INTEGRATION OF LIGNIN REMOVAL INTO A KRAFT PULP MILL AND USE OF LIGNIN AS A BIOFUEL

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There are important consequences for a pulp mill when either new or traditional technology is integrated into the production system. When a flexible technology, such as lignin removal, is introduced into the production system many new opportunities will arise, therefore, it has to be decided what needs to be achieved in the initial phase of operation and what the next step will be to improve the lignin value and the overall value for the pulp mill. The focus of this work is mainly on changes in the power balance and improved use of the wood source as a biofuel when the LignoBoost process is installed in a greenfield mill for production of *Eucalyptus urograndis* market pulp.

Keywords: biorefining, kraft pulping, lignin, biofuel

INTRODUCTION

Today's market pulp mills are in most cases self-sufficient in steam from the black liquor alone and have great potential to supply energy to other industries and society. The energy surplus in the mill can be exported in different ways, as electricity, biofuels (bark, lignin, etc) or heat for district heating. The most favourable alternative for a specific mill depends on the mill situation and needs to be evaluated for each mill.

Lignin separation from black liquor gives a potential to produce extra tonnes of pulp if the recovery boiler capacity is the limitation for the annual pulp production. The separated lignin can then be used as mentioned above, as a valuable by-product and give the pulp mill new revenues. The most obvious use of a continuous bulk flow production of lignin is, in a short time perspective (0-5 years), to use it as a biofuel internally in the pulp mill or sell it as a biofuel when companies want to switch from fossil fuels. The opportunity would then be to develop the pulp production towards a completely fossil-fuel-free production, to produce more pulp and to develop opportunities for new revenues for pulp mills.

The integration of lignin extraction – the LignoBoost process – into a pulp mill will affect the energy balance as well as the water and material balances. This has to be studied in detail for each individual pulp mill to evaluate its business potential in relation to the concept.

Lignin as a solid biofuel puts certain demands on the system design (as all solid fuels do). There are a lot of different aspects to take into consideration, examples are silo storage design, feeding into and out of the silo, drying of the product, explosion risks and moisture effects. A way to avoid some of these aspects could be to mix lignin into another liquid fuel, for example into fossil fuel oil (increasing the share of biofuel used), tall oil pitch or other liquid biofuels. However, there are limits for how much lignin it is possible to mix into these types of solid/liquid slurries.

MATERIAL AND METHODS

General description of LignoBoost

In the LignoBoost Process, a stream of black liquor is taken from the black liquor evaporation plant (see Fig. 1). The lignin is then precipitated by acidification, CO_2 (g), and filtered ("Chamber press filter 1" in Fig. 1). The filter cake is then re-dispersed in acidic recycled filtrate ("Cake re-slurry" in Fig. 1), where additional H_2SO_4 or spent acid from chlorine dioxide production, is added to reach pH 2-3. The resulting slurry is then filtered and washed by means of displacement washing ("Chamber press filter 2" in Fig. 1).

The filtrate from chamber press filter 1 (Fig. 1) should be recycled to the black liquor evaporation plant after the point at which the feed stream to LignoBoost is taken. This should be done to avoid a decrease in the lignin concentration in the stream fed to the LignoBoost operation. The filtrate from chamber press filter 2 should be recycled to the weak black liquor.

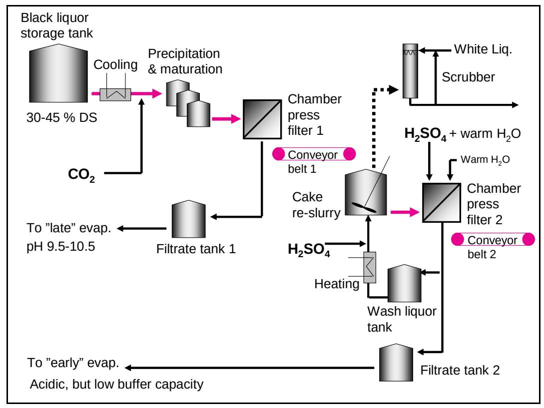


Figure 1: General layout of the LignoBoost lignin removal process
(post-treatment, drying and pulverizing are excluded)

Figure 2: Lignin produced in the LignoBoost demonstration plant – filter cake and lignin pellets

Table 1
Typical material properties of Kraft lignin from the LignoBoost process

Property	Unit	Value
Heat value (Hcal)	MJ/kg DS, ash free	25-27.5
Heat value (Heff)	MJ/kg DS, ash free	24-26.5
Moisture content	wt%	30-40% from the process or dried to below10%
Bulk density	kg/m^3	About 500 from the process or about 700 as a dry powder
Ash content	wt% DS	0.01-1.4
Sulphur content	wt% DS, ash free	2-3
Chlorine	wt% DS, ash free	0.01
Sodium content	g/kg ash	100-400
Potassium content	g/kg ash	1-100
Calcium content	g/kg ash	1-200

Lignin from the LignoBoost process is a moist filtercake, 30-35% moisture, of lignin (Fig. 2). The lignin product has a heat value in the range of coal (Table 1) and it is hydrophobic. The purity is typically 95-98% kraft lignin with inorganics, some traces of carbohydrates and even smaller amounts of extractives (if any at all).

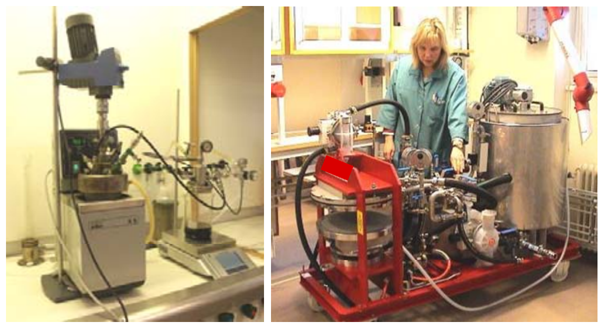
Collection of basic LignoBoost data for calculations and design

There is a need for experimental trials to get basic data before a proper design of a LignoBoost is possible. The typical data comprise consumption of chemicals (H_2SO_4 and CO_2) as well as filtering resistance.

This is done for the specific black liquor of interest and is initially done on a small scale, which is practical for the screening of parameters. However, studies on larger filters with more realistic operation compared to industrial filters, as well as studies of fresh black liquors, are necessary to collect design data.

Mill description

We have, in co-operation with Metso, used a simplified pulp mill model to simulate energy balance changes when LignoBoost is introduced into a pulp mill. These changes differ of course from one pulp mill to another depending on the specific local situation. For our calculations, we have chosen a modern greenfield pulp mill which produces 1000000 ADt bleached *Eucalyptus urograndis* kraft pulp/year (Table 2).



Laboratory scale equipment
~ 10g lignin per filtration-batch.

Pilot scale equipment
~ 0.5 - 1 kg lignin per filtration-batch

Figure 3: Equipment of different size used in evaluation of the LignoBoost concept

Table 2
Summary of key operating data of the pulp mill used in this study

Pulp production, ADt/day	3200
- *ditto*, ADt/y	1000000
Dried pulp from dryer, ADt/24 h	3200
Operating days, d/a	355
Mill availability, %	90
Wood yard	
Wood to digester (dry), t/24 h	6010
Bark and wood waste (dry), t/24 h	615
Basic wood density, kg/m^3	510
Digester plant	
Kappa number	17.5
Unscreened deknotted digester yield, %	52
Alkali charge on wood as effective alkali, NaOH, %	18
Sulphidity (white liquor), mole %	30
Oxygen stage	
Kappa number after oxygen stage	10
Oxygen stage yield, %	97
Alkali charge as NaOH, kg/ADt	23
Oxygen charge, kg/ADt	20
Washing and bleaching	
Dilution factor in the last stage, m^3/ADt unbleached	2.5
Yield bleach plant, %	97.5
Evaporation plant	
Weak black liquor to evap., excluding spills, t/h	1246
- *ditto* dry solids content, %	14.4
Weak black liquor temperature, °C	110
Strong black liquor, DS content including ash, %	80
Total evaporation, including spills, t/h	1026
Number of evaporation effects	6
Recovery boiler	
Estimated higher heating value (virgin), MJ/kg DS	14.2

Strong liquor virgin solids to mixing tank, t DS/24 h	4235
Steam temperature, °C	485
Pressure, Bar	85
Flue gas exit temperature, °C	175
Condensing steam turbine	
Condensation temperature, °C	55
Causticizing and lime kiln	
Causticizing efficiency, mole %	82
Total white liquor production, m^3/24 h	9602
Lime kiln load, t/24 h	753
Active CaO in lime, %	85

RESULTS AND DISCUSSION

Typical results from experimental evaluation of LignoBoost

The most important results from an experimental LignoBoost design data study is the consumption of chemicals, such as CO_2 (g) and H_2SO_4, as well as the specific filterability (Figs. 4-7).

The amount of CO_2 (g) needed to lower the pH to about 10 (Figs. 4 and 5) mainly depends on the residual alkali in the black liquor. The results from the ongoing LignoFuel R&D Programme show a great opportunity to use lime kiln flue gases as the CO_2 (g) source. Experimental work in small pilot plant scale has resulted in a possible design. The use of lime kiln flue gases, with a CO_2 (g) content of about 15-30%, instead of concentrated gas delivered by a gas supplier will of course decrease the total operating cost. The cost related to consumption of chemicals (CO_2, H_2SO_4 and NaOH) is expected to decrease roughly by 20-25%.

Sulphuric acid is needed to lower the pH down to pH 2-3 and to wash the lignin (Fig. 6). One way to maintain the Na/S balance, due to intake of sulphur through charge of fresh H_2SO_4, can be by using spent acid from the chlorine dioxide plant. However, the potential of this measure depends on how the mill handles the spent acid: whether it is already included into the Na/S balance or not. It is also important to remember that the way the produced lignin is used will affect the Na/S strategy as well.

Sulphur will be discharged with the lignin if lignin is used externally, and it will be introduced into the Na/S balance again if lignin is used in the lime kiln as a biofuel. The amount H_2SO_4 needed to lower the pH to 2-3 is mainly controlled by the DS content in the black liquor to the LignoBoost plant and the dewatering efficiency in the first filtration step, with respect to achieved DS content in the lignin filter cake. The specific filtration resistance is an important parameter when the filter size is calculated (Fig. 7).

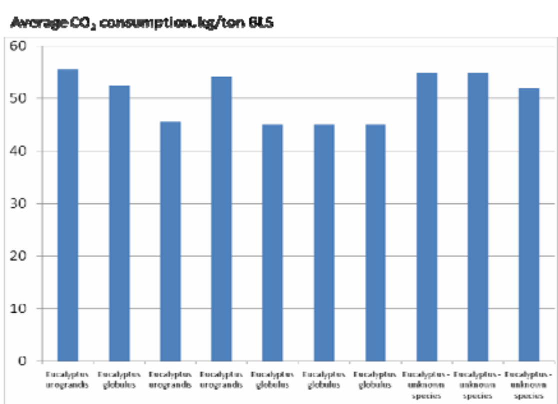


Figure 4: Average consumption of CO_2 (g) to lower the pH value, expressed as kg/ton BLS. The results are collected from black liquors from pulp mills producing Eucalyptus pulps; some results are from laboratory trials and some from pilot scale trials collected from fresh black liquors at these mills

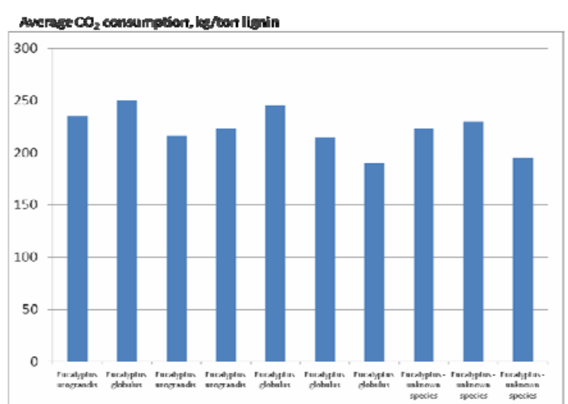


Figure 5: Average consumption of CO_2 (g) to lower the pH value, expressed as kg/ton produced lignin. The results are collected from black liquors from pulp mills producing Eucalyptus pulps; some results are from laboratory trials and some from pilot scale trials collected from fresh black liquors at these mills

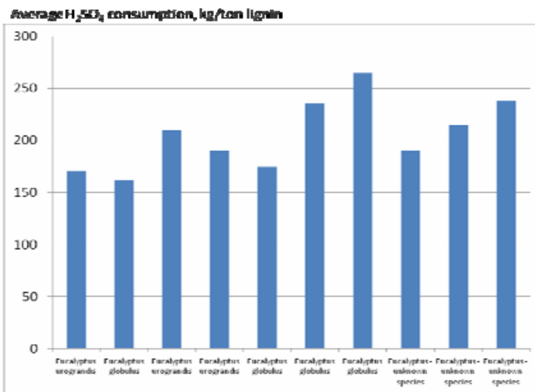


Figure 6: Average consumption of H_2SO_4 to get good washing, expressed as kg/ton produced lignin. The results are collected from black liquors from pulp mills producing Eucalyptus pulps; some results are from laboratory trials and some from pilot scale trials collected from fresh black liquors at these mills

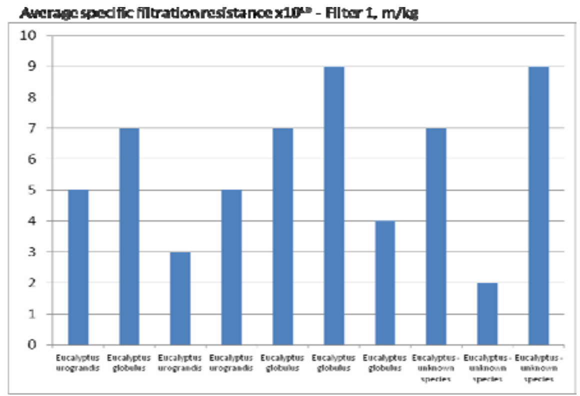


Figure 7: Specific filtration resistance in the first filtration step. The results are collected from black liquors from pulp mills producing Eucalyptus pulps; some results are from laboratory trials and some from pilot scale trials collected from fresh black liquors at these mills

A change from $1x10^{10}$ to $1x10^{11}$ means a 2-3 times larger filter area to get the same filtration capacity. Figure 6 shows some experiences from different Eucalyptus black liquors when precipitated lignin is filtered in the first filtration step. Note also that the black liquor viscosity is another very important parameter, which affects the requested filter area.

The filterability varies of course with the temperature, precipitation pH, the black liquor DS content and some other parameters. In some cases, there is a difference in the results obtained from a small-scale laboratory trial and those from a pilot scale trial, where fresh black liquors are used. Since the investment cost for pressure filters represents a large part of the total investment cost in the LignoBoost concept, this evaluation is very important to optimize the investment cost already in the beginning of the project.

Pulp mill calculations – the power balance

Operation without power boiler is an option in a greenfield mill. Debarking of the wood can then be done in the forest, which might be beneficial in some cases. Bark can be left in the forest land to fertilize the land or can be sold to other users willing to pay. A power boiler at the pulp mill has the potential to supply the grid with electricity, but the driving force for a power boiler becomes very low when this option is not available.

In this study we have focused on the power balance for the pulp mill described above (Table 2) and on how it changes with and without lignin removal by the LignoBoost process. Case 1 is a reference case, which describes a pulp mill with a power boiler, where bark from the logs and rejects are fired. In case 2, also a reference case, we describe the same type of pulp mill but without a power boiler. The difference is then if the pulp mill buys debarked wood or not, which of course is a major difference in the power balance.

Case 1 (reference case 1): No lignin extraction, power boiler

The result is that the process produces 61 MW excess power available for selling to the grid. Of these 61 MW, 48 MW is condensing power. The total power production in the mill is of 138 MW and the process consumption – of 77 MW.

Case 2 (reference case 2): No lignin extraction, no power boiler

The power production is of course lower since we do not debark the wood at the mill and we do not have a power boiler, just a small unit for start-up situations. The result is 36 MW excess power available for selling to the grid. Of these 36 MW, 26 MW is condensing power. The total power production in the mill is of 110 MW and the process consumption – of 74 MW.

Case 3: Lignin extraction, power boiler

Lignin extraction is done with the aim of avoiding electricity selling to the grid and, of course, related investment. In this case 186000 tonnes lignin/year is removed. This corresponds to 0.18 tonne lignin/ADt pulp, which is about 36-37% of the lignin available in the black liquor. This lignin lean black liquor should, with some measures, be possible to handle in the recovery boiler.

Lignin extraction results in a decreased thermal load on the recovery boiler, which means an opportunity to produce more pulp. Alternatively, since we are talking about greenfield mills, we have the option to build a smaller recovery boiler already from the start.

The pulp mill operation is still calculated to consume 77 MW, which results in a need of 5 MW condensing power. We have not tried to optimize the size of condensing power, but we expect that it can be reduced.

The moist lignin product (65-70% DS content) could be used for efficient power production with a total efficiency of 45%. This would result in roughly 78 MW, which is about 30% more power compared to reference case 1 (above). This external production of power makes it also possible to deliver power as top load in the power system, usually resulting in a better power price.

By extraction and selling the produced lignin the Na/S balance is adjusted in a positive way. Lignin contains about 2-3% sulphur, which means that it is an opportunity to maintain the Na/S balance by lignin removal. If we need to keep some sulphur, this can be managed by returning lignin as a biofuel in the lime kiln or by choosing another sulphur rich fuel.

Case 4: Lignin extraction, no power boiler

Lignin extraction is done and no electricity is sold to the grid. In this case 108000 tonnes lignin/year is removed to balance the pulp mill with respect to this desired power situation. This corresponds to 0.10 tonne lignin/ADt pulp, which is about 20% of the lignin available in the black liquor. This amount of lignin removed from the black liquor is normal for the LignoBoost concept.

Lignin extraction results in the fact that thermal load on the recovery boiler is decreased, which means an opportunity to produce more pulp. Alternatively, since we are talking about greenfield mills, we have the option to build a smaller recovery boiler already from the start.

The pulp mill operation is still calculated to consume 74 MW. This results in a need of 2 MW condensing power, but we believe that the power demand can be optimized so no condensing power would be needed. However, a condensing turbine, even if it is small, could be beneficial in order to operate the pulp mill in a smooth way. The moist lignin product (65-70% DS content) could also in this case be used for efficient power production with a total efficiency of 45%.
This would result in roughly 45 MW, which is about 25% more power compared to reference case 2 (above).

Table 3
Summary of power balance calculation results

Case	Reference case 1	Reference case 2	Case 3	Case 4
Power boiler	Yes	No	Yes	No
Lignin extraction – LignoBoost*	No	No	Yes	Yes
Total power production from internal boilers, MW	138	110	77	74
Lignin production, tonnes/year	0	0	186000	108000
Consumed power for pulp production, MW	77	74	77	74
Excess power – possible delivery to the grid, MW	61	36	0	0
Condensing power – part of the total power production, MW	48	26	5	2
External power production from extracted lignin,** MW	0	0	78	45
Total excess energy,*** MW	61	36	78	45

*The size of lignin removal is balanced to avoid delivery of power directly from the pulp mill to the local grid;
**These numbers relates to when lignin, exported from the pulp mill, is used in a power boiler with 45% total efficiency;
***Total excess energy possible to deliver from the pulp mill. Power production from lignin is set to have 45% efficiency in an external power boiler

In this case, we will also be able to select the timing for the power delivery and focus on top load situations to improve the revenues.

Similarly to case 3, the Na/S balance can be adjusted with lignin extraction.

Another use of LignoBoost kraft lignin as a biofuel

LignoBoost kraft lignin has been tested extensively as a biofuel in both small-scale and large-scale commercial boilers, including a lime kiln.

Trials in a 12 MW research CFB-boiler

Trials with co-firing kraft lignin and bark in a fluidized bed boiler[1] showed that this can be done easily. The combustion performance was normal and was not influenced by the lignin. The sulphur content in kraft lignin had a significantly positive effect in reducing the alkali chloride content in the deposits, thus reducing the risk of sticky deposits and high temperature corrosion occurring. When kraft lignin was co-fired with bark, the sulphur emission increased, when compared to what happens when bark is fired by itself. However, in this case, most of the sulphur was captured by calcium in the bark ash. The conventional capture of sulfur was also demonstrated with the addition of limestone to the bed. The addition of kraft lignin had no measurable effect on the sintering properties of the bed material. However, the sintering temperature of the cyclone bed material was decreased when limestone was added.

Full-scale substitution of coal in a Pressurized Fluidized Bed Combustion (PFBC) boiler

LignoBoost kraft lignin was mixed with coal and fired in full-scale trials in the PFBC boiler plant at Värtaverket in Stockholm,[2] with each of the two modules having a thermal capacity of 210 MW. The extensive long-term trials involving the co-firing of kraft lignin and coal showed that continuous co-firing had no effect on the important combustion parameters. A substitution rate of up to 15%, on an energy basis, was demonstrated and a substitution rate of 20-30% seems to be possible. In total, more than 1500 tonnes of kraft lignin were used in 2008. Fuel handling and the preparation proved to be the most difficult tasks.

Trials in a full-scale lime kiln

One appealing application is to replace fossil fuel fired in the lime kiln with dried kraft lignin powder, which has a higher energy value, when compared to many other biofuels. Full-scale tests, involving firing lime kilns with kraft lignin, were carried out at a kraft mill in Sweden.[3] This lime kiln has a capacity of 275 tonnes of burned lime per day. The kiln is equipped with a lime mud dryer and a lime product cooler. The burner is designed for the simultaneous co-firing of oil, biomass powder, gas (NCG) and methanol. The existing powder fuel feeding system at the mill is designed to supply the two lime kilns with dried and pulverized bark or wood.

Kraft lignin powder/oil mixtures were evaluated up to a level of 100% kraft lignin. During a total of 32 hours, 37 tonnes of kraft lignin were co-fired with fuel oil. For approximately 15 hours, the kraft lignin heat input was above 50% of the total heat input. At the end of the trial, the fossil fuel oil was completely shut off and the kiln was operated on 100% kraft lignin for approximately 2 hours. The experience gained from the full-scale combustion trial and the shorter lime kiln feeding trial show that it is possible to achieve a stable and continuous operation of a lime kiln when kraft lignin is used as a fuel. It was possible to use the standard powder burner and feeding equipment when firing dried and sieved kraft lignin. The temperature levels in the kiln were approximately the same when kraft lignin was fired, as when fossil fuel oil or wood powder was fired. It was possible to produce lime with a consistent quality, when firing with kraft lignin. The temperature reached in the burner zone was sufficient for the proper sintering of lime nodules. White liquor could be produced from the lime with the same causticising efficiency and at the same rate as during normal operation. We saw no significant influence on the emissions of CO, H_2S, NO_x and SO_2 and according to the operator, the kiln could be controlled easily when firing kraft lignin.

CONCLUSIONS

- Basic data for the LignoBoost concept has been evaluated by experimental work for different Eucalyptus black liquors. The consumption of chemicals (CO_2 and H_2SO_4) differs quite a lot between these liquors. The same holds true for the specific filtration resistance. It is important to collect these basic data for each specific fresh black liquor to get proper design data and proper data for the evaluation of the business concept.

- The LignoBoost concept gives flexibility to the greenfield pulp mill chemical and energy balances, which can be an interesting opportunity:
  - Sulphur can be discharged by the kraft lignin product. This can be balanced by use of kraft lignin as a biofuel in the lime kiln. Kraft lignin can be used as dry powder directly or added into a liquid fuel such as fossil fuel oil, methanol, ethanol, glycerine or other fuel working as a "carrier".
  - The power production from a certain amount of wood raw material going into a kraft pulp mill could, in our calculation, be increased roughly by 25-30% when kraft lignin is extracted and burned in an external boiler optimized for power production.
  - If distribution of electricity to the grid is not an obvious option, extraction and distribution of lignin can be an opportunity to utilize the excess of energy as a first step. The next step would be to find a higher value for this kraft lignin, such as the use for carbon fibers, active carbon, binders etc. It is clear that when kraft lignin can be sold for these higher value products, lignin removal will be important to achieve.
- LignoBoost kraft lignin has been successfully used in several combustion applications, such as a lime kiln, a CFB operating on bark and a PFBC normally operating on coal.

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