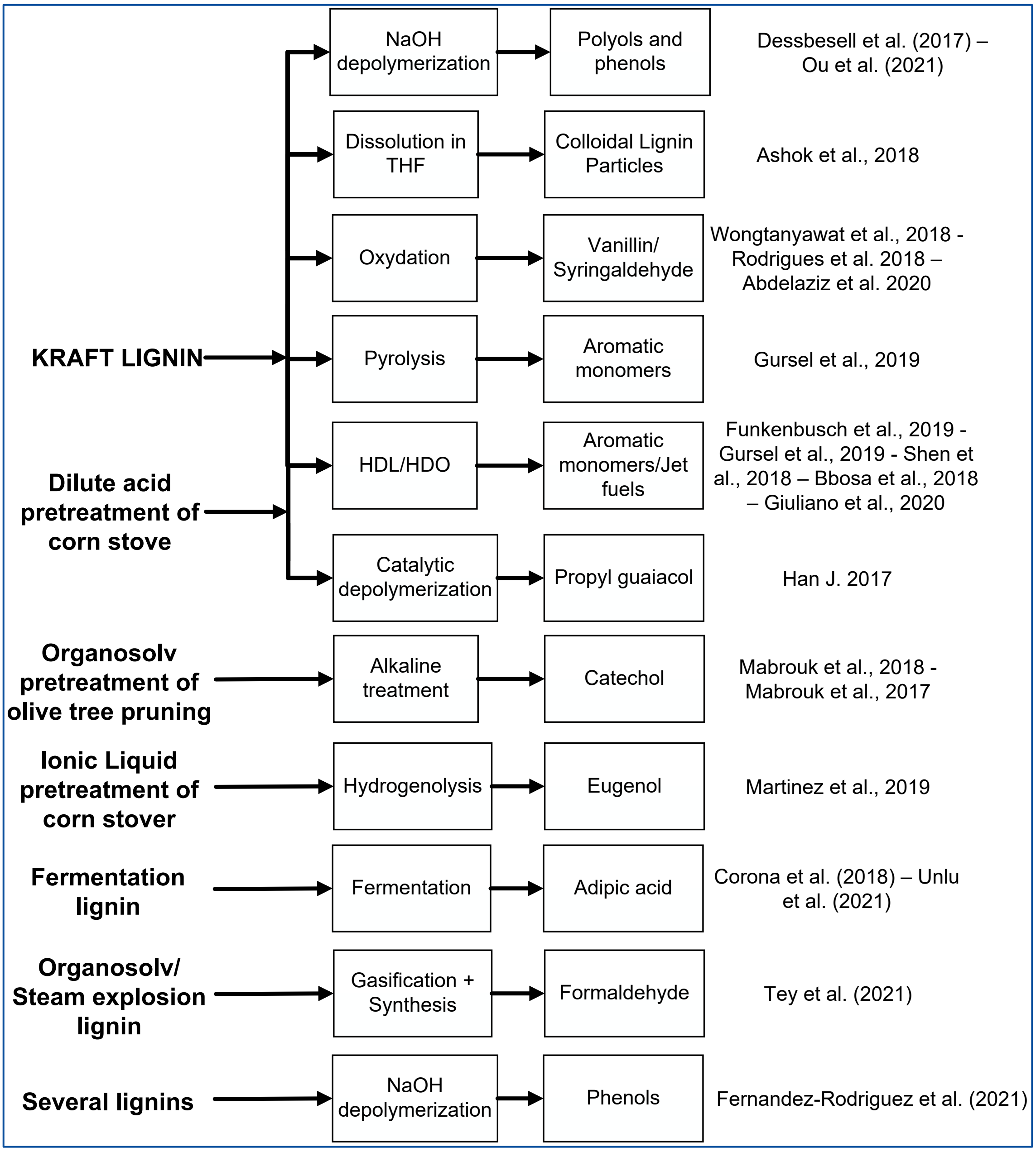

Figure *4. 1*- State of the art of lignin valorization assessment

4.2 MARKET SIZE OF LIGNIN-BASED PRODUCTS

Table 4. 2 presents the selling prices of the main lignin-based products and the product market size. Generally, higher value products correspond to lower potential estimated yields. Larger market sizes correspond to lower selling prices. In addition, the lignin quality is correlated with the potential product obtainable. High purity lignins can be used to produce high-added value compounds (e.g., vanillin), and low purity lignins can be used to produce products with lower economic values [23].

Table 4. 2 Market size of lignin-based products

Main lignin-based product	Estimated yield % (kg/kg$_{LIGNIN}$)	Market size (kt/y)	Product selling price (€/t)	Work
Colloidal Lignin Particles	100	5,000-20,000	800-1,500	[33]
Vanillin	8	16	14,000	[26]
Catechol	2.6-28	15-20	985-2,000	[35] - [15] - [18]
Propyl guaiacol	12			[26]
B/T/X	10-25	40,200/19,800/42,500	1,200	[26]
Jet fuels		246,000	500	[26]
PHA		1,700	3,000-5,000	[26]
Carbon fibre		100.5	38,000	[36]
Polyurethane foams (as polyol)		20,000	1,500	[37]
Eugenol	3	37	8,000	[19]

Although the recent literature reports already provide interesting data on the techno-economic features, they typically suffer from some limitations due to the lack of information about the differences between the use of different lignins. Therefore, the analysis results are insufficient to identify the best process pathway for each type of lignin.

Simulations and modelling based on the analysis of a process superstructure would offer the advantage of identifying the best process and the best lignin-based products by changing the characteristics and type of feedstock. Therefore, the analysis can identifying the limits and opportunities of each process pathway and each raw material considered. Development of mathematical models and simulation tools correlating the chemical-physical characteristics of a lignin to its use to develop specific applications and future opportunities. The majority of the reports in the literature provide preliminary assessments of the valorization schemes starting from a selected lignin stream to produce a single product.

4.3 USEFULNESS TO DEVELOP TECHNO-ECONOMIC ANALYSIS TOOLS TO FIND THE OPTIMAL LIGNIN-BASED PROCESS PATHWAYS AND PRODUCTS

This section aims to provide some outlines to develop integrated simulation tools for the technical-economic evaluation of lignin-based biorefinery schemes.

The main steps are:

- assessing the target products and the main conversion pathways; and
- gathering process yield data.

Table 4. 3 summarizes the specific process conditions required to achieve aromatic monomers, polyurethane foams, carbon fibres, phenols, eugenol, phenol-formaldehyde resins, and adipic acid.

Table 4. 3: Process conditions and chemical requirement of each lignin conversion process considered in the main techno-economic analysis

Main product	Processes	Catalysts/solvent	Reactants	Temp. (°C)	Press. (bar)	Reference
Aromatic Monomers	Pyrolysis	-	-	500	1	[38]
	Liquid/gas cooling	-	-	5	1	[27]
	HDO	NiMo	H2	400	150	[38]
	Distillation	-	-	102/226/394	1/2	[27]
	Hydrothermal Liquefaction	Pd/C	NaOH	250	55	[39]
Polyurethane foam	Diisocyanate reaction with polyols	H_2O and Pentane (blowing agents)	water/isocyanate and polyol/isocyanate			[40]
Carbon Fibres	Hydrothermal Base Catalysed Treatment			300	180	[34]
	Spinning			100–230 (depends on lignin)		[4]
	Thermal stabilization			105 for 1 h then 200 for 24 h		[4]
	Carbonization	O_2 free, Ar or N_2		>900		[4]

Cathecol + Phenol + Cresol	Hydrothermal Liquefaction			350	207	[18]
	Flash			347	204	[18]
	Reactive extraction	MIBK or Ethyl acetate/Water (anti-solvent)	NaHSO$_3$ or NaOH	23	1	[18], [41]
	MIBK recovery			50	0.092	[41]
	Aqueous phase distillation	-	-			
	Organic phase distillation	-	-			
Eugenol (Ionic Liquid Pretreatment)	Hydrogenolysis Process	IPA and Ru		300	20	[19], [42]
	IPA recovery processes (for Flash, Extraction and Distillation)			81.4	1.013	[19]
	Distillaton of Eugenol	Ru/C, 3 h		300	0.1	[19]
	Distillation of Phenolics	Ru/C, 3 h		300	0.1 or 0.85	[19]
Vanillin + Vanillin acid + Acetovanillone + Guaiacol	Oxydative depolymerization		O$_2$	161	8.0	[25]
	Membrane filtration			50	7.5	[25]
	Distillation			185	10.4	[25]

Phenol-formaldehyde resins	Hydrothermal liquefaction	Ethanol		350	20	[43]
	Dissolution in DES	DES		100	1	[44]
	Phenol exctraction	NaOH - H_2SO_4 - Ethyl Ether		65–85	20	[43]
	Resin synthesis	Water-NaOH	Formaldehyde	80	1	[43]
Formaldehyde	Thermal degradation to methanol			250	80	[32]
	Formaldehyde synthesis	Silver	O_2	600–650	3	[32] - [45]
Adipic Acid	Catalysed Depolymerization	NaOH		120–160	3.3	[30] - [31]
	Microbial conversion		Nutrients	32	1	[30] - [31]
	Upgrading to Adipic Acid	H_2SO_4 - Ethanol		24	24	[30] - [31]

One lignin valorization process superstructure is shown in Figure 4.2. Kraft lignin and lignin derived from many biorefinery operations are considered to feed several main processes to produce eight different products. In particular, three products have a polymeric structure (carbon fibres, polyurethane foams and phenol-formaldehyde resins), and five are chemicals or fuels (vanillin, aromatic monomers, phenols, eugenol and adipic acid).

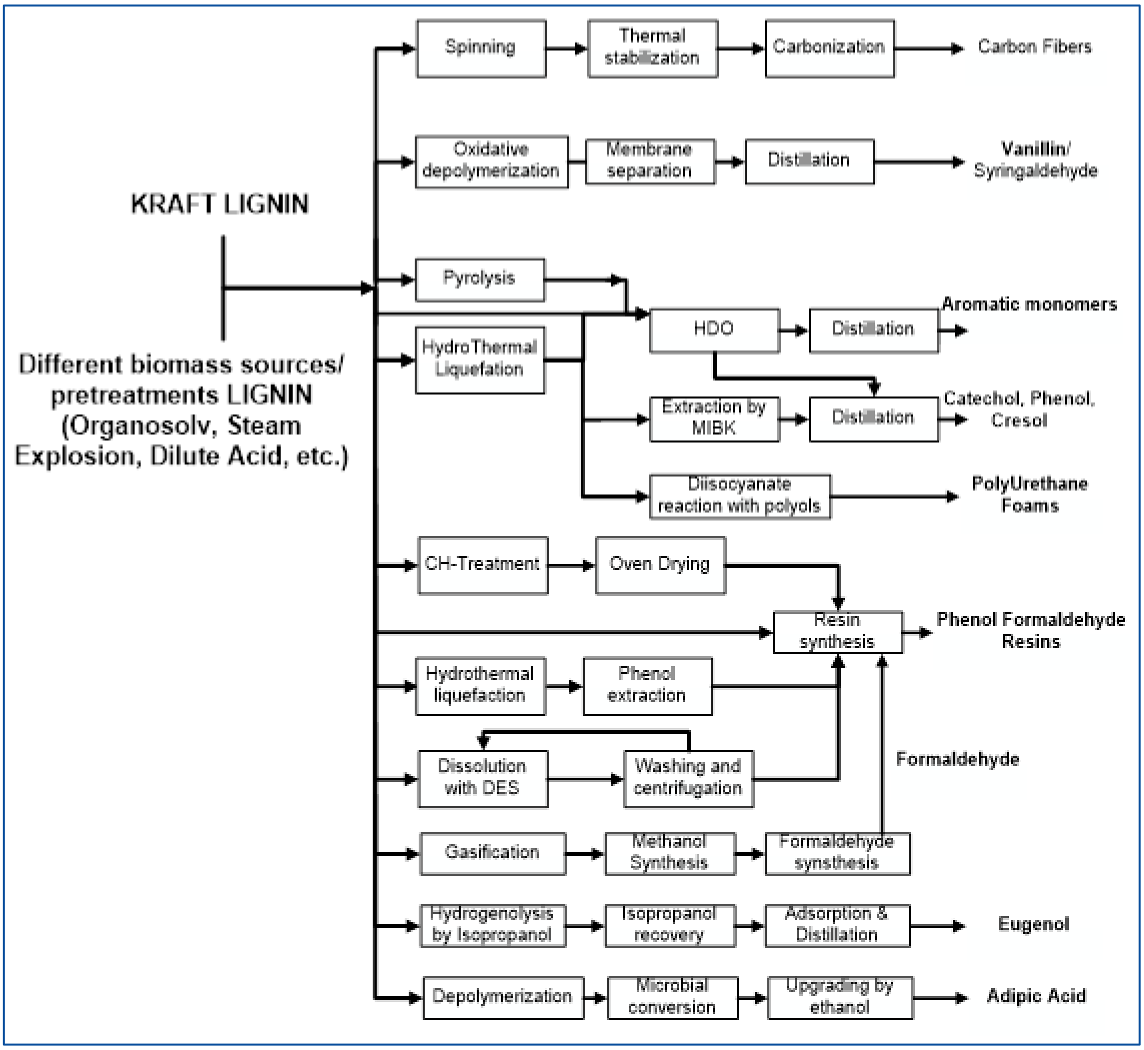

Figure 4. 1 Process superstructure for lignin valorization

4.4 PRELIMINARY WORK AND RESULT

On the basis of the whole superstructure of Figure 4. 2, a simpler preliminary superstructure was built with the most commonly used pathways according to an accurate literature survey. In particular, it consists of six lignin pretreatment routes, two product synthesis processes and two purification technologies, as summarized in the preliminary superstructure of Figure 4. 3. In this preliminary superstructure, only two main products were considered target products: aromatic monomers (AMs) and phenol-formaldehyde resins (PFRs).

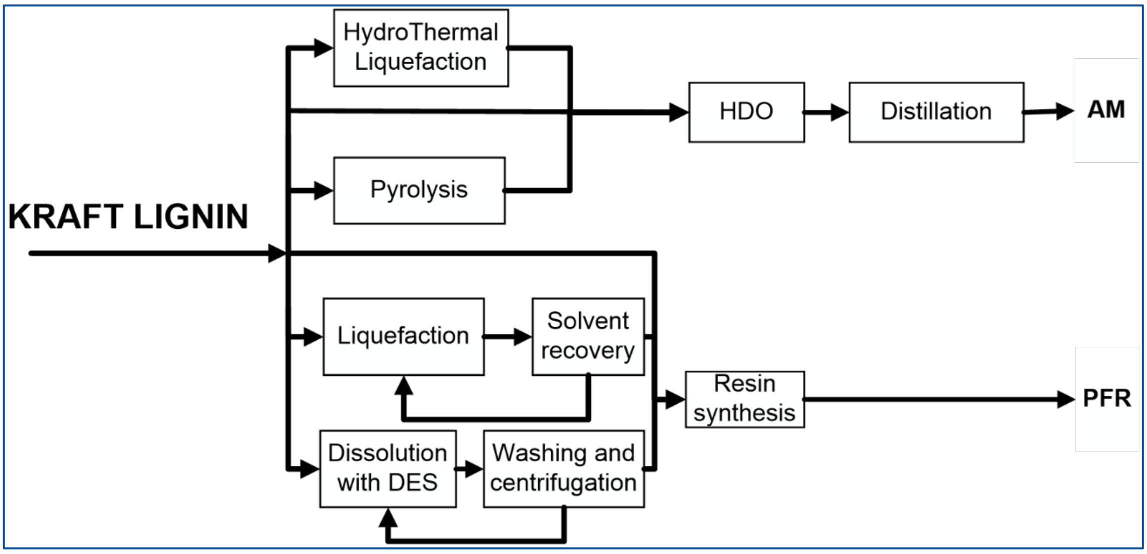

Figure 4. 2 Preliminary superstructure producing Aromatic Monomers and Phenol-Formaldehyde Resins

The optimization problem consists of finding the optimal process flowsheet and the optimal feedstock allocation to products for a lignin-based biorefinery, given an objective function. The lignin-based biorefinery optimization problem aims at deciding which route to take through the network and the relevant flows entering and leaving each layer to maximize the maximum lignin cost (MLC). The latter MLC was derived as the maximum cost of dry lignin that allows a positive net profit from the biorefinery operations:

$$MLC = \max c_L$$

To set the economic analysis, the following constraints were considered:

$$\begin{cases} NetProfit = F_{3,AM}p_{AM} + F_{3,PFR}p_{PFR} - TAC - AIC = 0 \\ TAC = RMC + WWC + UTC + OMC \\ RMC = F_a c_a + F_{IN,L} c_L \end{cases}$$

where $F_{3,AM}$, and $F_{3,PFR}$ are the flowrates of the aromatic monomers and phenol-formaldehyde resins, respectively, p_{AM}, and p_{PFR} are the product selling prices, *TAC* is the Total Annual Cost, *AIC* is the Annualized Investment Cost, *RMC* is the Raw Material Cost, *WWC* is the wastewater treatment cost, *UTC* is the Utilities Cost, *OMC* is the Operating & Maintenance Cost, F_a is the auxiliary material flowrate, c_a is the chemicals/auxiliaries cost and $F_{IN,L}$ is the dry lignin feedstock flowrate. Data tables and details about this analysis can be found in Galanopoulos et al. [46].

The results of this work consist of the *MLC* value, which allows the biorefinery to be economically viable. Values of *MLC* lower than 50 €/t are considered too low, as the cost of producing/processing the feedstock to make it suitable for pretreatment can be high.

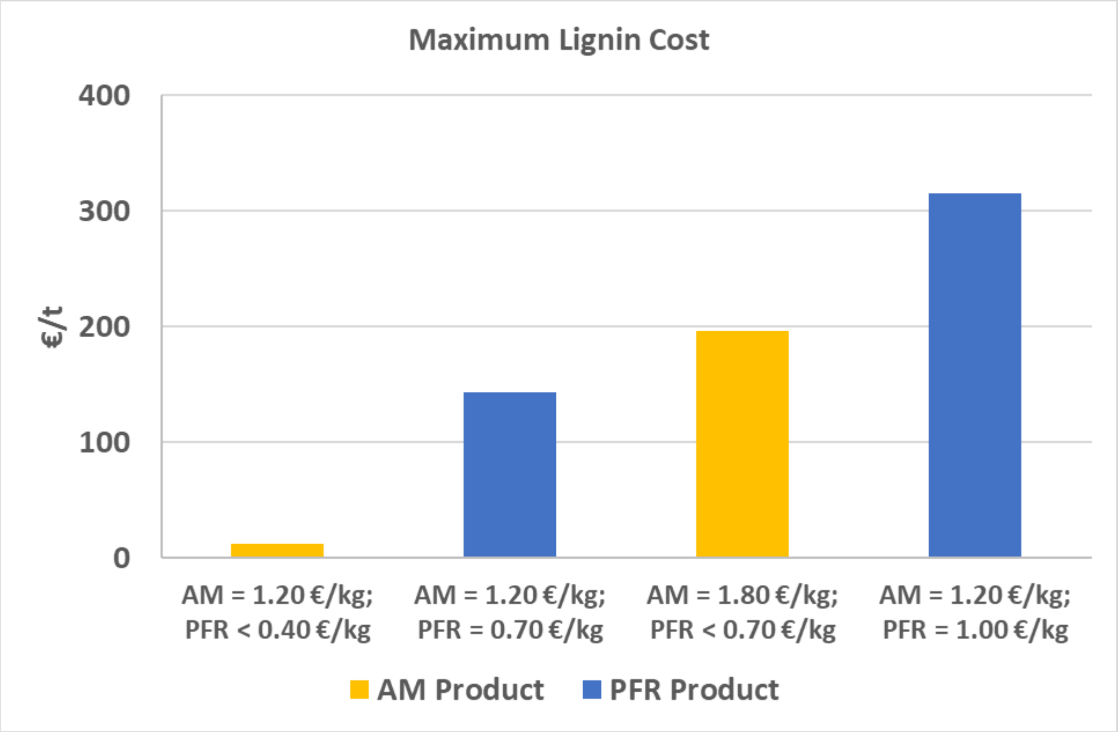

Figure 4. 3 Maximum Lignin Cost (MLC) as a function of the PFR (Phenol-Formaldehyde Resins) and the AM (Aromatic Monomers) selling prices

To evaluate the impact on the optimization of two main economic parameters, a sensitivity analysis varying the PFR and AM selling prices was performed. The base price of AM, assumed to be equal to 1.20 €/kg [26], was increased and decreased by 50%. Because the different final properties of resins are difficult to evaluate in the present analysis, the PFR selling price was varied over a wider range (0.10 €/kg and 1.00 €/kg).

Figure 4. 4 presents the MLC, *CC* and *OC* as a function of the AM price and of the PFR price. The main expected result consists of a general decrease in the MLC with decreasing p_{PFR}. In particular, for the case of p_{AM}=0.60 €/kg, a minimum value of p_{PFR} equal to 0.40 €/kg is necessary to obtain a nonnegative MLC value. For p_{PFR} >0.60 €/kg, the optimal product is always the PFR, regardless of the AM price over the investigated range. For higher values of p_{AM} (1.20 and 1.80 €/kg), a threshold value for p_{PFR} is observed, below which the MLC value remains constant and positive. In particular, for p_{AM} equal to 1.20 €/kg, AM is the optimal product only for p_{PFR} <0.40 €/kg with a very low MLC (approximately 12 €/t). For p_{AM} equal to 1.80 €/kg, AM is the optimal product for p_{PFR} < 0.60 €/kg, with a higher MLC (196 €/t).

Overall, a simplified preliminary superstructure model was evaluated considering the production of aromatic monomers or phenol-formaldehyde resins using kraft lignin. The main preliminary results highlighted the resins as the optimal target product (maximizing the maximum lignin cost), but this result was conditioned by the resin selling price (or real final properties of the lignin-based resins). Compared to the literature works described above, all possible process flowsheet are evaluated simultaneously by the software, identifying only one optimal flowsheet. This approach can be replicated for a large number of products and lignin sources at the same time, this is the main advantage and the main potentiality.

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Conclusions

Lignin-derived chemicals such as phenols for the production of adhesives and resins have rapidly increased in the last 5–10 years. Additional applications close to the market include asphalts and additives for concretes (i.e., polyurethanes),

The major part of the developed applications uses lignin as a macromolecular stream. Kraft lignin and lignosulfonates are the most abundant technical lignins already tested for several applications.

In the short term, the production of lignin-derived SAFs could have a chance to be rapidly integrated in existing oil refinery infrastructures to produce drop-in fuels, especially for the aviation and marine sectors.

- The volume of Kraft and lignosulfonates could decrease in the future due to the reduction in printed paper and the increasing trend in the use of recycled paper. In contrast, technologies for biorefineries are expected to reach higher TRLs and to be more widely available in the market. This could increase the volume of technical lignins through biorefinery applications.
- In addition to phenols, fine chemicals from lignin with huge potential include aldehydes and BTX.
- The use of innovative and light materials with improved mechanical and technical properties will progressively involve wide sectors in the future. In this regard, lignin-derived carbon fibres could have an important market share. In the long term, the main application could be the progressive replacement of steel with carbon fibre. At the same time, lignin could be used as a coke replacement in the iron and steel industry.

Research in the short term must include a higher exploitation of the most abundant technical lignins, namely kraft and lignosulphonates, mainly for the production of macromolecules (i.e. adhesives, resins, carbon fibers).

Research in the medium to long term must include:

- the development of novel value added applications (i.e. nanoparticles, smart materials);

- the development of novel biorefinery layouts yielding high purity lignins and to prove their scalability;

- integrated techno-economic and environmental assessments

Finally, a deep knowledge of the lignin structure is a key element to tailor the lignin chemistry and to achieve streams with standardized properties.

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