Precipitation and Valorisation of Lignin in South African Kraft Mill Black Liquor – First Stages

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1. INTRODUCTION

Worldwide, the pulp and paper industry is in decline due to a number of factors such as high production costs, the growing utilization of electronic media that compete with print media and books, as well as pressure for the industry to be more environmentally sustainable. The yield in Kraft pulping mills is about 50%; a major obstacle observed in attempting to increase production in many Kraft mills is bottleneck in the recovery unit operations. One way to off-load the bottleneck is to divert the excess black liquor and utilize it to recover lignin by precipitation.

The Biorefinery concept introduces the practice where almost all of the biomass could be utilised. For an example, the pulp and paper industry can extract even more chemicals, materials and energy, in addition to producing cellulose (pulp). Due to a decline in the fossil fuel sources and their impact on the environment, utilization of renewable resources is needed for sustainability of the planet. Thus, extraction of lignin from the Kraft pulping process is essential, not only to offload the mill requirements to run more efficiently, but also to introduce a product new stream that could add into the mills' profitability. Second to cellulose, lignin is the most abundant renewable carbon resource that is very under utilised in the industry, however with a potential to add value into multiple industries, including the chemical, materials, energy, etc. Lignin is said to be the natural glue that holds the plant cell together. It is composed of phenyl-propane units resulting in a branched complex polymer (fig. 1).

The aims and objectives of the current project is to precipitate and characterize lignin from Kraft black liquor with an attempts to obtain narrow molecular weight lignin that can further be valorised to encourage Biorefineries in South African pulping mills.

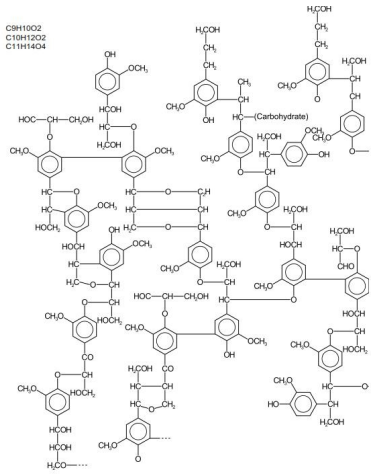

Fig.1 Lignin polymer structure

2. METHODOLOGY

Black liquor obtained from Kraft pulping mill, prior to evaporation (weak black liquor) was utilized for all precipitation experiments. Analysis on the black liquor included, total solids, the ash content, and total lignin.

Precipitation experiments were performed by adding 6M sulphuric acid (H_2SO_4) to 100 g of black liquor to decrease the pH (13.5) of the black liquor. Lignin precipitation is observed at around neutral pH, forming a colloidal type solution. The solution was further stirred for 1-2 hours for the lignin particles to completely grow. The lignin precipitate was then recovered by centrifugation (20 mins, 8g), further washed with acid water in multiple steps by utilizing the centrifuged. Filtrations and vacuum drying was finally used to recover the final lignin product.

Size exclusion chromatography (SEC, fig. 2) was utilized to determin molecular weight distribution (MWD) of the obtained lignin. Scanning electron microscopy (SEM, fig 3) was also utilized to visualize the surface morphology of the obtained lignin. Further structural analysis will include FT-IR, NMR, EA, Py-GC-MS.

3. RESULTS

Black Liquor Analysis

total solids	14.70 – 15.03 %
ash content	8.95 – 9.78 %
total lignin	47.15 – 51.12 g/L

Lignin was recovered in moderately high yield, *ca* 82.65 % with respect to the total concentration in black liquor. A mass balance showed that *ca* 5.80 % of the lignin found in black liquor was acid soluble, while the rest of is probably lost during the washing stages. MWD chromatogram showed two distinct peaks with the following data.

Averages	Peak 1	Peak 2
Mn (g/mol)	5.37e+03	5.033e+04
Mw (g/mol)	6.74e+03	5.42e+04
Mz (g/mol)	1.05e+04	5.05e+04
Pdi	1.25 ±0.132	1.002±0.071

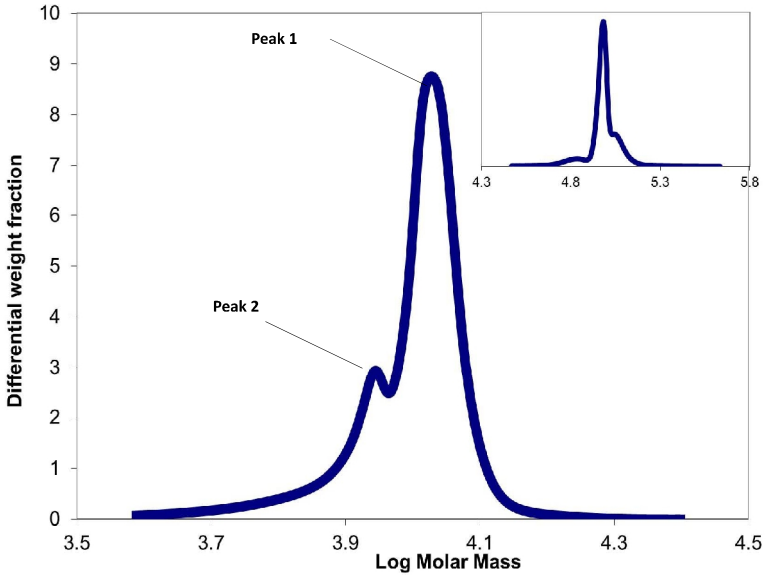

Fig.2 MWD of lignin precipitated with 6M H_2SO_4 with a UV detector (insert, RI detector).

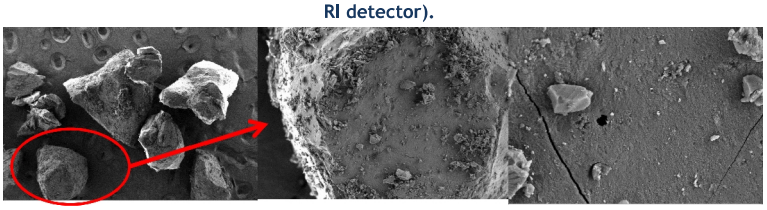

Fig.3 SEM micrographs showing the surface morphology of the precipitated lignin

4. SUMMARY

First stage of experiments have shown that lignin precipitated from black liquor with H_2SO_4 has good recovery and shows a narrow molecular weight distribution. Lignin with a narrow molecular weight distributions are desired, because they can be easily valorized. Preliminary surface analysis studies show interesting particles that may need further analysis. Future work will include a more precipitation reactions and detailed chemical and structural analyses.

References

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