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Lignin – a natural resource with huge potential

Petroleum is the lifeblood of the chemical industry. It is the raw material for basic chemicals and is used to produce a tremendous wealth of products. Growing demand and dwindling resources mean that the chemical industry is increasingly focusing on renewable resources. Lignin is a wood component that is proving to be a particularly promising resource. It is currently almost exclusively used for generating energy, although it could also be used for many other purposes. In Baden-Württemberg, a research consortium is specifically focused on exploring the potential of this wood component.

Wood processing plant in the city of Buchenbach. © Juliette Irmer

Lignocellulose (Latin lignum = wood) gives plants shape and stability. Lignocellulose biopolymers strengthen the cell wall of plants and consist of three main components: cellulose and hemicellulose form a framework in which lignin is incorporated as a kind of connector, thus solidifying the cell wall. Cell wall lignification makes plants resistant to wind and pests.

In contrast to fossil petroleum, lignocelluloses derived from wood, straw or Miscanthus are renewable raw materials, they can be grown on fields and in forests and are climate neutral. Moreover, the amount of carbon dioxide released into the atmosphere by burning wood and woody materials does not exceed that stored by the trees as they grow. But are lignocelluloses a serious alternative to petroleum?

From petroleum refineries to biorefineries

The chemical industry entirely depends on carbon compounds for creating products such as paints, adhesives, artificial fibres, fertilisers, pesticides and, above all, plastics. In Germany, petroleum, natural gas and coal account for roughly 87 percent of all carbon compounds used for these purposes.

However, carbon also occurs in plants. During photosynthesis, plants bind atmospheric carbon dioxide and use it to produce energy-rich molecules, primarily sugar compounds. The chemical industry already uses renewable resources to a limited extent (13 percent), mainly vegetable oil, starch, natural rubber and cellulose.

The objective is to increase this percentage in the future. "Our long-term goal is to establish biorefineries in which renewable raw materials can be used in their entirety in an optimised value chain," says Dr.-Ing. Daniel Forchheim from the Karlsruhe Institute of Technology and coordinator of the Lignocellulose consortium in Baden-Württemberg. The consortium is currently working on 19 projects that study the entire flow of material from field to product. The major research areas are the cultivation of the raw material, i.e. the selection and breeding of lignocellulose-producing plants, the testing of novel extraction methods and biotechnological and chemical synthesis strategies for the development of biobased products.

Lignin – the new petroleum?

Phenylpropane building blocks of lignin coumaryl alcohol (1), coniferyl alcohol (2) and sinapyl alcohol (3). Source: Yikrazuul / Wikimedia Commons | public domain / https://commons.wikimedia.org/wiki/File:Monolignols_general.svg?uselang=de

Lignin, which represents up to 30 percent of the lignocellulose biomass, is an unexploited treasure – at least from a chemical point of view. The resinous substance consists of different aromatic basic building blocks, so-called phenylpropanoids, which are extremely useful. Aromatic compounds are normally extracted from petroleum and used to produce plastics, drugs and paints. The potential of lignin is therefore quite high: besides cellulose and chitin, lignin is the most abundant polymer in nature - and the only one that contains such a large number of aromatic compounds.

Every year, approximately 50 million tonnes of lignin are produced worldwide as by-products of the paper industry. Lignin is usually extracted from wood pulp using a sulphate process during which debarked wood chips, straw or crushed corn stalks are boiled for several hours in large pressure vessels with sodium hydroxide in order to remove the lignin from fibruous cellulose. Lignin is a by-product of this process and accumulates in the form of black liquor. The material potential of lignin remains largely unused: 98 percent of lignin is burned.

However, lignin can also be produced from straw or Miscanthus, a giant grass with a particularly promising potential. Miscanthus x giganteus grows on nutrient-poor soils, achieves high yields and defies many stress factors. It is also used as the pilot plant in a subproject being carried out by researchers from the Center for Organismal Studies at the University of Heidelberg. “We are studying the influence of environmental factors on an important metabolic pathway in plants called the phenylpropanoid pathway,” says Linn Voß from the Center. The phenylpropanoid pathway starts with the amino acid phenylalanine. Plants have a certain pool of this compound, which they use to synthesise compounds that provide e.g. protection against herbivores and pathogens as well as lignin. Plants are able to alter the quantity of phenylpropanoids in response to changing environmental conditions. During dry conditions or when they are infected with insects, plants produce more defence substances and less lignin. “Miscanthus is very robust and seems to be very efficient in its use of phenylalanine. We now want to understand how plants are able to alter these quantities,” says Voß.

The different lignin building blocks form a network.

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In addition to basic research, the research consortium is also looking at developing new conversion methods. A distinction needs to be made between the separation of lignocellulose into its three main constituents and subsequent processes which break down cellulose, hemicellulose and lignin into their basic building blocks. This is particularly difficult for lignin as the phenylpropanoid building blocks coniferyl, cumaryl and sinapyl alcohol are linked together in different ratios and form a dense, three-dimensional network that is difficult to break up chemically. Due to its complex structure, breaking down lignin requires high temperatures (up to 500 degrees Celsius) and high pressure (up to 200 bar). This is the reason why researchers are specifically focused on developing methods that do less damage to the cellulose and hemicellulose and are more economical.

Reaching the goal with bacteria and fungi

The researchers are using nature as a model: white rot fungi break down lignin using an enzyme cocktail. But this is a very slow process. The fungi break down lignin mainly with the aid of laccase and peroxidase enzymes. However, the results obtained in the laboratory are not always satisfactory. “The enzymatic processes do both, synthesise new molecules and break down others. The enzymes break down lignin into its building blocks, but also assemble them again,” says Dr. Susanne Zibek from the Fraunhofer Institute for Interfacial Engineering and Biotechnology in Stuttgart. Another approach which aims to break down lignin directly with the aid of bacteria and fungi might be more promising. “Bacteria and fungi possess the pathways we have in mind,” says Dominik Rais from the Institute of Interfacial Engineering and Plasma Technology at the University of Stuttgart. The researchers use genetic engineering methods to make the bacteria express more enzymes of interest or turn off unwanted ones. The ultimate goal is to produce specific lignin building blocks only. However, the method is still in an early phase of development.

Chemists from the Max Planck Institute for Coal Research in Mülheim an der Ruhr have developed a process that aims to make lignin easier to use. Thanks to two catalysts and three interconnected chemical reactions, lignin can be broken down at 150 degrees and less than 40 bar. Above all, the process does not produce the wild mixture of aromatic compounds which is usually obtained during the thermochemical separation of lignin and that is difficult to separate, but a more uniform group of aromatic carbon compounds that are easier to isolate.

The first applications that use lignin as a material already exist: a company called TECNARO from the Baden-Württemberg city of Ilsfeld blends lignin with other natural fibres such as flax or hemp to produce a fibre composite called ARBOFORM® (Arbor, Latin = tree) that can be shaped at elevated temperatures. This composite is also called liquid wood because it can be turned into any shape whatsoever, including steering wheel segments, mobile phone housings or musical instruments such as flutes. In addition, lignin can be used to produce artificial vanillin on the industrial scale. Approximately three kilograms of vanillin can be produced from around one tonne of wood.

Cellulose and hemicellulose building blocks can also be used as materials. A group of researchers at the University of Hohenheim uses genetically modified yeast to produce ethanol from agricultural waste such as straw. The Swiss company Clariant has also managed to do this. Their demonstration plant in the city of Straubing can produce up to 1,000 tonnes of ethanol per year. This cellulosic ethanol is already used in cleaning agents.

Biomass is not unlimited

Organisation of the Lignocellulose consortium.
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Lignin has huge application potential. However, the quantity of lignin that will be used in the chemical industry in the future depends on many factors: on the one hand, it depends on the progress of crude oil prices, and on the other on progress in research. The research consortium is also dealing with potential ecological constraints associated with the use of lignin: how intensively can lignocellulose be used for extracting lignin before it has a severe environmental impact? ”One group of researchers is focusing on the question as to how much dead wood there needs to be in a forest. "This is an important aspect to investigate as lignin is an important soil former," says Forchheim.

Another subproject is investigating the regional availability and sustainable use of lignocellulose: "Wood is a resource that is produced sustainably and it is not in direct competition with food production. So there is no ethical problem. However, lignocellulose is already being used intensively and there is little room for expansion," says Dr. Marcus Lingenfelder, a forestry researcher from the University of Freiburg. Making wood-derived lignocellulose available in a sustainable way for the bioeconomy would require replacing the use of wood for energy production in the long term with other renewable energy sources such as sunlight, wind and water. "This would be quite a sensible strategy as it is much more area efficient than biomass combustion. In addition, the incorporation of lignocellulose into durable products would trap more atmospheric CO_2 for longer," says Lingenfelder.

Using the fast-growing Miscanthus grass is not without its difficulties either. Although Miscanthus is a non-food biomass, its cultivation nevertheless competes with the production of food and feed as agricultural land is not only limited in Germany but also elsewhere. Therefore lignin produced from agricultural residues or as a by-product in the paper industry and is currently mainly burnt seems a rather good alternative. The added value that will generate higher revenues when lignin is used for more than just energy generation will expand the range of possibilities for green products. Although lignocellulose will probably not replace petroleum in the near future, it is likely to complement it.

Dossier

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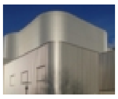

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