

THE KRAFT PULP MILL AS A BIOREFINERY

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ABSTRACT

Lignin removal from black liquor and utilization of lignin into energy and chemicals is the main focus of STFI-Packforsks biorefinery efforts. In close cooperation with Chalmers a process for efficient removal of lignin from black liquor, LignoBoost, has been developed. Lignin is precipitated with carbon dioxide, dewatered in one stage and dewatered/washed and in a second washing stage. Washing is done counter-currently. This eliminates the risk for lignin dissolution which is a main drawback in the conventional one-stage process. Compared to the one-stage process the water use is lower, lignin is cleaner with respect to ash and sodium and the capacity is significantly higher. Typical data with less than 2 tonnes of wash water per tonne of lignin are ash and sodium less than 0.4 and 0.1 % respectively. The lignin has been shown to be a promising fuel. The LignoBoost-technology is currently being tested in a demonstration plant with a production of 4000 tonnes of lignin per year. The demonstration started the operation December 2006. The LignoBoost-process also offers significant technical and economical potential for future development such as xylan removal from black liquor, ethanol fermentation and gasification of biomass.

Keywords: Biorefinery, lignin, energy, kraft pulping

INTRODUCTION

A large research effort is today directed in finding new areas of usage of by-products from kraft pulping, often called the "Pulp Mill Biorefinery". STFI-Packforsk has been active in the area for some years. The activities include separation and purification of lignin and xylan from black liquor, glucomannan, xylan and glucomannan from wood chips/forestry residuals and extractives from bark. This paper is directed mainly towards lignin and will describe the whole story from the original idea 1996 to the current situation 2007. During these years researchers at STFI-Packforsk and Chalmers Technical University have developed a new and cost-efficient process for extracting high-quality lignin from kraft black liquor. The new process is named LignoBoost. The LignoBoost-process is the result of R&D carried out within the framework of the KAM- (the Ecocyclic Pulp Mill) and FRAM- (the Future Resource-adapted Pulp Mill) programmes. The total budget for the lignin activities in the KAM- and

FRAM-programms is 95 MSEK (until 2006 the budget is 65 MSEK). The main financers for these programs were the Swedish Foundation for Strategic Environmental Research, pulp and paper industry and the Swedish Energy Agency.

THE LIGNOBOOST R&D-HISTORY

The main steps in the progress during these years are described in Figure 1.

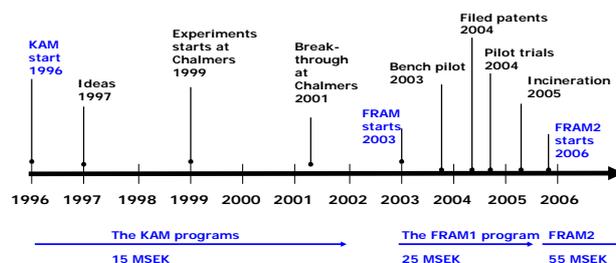


Figure 1. The R&D history of the LignoBoost-process.

KAM starts 1996

The "Ecocyclic pulp mill" ("kam") programs aimed at the development of realistic and environmentally optimal solutions for the production of high-quality bleached kraft pulp, which minimize the use of non-renewable resources and capital. Another aim was education of research scientists (resulting in 21 licentiate and 4 PhD thesis). The KAM-programs engaged a broad Swedish university network in close cooperation with the industry. The key issues were: mineral balances, minimizing solid residues, reduced energy consumption, utilization of surplus energy, high degrees of system closure and alternatives to the kraft process. The main results from the KAM-programs are given in (1, 2, 3).

Ideas 1997

During 1997 two ideas were identified to give significant future technical and economic advantages, Figure 2. One of these ideas was removal of non-process elements prior to cooking. The other was removal of lignin from black liquor. Regarding lignin it was clear that lignin removal would offer two significant future advantages. One being less capital demanding increase the pulp capacity compared to a rebuild and expansion of the recovery boiler capacity. The other being increased revenues due the value of lignin as a fuel and chemical feed-stock. Two methods for removal of lignin were carefully evaluated (4, 5):

- precipitation by acidification of partially evaporated black liquor followed by dewatering/washing
- membrane fractionation followed by the combination acid precipitation/traditional filtration.

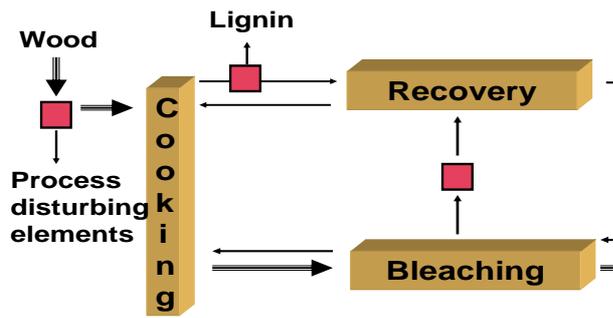


Figure 2. Identified areas with significant technical and economic advantages for future resource efficient kraft pulp mills.

For production of lignin, acid precipitation was selected as the most potentially promising route. For production of xylan, membrane fractionation was selected as the most promising route. These two methods can be successfully combined.

Lignin precipitation by acidification of black liquor followed by washing is not a new approach. In the literature, a fairly extensive material has been found, but mostly concerning the precipitation step (6, 7). The conventional process for lignin is described in Figure 3. Literature search and personal contacts indicated clearly that this approach gives lignin with a relatively low dry solid content, high ash (and sodium) content and poor dewatering properties. The result is a lignin product which cannot directly be used as fuel.

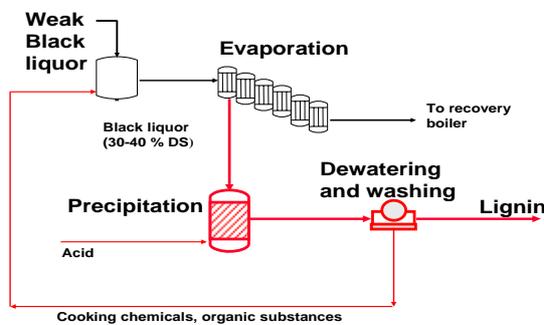


Figure 3. One stage dewatering/washing process for production of lignin from kraft black liquor.

Experiments start at Chalmers 1999 (4)

The focus was to study the separation of the precipitated lignin from the black liquor (by filtration) and washing of the lignin to improve its purity. The yield of precipitated kraft lignin at various precipitation temperatures and pH can be seen in Figure 4.

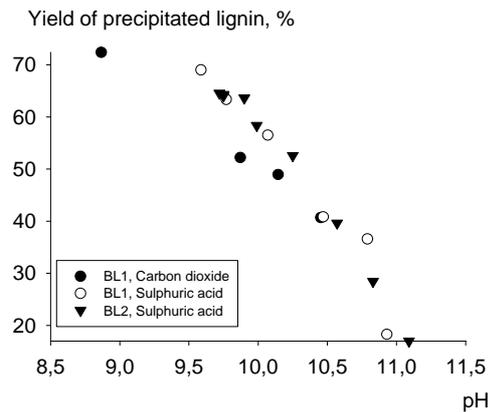


Figure 4. Yield of softwood lignin precipitated with carbon dioxide and sulfuric acid at 80°C and varying pH. BL1 and BL2 are different batches of black liquor from the same softwood kraft mill (4).

The lignin starts to precipitate at a pH of approximately 11.5, with the yield increasing to approximately 60 % of the original lignin content at pH 10. Precipitation with addition of the weak acid carbon dioxide gave slightly lower yield than precipitation with sulfuric acid, but for pulp mill process economy carbon dioxide was chosen for future studies.

The filtration properties of the lignin precipitate was systematically investigated by using a test filtration equipment with well-defined conditions (constant pressure, constant solid concentration of the feed and minimized the influence of sedimentation). The average specific filtration resistance of the filter cake was found to strongly depend on both precipitation pH and precipitation temperature. The large differences in filterability were shown to be caused by smaller lignin particle sizes formed at higher precipitation pH and/or at lower precipitation temperatures.

Washing the lignin after precipitation is important for the removal of residual black liquor and metal ions (especially sodium). Examples of wash curves obtained can be seen in Figure 5. Washing is more efficient at low pH, with lower residual sodium content in the lignin. Above a wash ratio of approximately 1.5-2.0 the sodium concentration was relatively constant.

The conclusions 2001 were as follows: The traditional process for lignin precipitation and separation from kraft black liquors results in severe problems with complete or partial plugging of the filter cake and/or the filter media. The case of more or less complete plugging results in an extremely low flow of wash liquor through the cake (virtually zero). A partial plugging of the filter cakes, on the other hand, results in very high levels of impurities in the lignin.

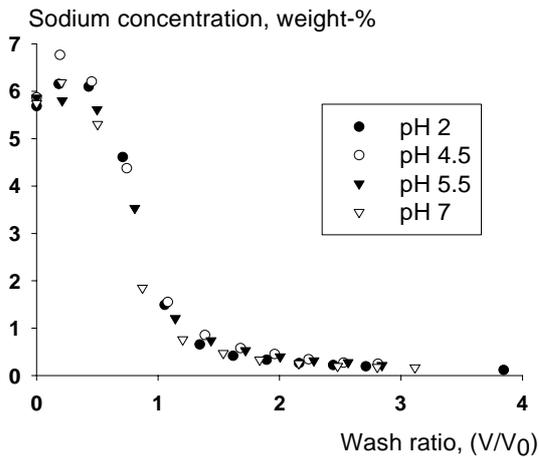


Figure 5. Wash curves when pH of the wash liquor is varied at a constant temperature of 20°C and a precipitation pH of approximately 10. V/V₀ is the ratio between the volume of added wash water and the volume of mother liquor in the filter cake before washing (5).

Breakthrough results at Chalmers 2002 (4)

The problems with filtering and dewatering were shown to be caused by changes in lignin solubility, caused by excessive pH and ionic strength gradients in the lignin cake during the washing process, Figure 6. In the early stage of washing the pH is still high due to buffering effects, while the ionic strength has decreased to very low values compared to the initial concentration of the entrained liquor in the cake. A high pH combined with low ionic strength will lead to lignin dissolution. As these problems with lignin solubility were recognized to be caused by large gradients in pH and ionic strength, it was realized that desirable to even out these profiles during washing.

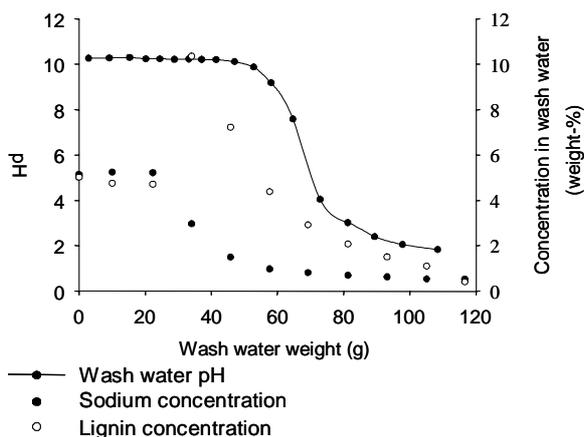


Figure 6. Effect of varying amount of wash water on filtrate pH (left y-axis, solid line, incoming wash water pH 1.05, 20°C, precipitation pH 10) and on the right y-axis sodium and lignin concentrations in filtrate (4).

A new process solution & start of FRAM1 2003

A process taking advantage of these findings is shown in Figure 7, where precipitated lignin is dewatered as in the conventional process. Instead of washing the lignin directly after dewatering the filter cake is re-dispersed with filtrate from the second dewatering/washing stage. When filter cake from the first dewatering stage is re-dispersed in liquor where the pH and temperature are controlled to approximately that of the final wash liquor, the gradients during the washing stage will be small. The pH change and most of the change in ionic strength, and thus the resulting change in lignin solubility, will then take place in the re-suspension stage instead of in the filter cake during washing.

One consequence of applying the two-stage process is that the sodium content for a given amount of wash water will be significantly lower, Figure 8. The process solution was further developed within the FRAM1 program and two patent applications were filed (8).

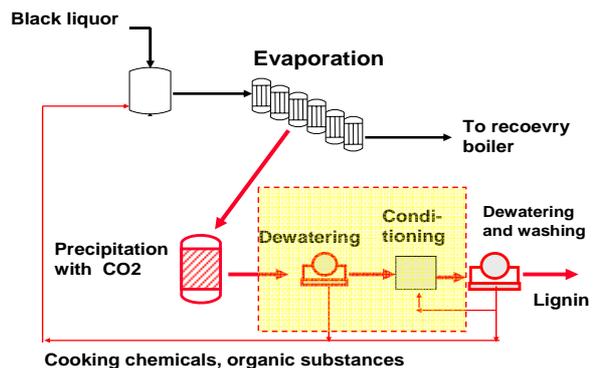


Figure 7. The two stage washing/dewatering process, LignoBoost, for washing lignin precipitated from black liquor. The new components are marked within the box.

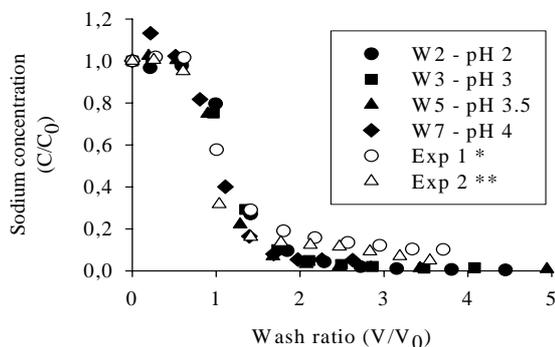


Figure 8. Wash curves when pH of the wash liquor is varied at a constant temperature of 20°C and a precipitation pH of approximately 10. Open symbols conventional one-stage process. Filled symbols two-stage LignoBoost-process. V/V₀ is the ratio between the volume of added wash water and the volume of mother liquor in the filter cake before washing (3).

Bench pilot 2003

Based upon the laboratory experiments a mobile equipment which could simulate the LignoBoost process was constructed. After being tested with good results it was operated in a mill using live black liquor. The results fully verified the laboratory results. Of particular interest are the ease of operation, the high capacity and the very low level of sodium, (below 0.1%) in the produced lignin using less than 2 m³ tonne of water per tonne of lignin.

Pilot trials 2004

Within the FRAM1-program mill pilot trials were carried out according the LignoBoost concept. We were generously given the opportunity to use the one stage washing lignin plant i Bäckhammar owned and operated by LignoTech Sweden AB and to borrowed a mobile press filter from Larox Oy for the second dewatering/wash stage. A total of about 10 tonnes of lignin was produced. Figure 9 shows the lignin as it came out from the second wash filter. The lignin produced had very good properties, Table 1. The pilot trials fully verified the laboratory results and it was realized that we were one step closer to industrial implementation.



Figure 9. High quality kraft lignin from mill pilot trial 2004 with LignoBoost process.

Table 1. Properties of lignin produced in the pilot mill trial 2004.

Dry solid content, % on dry weight	55-70
Ash content, % on dry weight	0.4
Effective heat value (dry)	25.4 MJ/kg DS
Effective heat value (30% moisture)	17.1 MJ/kg DS
Elemental composition (% on dry weight):	C 64.6, O 26.4 , H 5.7, Cl 0.005, Na 0.03

In a trial 200 kg lignin pellets with high density (700 kg/m³) was produced using a saw dust pelletizer.

It was observed that the capacity increased compared to using sawdust. This can be explained by partial surface melting of the lignin due to friction in the equipment.

Incineration trials

A test over two days was done at TPS in Studsvik with 20 kW fall-tube oven with an internal diameter of 125 mm and with a total length of approx. 3.5 m. The results clearly showed that lignin is more flammable than wood powder but it burns out more slowly, Figure 10. The faster ignition is most likely due to the smaller particle size of the lignin. The slower combustion is likely due to the higher energy content of lignin. The main conclusion is that 100 % lignin can be fired in a conventional burner for wood powder without auxiliary firing.

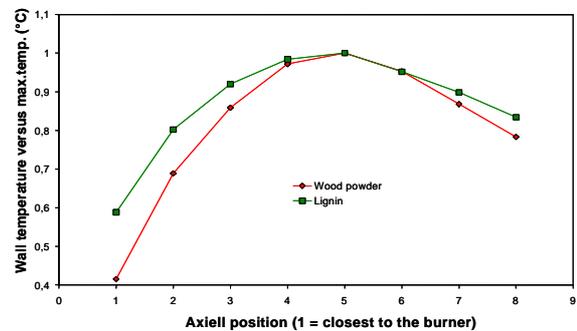


Figure 10. Normalized temperature vs maximum temperature in measure point 5.

Another application for lignin tested was as co-fuel in a 410 MW liquid coal PFBC (Pressurized Fluidized Bed Combined-cycle) CHP plant, the Värtan Heat and Power Station in Stockholm. The two PFBC modules operate under variable air pressure up to 12 bar at full load and steam data 135 bar/535°C. Air emissions are kept low by adding dolomite to the fuel, SNCR for NOx reduction and dust separation cyclones. A coal paste was successfully prepared with addition of lignin. The operating time with a mixed “coal lignin paste” was about 3 hours. The results from the short combustion tests were very promising and did not reveal any handling problems. Laboratory experiments showed that up to 10-15 % lignin fuel could be readily miscible in the coal paste without impairing the handling characteristics of the paste.

FRAM2 starts 2006

In the on-going FRAM2-program (October 2005 to December 2008) the LignoBoost-process and lignin incineration applications are developed into industrial practice. The following issues are studied:

- Effect of wood species and cooking on the LignoBoost process.
- Design data for lignin removal using the bench equipment in mills.

- Reduction of investment and operational costs.
- CO₂ from lime kiln flue gases.
- Mill trials in lime kilns, in heat/power plants and bark boilers including handling of the lignin.
- Case studies for 3-4 mills.

LIGNOBOOST AB

The results from lignin removal from black liquor were so promising that the board of STFI-Packforsk decided to establish a subsidiary 2006, LignoBoost AB, for exploitation of the technology.

DEMONSTRATION PLANT

The LignoBoost technology is now realized in a demonstration plant located at the Bäckhammar unbleached kraft pulp mill. The demonstration plant is operated as a subsidiary to STFI-Packforsk, LignoBoost Demo AB. The demonstration plant is to a large extent utilizing a lignin production plant earlier owned by Lignotech. The plant has been modified and converted to make lignin removal according to the LignoBoost-process possible. The demonstration plant is planned to produce approximately 4 000 tonnes of lignin annually from 2007. Nearly all lignin produced will be used in different incinerators such as lime kilns, bark boilers and Fortum's heat & power plant in Stockholm. Some of the lignin will be used in STFI-Packforsk's different biorefinery projects aiming at different chemical products.

On December 21st, 2006, 500 kg of lignin was produced. Regular production will begin in January 2007. An official inauguration will take place on February 12th 2007.

FUTURE POSSIBILITIES

Lignin removal with the LignoBoost process opens up new opportunities for further conversion of a kraft pulp mill to a bio-refinery. Examples of such opportunities are xylan removal from black liquor, ethanol fermentation and gasification of biomass.

Xylan removal from black liquor

High molecular weight xylan can be separated from black liquor by membrane separation. A mill trial was carried out in FRAM using a ceramic membrane in the black liquor in continuous two-vessel digester system (4). The lignin separation was performed between 145 and 155°C at full digester pressure without adjustment of the pH. Ceramic membranes with cut-off between 5 and 15 kDa were used. The retentate is mixture of lignin and xylan and further fractionation is needed. Another option is to apply membrane separation immediately before or after the LignoBoost process. In the former case the performance of LignoBoost will be

improved and the lignin will be purer. In the latter case the retentate will be relative pure xylan as the high molecular weight lignin is precipitated in LignoBoost.

Ethanol fermentation

Precipitation of lignin requires carbon dioxide. The bulk of the variable cost is due to carbon dioxide if commercial product is used. It may be possible to use carbon dioxide from the lime kiln- but gas cleaning is a challenge. Carbon dioxide from ethanol fermentation yields about one tonne of pure carbon dioxide per tonne of ethanol produced. Currently sized ethanol plants are too small to justify recovery of the produce carbon dioxide. By combining lignin production with ethanol production the carbon dioxide can efficiently be utilized and the economical performance significantly improved.

Gasification of biomass

The amount of lignin (and xylan) that can be removed from black liquor is depending on mainly on the status of the recovery boiler. At a certain amount of heat value in the fired black liquor the performance is deteriorated. In many mills this critical level is between 10-30 % of lignin removed. One interesting way to handle this is to add fuel gas from gasified biomass and thus compensate for lost heat value, Figure 11. Produced carbon dioxide can also be used for lignin precipitation (9). The ultimate development would be removal of all valuable organic components from the black liquor such as lignin, xylan and sugar acids and instead obtain all the fuel need from gasified biomass such as forestry residuals. Such an approach would make a complete removal of organic components in black liquor possible. The traditional recovery boiler may also be replaced with less capital demanding and less complicated techniques. STFI-Packforsk and VTT is currently, together with selected partners, working applying for a large collaborative EU-financed project based on these ideas in the EU 7th research program.

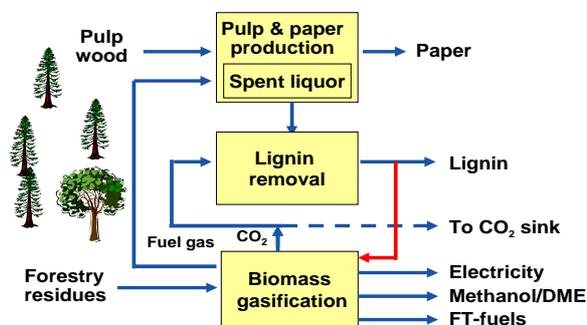


Figure 11. Integration opportunities between LignoBoost and gasification of forestry residues proposed by STFI-Packforsk and VTT (9).

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