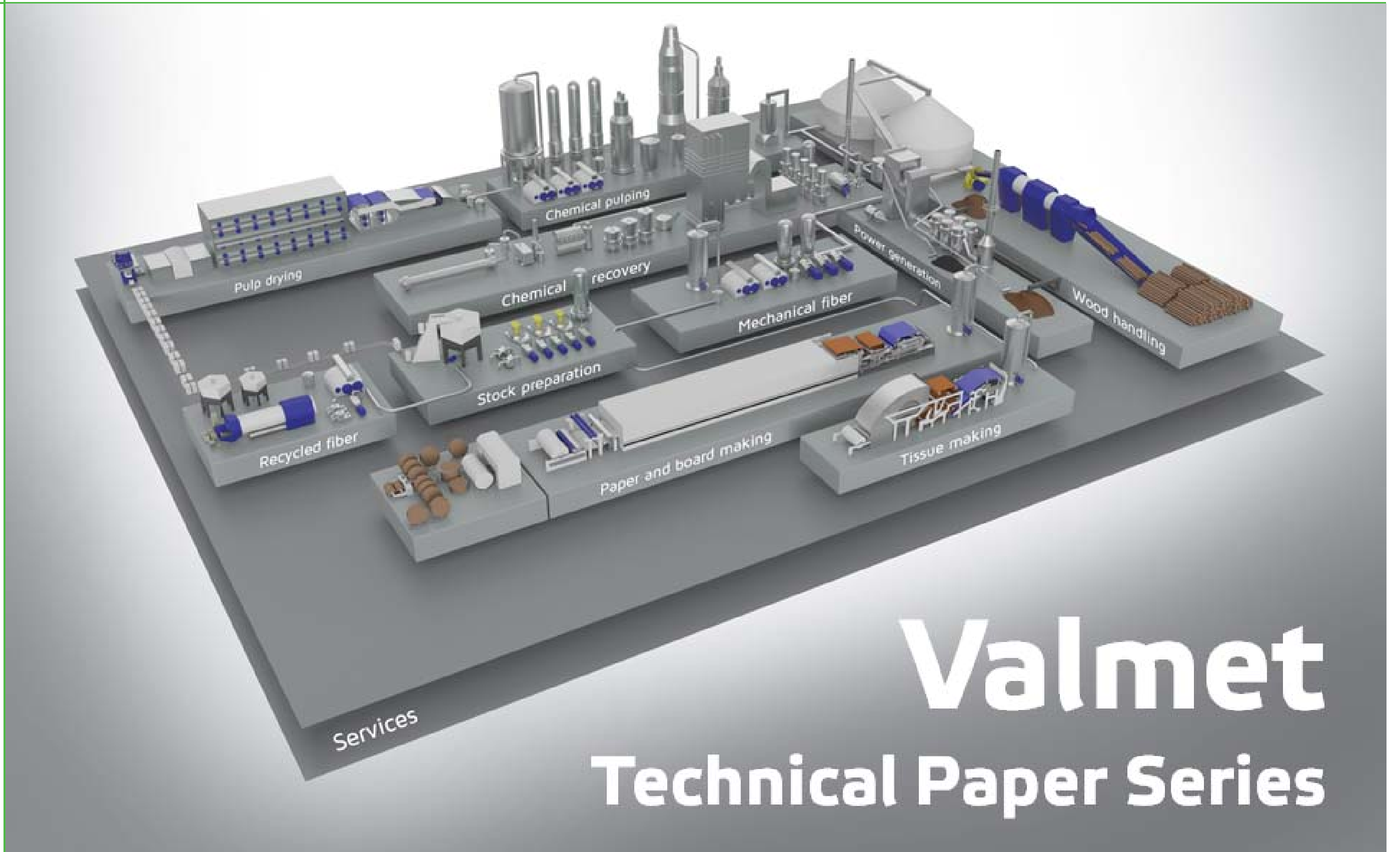

The next generation LignoBoost – tailor-maid lignin production for different lignin bioproduct markets

Executive Summary

The list of end products that can be made from lignin ranges from fuel applications to carbon fibers and fine chemicals. As more lignin becomes available on the market one key question that needs to be addressed is, of course; What to do with the produced lignin? This paper describes highlights and important results from collaborations aimed to develop add-on processes that will produce lignin with a tailored specification.

Pilot scale trials have been carried out producing a bio based carbon black from lignin. Carbon black can be used as reinforcement filler in rubber products. It was also shown that an odor free lignin could be produced by decreasing the guaiacol content in the lignin from 1.42 mg/kg to 0.04 mg/kg. The odor free lignin concept is ready for commercialization enabling production of a completely odor free bio-composite from lignin.

Introduction

Kraft lignin production at large scale is commercial and purified lignin is sold globally. Known trade names for lignin are BioChoice™ (Domtar) and BioPiva™ (UPM). Several pulp and paper manufacturers, such as Stora Enso, Domtar, UPM, Metsä Fibre, Suzano and Fibria, are changing their image to a broader bioproduct scope, including a production of lignin.

When producing pulp according to the traditional kraft method the overall yield going from wood to pulp is about 50%. Part of the other 50% is used to produce new cooking chemicals, electricity and heat. Modern mills require less energy due to the latest development in energy efficiency.

Lignin is the major energy carrier in the black liquor and by removing part of the lignin the heat load to the recovery boiler decreases. That means more black liquor can be combusted in the boiler and if no other bottlenecks exist the pulp production can be increased with approximately 1.2 – 1.5 ADt/tonne extracted lignin.

A large modern mill today, of about 1.5 MADt/y, can produce about 80-100 MW electricity to the grid. This corresponds to an energy surplus in the black liquor of about 430 MW or a lignin extraction plant of 450,000 tpa (using 26.5 MJ/kg as heating value for lignin). Hence, there is great potential in a modern mill to turn the operation into a biorefinery and produce new products, e.g. lignin.

How much lignin that can be removed will depend on several things, such as energy situation, what kind of raw material the mill uses, combustibility of the black liquor and the operability of the recovery boiler. The limit will vary from case to case. In the calculation example above the lignin extraction rate is 300 kg/ADt.

Even for existing mills a relatively high lignin extraction is within reach without doing major changes, such as rebuild of the evaporation plant to increase final dry solids of black liquor. The lignin recovery rate at the Stora Enso Sunila mill is 135 kg/ADt *[Wallmo et al, NWBC 2015]*. A general softwood kraft black liquor contains about 510 kg lignin/ADt which means that the removal rate in Sunila is slightly more than 25% of the total lignin amount.

The list of end products that are possible to produce from lignin is very long - ranging from the most obvious, which is to use the lignin as fuel, to carbon fibers and fine chemicals such as vanillin. Market volume and lignin price are linked and usually big market volumes are connected to a lower value. Today about 1.2 million tonnes of lignin are produced worldwide and it is dominated by the production of lignosulfonates, mainly from sulfite mills, which accounts for about 90% of the produced lignin *[Miller et al, RISI report 2016]*.

The first plant, with a capacity of 8,000 tonnes/year, started up in 2006 as a demonstration plant at the Nordic Paper Bäckhammar mill in Sweden. The first commercial plant was built in North America in 2012 at Domtar's pulp mill in Plymouth, North Carolina, and started production in 2013. It has a capacity of 74 tonnes per day, or 25,000 tonnes per year. The process reduces the load on the recovery boiler, effectively enabling increased pulp production.

The third plant started up in 2015. This plant has a capacity of 50,000 tonnes/year and is located in the Stora Enso Sunila Mill in Finland. In addition to lignin extraction Stora Enso also installed a ring flash dryer, equipment for using the lignin as fuel in the lime kiln and a bagging plant. Lignin production has made it possible to replace fossil fuel and to reduce CO_2 emissions by 27,000 tonnes/year (Lignin Solutions, Stora Enso Biomaterials). All plants produce lignin of high value and consistent high quality, enabling commercial use. Known trade names for lignin from these plants are BioChoice™ (Domtar) and BioPiva™ (UPM).

The LignoBoost Process

The plant is located in the recovery island in the pulp mill, processing a part of the black liquor going through the evaporation plant (**Figure 1**).

Figure 2 shows a simplified schematic figure of the process. The main process steps are well-known unit operations including gas absorption, precipitation, solid liquid separation and displacement washing. All processed streams are sent back to the mill for recovery of cooking chemicals, giving a totally effluent free process.

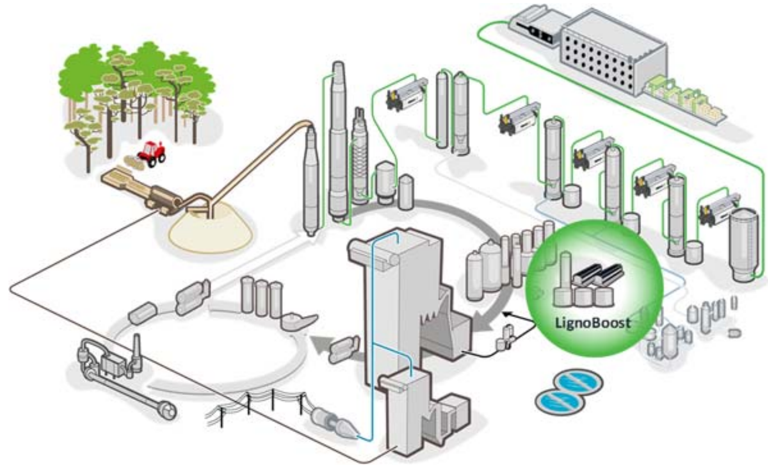

Figure 1 The location of a lignin extraction plant inside the pulp mill

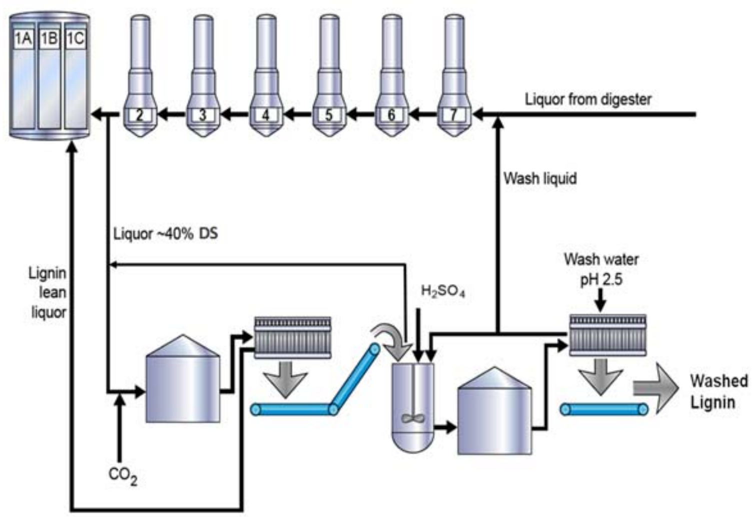

Figure 2 Simplified process description

Lignin is precipitated by injecting carbon dioxide gas (CO_2) to lower the pH. After precipitation, the slurry is conditioned in order to create larger agglomerates before the solid lignin is separated from the black liquor in a filtration step. Lignin cake from the filtration process, containing precipitated lignin and black liquor carryover, is transported to a re-suspension step where the cake is mixed with spent wash water from the downstream displacement washing and fresh sulfuric acid (H_2SO_4) to rapidly lower the pH to 2.5-4.0. Slurry in the re-suspension step is matured before it is dewatered and washed in a combined filtration and washing stage where, after cake formation, acidic wash water is pressed through the cake to wash away impurities.

The process has supplied even quality kraft lignin to the market for 11 years.

Lignin market and possible end products

Lignin extraction from black liquor has been of great interest for a long time and it is generally perceived to have a great potential. Yearly about 55 million tonnes of kraft lignin are produced worldwide in pulp mills during the pulp production and the extraction potential is believed to be about 40 million tonnes *[Gellersted et. al 2013]*. It is seen as an emerging market and is expected to grow. Kraft lignin is the only one of today's existing lignins (lignosulfonates, soda lignin, kraft lignin, organosolv lignin and biorefinery lignin) that is commercial and has the combination of a growing market and a high level of purity in the end product.

Also, in the research area lignin and its transformation into different end products is heavily investigated. This can be seen in intellectual property activity where new applications with lignin as a topic are increasing exponentially *[VTT lignin webinar 2016]*. The five most dominant areas in the intellectual property area are: surface active agents, resins, thermoplastics, chemicals & fuel and concrete additives. Although lignin extraction technologies exist there are pieces missing in the value chain to monetize lignin. In some cases, the connection between commercial lignin producers and the end-user is missing, and researchers are doing great work, but without talking to both producer and end-user. To be successful, collaborations with all players (producer, "refiner" and user) are needed.

Tailor making lignin

For some end markets a specific requirement and/or specification is needed in order to reach the conditions set for the final product, e.g. a highly purified lignin (at least <500 ppm ash) is a prerequisite for producing carbon fibers. Lignin from different raw materials could be quite different and it is an advantage if the technology development in refining lignin could balance feedstock variability. Also, there must be optimization in the downstream process that produces the end product. Lignin could not in every case be seen as a drop-in replacer. To tune the extraction process or add a process step in order to reach a specific requirement is needed in many cases, but processors of the lignin must also optimize their process from a "lignin use point-of-view".

Valmet has, through strategic partnerships and collaborations, focused research toward selected end markets. In **Figure 3** the different end markets and the general refining work that is needed in order to produce the quality required by that market are described. This diagram illustrates opportunities and potentials for the pulp and paper industry to turn their operation into a biorefinery based on lignin. It also shows how lignin extraction could be redesigned to meet required specifications.

Figure 3 Several potentials for turning lignin extraction into higher value products

One of the collaborations is about making kraft lignin water soluble through e.g. sulfonation. Sulfonating kraft lignin has traditionally been done using formaldehyde, which poses several risks to both workers and the environment. Using a new process that has been developed together with RISE Bioeconomy, lignin can be sulfonated to a very highly purified product without the use of formaldehyde. Since this is done using washed lignin, the content of lignosulfonate is about twice as high as in traditional lignosulfonates produced from sulfite pulping liquor. Sulfonated lignin is a well-established product with a wide range of uses and a current world production of more than one million tonnes/year.

Another example of a collaboration with an aim of unlocking the potential of lignin is the one made with BioChemtex. The overall target is to provide the market with a second generation biochemical (para-xylene) using lignin as raw material. The aim of the project is to optimize a combination of two technologies, LignoBoost and Moghi, and to integrate the combination in a pulp mill environment. Lignin samples with varying quality have been produced and treated in laboratory and pilot scale studies in order to convert lignin into para-xylene. Para-xylene can be oxidized to terephthalic acid that can be reacted with ethylene glycol to produce a renewable PET bottle.

The use of lignin for producing carbon fibers has been seen as the holy grail of lignin. The issue so far has been that the lignin is not as uniform as the other fiber precursor, polyacrylonitrile (PAN), derived from fossil oil or natural gas. Variable conformation and quality of the lignin limits the individual fiber strength properties compared to PAN fibers. However, there are benefits of using lignin. One is that less energy is needed to convert the precursor fiber into a carbon fiber. An issue of using lignin as precursor is the varying melting property. This may be improved by fractionating the liquor prior to precipitation. This would lead to more uniform melting properties. Also, the purity of the lignin could be increased in order to reach the target of less metals. The target for the ultra-pure lignin is to attain less than 250 ppm ash in the final lignin product.

Based on the findings in the collaborations several add-on processes have been developed which enable production of a tailored kraft lignin (**Figure 4**). The aim has been to meet the specifications needed for a particular end market product, while keeping the variability of the starting material in mind. These add-on processes have been tested ranging from lab scale to pilot scale to verify that they meet the intended specification. The odor free lignin concept is ready for commercialization.

Lignin quality	LignoBoost concepts	Application
Pure lignin	LB 1 → LB 2	Solid fuels
Odor free lignin	LB 1 → LB 2 → Odor free	Binders/Bioplastics/ Technical carbons
Ultra pure lignin	LB 1 → Purification → LB 2	Bioplastics/ Carbon fiber
Crude lignin	LB 1	Transportation fuel/ Bioplastics/ Technical carbons
Carbon green	LB 1 → LB 2 → HTC	Technical carbons
Fractionated	Fractionation → LB 1 → LB 2	Bioplastics/ Carbon fiber
Water soluble	LB 1 → LB 2 → Soluble	Lignosulfonates/ Dispersants

Figure 4 The process concepts that convert lignin to a refined lignin and the intended end use market. LB1 refers to the alkaline part of the lignin extraction process and LB2 refers to the acidic part.

Odor-free kraft lignin

The odor of lignin has earlier been seen as an obstacle in producing different consumer products from lignin. Especially when making a composite containing lignin (such as bio plastic, binder or coating), the final product has, despite using pure lignin, still had a characteristic smell. The general perception has been that the sulfurous compounds are to blame for this smell and that "a sulfur free lignin is an odor free lignin." There is an analysis method designed to detect and measure the odor threshold from a product; olfactometric analyze. The method involves heating up a sample, leading the fumes through a gas chromatograph and then simultaneously to a mass spectrophotometer and to a human sniffing port. The evaluator should try to describe the nature/characteristic of the smell and rate the odor (on a 1 to 5 scale) by intensity and how nasty the smell is. From such an analysis of lignin it was determined that it was not the sulfurous compounds (dimethyl disulfide, dimethyl trisulfide and dimethyl tetrasulfide) that were the major contributors to the smell; it was guaiacol and ethyl-guaiacol (**Table 1**).

Compound/From instrument (GC-MS)	Ret time (x;y)	Intensity Rating	Nasty-smelling Rating	Odor character
DMDS	19.0	4	2	Nasty/bad; sulfur
DMTS	30.2	3-4	2	sulfur
Guaiacol	35.2	4-5	3-4	Burnt wood/like the sample
DMTetraS	38.0	1-2	0	sulfur

Table 1 Extract from results of olfactometric analysis on lignin

By drying lignin samples in an oven (105 °C) the sulfurous compounds were removed, while the guaiacol compounds still remained. Removing the sulfurous compounds, either before precipitation by e.g. black liquor oxidation or from the final lignin by heating, the final lignin will still contain guaiacol. Hence, in order to produce a totally odor free lignin also the guaiacol must be removed. Based on these conclusions two concepts to remove the guaiacol have been developed (two patents pending). In the first concept the guaiacol removal treatment takes place inside the lignin precipitation and washing process. In the second concept the washed lignin is treated, i.e. post lignin extraction and washing treatment. The odor reduction has been evaluated as guaiacol removal. Compared with a normal washed lignin, about 60% of the guaiacol is removed using the first concept. The second concept starting with a washed lignin removes about 97% (**Table 2**). The odor free concept is ready and large scale production (>1 tonnes per concept) will be made in Q3 2017 using the Bäckhammar demonstration plant. The produced lignin is targeted to be used in end user application testing.

Sample	Treatment	Guaiacol [mg/kg]	Ethyl guaiacol [mg/kg]	Compound Removal efficiency [%]
Ref	Reference	1.42	0.19	n.a.
C1	Concept 1 (inside treatment)	0.61	0.08	57% / 58%
C2	Concept 2 (post treatment)	0.04	n.d.	97% / 100%

Table 2 Results from pilot trials, odor reduction concept

Bio-based carbon black

Carbon black is the trade name for a black powder used as reinforcement filler in rubber products. In almost all rubber products exposed to high wear and tear carbon black is used. By blending carbon black with a rubber mixture (up to 50% by weight) before vulcanization the tensile strength could be multiplied; up to 10 times higher. Carbon black is primarily classified by particle size.

As world production was more than 12 million metric tonnes per year in 2015, and as the current raw material is heavy fractions of oil, replacing carbon black with a CO_2-neutral alternative represents a true opportunity for the pulp and paper industry. Together with the partner SunCoal, a high temperature carbonization process has been developed that converts kraft lignin into carbon green, a new alternative that meets the specifications for several grades of carbon black. Experiments have been carried out in a pilot facility in Germany (**Figure 5**) and tonnes of lignin have been converted to bio coal with good properties. Potential applications have been identified and end user tests are being carried out.

The bio coal from the process could also be activated and used as activated carbon in different purification techniques, such as water or gas purification.

Figure 5 Hydrothermal carbonization pilot where lignin experiments have been carried out

Conclusions

LignoBoost process is commercial and high purity lignin from the process is produced worldwide and sold globally. Add on processes are developed for lignin Bio-products market with the aim to meet a certain specification.

It has been shown that the compound contributing the most to the characteristic smell of lignin is not the sulphurous compounds; it is guaiacol. By decreasing the guaiacol content in the lignin from 1.42 mg/kg to 0.04 mg/kg an odor free lignin could be produced. This means that a completely odor free biocomposite can be produced from lignin. The odor free lignin concept is ready for commercialization.

Lignin can be tailored to meet several quality specifications. A bio based carbon product can be produced from lignin by hydrothermal carbonization. The product could be used as reinforcement filler in rubber products or be activated and used in e.g. gas cleaning.

By jointly collaborate to commercialize lignin quality it is possible to:

- Add revenues for all development partners
- Increase product diversification
- Minimize dependence on fossil raw material use
- Decrease time to market for high value lignin qualities

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