

## Techno economic evaluation of lignin extraction in a dissolving pulp biorefinery

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### Abstract

Material and energy balances of a modern theoretical dissolving softwood kraft pulp mill, using pre-hydrolysis in water, have been established. The mill produces 1000 ADt/day and there is an energy excess in the mill that could be used to produce power. If lignin is removed with the LignoBoost process the recovery boiler is unloaded enabling an increased pulp production. With a lignin removal of 0.2 ton/ADt the pulp production could increase 8.5%. According to a sensitivity analysis the lignin price has the largest impact on the economic performance.

### Introduction

Full mill simulation models for market kraft pulp production have been developed in different projects for European softwood, birch and eucalyptus [1]. The models have been used during a number of years both in research activities and in mill specific projects for trouble shooting and as a basis for evaluation of new process concepts. Recently, many mills have shown an interest in upgrading their process to production of dissolving pulp, which traditionally has a higher market price than the market pulp. To meet this trend a simulation model for dissolving pulp production using pre-hydrolysis kraft process was developed at Innventia. Material and energy balances have been established using the simulation program WinGEMS 5.0 and all data presented are for steady state operation. The model has been used to evaluate effects of a lignin removal combined with an increased pulp production.

### Process description

The model reflects a greenfield dissolving softwood kraft pulp mill producing 1000 ADt/day. The design of the mill should consider high energy efficiency and pulp quality, low specific consumption of wood, chemicals and water, maximized production of energy from biomass, as well as low emissions and cost efficient solutions. The dissolving pulp mill model is based on data obtained from major pulp companies, equipment suppliers and laboratory trials, representing best available, commercially proven, technology. The process layout is shown in *Figure 13*.

### Pre-hydrolysis stage

The fibre line consists of a separate pre-hydrolysis stage before the impregnation stage. Condensate from black liquor evaporation and steam are added to the pre-hydrolysis stage. After the pre-hydrolysis stage the liquor is removed from the chips and led to the evaporation plant. This is done to enable the use of the pre-hydrolysate for production of additional bio-refinery products which has not been evaluated in this study. In a real mill internal circulation of pre-hydrolysate would be used to decrease the amount of extracted pre-hydrolysate significantly. The pH in the pre-hydrolysis liquor remaining in the chip is 3-4 and if the temperature is increased rapidly, lignin condensation may cause high amounts of reject. To prevent this, cold white liquor is charged to the pre-hydrolysed chips at a temperature below 120°C.

### Fibre line

The pre-hydrolysed chips are thereafter subjected to impregnation, cooking and oxygen delignification in double stages. The oxygen delignified pulp is bleached in a four stage

sequence D<sub>1</sub>(EOP)D<sub>2</sub>P. EOP filtrate is recycled back to brown stock washing. With the use of wash presses both COD to effluent and effluent volume are kept low. Yield, charges etc. are presented in **Table 6**.

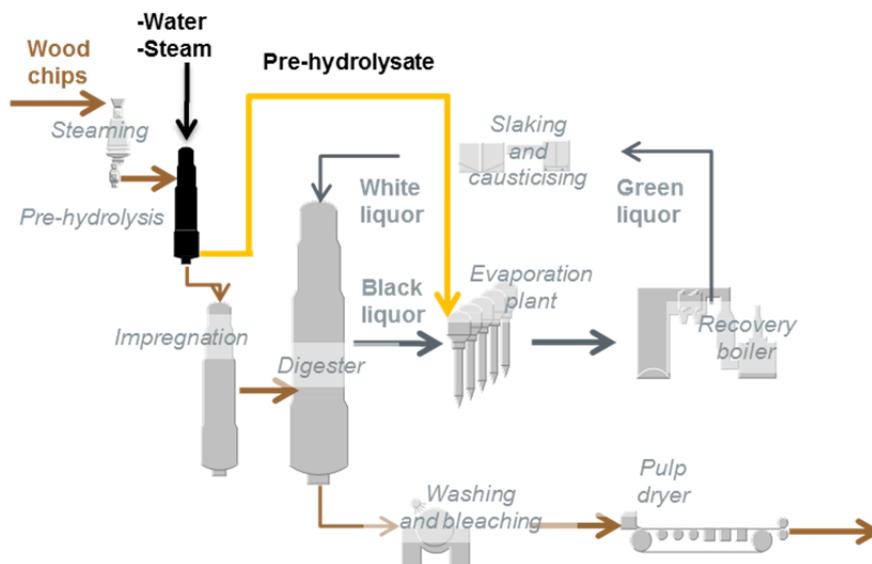


Figure 13 Schematic process layout for the dissolving pulp mill using pre-hydrolysis in water, the pre-hydrolysate taken to the evaporation plant.

Table 6. Summary of some key operating data for the fibre line compared with the market pulp mill model.

	Unit	Dissolving pulp	Market pulp
Pre-hydrolysis yield	%	82	-
Kappa number after cook		25	30
Combined cooking and pre-hydrolysis yield	%	37	47
Alkali charge on wood as effective alkali (NaOH)	%	22	20
Sulphidity (white liquor)	%	35	35
Kappa number after oxygen stage		5	12.5
Alkali charge as NaOH in oxygen delignification	kg/ADt	25	25

## Results and discussion

### Evaporation

With the pre-hydrolysate recycled back to the evaporation plant the load on the evaporation increases significantly. The pre-hydrolysate stands for approximately 30% of the total flow to the evaporation. Flow and dry solid content etc. are listed in Table 7.

Table 7. Flow and dry solid content in black liquor and pre-hydrolysis liquor to the evaporation plant.

	Unit	Dissolving pulp	Market pulp
Weak black liquor to evap., excl. spill	t/ADt	15	10
ditto dry solids content	%	15.3	16.4
Pre-hydrolysate to evap	t/ADt	6	-
ditto dry solids content	%	4.4	-
Strong black liquor, DS content incl. ash	%	80	80
Total evaporated (condensate)	t/ADt	18	9.1

### Energy, steam and power production

The process is very energy efficient and the black liquor alone produces enough steam to satisfy the process consumption in the mill. Steam use is listed in **Table 8**.

*Table 8. Steam use in process GJ/ADt.*

	Dissolving pulp	Market pulp
Recovery and power boiler (including soot blowing)	1.5	0.91
Evaporation	6.8	3.5
Pre-hydrolysis stage	3.7	-
Other process (pulping, bleaching, pulp machine, chem. prep. etc.)	4.9	4.3
Total process consumption	17.0	8.6
Back pressure turbine	5.4	3.0
Condensing turbine	6.3	5.8
- Of which is cooled away in turbine condenser	4.0	3.6

There is also an excess of steam from the recovery boiler and power boiler that is utilized in a condensing turbine to produce “green” power, **Table 9**. Compared to the market kraft pulp mill the process steam consumption is much higher for the dissolving pulp mill. However, the possibility to produce power is higher due to the much lower overall yield.

*Table 9. Power production and consumption in kWh/ADt.*

	Dissolving pulp	Market pulp
Back-pressure part of the turbine	1451	801
Condensing part of the turbine	644	588
Sum production	2094	1389
Process	808	716
Sold	1286	673
Sum consumption	2094	1389

### Non-process elements, NPEs

When evaluating biorefinery concepts the effects on the process chemicals as well as the energy use need to be addressed. However, in order to fulfil both process availability and sustainability requirements, a special focus has to be put on NPEs from the beginning of the concept development, as they will have large influence in biomass-based processes. NPEs are elements not taking part in desired chemical reactions within a given process stage. Data for the NPE content in wood and pre-hydrolysate is presented in **Table 10** and result from laboratory **Figure 14**.

*Table 10. Wood composition and NPEs to the evaporation with the pre hydrolysate.*

	Al	Ba	Ca	K	Mg	Mn	P	Si
Wood composition (mg/kg dry wood)	9	6	630	373	126	50	55	15
% of incoming with wood to evaporation with pre-hydrolysate	22	43	42	53	45	43	48	43

In the pre-hydrolysis NPEs are dissolved and will follow the pre-hydrolysate to the recovery cycle. This decreases the content of NPEs in the dissolving pulp. For some elements, i.e. P and Si, the increased level in the recovery area will have an impact on the chemical balance in the mill. Silicon and phosphorous are elements accumulating in the lime cycle [2] and with the dissolving pulp concept the total amount to the lime cycle increases compared to a kraft market pulp mill. The free CaO had to be decreased to 85% (in kraft market pulp model is 90%) to not increase the lime make up need. As a

consequence, the lime kiln load is higher compared to a market pulp mill (385 ton/ADt for dissolving pulp and 261 ton/ADt for market kraft pulp as lime from kiln).

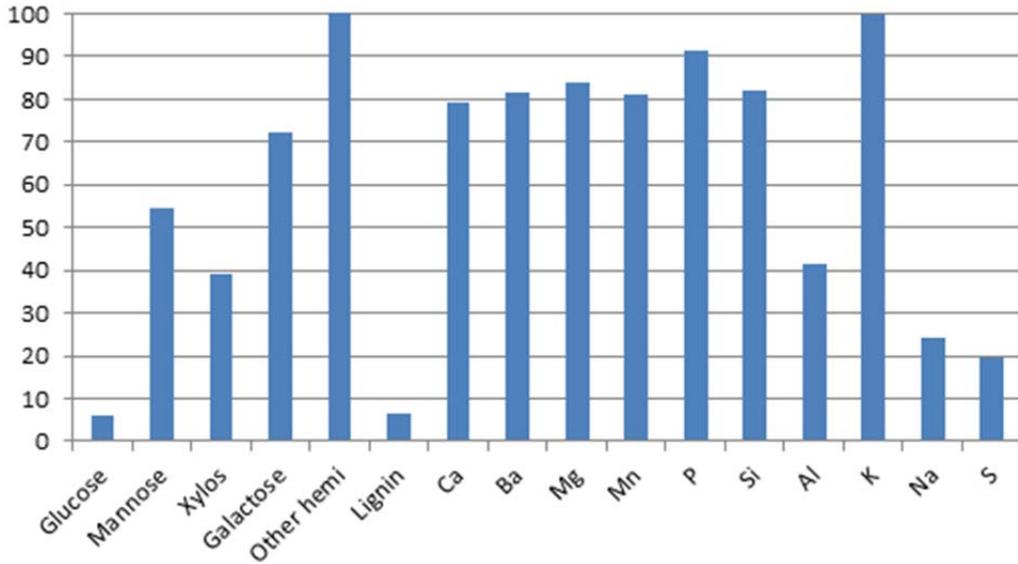


Figure 14. Dissolution of organic components and selected elements in the pre-hydrolysis stage in laboratory trials. The result is presented as percent dissolved of what was present in the wood. In case of more present in the pre-hydrolysate than in the wood a dissolution of 100% was assumed (other hemi and K).

**Lignin removal**

Lignin removal is an excellent way of unloading the recovery boiler that is often the limiting factor in a kraft pulp mill planning for an increased pulp production. In this model (a green field mill) the capacity of all unit operations is in balance and a pulp production increase, enabled by unloading the recovery boiler through the lignin removal, assumes an expansion of the other unit operations. This is in general less costly than a capacity increase in the recovery boiler.

Black liquor is acidified with carbon dioxide to pH 9-10 and lignin precipitates. The lignin is filtered and the lignin lean black liquor is returned to the evaporation plant. The lignin is thereafter re-slurried in an acidic stage with sulphuric acid at a low pH. Thereafter the lignin is displacement washed in a press filter. The wash liquor is returned to the evaporation plant. Process scheme of the concept is shown in Figure 15. [3]

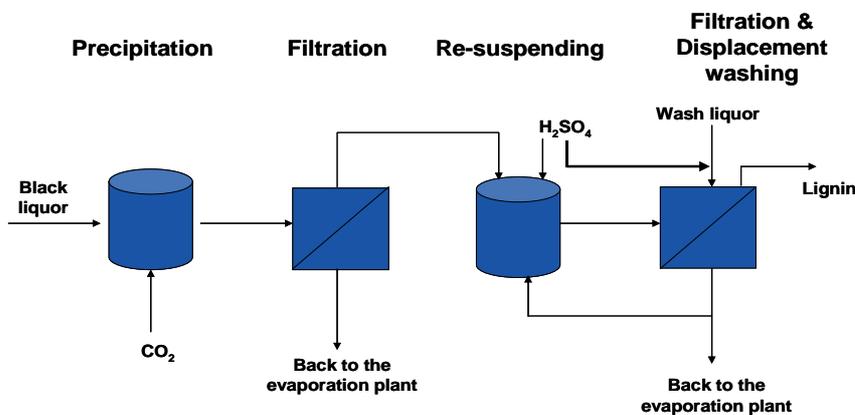


Figure 15. Schematic process layout of the LignoBoost concept.

The lignin removal was assumed to be 0.2 ton lignin /ADt. Lignin removal will have a large impact on the sodium sulphur balance, see **Figure 16**. The effect of lignin removal on the sulphur intake to the mill is significant. Some of the sulphur is removed with the lignin but the main part has to be taken out, normally with the ESP dust. The removal of ESP dust has to increase more than four times and the demand for sodium hydroxide make up increases consequently. In a real mill implementing a LignoBoost unit this is most likely considered as too high and the possibility to decrease other sulphur intake to the mill has to be investigated. The use of spent acid in the LignoBoost process other than elsewhere in the mill could decrease the overall intake of sulphur to the mill. There is also a lot of ongoing activity to decrease the need of sulphuric acid in the LignoBoost. Internal production of sulphuric acid is also an alternative. With the lignin removal the steam production decreases at the same time as the steam consumption in the process increases. However, as the pulp yield is relatively low for dissolving pulp production there is still an excess of energy in the mill. The sold power decreases from 1 290 kWh/ADt to 700 kWh/ADt with the lignin removal.

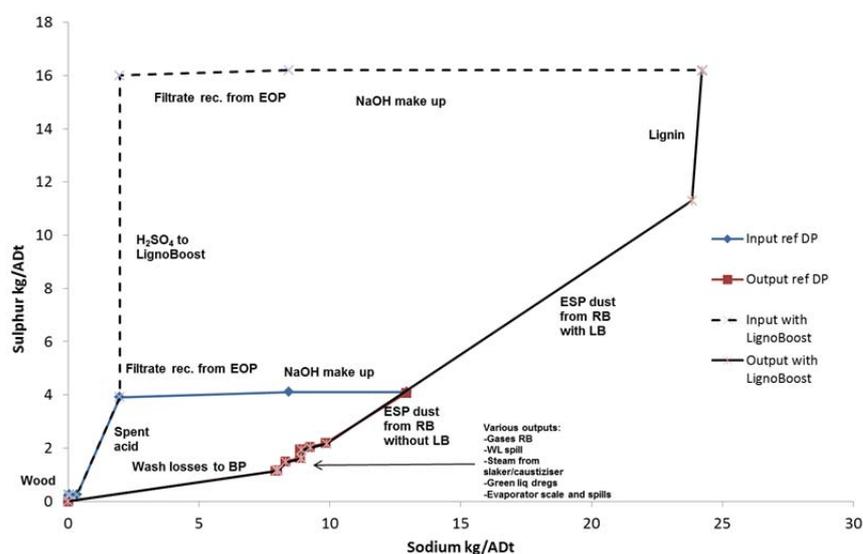


Figure 16. Sodium sulphur balance for dissolving pulp mill with and without lignin extraction (LB).

### Conclusions

With a lignin production of 0.2 ton/ADt the pulp production could increase with 8.5%, see Table 11. The heat value of the black liquor will decrease but will still be high enough for stable and favourable combustion properties in the recovery boiler.

Table 11 Increased load on selected unit operations per hour (h), day (d) or year (y).

	Dissolving pulp	Dissolving pulp including lignin removal	Lignin removal, increased pulp production	% increase
Pulp production (ADt/d)	1000	1000	1085	8.5
Wood (t/d)	2563	2563	2780	8.5
Evaporated water (t/h)	747	774	839	12.4
Dry solids to recovery boiler (t/d)	2520	2324	2520	0.0
White liquor incl. makeup (m <sup>3</sup> /d)	5 150	5 151	5 586	8.5
Lime kiln load (t/d)	385	368	399	3.6
Lignin production (t/y)	0	65 387	70 912	

Yearly income from lignin and dissolving pulp minus variable production cost is shown in **Figure 17**. As a reference point the power price was 50\$/MWh, dissolving pulp price 714€/ADt and the lignin price was 508€/ton lignin. Lignin is not a commodity product with a known market price and the number 750\$(CAD)/ton lignin was taken from Browne [4] described as conservatively estimated at the plant gate. Lost income from power production due to lignin removal was considered as a production cost. The power price was varied from 50€/kWh  $\pm 100\%$  where -100% corresponds to a mill without condensing turbine. The lignin price was varied  $\pm 50\%$ . Dissolving pulp price was varied  $\pm 30\%$ . The additional income has to cover all necessary costs related to the lignin removal and increased pulp production i.e. equipment for lignin separation and increased pulp production, rebuilding the mill, land preparation, upgrading of the lignin to high value product if necessary etcetera.

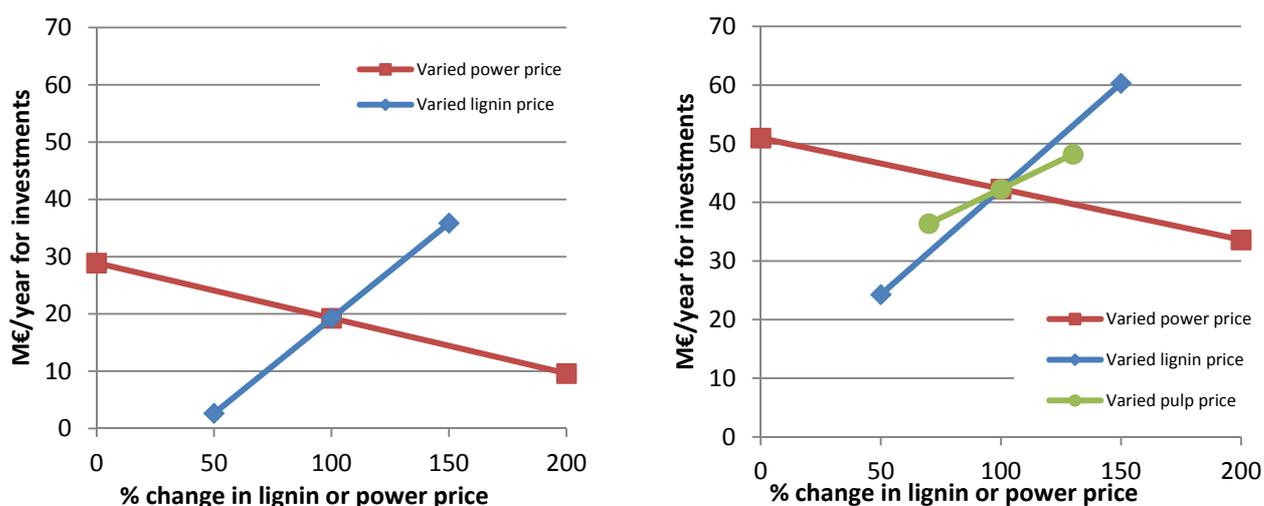


Figure 17. Effect of changes in lignin and electricity price on the economic capacity for investments after the variable costs has been covered. Left diagram is without increased pulp production, to the right with increased pulp production. Lost electricity production has been considered as a variable cost.

Of the studied parameters, the lignin price has the largest impact on the economic performance. An increased pulp production is enabled by lignin removal and is economic viable especially if the possibility to produce electricity is low.

### Acknowledgements

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## Evaluation of Commercial Scale Solvent-Based Processes for Fractionation of Kraft Lignin

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### Abstract

A generic design for the fractionation process was developed and tested against eight organic solvents. Modelling and simulation using Aspen Plus<sup>®</sup> was used to establish the mass and energy balances and the efficiency of solvent recovery for the alternatives considered. In addition, the solvent recovery yield was determined as it is essential for the economic feasibility of the process. Solvent losses in the process could be as high as 23%. The capital and operating costs as well as the minimum value of the fractionated lignin were determined using the most common economic metrics. The environmental, health and safety (EHS) impact for each solvent was evaluated and expressed as an EHS score. The results showed that the impact of the solvent type and recovery process on the energy balance and the environmental footprint of the fractionation processes cannot be ignored for designing and scaling-up such processes.

### Introduction

Commercial scale processes for lignin extraction such as the LignoBoost<sup>™</sup>, LignoForce System<sup>™</sup> as well as the Sequential Liquid-Lignin Recovery and Purification (SLRP<sup>™</sup>) that is at an advanced stage of development, now offer the opportunity to have an abundant supply of lignin recovered from Kraft weak black liquor. However, this has not led to the proliferation of high value lignin applications and derivatives. This is due to some technical constraints that can lead to economically uncompetitive performance. The main difficulties associated with the conversion of lignin into derivatives include its polydispersity and structural heterogeneity [1], which limits the miscibility and reactivity with other polymers and solvents. Specifically, Kraft lignin is characterized by a wide range of molecular weight, insoluble in water, soluble in alkali, contains several phenolic units in addition to impurities such as sulphur and metals. The reactivity due to the presence of phenolic unit as well as low methyl content can favour its use in phenol formaldehyde resins. Klett *et al.* [2] has also reported that for Kraft black liquor lignin, it is necessary to have a metal (Na) content lower than 100 ppm for high value applications such as carbon fibres because higher fraction can create flaws during carbonization. Some of the methods that have been proposed to produce Kraft lignin with suitable properties (low polydispersity, more homogeneous structure and free of impurities) for direct use include selective precipitation, black liquor ultrafiltration and fractionation with organic solvents [3]. The use of organic solvent is one of the most reported methods for lignin fractionation and it has also been demonstrated that sequential extraction leads to a less dispersed fractions. One of the most recent comprehensive works on lignin fractionation is that by Duval *et al.* [4]. A wide range of solvents was screened based on lignin solubility as indicated by the Hansen solubility parameters, health and safety factors, regulatory considerations, classification of the solvents (alcohols, ketones and esters) and low boiling points to prevent lignin degradation as well as enhance energy savings and recovery. This led to the selection of eight organic solvents, namely methanol, ethanol, 1-propanol, iso-