

Extracting Valuable Lignin for Biorefinary Production and
Replacement of Fossil Fuels

Extrayendo valiosa lignina para Producción en Biorefinería y
sustitución de Combustibles Fósiles

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Abstract

Constantly investing in R&D, Metso Power offers a novel method to extract lignin from black liquor dedicated to recovery boilers.

Developed by STFI-Packforsk and Chalmers University of Technology, it can be utilized as integral part of the liquor cycle in the pulp mill.

This new technology is a stand alone plant and integrated to the evaporation train, allowing to be built while the mill is running flat out.

By treating part of the black liquor stream, the recovery boiler will be thermally off-loaded. That will allow an increase in pulp production without performing significant extensions in the recovery boiler.

The extracted lignin can be dried and used as fuel, replacing oil or natural gas in the lime kiln or power boiler. Alternatively, lignin can be used as raw-material for various chemicals and in a longer perspective to produce LCCF (Low Cost Carbon Fibres).

This paper presents a description of the technology, the necessary equipment required for its operation and characteristics of a typical installation.

Introduction

Looking at the majority of Kraft pulping processes worldwide, it will be possible to notice a common factor in all of them: they are limited in recovery boiler capacity and the recovery cycle turns itself into the bottleneck of the production line.

Any pulp production increase tentative most likely would have to either be followed by an upgrade in the existing recovery boiler or, depending on the financial circumstances and the projects characteristics, demand a new one.

A retrofit or upgrade requires several days of equipment shutdown (10 to 60 days, depending on the project complexity), causing considerable pulp production loss. When adding those losses to the necessary investment cost to develop the project, the financial indicators may turn the project not viable.

An alternative to those cases would be a parallel installation to the existing system, causing few or even no impacts to the current process.

The subject presented in this paper is an innovative method of extracting lignin from the black liquor, off-loading the recovery boiler and giving different possibilities to the final usage of the extracted lignin, working as a fossil fuel substitute or as a raw material to chemicals production.

Process Description

A typical flow scheme can be viewed on Figure 1.

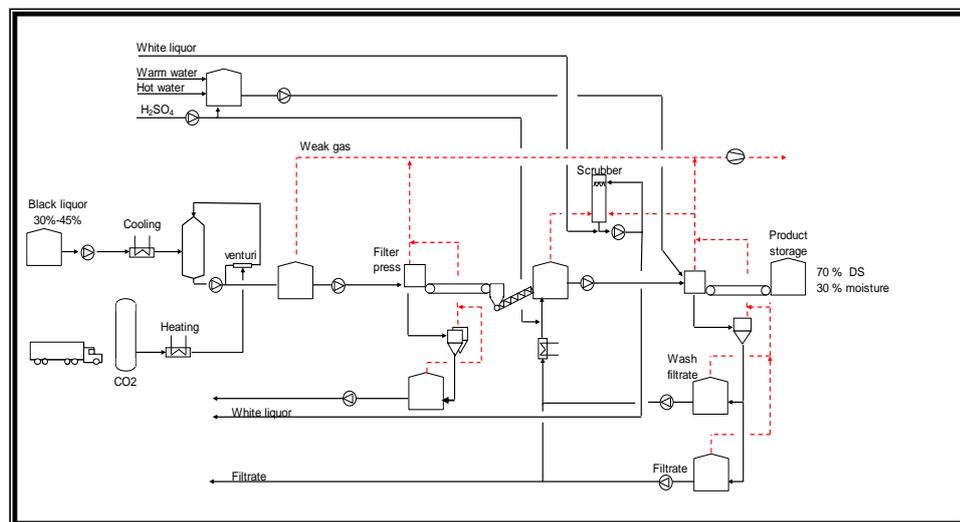


Figure 1: Process – Flow Scheme

Part stream of black liquor is taken out at 30% to 45% dryness from the evaporation plant. The black liquor is treated with carbon dioxide (CO₂) and as the carbon dioxide is absorbed in the black liquor, pH value decreases and the lignin becomes increasingly hydrophobic and eventually precipitates.

The slurry is taken out to a vertical pressure filter (VPA) for dewatering. Effective washing is necessary after dewatering of the precipitated lignin. Sodium is enriched

in the precipitated lignin and has to be washed out, both for maintaining the sodium balance in the mill and to lowering the ash content in the final lignin product. Low content of alkali metals is very important when lignin is used for combustion.

About 70% of the lignin is precipitated and removed from the original liquor. The precipitated lignin is further purified by re-suspension of the lignin cake, dilution followed by filtration and displacement washing. It has been shown in earlier research that filtration and washing in only one step results in rather severe problems with plugging of the filter cake, giving a high ash content in the final product. These effects were believed to be caused by changes in the lignin structure in the lignin cake due to the pH and the ionic strength gradients in the filter cake during the washing process.

Remaining black liquor from precipitation and pressing is sent back to the evaporation plant as lignin lean black liquor stock. Re-alkalization of the lignin lean filtrate is usually not required when moderate amount of lignin is extracted.

The accepted portion from the press filter (the lignin) is crushed and transported for treatment with sulfuric acid (H_2SO_4) or spent acid at pH 2.5 to 4. The solid concentration of lignin in the slurry is kept between 10 and 20%.

During the acidification, hydrogen sulfide (H_2S) gas is released. This gas is recovered to the process by a white liquor scrubber or sent to the weak gas system. The use of sulphur in the form of H_2SO_4 in the process will result in an additional sulphur intake to the pulp mill.

The treated lignin is again dewatered in a second vertical press filter. After the pressing, a pelletizer will compact the lignin to pellets. Precipitated lignin is hydrophobic and easily dewatered to 70% DS. Generally, the optimum temperature is higher for softwood (65-70°C) compared to hardwood (50-65°C).

Pellets can be used as a high quality green fuel. Lignin gives higher adiabatic combustion temperature than wood because of its very high heating value, as it can be shown on Figure 2.

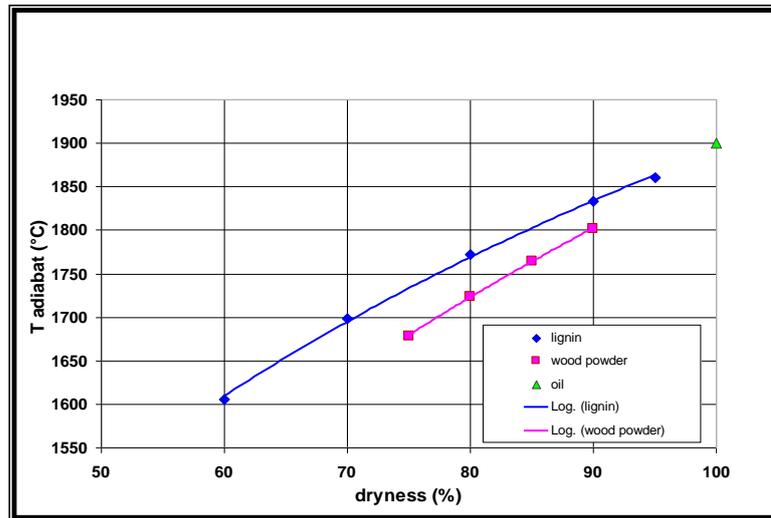


Figure 2: Adiabatic combustion temperature for different fuels

It is known that black liquor properties are quite dependent upon the wood and the cooking process in the pulp mill. Therefore, lignin exiting the plant will also have its properties depending upon those factors.

Impact of Lignin Extraction on Black Liquor Properties

Chemical Analysis

Extraction of lignin implies changes in the physic-chemical properties of black liquor which must be considered in the design and development of different processes in the chemical recovery system.

As an example, liquor from a Swedish mill is taken at 14% solids content (sample BL). The other liquor is obtained as a filtrate from a lignin precipitation process at 22.4% solids content (sample F).

The main liquors, BL and F, were analyzed with respect to their content of organic and inorganic components. Results of this analysis are presented in Table 1 and shows that lignin content in the solids is about four times higher in liquor BL compared to liquor F. The content of carbohydrates is generally lower in liquor F, which may be explained by carbohydrates adhering to the lignin cake during filtration.

The higher salt concentration in the solids in liquor F is partly due to lower amounts of organics being present in these solids, and partly due to acidification in the precipitation step with CO₂ and H₂SO₄, which explains the higher concentrations of carbonate and sulphate in liquor F.

Components	<i>BL</i> (mg/g dry solid)	<i>F</i> (mg/g dry solid)
Na ⁺	156	202
K ⁺	24	25
S-total	50.4	62.6
S ₂ O ₃ ²⁻	30.1	36.3
SO ₄ ²⁻	23.1	96.2
SO ₃ ²⁻	4.0	2.9
CL ⁻	2.1	3.1
CO ₃ ²⁻	86.8	137.6
HS ⁻	29.7	29.5
OH ⁻	20.3	0.1
Klason lignin	314	77
Acid soluble lignin	65	30
Araban	5.6	6.3
Galaktan	4.9	2.9
Glukan	0.9	0.7
Xylan	34.1	17.8
Mannan	0.3	0.2

Table 1: Chemical composition of liquors *BL* and *F*

Viscosity

A comparison of *BL* and *F* in Figures 3 and 4 shows that viscosity of filtrate *F*, is generally lower at the same solids content; the largest difference in viscosity occurs at solids content above 50%.

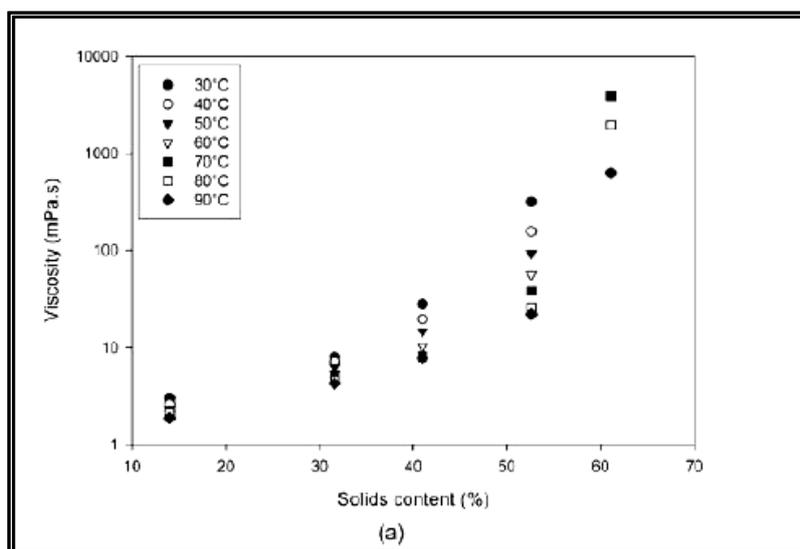


Figure 3: Viscosity of black liquor *BL* at different solids content and temperatures

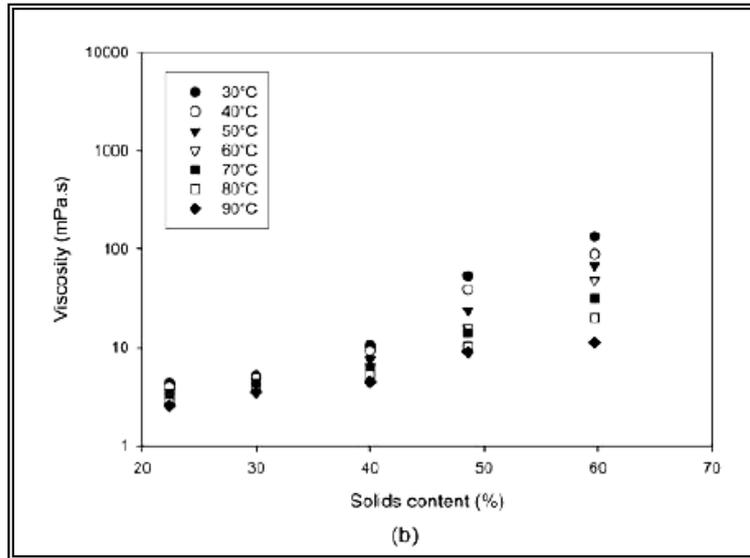


Figure 4: Viscosity of lignin-lean black liquor *F* at different solids content and temperatures

Results from viscosity measurements showed that viscosity of the liquor decreases with decreased lignin content at the same solids content and temperature.

Boiling Point Elevation (BPE)

Figure 5 shows the measured BPE of four liquors (BL, 25% F + 75% BL, 50%F + 50% BL and F) and as a function of solids content.

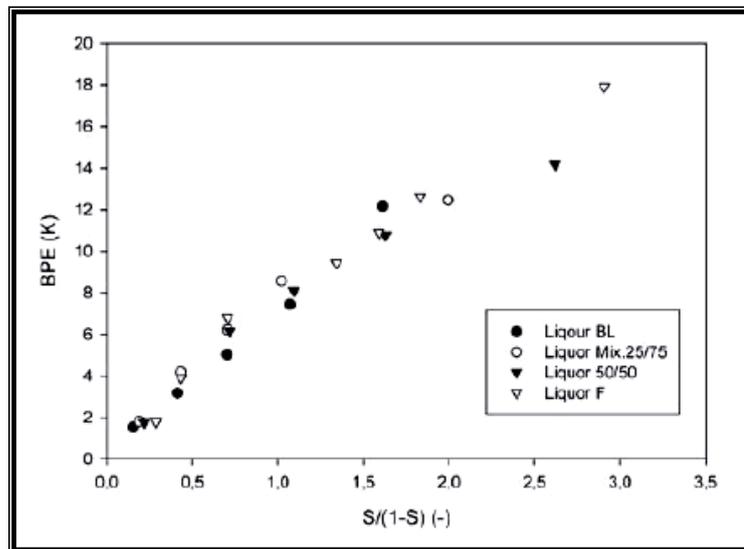


Figure 5: Boiling Point Elevation of black liquors at different solids content

As can be seen in Figure 5, lignin extraction does not affect the BPE to any great extent. Generally speaking, it can be seen that the filtrate, F, has a higher BPE at low solids content and a lower BPE at higher solids content. This may be explained by the fact that the solids in the filtrate contain higher amounts of inorganic materials due to lignin removal when compared to the black liquor, BL. At higher solids content, different precipitants of sodium sulphate and sodium carbonate may form and,

because of the higher ratio of inorganic to organic compounds for the filtrate, F, this may occur at a lower solids content compared to black liquor, BL.

Impact of Lignin Extraction on Evaporation Capacity

Results show that lignin extraction does not affect the evaporation process negatively with respect to BPE and viscosity. This means that chemical recovery processes have potential for further development, especially where evaporation plants are concerned.

Most likely the evaporation plant capacity will remain or be slightly improved by the lignin extraction. Crystallization point (risk for scaling) might change due to the changes in inorganic composition.

Increased evaporation demand from lignin wash water corresponds to 2 m³/ton lignin or 0.25 m³/ADt at 25% lignin removal rate. The amount of water to be evaporated might increase 5% to 10%.

Generally speaking, it is fair to say that overall efficiency of the evaporation plant is limited by water removal capacity and the dry solids flow. At high dry solids content the efficiency is lower, thus the increased capacity needed when extracting lignin from black liquor is to some extent counter balanced by the decrease in dry solids flow.

Impact of Lignin Extraction on Recovery Boilers Operation

Removing lignin from black liquor means that the organic part of the black liquor dry solids is decreasing. This will of course influence the combustion properties of the black liquor e.g. the adiabatic combustion temperature in the recovery boiler will decrease.

There are actions that can be taken to counterbalance the decrease in combustion temperature; e.g. increase the dry content of the black liquor entering the recovery boiler, increase combustions air pre-heating or increase air content entering at the lower part of the boiler i.e. the primary and secondary air.

However, it may increase the carry-over of fly ash since the flue gases generated in the lower compartment of the boiler is increased. A lower organic load to the recovery boiler means also that production of high pressure steam will decrease. To ensure that the steam production is maintained additional bark or forest residues can be

burnt in other boilers at the plant. Another action may be to lowering the steam demand in the process through steam savings.

Conclusions

Removal of lignin from black liquors causes a reduction in black liquor viscosity. This effect is more evident at solids contents above 40%. Boiling point elevation does not change drastically with the removal of lignin.

Lignin extraction does not affect the evaporation process negatively with respect to BPE and viscosity. Increased evaporation demand from lignin wash water corresponds to 2 m³/ton lignin or 0.25 m³/ADt at 25% lignin removal rate. The amount of water to be evaporated might increase 5% to 10%.

Removing lignin from black liquor means that the organic part of the black liquor dry solids is decreasing, which may affect the recovery boiler operation. However, there are some operating alternatives that can be performed in order to minimize the impacts on the boiler's standard operation.

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