EQUILIBRIUM OF LIGNIN PRECIPITATION

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ABSTRACT

Lignin is possibly one new product from the paper pulp mill. Lignin of relatively high purity can be separated from black liquor by using the so called "LignoBoost" process. The first step of the LignoBoost process is the precipitation of lignin by lowering black liquor pH. The efficiency of this step depends on the properties of black liquor and the process conditions in the precipitation step.

In this paper, a mixed softwood/hardwood black liquor was studied. The influence of pH, temperature and ionic strength on the solubility of lignin was investigated. Two different measurement methods were used to determine the lignin concentration in the filtrate: the Klason method and the standard UV method at a wavelength of 280 nm.

Results showed that lignin solubility decreased when the pH and temperature of black liquor were lowered and the ionic strength in the black liquor was increased. When compared with earlier studies, based on softwood black liquor, it was found that the yield in the precipitation step was lower when the mixed softwood/hardwood black liquor was introduced. Another conclusion was that the Klason lignin method and the standard UV method gave different results of lignin concentration of the filtrate. However, the Klason lignin method is the more accurate method.

Keywords: kraft lignin; precipitation; black liquor; pH; ionic strength

INTRODUCTION

In the pulp and papermaking industry, the yield of the raw material is only approximately 40-55% and, so far, it is only cellulose that has been utilized in an efficient way. In fact, most of the organic compounds dissolved in the cooking process end up in the black liquor. Lignin is a major constituent of these organic components. Considering that lignin has a high heating value, it has great potential as a fuel, and lignin is the greatest contributor to the heating value of black liquor. If lignin is extracted from black liquor, the heat load of the recovery boiler is decreased, which is important in pulp mills when the capacity of the recovery boiler limits the overall production rate of pulp. Producing a renewable material like lignin from black liquor may be a first step towards converting the pulp mill into a biorefinery, and improving the total material yield of the pulp mill.

LignoBoost is a novel process that extracts lignin from black liquor. Several physical and chemical operations are involved in this process: lignin precipitation, filtration, a step in which lignin cake is re-slurried, a second filtration and a final washing. Öhman *et al.*[1-5] have published papers that deal with the filtration and washing procedures. Alén *et al.*[6] have published papers on the precipitation of lignin. They have studied lignin precipitation from both softwood and hardwood by the introduction of carbon dioxide gas and found that when pressure was increased the carbonation time was shortened and the yield was greater. Alén *et al.*[7] have also reported that the highest yield of precipitated lignin was obtained with a dry content of 27-30% for softwood black liquor and 30-35% for hardwood black liquor. Uloth and Wearing[8, 9] have compared the lignin recovered from three different precipitation procedures: acid precipitation by using sulfuric acid and waste acid from chloride dioxide generation, carbon dioxide precipitation and ultrafiltration. The conclusion was that the precipitation of lignin through acidification provided a greater amount of lignin. Nevertheless, very few papers that examine how the process parameters influence the equilibrium of lignin precipitation can be found. Theliander[10] and Wallmo *et al.*[11] have investigated the solubility of lignin and how the filtration is influenced by changes in process conditions. Most of the papers above deal with softwood black liquor but very little is known about hardwood black liquor. It is also of importance to investigate mixed softwood/hardwood black liquor when considering the industrial application of the LignoBoost process in kraft pulp mills having mixed black liquors.

In this work, we have investigated the precipitation equilibrium of a mixed softwood/hardwood black liquor. Process parameters such as pH, temperature and ionic strength were investigated in order to gain a deeper understanding of how the equilibrium of lignin precipitation is influenced by different process conditions. The yield of the lignin in precipitation was calculated, by using both the Klason lignin method and the UV method with a standard absorption constant.

EXPERIMENTAL

Lignin Precipitation

The precipitation process was carried out on lab scale using the procedure proposed by Theliander[10]. The black liquor used in this study was obtained from a pulp mill producing both softwood pulp and hardwood pulp. The chemical recovery department at the mill, however, serves both fiber lines. In this study, 200 g of black liquor sample was weighed and placed in a plastic bottle with a magnetic stirrer. A certain amount of sodium ions was added (in the form of sodium sulfate) to the black liquor if greater ionic strength was required. The bottle was closed with a lid and placed in a water bath for 1 hour in order to reach the target temperature and shaken well every 10 minutes. The temperature was varied between 45 °C and 75 °C, see **Table 1**. When the target temperature was reached, 6M sulfuric acid was added to the sample. The amount of the acid depended on the target pH (see **Fig.1**). The sample was shaken every 10 minutes for 1 hour to obtain the apparent equilibrium. When the precipitation process was finished, the sample was filtrated through a Büchner funnel and the filtrate was collected for lignin concentration analysis. The detailed process parameters are given in **Table 1**.

Table1. The parameters in precipitation

Temperature (°C)	Na Content	pH
45, 55, 65, 75	Original	~11, ~10.5 ~10, ~9.5
45, 55, 65, 75	Original + 10 %	~11, ~10.5 ~10, ~9.5
45, 55, 65, 75	Original + 20 %	~11, ~10.5 ~10, ~9.5

Analytical Methods

The dry content of the black liquor sample was determined according to the Tappi (T) 650 method, and the content of sodium hydroxide and sodium sulfide was measured according to the Tappi (T) 625 method. The lignin concentration of the black liquor and the filtrate was analyzed by UV light absorption using a Hitachi UV-3200 spectrophotometer at a wavelength of 280 nm. Prior to the measurement, 10 g of the filtrate was prepared, and was diluted 5000-fold, and the pH value of the sample was adjusted to 11. The absorption constant used for all of the liquors was 24.6 (dm^3/g cm). Acid hydrolysis was performed on the filtrate liquors for Klason and acid soluble lignin, and hemicellulose content. The samples were placed in an autoclave at 125 °C, according to the Tappi T249cm-85 method. The insoluble residue referred to as Klason lignin was measured gravimetrically according to TAPPI T222 cm-00. The acid soluble lignin was determined using the UV method with a wavelength of 205 nm.

RESULTS AND DISCUSSION

Table 2 lists some important characteristics of the black liquor sample. It can be seen that the content of so called 'acid soluble lignin' is rather high, which is typical for a hardwood black liquor.

Table 2. Some important characteristics of the black liquor sample

Dry Content (%)	33.2
Na (g/kg liq.)	63.5
Lignin UV (g/kg liq.)	115.1
Lignin Klason(g/kg liq.)	88.9
Acid sol. Lignin (g/kg liq.)	28.2
NaOH (g/kg liq.)	12.8
Na_2S (g/kg liq.)	13.2

The curve of the acid consumption of the black liquor is presented in **Fig. 1**.

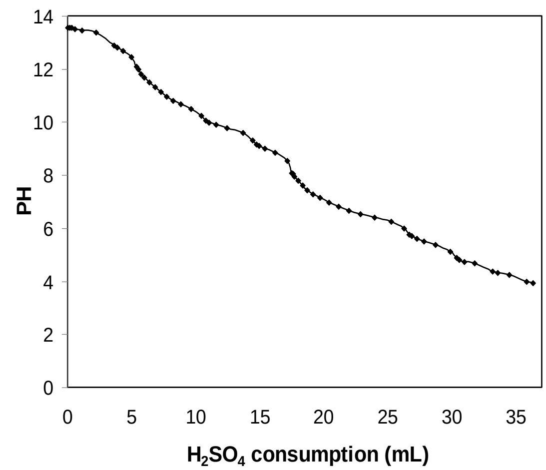

Fig. 1. The sulfuric acid consumption of the black liquor sample. The concentration of the sulfuric acid was 6 mole/L and the amount of black liquor was 200 g.

In this work, the yield of lignin in precipitation was calculated using the following **Eq. 1**.

$$Yield = \frac{L_{BL} - L_F}{L_{BL}} \times 100\% \qquad (1)$$

Where *Yield* is based on the UV or Klason measurement (%), L_{BL} stands for the original lignin concentration of the black liquor, and L_F stands for the lignin concentration of the filtrate after the precipitation step.

Fig. 2a to **Fig. 2c** show the yield of lignin in the filtrate (measured by using the Klason lignin method and the UV method) at different temperatures and pH values. As can be seen, there is a big difference between the results of the Klason lignin and the UV methods. The latter underestimated the concentration of the lignin in the filtrates, consequently, the calculated yield of lignin in precipitation was erroneously low. This is in agreement with earlier findings by Theliander[10]. The reason for this is probably because the recommended absorption constant for softwood black liquor, considered to be 24.6 (dm^3/g cm), was used in the calculation of the lignin concentration in the filtrates after precipitation. It is known that the absorption constant varies with composition, and in this case a lot of lignin was removed from the black liquor. Therefore it can be assumed that the UV method gave the erroneous results. Furthermore, considering that the black liquor sample investigated here was a softwood/hardwood mixture and that the absorption constant of hardwood black liquor is lower, 21 (dm^3/g cm), than the absorption constant of softwood, the calculated lignin yield based on this constant will be even lower. Therefore, the amount of lignin yielded is better determined using the Klason lignin method.

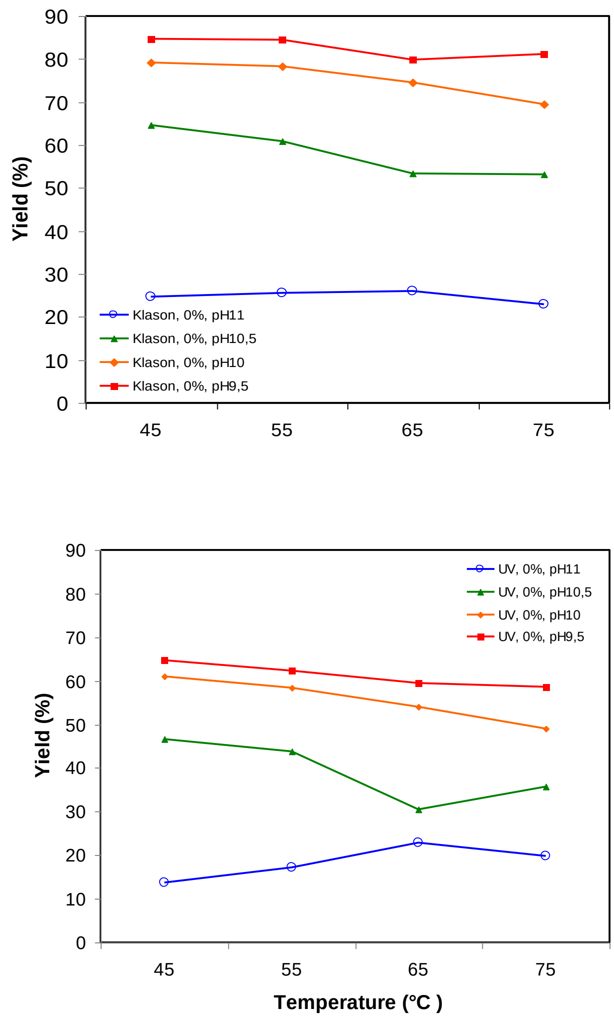

Fig. 2a. Yield of lignin in the filtrate (measured by using Klason lignin method and UV method) at different temperatures and pH values. No extra sodium content was introduced.

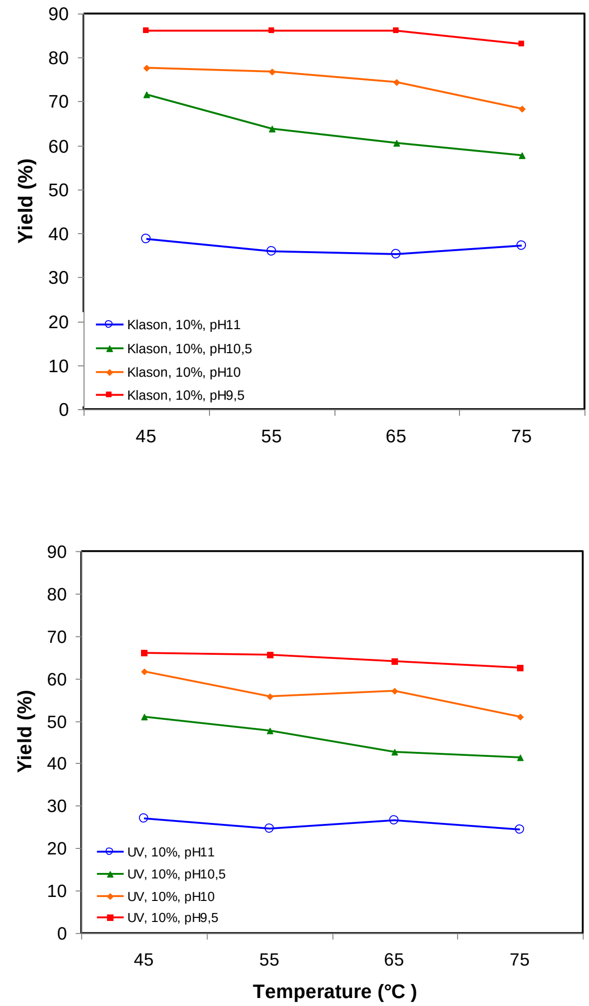

Fig. 2b. Yield of lignin in the filtrate (measured by using Klason lignin method and UV method) at different temperatures and pH values. 10% extra sodium content was introduced by the addition of sodium sulfate to the black liquor sample.

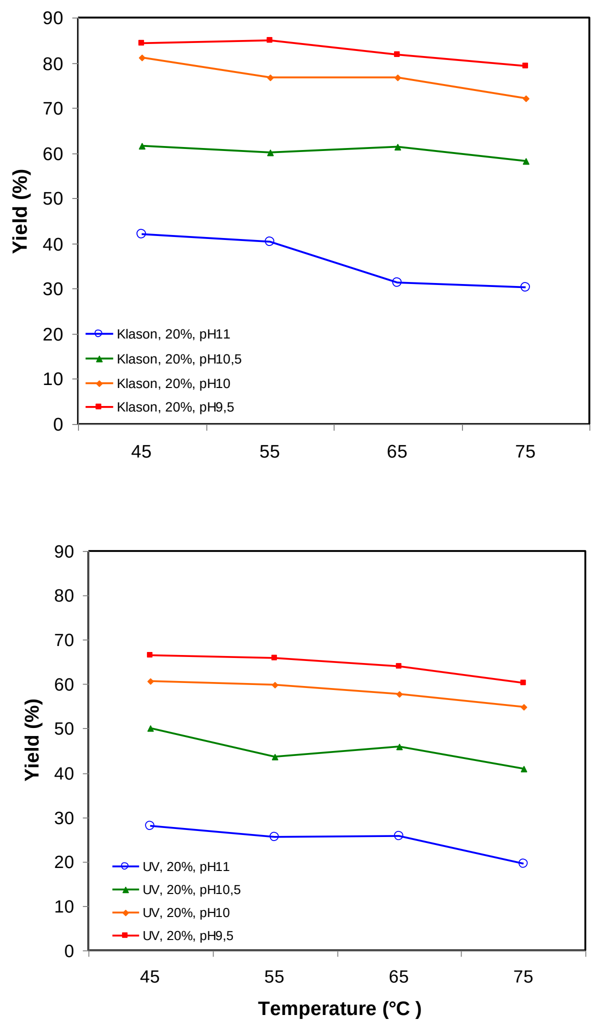

Fig. 2c. Yield of lignin in the filtrate (measured by using Klason lignin method and UV method) at different temperatures and pH values. 20% extra sodium content was introduced by the addition of sodium sulfate to the black liquor sample.

It can also be seen from **Fig. 2a** to **Fig. 2c** that the yield of lignin increased with a decrease both in black liquor pH and in the temperature of the precipitation step. Increasing ionic strength resulted an increase in the yield of lignin. These observations are in agreement with earlier investigations. Furthermore, when black liquor pH was decreased, the influence of the other parameters decreased.

Theliander[10] has developed a simple model (**Eq. 2**) for estimating the yield of lignin in the precipitation step which is valid for softwood black liquor.

$$Yield = a \times \exp\left(\frac{b}{T}\right)(H^+)^c(Na^+ + K^+)^d \qquad (2)$$

Where *Yield* is based on Klason lignin measurement (%), T is the temperature in Kelvin, H^+ is the hydrogen ion concentration (mole/L), and Na^+ and K^+ are the sodium and potassium ion concentrations (g/kg liquor). The parameters: a, b, c and d are determined by fitting the equation to experimental data, which are given in **Table 3**.

Table 3. Numerical values for the parameters in **Eq. 2** valid for softwood black liquor[10]

a	*b*	*c*	*d*
157	365	0.109	0.174

The results shown in **Fig. 3** are obtained if this model is applied with the data obtained from this study. It can be seen that the model, together with the numerical values of the parameters in **Table 3**, overestimated the yield for a mixed softwood/hardwood black liquor.

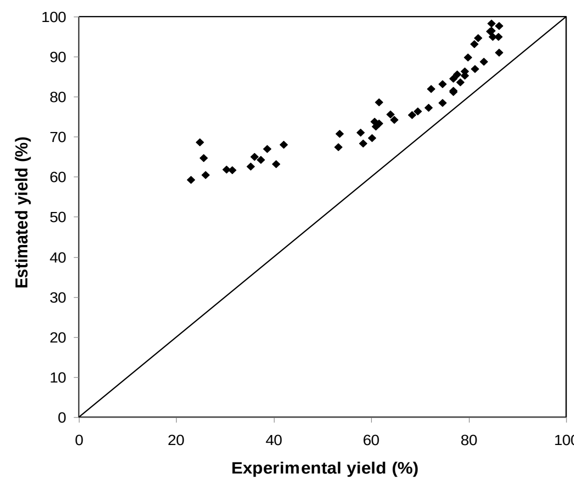

Fig. 3. Estimated lignin yield versus experimental lignin yield.

Comparing the experimental results from this study (mixed softwood/hardwood black liquor) with the results of previous study (softwood black liquor by Theliander [10]), the yield of lignin in precipitation is somewhat lower. This finding is also reported (only one measuring point) by Öhman *et al.*[4], who noticed that the hardwood black liquor had a lower lignin yield than the softwood black liquor in the precipitation step. The reason why softwood black liquor has a higher lignin yield than hardwood black liquor, is likely to be found in the fact that the composition of lignin is different in these two types of wood. Softwood lignin is almost pure guaiacyl lignin while hardwood lignin is a syringyl-guaiacyl lignin.

CONCLUSIONS

The conclusions we can draw from this study are that the yield of lignin increases when black liquor pH and temperature decrease. Increasing ionic strength can also improve the yield of lignin. Of these parameters, pH was found to be more dominant than the other two factors.

A mixed softwood/hardwood black liquor gives a lower yield in the precipitation step than a softwood black liquor.

The Klason lignin method was more precise for determining the lignin concentration of the samples than the UV method. Consequently, it is the preferred method when accurate data is required, e.g. when designing equipment, processes or troubleshooting.

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REFERENCES

1. Öhman, F.; Theliander, H. Washing lignin precipitated from kraft black liquor. *Paperi. Ja. Puu*. 2006, *88 (5)*: 287.
2. Öhman, F.; Theliander, H. Filtration properties of lignin precipitated from black liquor. *TAPPI Journal*, 2007, *6(7)*: 3.
3. Öhman, F.; Wallmo, H.; Theliander, H. A Novel method for washing lignin precipitated from kraft black liquor – Laboratory trials. *Nordic Pulp and Paper Research J*. 2007, *22(1)*: 9.
4. Öhman, F.; Wallmo, H.; Theliander, H. Precipitation and filtration of lignin from black liquor of different origin. *Nordic Pulp and Paper Research J*. 2007, *22(2)*: 188.
5. Öhman, F.; Wallmo, H.; Theliander, H. An improved method for washing lignin precipitated from kraft black liquor – the key to a new biofuel. *Filtration*, 2007, *7(4)*: 309.
6. Alén, R.; Patja, P.; Sjöström, E. Carbon dioxide precipitation of lignin from pine kraft black liquor. *Tappi*, 1979, *62(11)*: 108.
7. Alén, R.; Sjöström, E.; Vaskikari, P. Carbon dioxide precipitation of lignin from alkaline pulping liquors. *Cellulose Chemistry and Technology*, 1985, *19(5)*: 537.
8. Uloth, V.C.; Wearing, J.T. Kraft lignin recovery: Acid precipitation versus ultrafiltration. Part I: Laboratory test results. *Pulp & Paper Canada*, 1989, *90(9)*: 67.
9. Uloth, V.C.; Wearing, J.T. Kraft lignin recovery: Acid precipitation versus ultrafiltration. Part II: Technology and economics. *Pulp & Paper Canada*, 1989, *90(10)*: 34.
10. Theliander, H. The lignoboost process: Solubility of Lignin. *Proceedings of the International Chemical Recovery Conference*, 2010, Williamsburg, VA.
11. Wallmo, H.; Richards, T.; Theliander, H. An investigation of process parameters during lignin precipitation from kraft black liquors: A step towards an optimized precipitation operation. *Nordic Pulp and Paper Research J*. 2009, *24(2)*: 158.