

Utilization of lignin Project: 2490: BioValue Spir, leverance 6	Prepared	LATO
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Growing populations and increasing consumption of energy, food and other goods combined with climate changes have created a need for new technologies that can produce sustainable alternatives to the fossil based products and ensure security of supply.

Utilization of residual lignocellulosic biomasses such as wood and straw have in many years been heavily investigated due to the large amounts available and most of them are used for low value applications such as energy production or simply just being plowed. In Denmark alone 2.6 million tons of straw was left at the fields in 2014.ⁱ Alternative utilization methods would increase the demand for straw and turn Danish farmers' residual product into a valorized feedstock.

Lignocellulosic biomass consists of cellulose, hemicellulose and lignin. Lignin has a complex structure (see Figure 1ⁱⁱ below) and can be found in the cell wall of the plants. Lignin gives the plants structural stability and biological resistance. The properties of lignin do, however, also make it more difficult to convert and utilize the lignin than the cellulose. The biomass type, harvesting type and processing method all have influence on the structure and characteristics of the lignin.

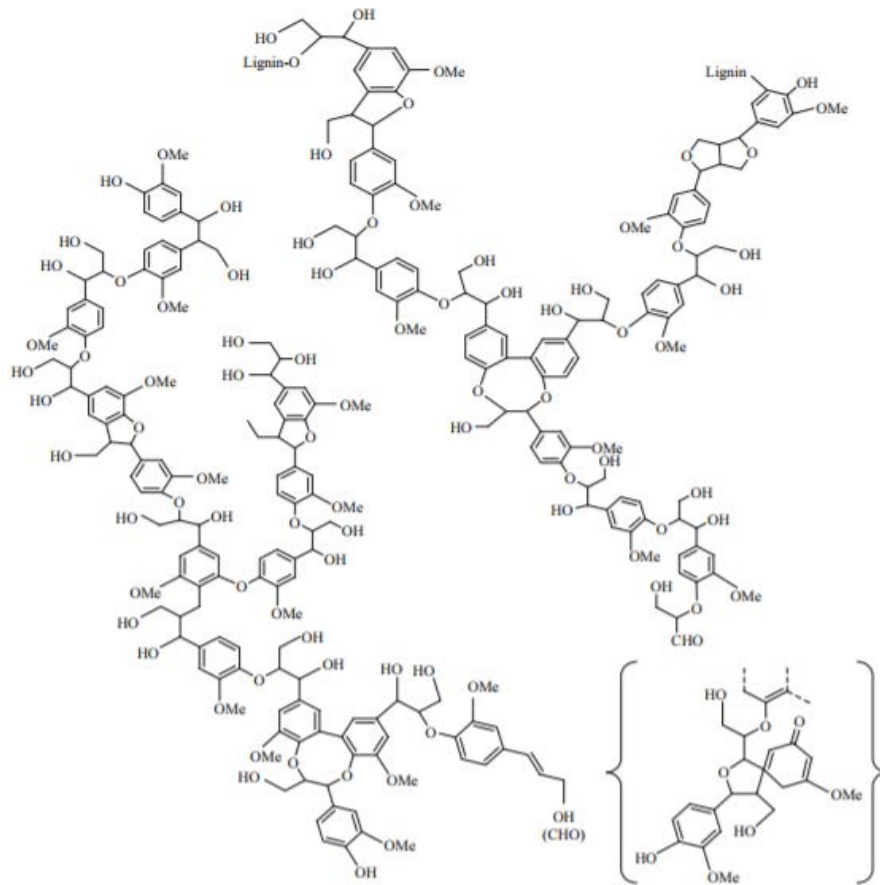


Figure 1: Chemical structure of softwood lignin.

The use of lignocellulosic biomass for biorefining has accelerated in recent years and in November 2017 nine commercial plants were in operation in Europe.ⁱⁱⁱ Generally the utilization of the biomass has been focused on converting the more easily accessible cellulose and hemicellulose content into higher value products such as paper, ethanol, sugars and additives as indicated in Table 1 below where the products made at nine European commercial scale biorefineries are specified along with the lignin utilization. The processing of the biomass typically leads to formation of a lignin containing co-product that normally is used for energy production due to its high calorific value (HHV ~ 22 GJ/t^{iv}) and good burning properties.

Table 1: European biorefineries treating lignocellulosic biomasses, their products and how lignin is utilized.

BIOREFINERY	BIOMASS	PRODUCTS	LIGNIN UTILIZATION
Lenzing Pulp Mill (A)	Wood	Cellulosic fibres	Energy production
		Sweeteners	
		Acetic acid	
		Furfural	
Pöls Biorefinery (A)	Wood	Pulp	Energy Production

		Paper	
		Tall oil	
Metsä Bioporduct mill (FI)	Wood	Pulp	Energy production
		Tall oil	
		Biocomposites	
Joensuu Bio-oil Plant (FI)	Forest residues	Bio-oil	Bio-oil
Biowert Biorefinery (D)	Grass	Cellulosic fibres	
		Nutriens	
		Biogas	
Caserta Levulinic Acid Plant (I)	Cellulosic biomass	Leveulinic acid	?
Sarpsborg Biorefinery (N)	Wood	Cellulose	Vanillin
		Ethanol	Energy production
		Vanillin	
Domsjö Pulp Mill (S)	Wood	Cellulose	Lignin powder
		Ethanol	
		Lignin	
Crescentino (I)	Poplar	Ethanol	Energy production

The lignin content and the actual properties of the lignin products depend strongly on the processing methods, as shown in Table 2 below, where purified and concentrated lignin from the pulp & paper Kraft process are compared with lignin produced via hydrolysis.

Table 2: Comparison of the properties and yearly production of hydrolysis and LignoBoost lignin

LIGNIN PRODUCTS	UNIT	HYDROLYSIS LIGNIN ^v	LIGNOBOOST LIGNIN ^{vi}
HHV	GJ/t	22	26
Lignin content	% of dm	~50 ^a	94
Ash content	% of dm	10	<1
Yearly production	1000 tons dm	400 ^b	75 ^c

^a Lignin content is calculated from a Solid Biofuel yield of 385 kg/t dm^{iv}, a lignin content in straw of 18,5% of dm^{vii} and the assumption that all lignin ends up in the Solid Biofuel (Hyrolysis lignin).

^b Yearly production is based on the nameplate capacity of Beta Renewables Crescentino, Project Liberty, Dupont's plant in Nevada, GranBios plant in Alagos and Raizens plant in Piracicaba and an assumed yield of hydrolysis lignin of 1,5 kg lignin/kg ethanol.

° Yearly production from the Sunila Mill in Finland^{viii} and Domtar in USA^{ix}

The LignoBoost technology where lignin is precipitated and from Kraft black liquor has been developed by Valmet. ^x Black liquor is a liquid solution that mainly contains lignin, hemi-cellulose and inorganic salts originating from the chemicals added in the process (NaOH and NaS). The LignoBoost lignin has a very high lignin content whereas the hydrolysis lignin typically contains residual nonconverted cellulose and hemi-cellulose and inorganics. Today only two full scale LignoBoost plants are in operation in respectively Finland and America.^{xi} The different properties and lignin content means that the two types can't be considered as group of whole but one must take into consideration what type of properties and application it can be used for.

The unique structure and properties have led to increasing interest in production of different products from lignin such as heavy fuel oil (b21st), concrete plasticiser (ligniOx), Lignoflag. Kraft and

Table 3: Selected development projects working with lignin utilization. Kraft and Organosolv are both pulping processes

PROJECT	LIGNIN TYPE	LIGNIN UTILIZATION
APSE	Hydrolysis	Asphalt
B21st	Hydrolysis	Chemicals Maritime fuels
LigniOx	Hydrolysis Kraft Organosolv	Dispersants

Other applications where the use of lignin has been evaluated is the use as a precursor in the production of carbon fibers, where expensive fossil derived polyacrylonitrile currently is being used.

Hydrolysis lignin has recently been successfully used as a replacement of a part of the traditional oil-based additives that are used for bitumen production in a trial road in Poland within the EU-funded APSE-project.^{xii} Additional production of a trial road in Madrid has been planned.^{xiii}



Figure 2: Construction of trial road in Poland where bio-based lignin has been in the asphalt. (Source: <https://apseproject.eu/5704>)

The replacement of CO₂-intensive bitumen is not only good for the environment it also has great influence on the economy of the lignin producer since bitumen has a high selling price compared to the current selling price of lignin (135 EUR/t, 2015) which is based on the market price of wood pellets. The actual cost of bitumen follows crude oil price and within the last 8 years the price has fluctuated between 200 – 700 USD/ton.^{xiii} Currently (2017) the consumption of bitumen in Europe alone is 12 million ton and Hydrolysis Lignin is expected to replace 10% of the bitumen leading to market potential of 1.2 million tons in Europe alone. The consumption of bitumen depends on the road construction and maintenance activities.

High value utilization of lignocellulosic biomasses will increase the create new market opportunities and increase the consumption of the lignocellulosic biomasses and thereby create a market. The market potential as bitumen replacement is huge and in order to produce the 1.2 million tons lignin in Europe one would require approx. 4 million tons of biomass (e.g. straw)/year.

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- ⁱⁱⁱ <https://biorrefineria.blogspot.dk/p/listado-de-biorrefiern.html>
- ^{iv} <http://www.tappi.org/content/events/09IBBC/papers/49.1.pdf>
- Larsen, Jan - Status of the Inbicon Technology by end of 2014 **2014** <https://biorefiningalliance.com/wp-content/uploads/2015/03/Status-for-the-Inbicon-technology-by-end-of-2014.pdf>
- ^v <http://www.inbicon.com/en/key-advantages/end-products>
- ^{vi} El Mansouri, N-E., Salvadó, J. Structural characterization of technical lignins for the production of adhesives: Application to lignosulfonate, kraft, soda-anthraquinone, organosolv, and ethanol process lignins. **2006** Industrial Crops and Products (24), 8-16
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- ^{viii} <http://www.metso.com/news/2013/10/future-valmet-to-supply-a-lignoboost-plant-for-the-new-biorefinery-at-the-stora-enso-sunila-mill-in/>
- ^{ix} <http://www.metso.com/news/2013/10/future-valmet-to-supply-a-lignoboost-plant-for-the-new-biorefinery-at-the-stora-enso-sunila-mill-in/>
- ^x <http://www.valmet.com/pulp/chemical-recovery/lignin-separation/lignoboost-process/>
- ^{xi} <http://www.valmet.com/more-industries/bio/lignin-separation/>
- ^{xii} <https://apseproject.eu/>
- ^{xiii} Raquel Casado CONCEPT OF SUSTAINABLE ROAD STRUCTURE – LIFE CYCLE COST ANALYSIS **XXXVI Seminarium Techniczne PSWNA**