Fraunhofer CBP

Fraunhofer Center for Chemical-Biotechnological Processes CBP

Material Use of Lignocellulose

Process development and scale-up


Fraunhofer
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Lignocellulose biorefinery

Pulping of wood and material use of lignin

In order to meet challenges such as increasing raw material prices and limited fossil resources, the utilization of renewable raw materials is becoming increasingly important. In our pilot plant, we are using a biorefinery process to sustainably produce basic and fine chemicals from wood.

Lignocellulose: valuable renewable raw material

Lignocellulose – bulk material of the cell walls of all woody plants – is the most common natural and renewable raw material. Lignocellulosic materials consist primarily of polymeric C6 and C5 sugars (cellulose, hemicellulose) and of the biopolymer lignin. As it is the main component of straw or wood, its extraction and utilization does not interfere with the production of food and feed. Thus, lignocellulose represents a renewable raw material source for cellulose-based fiber materials and platform chemicals based on sugars or phenols.

Fractionation for complete utilization of lignocellulose

Lignocellulose is highly resistant to enzymatic degradation, chiefly due to its compact structure and lignin content. In order to be able to extract the sugars bound in the lignocellulose and the lignin from plant materials containing lignocellulose, the lignocellulosic material has to be pretreated by pulping. However, harsh physical-chemical treatment methods result in decreased yields or qualities of individual fractions. New methods and combinations of methods are thus necessary to obtain technically usable building blocks for subsequent chemical reaction products. At Fraunhofer IGB and our institute branch in Leuna, the Fraunhofer Center for Chemical-Biotechnological Processes CBP, we are developing utilization pathways for the lignocellulosic biorefinery.

left:
In order to use lignocellulose as a raw material, wood has to be separated into its chemical components

Cover picture:
Wood waste is a valuable raw material

Pilot plant at Fraunhofer CBP

As part of the "Lignocellulose Biorefinery" project funded by the German Federal Ministry of Food and Agriculture (BMEL), Fraunhofer CBP was able to transfer the process steps of the so-called Organosolv technique to pilot scale. In an integrated pilot plant, wood is pulped in a 400-liter reactor with organic solvents under pressure and at up to 200°C in order to separate it into its basic chemical components.

Organosolv digestion for the production of high-purity Organosolv lignin

In an ethanol-water mixture, the lignocellulose of the wood is fractionated into cellulose, hemicellulose and lignin under pressure and high temperatures.

- The cellulose-rich pulp can be used in applications such as textiles or can be further hydrolyzed by cellulolytic enzymes to glucose to serve as substrate for fermentations.
- Lignin is dissolved in the digestion solution and can be precipitated and separated from it using a patented process. In contrast to other digestion processes, lignin is obtained in a very pure form and without sulfur impurities, which opens up a wide range of material applications.
- The C5-rich hemicellulose is concentrated into a stable, fermentable solution after removal of lignin and solvent. The fermentability of the digestion solution can be significantly increased by detoxification (enzymatic or adsorptive).

In addition to providing a high-purity lignin fraction, the Organosolv process is characterized by easy recovery of the pulping chemicals.

Integrated plant for universal piloting

The integrated pilot plant includes a large number of individual process steps for manufacturing fibers, concentrated sugar solutions and lignin and is available to investigate and develop processing and fractionation technologies from wood or other lignocellulosic raw materials. Up to 70 kg of biomass can be processed every day. The facility was designed in such a way that the material and energy cycles form closed systems and can therefore be completely balanced.

Universal design

In addition to the Organosolv process, the universal design of the pilot plant also enables the optimization of other pulping or extraction methods at pilot scale (for example aqueous hydrolysis, pulping by means of acid or the soda process). Comprehensive analytics are available to provide mass balances of the individual process steps. Questions in the area of thermal separation technology and extraction can also be answered using individual process-technological units in the plant.

The pilot plant is used in international and national research projects to further optimize the process, to integrate the intermediate products obtained in various value chains and finally to pave the way for the industrial implementation of the technology.

FABIOLA™ Organosolv digestion

In the BBI-EU project UNRAVEL, the novel FABIOLA™ Organosolv digestion of lignocellulose was piloted for the first time. Acetone is used as solvent. Compared to ethanol, the process can be operated at milder temperatures thus reducing the energy required for solvent recovery.

Integrated pilot plant with 400-liter reactor for lignocellulose digestion at Fraunhofer CBP


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Process development for products made of wood

Value creation from lignocellulose

Saccharification of cellulose and hemicellulose

From the cellulose and hemicellulose fractions, monomeric sugars are obtained by enzymatic treatment, which can be used as fermentation substrates for a variety of biotechnological conversions.

Fibers

Alternatively, the cellulose-rich pulp obtained from Organosolv digestion can be used as cellulose pulp for classical applications such as papers or textile fiber after subsequent fiber bleaching. Also, further processing to carbon fibers is possible. We are happy to provide sample quantities of fibrous materials from straw, wood, hemp or other raw and residual materials for customers' own investigations into application development.

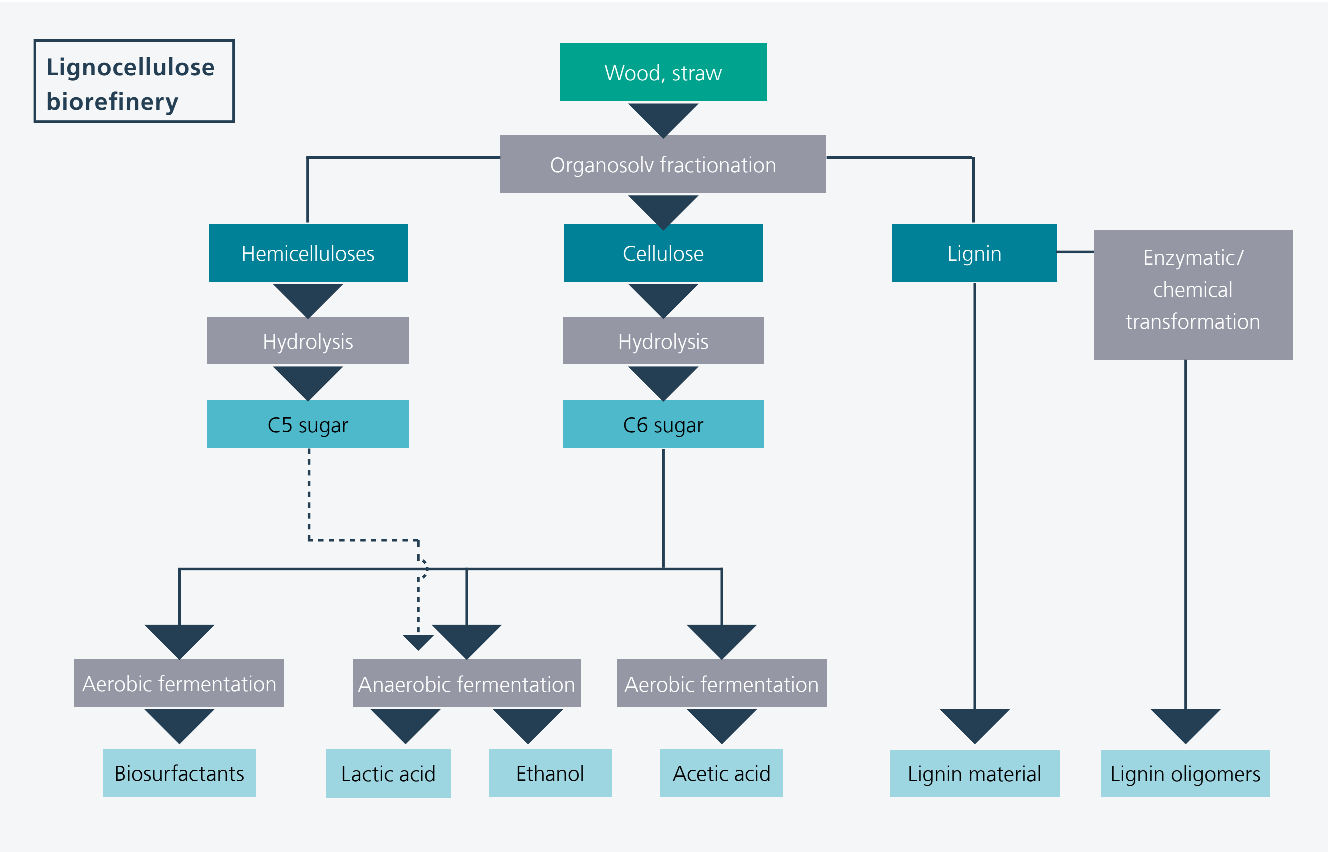
Lignin

Due to its good thermoplastic properties, our Organosolv lignin can be used directly in compounds for the extrusion of molded parts.

Likewise, lignin serves as an alternative for petroleum-based phenol in resins and polyurethane compounds. Thanks to the high purity of Organosolv lignin, it can potentially be used in high-end applications such as food, cosmetics or pharmaceuticals.

In addition, at Fraunhofer CBP we are investigating and scaling up various processes for the modification and depolymerization of lignin that preserve or enhance its structure and functionality. In this way, new, previously inaccessible aromatic structures with new functionalities and thus a new performance spectrum are being identified, which can be used in a wide range of industrial applications. We will present these to you on the following pages.

Container for precipitation of lignin from cooking liquor



Pulping of lignocellulose by Organosolv process and utilization of the individual fractions

Lignin – sustainable source for new materials or aromatic chemicals

Lignins are mainly generated from three phenylpropane units, which are formed from the precursors *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol.

Utilization of lignin

The basic building blocks of lignin are substituted phenols, mainly guaiacol, syringol and *p*-hydroxyphenol, which vary in proportion depending on the type of wood. Lignins can therefore be used, for example, as an alternative for petroleum-based phenol in resins and polyurethane compounds or added to plastics in compounds.

In the Kraft process, also known as the sulfate process, primarily used worldwide for pulping coniferous wood, sulfur-contaminated lignin-containing lyes are produced as a by-product, which are in general just utilized thermally. Since lignin is considered the largest source of biobased aromatic molecules, a material use of these residual material streams is of great interest in order to reduce the demand for fossil raw materials.

LignoBoost Kraft lignin

Kraft lignin is a type of industrial lignin that is produced in large quantities in the pulp industry. In the Kraft cooking process, about 90 to 95 percent of the lignin is dissolved in the cooking liquor containing sodium hydroxide and sodium sulfide. In the pulping process, the lignin macromolecules are broken, the lignin is dissolved in alkaline solution and then precipitated by the LignoBoost process.

Properties of LignoBoost Kraft lignin

Molar masses [g/mol]	
M_w	3140
M_n	680

Composition	
Dry matter	93.3 %
Lignin soluble	2.5 %
Glucose	0.0 %
Xylose	1.2 %
Ash	4.0 %

Elemental analysis	
Carbon	61.4 %
Hydrogen	5.6 %
Oxygen	26.8 %
Sulfur	1.5 %

P-NMR [mmol/g]	
Aliphatic OH	1.5
Carboxyl-OH	0.3
Syringyl-OH	0.5
Guaiacyl-OH	0.5
Catechol- & *p*-hydroxyphenol-OH	0.0

Lignosulfonate

Lignosulfonate is isolated in the Kraft cooking process in a cooking liquor containing sodium hydroxide, sodium sulfide and sulfonic acid salts. The dissolved lignin is then precipitated by acidification with sulfuric acid.

Properties of lignosulfonate

Molar masses [g/mol]	
M_w	4130
M_n	2080

Composition	
Dry matter	94.7 %
Lignin soluble	2.5 %
Glucose	0.1 %
Xylose	0.3 %
Ash	1.3 %

Elemental analysis	
Carbon	65.0 %
Hydrogen	5.7 %
Sulfur	1.6 %
Nitrogen	0.1 %

P-NMR [mmol/g]	
Aliphatic OH	1.7
Carboxyl-OH	0.4
Syringyl-OH	1.6
Guaiacyl-OH	1.7
Catechol- & *p*-hydroxyphenol-OH	0.3

Organosolv lignin

The Organosolv lignin produced in our pilot plant is of high quality and purity, which makes it ideal for both direct use and upgrading into high-value chemicals. Due to the high purity, Organosolv lignin may even be applied in food or pharmaceutical products..

Specifications

We deliver lignin based on customer needs in a reproducible quality for own studies. In our plant we can process lignocellulose from various feedstocks, such as beech, eucalyptus, spruce, miscanthus or wheat straw.

Variation in molecular weights

The properties of the Organosolv lignin obtained depend on the raw material (wood species, straw, etc.) and the digestion parameters selected. The choice of raw material influences the number average M_n and mass average M_w of the Organosolv lignin (see table).

Other variable properties

The so-called H-factor as a measure of the digestion time, temperature and the addition of sulfuric acid can also influence the glass transition temperature T_g of the lignin obtained as well as the proportions of aliphatic and aromatic hydroxyl groups.

Availability

Organosolv lignin from our pilot plant is available in kilogram scale. If requested, we can also produce larger quantities or meet specific quality requirements, depending on individual needs, and can extract tailor-made lignin very quickly. Please feel free to contact us so that we can provide you with a quotation.

Properties of Organosolv lignin (beech)

Composition	
Dry matter	93.6 %
Lignin soluble	1.9 %
Glucose	0.0 %
Xylose	0.5 %
Ash	0.0 %

Elemental analysis	
Carbon	64.8 %
Hydrogen	6.1 %
Oxygen	28.8 %
Sulfur	0.0 %
Nitrogen	0.0 %

P-NMR [mmol/g]	
Aliphatic OH	1.7
Carboxyl-OH	0.1
Syringyl-OH	1.4
Guaiacyl-OH	1.8
p-hydroxyphenol-OH	0.1
Phenolic OH total	3.3

Ranges of molecular masses of lignins of different wood species

Beech
M_n: 800 – 1390 g/mol
M_w: 1830 – 5870 g/mol

Eucalyptus
M_n: 1030 – 1060 g/mol
M_w: 2960 – 3400 g/mol

Spruce
M_n: 1030 – 1740 g/mol
M_w: 4090 – 10 490 g/mol

Residual forest wood
M_n: 910 – 1190 g/mol
M_w: 3030 – 6280 g/mol

Organosolv lignin

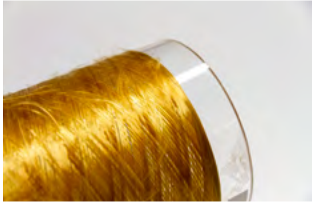
Reference

Rossberg, Christine; Janzon, Ron; Saake, Bodo; Leschinsky, Moritz (2019) Effect of process parameters in pilot scale operation on properties of organosolv lignin; BioResources 14(2): 4543 – 4559
https://publica.fraunhofer.de/entities/publication/9a3fe0ce-9a51-433e-9140-75aef50e3897/details

Applications

Fraunhofer CBP has already been involved in the investigation of various potential applications of lignins:

- Production of melt-spun fibers from Kraft lignin
- Production of fiber-reinforced plastics, e.g. flax fabric-reinforced lignin compounds
- Utilization of the fungicidal properties of lignin in crop protection
- Spinning of cellulose fibers reinforced with Organosolv lignin
- Processing into wood protective varnishes



IONCELL fiber made from cellulose and Organosolv lignin

Plant protection products

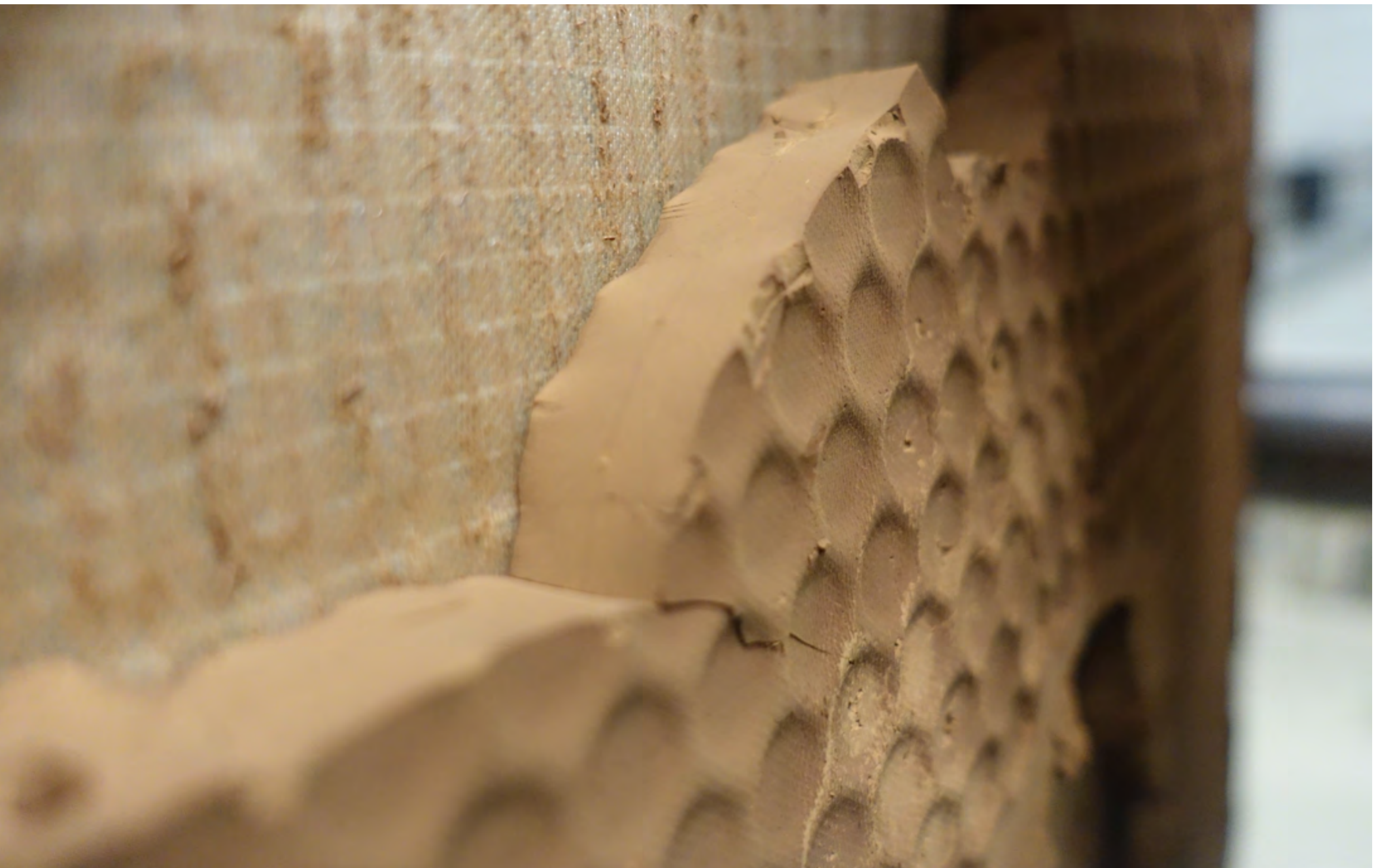
Piece of wood treated with lignin-based wood preservative stain

Lignin-based synthetic resin

Arboblend test specimen with Organosolv lignin (Tecnaro)

Polyurethane rigid foam with Organosolv lignin

Filter plates of the filter press filled with Organosolv lignin



Monomeric oils from lignin

In the case of the base-catalytic depolymerization of lignin, an oil with more than 30 monomers is obtained in addition to the solid oligomers. It contains, among other substances, the monomers guaiacol, catechol, syringol, phenol and vanillin, the content of which varies depending on the pulping process and lignin source.

The LignoBoost Kraft lignin oil contains an average of 0.4 percent vanillin and 1.0 – 1.7 percent guaiacol. Catechol varies between 0.0 and 2.6 percent depending on the process parameters.

Catechol can be up to 6.4 percent, vanillin up to 1.2 percent and guaiacol up to 3.8 percent in the oil from lignosulfonate.

The oil from Organolsolv lignin contains about 0.3 percent guaiacol, 0.0 percent catechol, between 1.3 and 3.0 percent syringol and about 0.3 percent vanillin. In the case of oil from coniferous organolsolv lignin, the proportion of guaiacol is significantly higher at 2.8 percent, and that of syringol is significantly lower at 0.1 percent. The levels of catechol and vanillin are comparable to those found in beech Organosolv lignin oil.

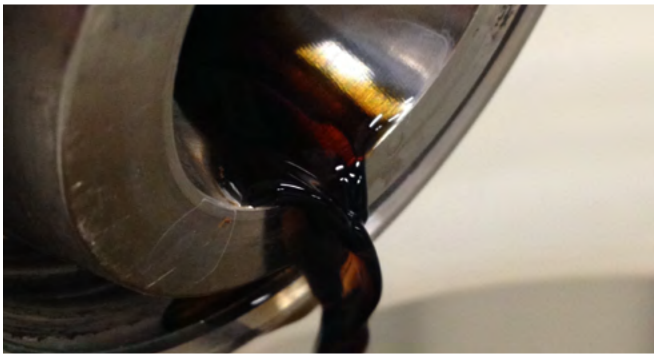
At Fraunhofer CBP, we have already examined various applications for the use of lignin-based oils:

- Epoxy/phenolic resins
- Polyurethane foams

Base-catalyzed depolymerization of lignin

The depolymerization of lignin enables the provision of low-molecular phenolic compounds from a renewable raw material source. When the lignin is cleaved, oligomers and monomeric oil are obtained.

Process
The base-catalyzed depolymerization of lignin takes place in a continuous flow tube reactor under a pressure of 250 bar and temperatures of up to 350°C in a dilute alkaline solution. It achieves hydrolysis of the lignin's ether bonds, thereby cleaving the macromolecule into monomeric, dimeric, and oligomeric alkyl-functionalized aromatic compounds. Targeted fractions can be isolated by membrane techniques. After separation and purification of the fractions, oligomeric polyphenols and an oil containing various monomers are obtained.



Lignin cleavage solution from the high-pressure plant

Contents and properties of different lignins in comparison
Monomers in the oil (in % lignin)

	Guaiacol	Catechol	Syringol	Phenol	Vanillin	M_w [g/mol]	Yield
LignoBoost Kraft lignin	1.0 – 1.7	0.0 – 2.6	0.0 – 0.3	0.0 – 0.1	0.3 – 0.5	260 – 270	10 – 12 %
Lignosulfonate	0.8 – 3.8	0.7 – 6.4	n. s.	n. s.	0.8 – 1.2	210 – 300	14 – 25 %
Organosolv lignin							
Beech wood	0.2 – 0.5	0.0 – 0.1	1.3 – 3.0	n. s.	0.1 – 0.4	340	8 – 14 %
Spruce	2.8	0.2	0.1	n. s.	0.4	n. s.	4 %

Low molecular weight phenolic oligomers from lignin

In order to break down the complex lignin molecules from the Organosolv lignin into simple building blocks, base-catalyzed and oxidative depolymerization have proven to be particularly promising processes.

Lignin oligomers from base-catalyzed depolymerization

The oligomers obtained from the base-catalyzed depolymerization achieve molar masses between 360 g/mol and 1310 g/mol (number average M_n) and between 1040 g/mol and 3480 g/mol (mass averages M_w).

The LignoBoost Kraft lignin oligomers are characterized by number averages (M_n) between 470 g/mol and 940 g/mol and mass averages (M_w) between 1170 g/mol and 2880 g/mol.

The lignosulfonate lignin oligomers are characterized by number averages (M_n) between 510 g/mol and 800 g/mol and mass averages (M_w) between 1240 g/mol and 1930 g/mol.

After cleavage of Organosolv lignin from beech, oligomers with number averages (M_n) between 360 g/mol and 870 g/mol and mass averages (M_w) between 1080 g/mol and 1910 g/mol are obtained. Upon cleavage of coniferous Organolsolv lignin, oligomers had the following molar masses: M_n 1460 and M_w 9230 g/mol.

Applications

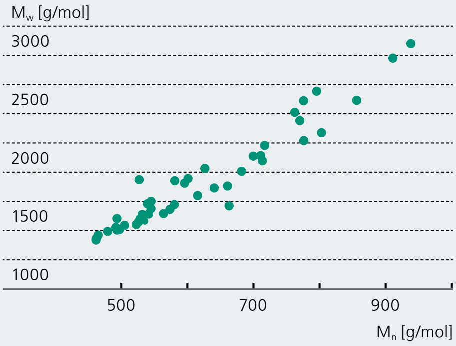
In different projects, partners have already used the lignin fragments created by base-catalyzed depolymerization for the following exemplary applications:

- Production of high-quality polyurethane foams
- Polyols for polyurethane coatings of slow-release fertilizers

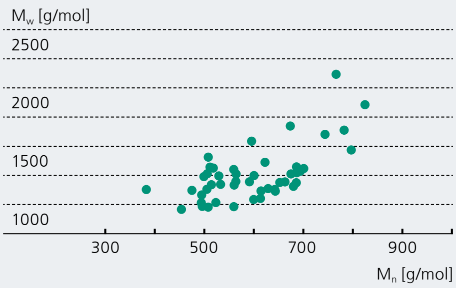
Initial application tests showed positive properties, some additional benefits such as biodegradability.

Dependence of the number averages M_n on the mass averages M_w of the oligomers

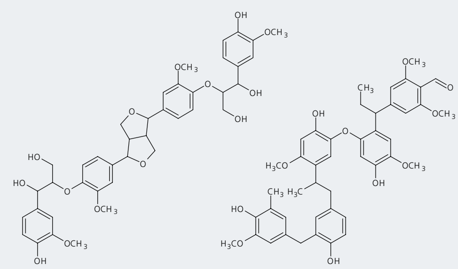
Oligomers from LignoBoost Kraft lignin



Oligomers from lignosulfonate



Oligomers from Organosolv lignin



left: Coatings made from lignin-based bitumen

right: Exemplary structures of lignin oligomers

Modification of lignin and lignin oligomers

Oxidative depolymerization to obtain carboxyl-rich oligomers

LignoBoost Kraft lignin can be depolymerized by oxidation using hydrogen peroxide. The obtained oligomers are characterized by an increased proportion of carboxyl groups, which can be up to 2.54 mmol/g lignin. This can be specifically adjusted.

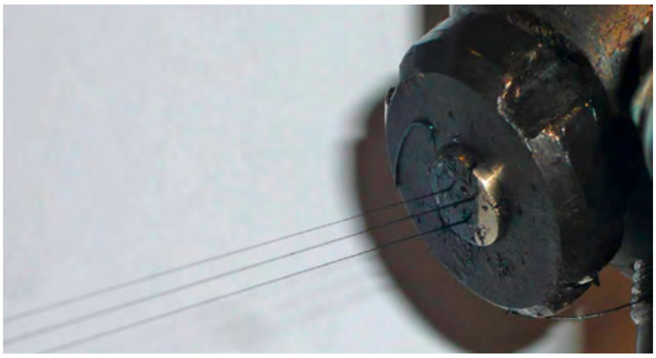
The carboxyl-rich oligomers can be used, for example, as hardener components in epoxy resins.

Production of non-polar lignin derivates

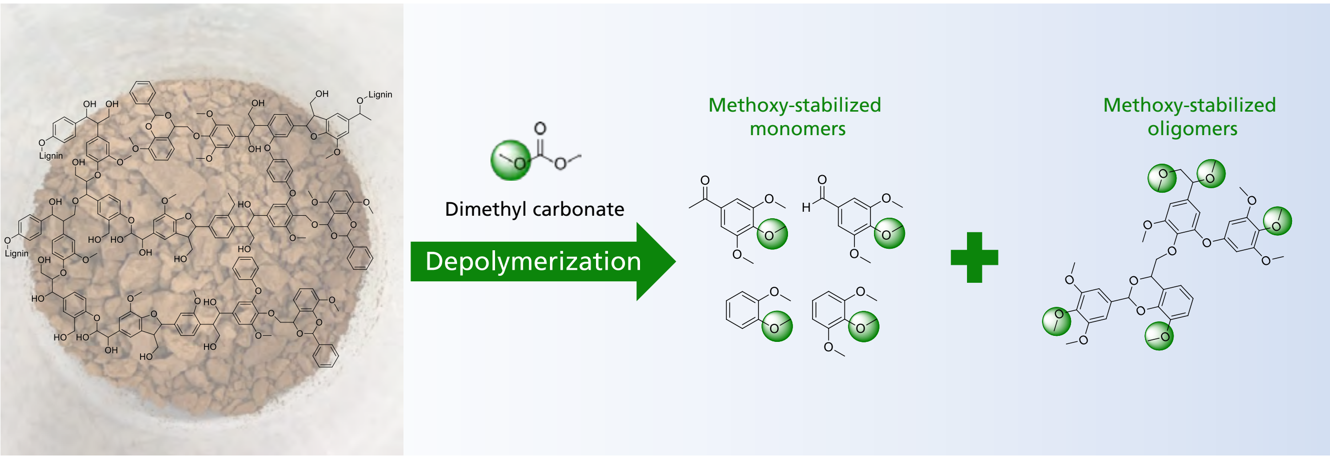
In the base-catalyzed depolymerization of lignin, subsequent reactions of the cleavage products take place limiting the yield of certain products. This can be prevented by depolymerization in dimethyl carbonate as a solvent. Dimethyl carbonate acts as a non-toxic and environmentally friendly "green" solvent and at the same time as in-situ methylating agent for hydroxyl groups. In the process, phenol groups are completely methylated and carboxyl groups are methylated up to 90 percent.

Acrylation with methacrylic acid

Lignin can be functionalized by acrylation, e.g. using methacrylic acid. This enables the plasma-induced cross-linking and stabilization of lignin with advantages in the production of carbon fibers.



Spinning of lignin-based carbon fibers



Non-polar lignin derivates are suitable, for example, for use in wood protection glazes

Range of services

Fractionation and material use of lignin

With our flexibly operational pilot plant and excellent equipment for conversion and processing procedures, we develop and scale biotechnological and chemical processes for the utilization of wood components up to application-relevant dimensions and support small and medium-sized companies in particular for faster product development and market launch.

We cleave lignin from various sources into oligomers or monomer-containing oils using different methods and characterize them with comprehensive analytics. Thereby we can adjust the molar mass as well as the functionality of the obtained products according to the application requirements.

We are happy to provide companies with oligomers as well as oil samples according to the desired specification, and we also provide support in application-related investigations.

- Development and piloting of pulping processes for lignocelluloses from different sources
- Recovery of lignocellulosic ingredients (extractives, hemicellulose, lignin, cellulose) with specific properties
  - Provision of fiber material, for example for the production of fiber composites
  - Provision of Organosolv lignin for e.g. thermoplastics, carbon fibers, but also cosmetic applications
  - Oxidation or base-catalyzed cleavage of lignin (including Organosolv lignin, Kraft lignin) to aromatic monomeric and oligomeric building blocks
  - Modifications such as acrylation of lignin to reactive lignin derivatives
  - Depolymerization of lignin to methoxylated oligomers as well as oil
- Extraction of other plant constituents such as bark extractives

High pressure reaction plant with continuously operated flow tube reactor

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The Fraunhofer Center for Chemical-Biotechnological Processes CBP develops and scales up chemical and biotechnological processes for the utilization of renewable raw materials. By providing infrastructure, pilot plant facilities and a staff of highly qualified experts, the CBP closes the gap between laboratory and industrial implementation and enables partners from research and industry to scale up processes to production-relevant dimensions, and thus accelerate process developments. To this end, Fraunhofer CBP offers a unique, modular platform for realizing complete process chains – from biomass fractionation and various conversion processes to product separation and purification. Fraunhofer CBP is a branch of the Fraunhofer Institute for Interfacial Engineering and Biotechnology IGB.

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