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Technical note on lignins and their applications

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LIGNINS TODAY

LIGNIN AND LIGNIN PYROLYSIS OIL AS SUBSTITUTES FOR PHENOL IN PHENOL-FORMALDEHYDE (PF) RESINS

In BIOCORE, CHIMAR (Greece) is investigating how Biolignin™ and Biolignin™-derived pyrolysis oil can be used for the production of PF-based adhesives, suitable for the manufacture of wood-based panels.

Unmodified, milled Biolignin™ can directly replace approximately 40% of phenol in PF resins. However, prior chemical modification of the Biolignin™ affords much higher levels of phenol substitution. So far, up to 70 % phenol substitution has been achieved using modified Biolignin™ that affords decreased use of formaldehyde. This is a clear advantage for a future biobased product.

An alternative way to use lignins, is to break them down into smaller aromatic compounds. The Energy research Centre of the Netherlands (ECN) achieves this using pyrolysis technology, which converts Biolignin™ into a phenolic pyrolysis oil. In BIOCORE, this oil has been tested by CHIMAR to make PF-based adhesives, replacing a part (10 %) of the phenol component by pyrolysis oil. Results so far are promising and indicate that a greater proportion of pyrolysis oil could be used.

Plywood panels produced using adhesives that contain Biolignin™ or Biolignin™-derived pyrolysis oil generally display similar physical and mechanical properties to conventional wood panels made with standard PF resin. The new 'bio-based' panels reach European standards (EN314.1 and 2), meaning they can be used for outside purposes.



Biolignin™ based plywood production at CHIMAR lab.
© CHIMAR

Moreover, the panels have extremely low formaldehyde emissions and can fulfill the CARB II requirements.

CONCLUSION

The development of biorefineries using advanced technologies, such as organosolv, to process lignocellulosic biomass is set to transform the lignin market, providing high quality, sulfur-free phenolic-based building blocks for a wide range of applications. While significant R&D will still be required to make certain lignin applications economically viable, BIOCORE researchers are revealing that others are already mature and will become commercial as soon as sufficient quantities of lignins are available.



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A biorefinery concept for the transformation of biomass into 2nd generation fuels and polymers

TECHNICAL NOTE ON LIGNINS AND THEIR APPLICATIONS



<http://www.biocore-europe.org>

EDITORIAL NOTE

The European FP7 project BIOCORE aims to demonstrate the feasibility of an industrial lignocellulosic biorefinery concept, which includes deriving value from lignin, beyond its calorific value. To achieve this, BIOCORE partners are devising extraction and conversion methods for lignin, which will allow the production of chemicals, polymers and materials.

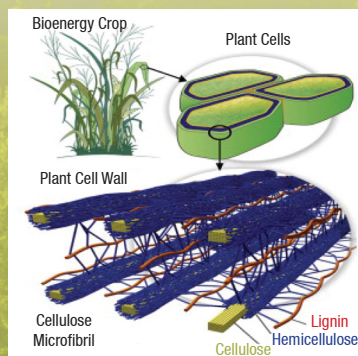
After two years, BIOCORE's first achievements are now tangible, with lignin being used to make several products, including glues (for wood panels) and plastics. Therefore, it is timely to present the potential of lignin-based technology and to start to imagine tomorrow's bio-based commercial products.

BIOREFINING AND LIGNINS

Like the paper industry, the emerging biorefining industry will produce large amounts of lignins, which are major components of lignocellulosic biomass (approximately 20 % dry weight). Therefore, a challenge for biorefiners is how to best use lignins. Should they be simply used to generate onsite power and heat? Or, should they be viewed as valuable chemical phenolic-based intermediates that can be used to develop a whole range of added value finalized products? This article aims to reveal what options exist for lignins as building blocks for the manufacture of biorenewable products.

Lignins are major structural components of plants, and confer to woody biomass its mechanical structure and resistance to environmental stress and microbial decay. From a chemical perspective, lignins are highly complex ramified polyphenolic polymers, whose structures are not completely defined despite many decades of research.

From an environmental perspective, lignins are a renewable source of aromatic compounds which can substitute oil-based phenolics.



Plant cell wall utilization of lignin, hemicellulose and cellulose.

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LIGNINS TODAY

Today's sources of lignins

Lignins produced by paper pulping processes are the most common and widely available lignins today (several Mt¹ per annum at the global scale). Lignins from Kraft pulping are most common though rarely used as chemicals. Instead they are burnt to generate heat and power. Currently, the main source of isolated industrial lignins (approximately 1 Mt per annum) is the Sulfite pulping process, which employs sulfur dioxide. This process produces water soluble lignosulfonates that are quite different from lignins obtained in other processes. Currently, one mill is pulping annual crops based on straw and grass and is producing soda lignin at 5-10 Kt¹ per year.

The growing biorefinery industry is also now set to produce lignins, whose characteristics will differ from those obtained in conventional paper pulping processes. The prospect of high level production of cellulose ethanol means that lignins from biorefineries will become increasingly available, thus creating an even greater commercial offer and opportunities for new products. Rough estimates of future lignin availability indicate that in Europe alone (EU-25), up to 16 Mt/year of lignin could be produced by biorefineries in the next decades.

The first wave of lignocellulosic biorefineries will use variants of the biomass separation technology known as steam explosion. In this technology, biomass is treated at high temperature and pressure for short periods of time, before rapidly releasing the pressure. This process leads to a profound disruption of the lignocellulosic network and allows the isolation of a cellulose fibre-enriched fraction. The lignins obtained in steam explosion processes are sulfur-free and generally display a medium level of purity

when compared to commercial Kraft lignins. Moreover, because the steam explosion process does not induce major changes in the structure of the lignins, it is thought that lignins obtained in this process to some extent resemble native lignin.

Organic solvents have long been used to separate woody biomass into its component parts. Therefore, it is logical that these form the key constituents of so-called organosolv processes that were originally developed to replace Kraft pulping in the paper industry. Many organosolv processes have been described, but two (based either on the use of alcohols or organic acids) are currently dominant. The widely studied ethanol-water solvent system has been operated at pilot scale by Lignol Energy Corporation (Burnaby, B.C.) for several years, while a formic/acetic acid solvent system forms the basis of the technology that has been developed to pilot scale by the CIMV company (Levallois-Perret, France). Advantageously, lignins obtained from organosolv processes are sulfur-free, water insoluble and display relatively high purity compared to lignins obtained from other processes.

Current uses for lignins

Most Kraft lignins are burnt within paper mills to generate heat and power, thus providing energy autonomy and lowered operating costs. The majority of lignosulfonates are used as additives in the building sector, where they provide plasticity and flowability to concrete. Lignosulfonates are also used as binders in animal feed pellets and can also be used as additives in animal feed preparations. Moreover, lignosulfonates are employed in other sectors such as road building, oil well drilling and even

as dispersants in pesticides used for agriculture. In addition to these applications, there are a myriad of minor uses, which includes the use of soda lignins in wood adhesives. However, the current quality of available lignins has only allowed very modest progress in this sector.

LIGNINS AND LIGNIN DERIVATIVES AS BIORENEWABLE BUILDING BLOCKS: EXAMPLES FROM BIOCORE

In BIOCORE, CIMV biolignins™ are being used in the manufacture of wood panels, polyurethanes, polyesters and phenolic resins, thus covering both the glue and bioplastics sectors.

The CIMV organosolv process provides a lignin fraction (Biolignin™) that displays limited solubility in polar and non-polar organic solvents. Physically, this fraction is obtained as a brown powder that displays a density of 0.9 g/cm³ (1.30 g/cm³ in solid state) and an average particle size of circa 2 microns.

Lignins as building blocks for polyurethanes (PUs) PU Films

In BIOCORE, IWC (Latvia) has investigated the synthesis of polyurethanes with CIMV Biolignin™. This research has shown that the lignin's function goes beyond a simple crosslinker role, providing higher thermostability to the PU. The fractionation of CIMV Biolignin™ using organic solvents (studied by

DLO and IWC) allows the isolation of soluble fractions that can be incorporated (up to 40 %) into polyether diol-based PU films. This drastically enhances the glass transition temperature, the ultimate stress and the Young's modulus upon elongation of the final polymer. PU films containing 20 % soluble lignin display properties (notably tensile strength) that are comparable to that of a 3-functional Lupranol-based film, and incorporation of 5-10 % of soluble lignin increases the ultimate strain of the PU, compared to a lignin-free PU.

PU foams

IWC (Latvia) has established that mechanically-pretreated Biolignin™ can also be used as a PU filler. The use of up to 30% in foams does not affect mechanical properties. When Biolignin™ is combined with Tall oil, it is possible to make rigid bio-based PU foam that could be used in the construction or refrigeration sectors.

PU cast resins

Another BIOCORE partner, SYNPO (Czech Republic), has developed a solvent-free process for the production of a novel PU cast resin, synthesized using 100 % bio-based polyol, which displays interesting properties. Novel PU cast resin, containing 20 wt. % of Biolignin™, displays, compared to Veropal 3B, a commercial SYNPO product, increased tensile strength, toughness, surface hardness and high electrical resistivity. The developed technology is currently being patented.

¹ Mt is a million metric tons and Kt is a thousand metric tons.