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Precipitation of lignin from kraft black liquor

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Abstract

The separation of lignin from kraft black liquor is an attractive option to consider for pulp mills. Many pulp mills are limited by the heat transfer capacity of their recovery boiler. Removing part of the lignin from the black liquor decreases the heat load necessary on the recovery boiler and more pulp can be produced. Moreover, if energy is needed into the process, energy from lignin can be used to replace fuel oil in the lime kiln or be combusted in a power boiler. Separated lignin can either be used as a solid biofuel or in a more futuristic perspective as a raw material for the production of “green” chemicals and/or materials to replace oil as a raw material.

In this thesis, the extraction of lignin from kraft black liquor using the “LignoBoost” process was investigated, in particular the precipitation step of lignin. Firstly, it was studied how the concentration of lignin after precipitation and the yield are influenced by some conditions: pH and temperature. The lignin concentration in the liquors was measured using the standard UV method at 280nm as well as using the Klason method. The concentrations of lignin (using Klason method) and carbohydrates (using an Ion Chromatography) in the solid precipitated and in the filtrates were also measured.

One of the most important conclusions of this work is that there is a difference between the results obtained when the lignin concentration is measured using UV method compared with Klason method with standard absorptions constants. The Klason method is preferred. It was found that the yield in the precipitation step is influenced by pH and temperature. The composition of the precipitated solid was almost independent of the conditions in the precipitation and in the separation stage and was almost constant.

Key words: black liquor, lignin, kraft pulping, precipitation, LignoBoost

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Nomenclature

[Arabinose]	arabinose concentration obtained from the calibration curve of arabinose (mg/l)
[Galactose]	galactose concentration from the calibration curve of galactose (mg/l)
[Glucose]	glucose concentration from the calibration curve of glucose (mg/l)
[Mannose]	mannose concentration from the calibration curve of mannose (mg/l)
[Xylose]	xylose concentration from the calibration curve of xylose (mg/l)
A	Absorbance (nm)
a	parameter of the equations for determination of the amount of anhydro sugars
c	correction factor for the acid hydrolysis yield
V_{sol}	Volume of the solutions prepared after separation of Klason lignin from the carbohydrate content (l)
W_{lignin}	mass of lignin in the wood residue used for hydrolysis (mg)
W_{sample}	mass of wood residue used for hydrolysis (mg)

1 Introduction

1.1 Introduction

The chemistry of wood is very complex because it consists on a large number of substances varying their composition with the plant species. The chemical structure of wood is divided into four main components: cellulose, hemicellulose, lignin and extractives. But, in today's kraft pulp processes only cellulose is used in an efficient way.

However, recently a new process has been developed for the extraction of the lignin from black liquor, named LignoBoost. In this process, lignin is extracted from black liquor by three important steps, namely: precipitation, filtration and washing.

The separation of lignin from the black liquor is an attractive option that should be considered by pulp mills for many reasons: firstly, because many pulp mills are limited by the heat transfer capacity of their recovery boiler. So, removing part of the lignin from the black liquor decreases the heat load on the recovery boiler and more pulp can be produced. If 25% of the lignin is removed, the capacity of the recovery boiler can be increased, corresponding to 20-25% more mill pulp production. In the same way, if energy is needed into the process, energy from the lignin can be used to replace fuel oil in the lime kiln or be combusted in a power boiler.

Secondly, a solid biofuel is obtained when lignin is separated from black liquor by precipitation. This solid biofuel can be used by outside users. On the other hand, new processes for the production of biofuel for cars are under development and lignin is a good candidate as a raw material for such processes since it can be extracted in large quantities.

Finally because the separated lignin can be used as a first step in the production of new "green" chemicals and/or materials to replacing oil as a raw material, but it this a more futuristic perspective.

1.2 Objectives

In this thesis, the separation of lignin from kraft black liquor is studied, in particular, the precipitation step. Firstly, is studied how the concentration of lignin in the liquor after precipitation and the yield are influenced by some important process conditions (namely, temperature, concentration and pH). This has been accomplished by performing numerous precipitation experiments over different pH and temperatures.

Secondly, is present some data related to the chemical characterization of the lignin filter cakes and filtrates, so like that it could be possible detected differences in their organic composition.

2 Background

This chapter is divided into 5 sections.

The first part is focused on the traditional pulp and paper mill. General descriptions of the flow sheet of pulp and paper production are present.

In the second part the raw material of this work (black liquor) is present, as well as lignin is also characterized. Some general aspects are pointed out.

Thirdly, a summary of earlier publications in the field of lignin separation and precipitation is also given.

After this, the concept of lignin extraction (in particular, precipitation) is described. A schematic process for separating lignin from black liquor using precipitation method (acidification) is given.

Finally, in the last section is characterized a new process for the extraction of lignin from black liquor, called "LignoBoost".

2.1 Traditional pulp and paper mill

The forest industry is one of the most important industrial sectors in Sweden. The “kraft” process produces a pulp with good strength properties and because of that is the most common and important process in Sweden.

Figure 1 shows a general schematic representation of the kraft pulping mill process.

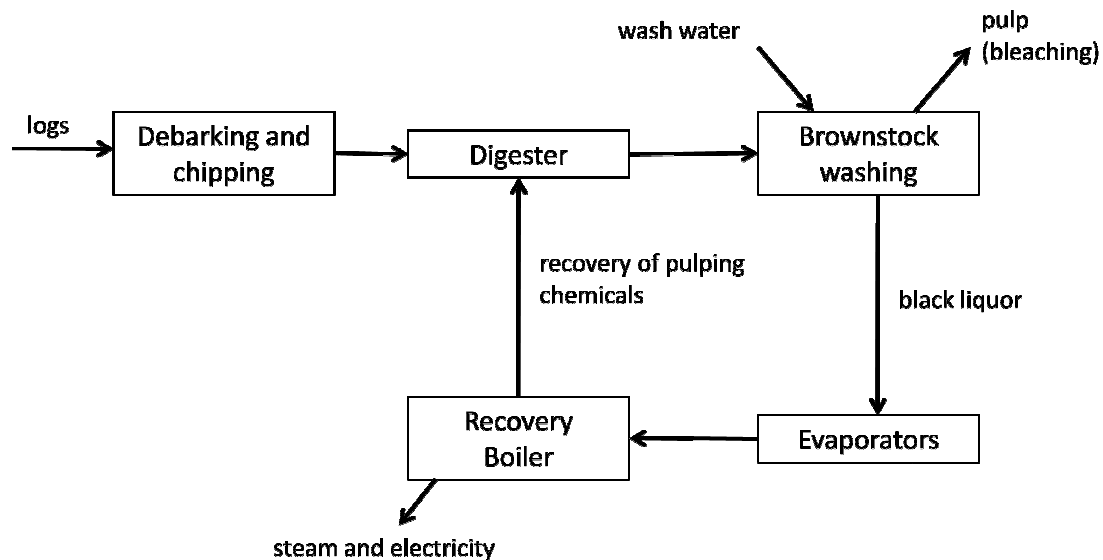


Figure 1: Schematic diagram of the kraft pulping mill

In a kraft pulping mill, after being stored, the wood logs are chopped into small pieces of wood called “wood chips”. The wood chips are then fed to digester, where they are impregnated with cooking liquor, which mainly contains sodium hydroxide and sodium sulphide.

At elevated temperatures (150°C-170°C), the hydroxide and sulphide ions react with lignin and the carbohydrates (mainly glucomannans and xylans). As a result of this, the cellulose fibres can be easily separated.

After the digestion process, the liquid consists of dissolved organic material, inorganic compounds and spent cooking chemicals, and is known as “black liquor”. The pulp and the black liquor are then separated in a washing process in a stage known as “brown-stock washing”. The washed pulp is transported to the bleaching plant if bleached pulp is to be produced. On the other hand, black liquor is then evaporated in several evaporation steps to a higher dry solids content.

After evaporation, the black liquor is transported to the recovery boiler to be combusted, and heat and electricity are produced for use in this process. However, the pulping chemicals (sodium carbonate and sodium sulphide) are recovered and used in the white liquor preparation plant to produce new cooking chemicals.

The black liquor processed in the recovery cycle can be considered to be a by-product the composition of which is of course, important when lignin extraction is being considered.

Dissolved lignin is by far the largest contributor to the heat value of black liquor.

2.2 Materials and products

2.2.1 Black liquor

Black liquor is a recycled by-product formed in the papermaking industry during the pulping mill of wood. Black liquor is a mixture of water, organic material and inorganic compounds from this pulping process. So, black liquor is a complex mixture.

Over the years, hundreds of chemical species have been found to exist in black liquor. The table below shows a typical chemical composition of the kraft black liquor.

Table 1: Chemical species of kraft black liquors from North American wood species (Frederick 1997)

Chemical species in black liquor	Amount
Alkaline lignin	30-45%
Hydroxy acids	25-35%
Extractives	3-5%
Acetic acid	5%
Formic acid	3%
Methanol	1%
Sulphur	3-5%
Sodium	15-20%

Table 2 shows typical values of the elementary composition of kraft black liquor.

Table 2: Elemental composition of Kraft black liquor from North American wood species
(Frederick 1997)

Elemental composition of black liquor	Amount
Carbon	34-39%
Hydrogen	3-5%
Oxygen	33-38%
Sodium	17-25%
Sulphur	3-7%
Potassium	0.1-2%
Chloride	0.2-2%
Nitrogen	0.04-0.2%
Others	0.1-0.3%

The composition of the black liquor depends on cooking conditions and the type of wood used. So, it is not possible to deduce a general composition. These different conditions influence the amount of the compounds present. So, it is very difficult to characterize black liquor because each of these components has an important role when determining the chemistry and properties of black liquor.

2.2.2 Lignin

Lignin is the second most abundant biological material on earth, exceeded only by cellulose and hemicelluloses, and comprises 15-25% of the dry weight of woody plants.

Lignin plays a very important role in plants life performing several functions indispensable for their life. First, lignin is distributed between and in the cell walls acting like a glue or cement on binding the wood fibres together. This gives the rigidity and mechanical resistance to compression, impact and bending that are well known in wood materials. Secondly, lignin also acts as water sealant across the cell walls playing a decisive part in the control of the internal transport of water, nutrients and metabolites. Finally, lignin makes the woody tissue more resistant against biological attacks by obstructing microorganism's penetration.

Lignin can be described as a three-dimensional amorphous macromolecule made of phenylpropane units that are formed during copolymerization of the three primary precursors: coniferyl alcohol, sinapyl alcohol and p-coumarly alcohol.

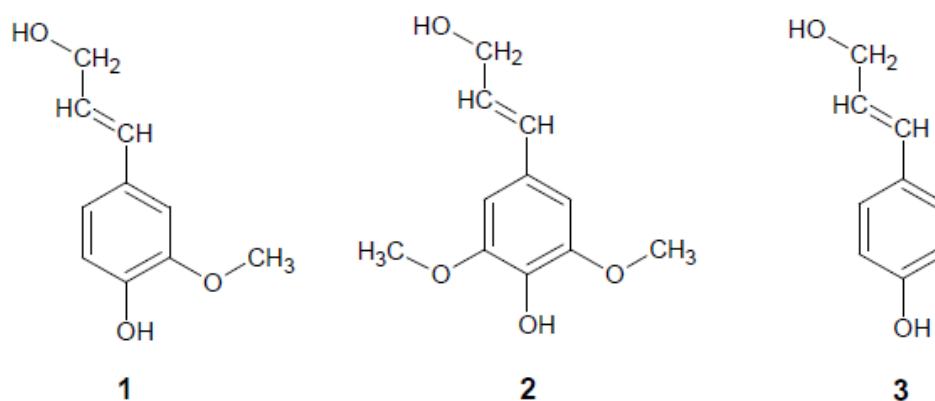


Figure 2: Primary precursors of lignin: (1) coniferyl alcohol, (2) sinapyl alcohol and (3) p-coumarly alcohol.

The biosynthesis pathway of lignin is initiated with enzymatic dehydrogenation of the monomers present in figure 2 with the formation of corresponding phenoxy radicals. Each of these free radicals is highly resonance-stabilised, as a result of its possible mesomeric forms (figure 3).

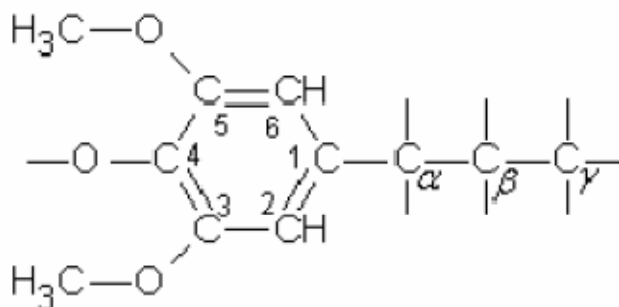


Figure 3: Common notation for addressing to the carbon atoms within each phenylpropane unit
(Wool and Sun, 2005)

The random coupling reactions between the phenoxy radicals result in structures disposed in very complex three-dimensional networks and with high heterogeneity in respect to its composition, cross-linkages, size and proportion of the characteristic functional groups (hydroxyl, carbonyl and carboxyl). So, because of this, it is not possible to attain a definitive structural model for the molecule of lignin in its native form. The most common of these models is the Adler's structure for native lignin that is shown in figure 4.

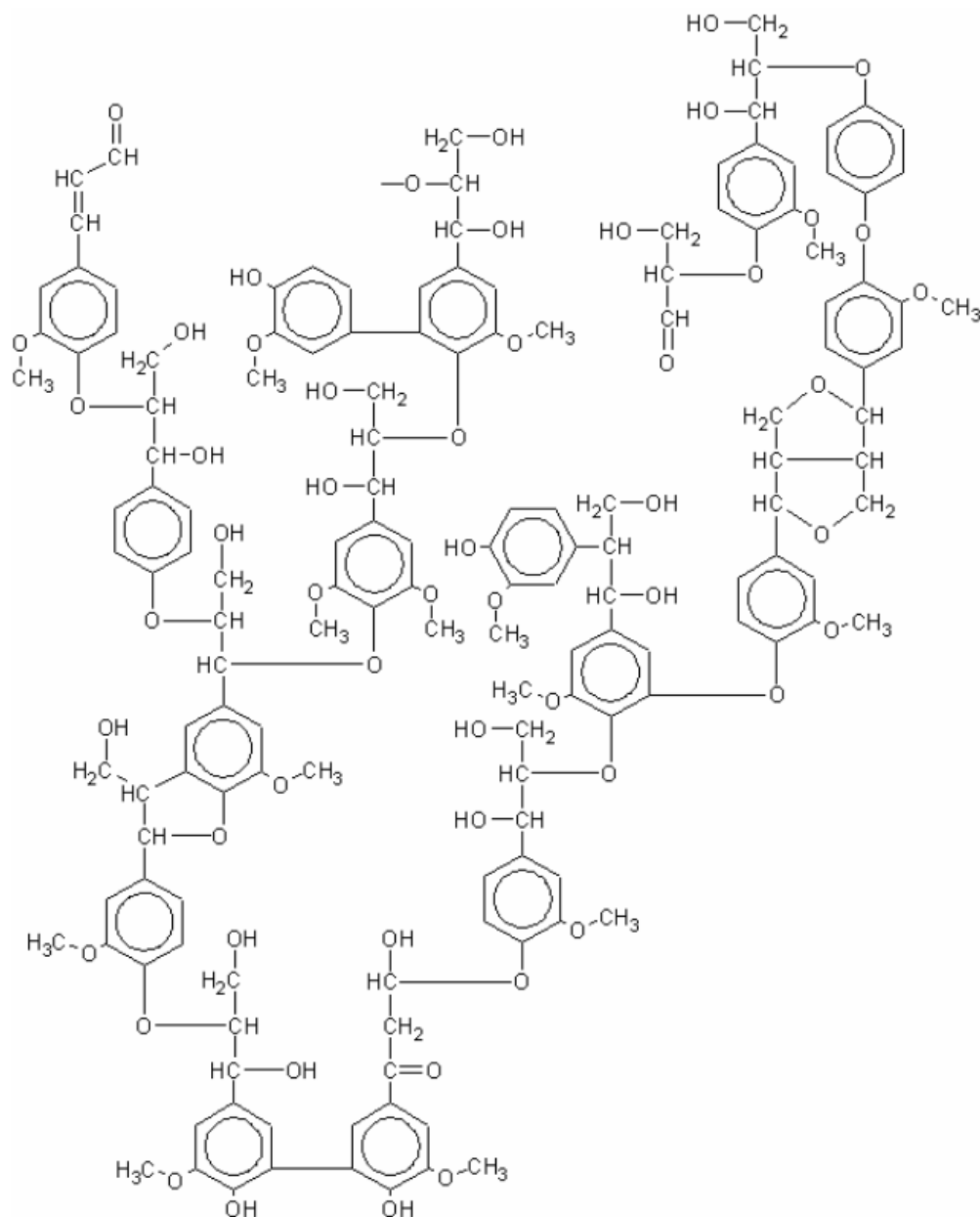


Figure 4: Structure of native lignin according to Adler (Adler 1977)

The lignin macromolecule also contains a variety of functional groups that have an impact on its reactivity. Lignin contains methoxyl groups, phenolic hydroxyl groups, and few terminal aldehyde groups. In the phenolic hydroxyl groups, only a small part of these are free. The most part are occupied in linkages to neighbouring phenylpropane linkages. Carbon and alcoholic hydroxyl groups are incorporated into the lignin structure during enzymatic dehydrogenation.

Table 3 shows the frequency of some common functional groups found in lignin (Sjöström 1993).

Table 3: Functional groups in native softwood and hardwood lignins (per 100 C₆C₃ units)
(Sjöström 1993)

Group	Softwood lignin	Hardwood lignin
Methoxyl	92-97	139-158
Phenolic hydroxyl	15-30	10-15
Benzyl alcohol	30-40	40-50
Carbonyl	10-15	

Analyzing the table above, it is possible to see that the number of functional groups differs amount different wood species. The guaiacyl propane unit is the most abundant unit found in native softwood lignin while syringyl propane is the most common unit in native hardwood lignin, in others words, the methoxyl group is more frequently present in hardwood lignin.

2.3 Literature Review

Lignin separation from black liquor is not a new idea, this concept has been treated in literature and patented over the years. The most common separation process is lignin precipitation from black liquor by acidification. Below, is presented a review of this process.

A patent regarding improvements in the recovery of lignin from black liquor was applied as early as in 1944 by Tomlinson and Tomlinson. In 1946, they treated black liquor with flue gases containing carbon dioxide. Tomlinson and Tomlinson noted differences between oxidized and non-oxidized black liquors, where lignin particles prepared from non-oxidized black liquors were filtered at a precipitation temperature (80°C), while this was not the case for oxidized black liquors.

Geisen, in 1957, proposed a continuous lignin precipitation process using as acidifying agent the carbon dioxide followed by filtration, washing and drying.

The lignin precipitation from eucalyptus black liquor using both carbon dioxide and sulphuric acid as acidifying agent was proposed by Merewether (1961/1962). He concluded that the precipitation temperature found to be critical when producing a filterable lignin, while lignin concentration and precipitation pH were of less importance. He also found the optimum temperature varied between 60°C and 90°C for different black liquors.

In 1979, Alén et al. studied lignin precipitation using pure carbon dioxide and flue gases as a acidifying agent. When pure carbon dioxide was used to acidify pine black liquor (softwood) in a pressurized vessel (1500 kPa) and with 80°C, the maximum lignin yield (77%) was found. Using a pressurized vessel during precipitation, the carbonation time was found to be shortened and the yield increased, when the pressure was increased.

The authors conclude in 1985 that the highest yield of precipitation was obtained at dry solids content at 27-30% for softwood and 30-35% for hardwood, when treating black liquor with carbon dioxide.

Uloth and Wearing (1989-a,b) compared three different precipitation methods: acid precipitation using both sulphuric acid and waste acid from chloride dioxide generation, carbon dioxide precipitation and ultrafiltration. They concluded that the amount of lignin recovered was higher with the acid precipitation method than with ultrafiltration. They also found that

the sodium content of the lignin, which limits its use as a fuel, was higher in the lignin obtained from ultrafiltration experiments than from acid precipitation.

In 2000, Howell and Thring used the same type of acid (waste acid from chloride dioxide generation) to precipitate lignin from hardwood black liquor. They found optimum separation properties at a temperature of 70°C together with slow rates of acid addition and stirring kept as slow as possible.

Cloutier (1993,1995) developed an electrolytic process that precipitated lignin from weak black liquor. Hardwood and softwood were used in these experiments.

In 2000, Sundin concluded that the mechanism for the lignin precipitation can be regarded as the coagulation of a colloid.

The stability of lignin solutions in black liquor is controlled mainly by three parameters, namely: ionic strength, pH and temperature, of which the most important are the first two (Norgren 2000). If the ionic strength is increased and/or the pH decreased to below a certain point, a precipitate will be formed.

In 2006, Öhman and Theliander concluded that the yield was almost the same for the precipitation using sulphuric acid (strong acid) or carbon dioxide.

Walmo et. al (2009) demonstrated was that the yield increases with decreasing temperature and increasing dry content.

2.4 Lignin precipitation – Schematic process description

Lignin is separated from the black liquor by precipitation, and the principles of this process are shown in figure 5.

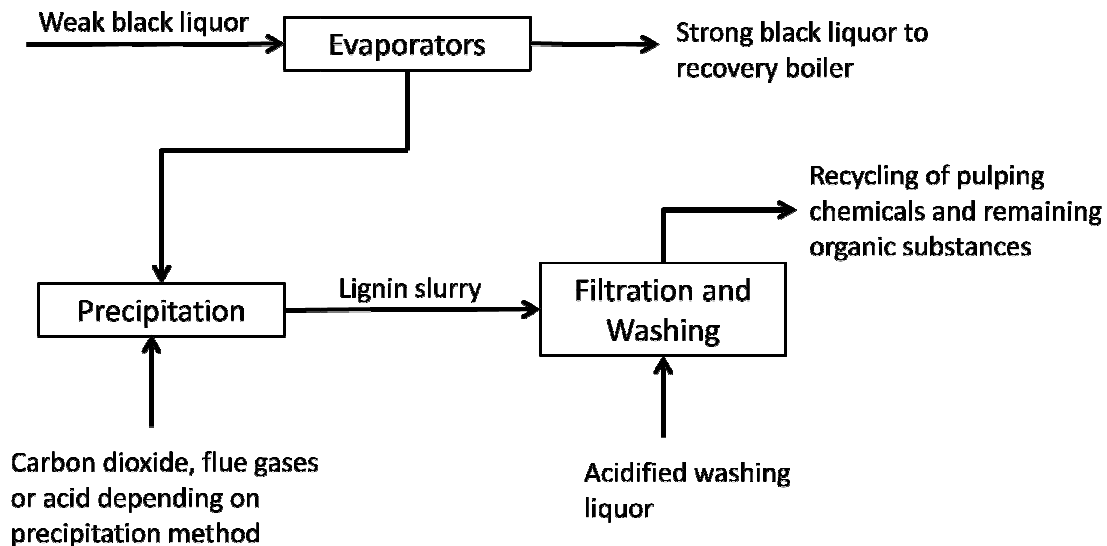


Figure 5: Technical procedure for lignin extraction from black liquor by precipitation

The precipitation reactor is fed by a part of the black liquor stream removed from the evaporators at approximately 30% dry solids content for optimum yield. In this reactor, the black liquor is acidified using carbon dioxide (either pure or in the form of flue gases), waste acid from chloride dioxide generation or sulphuric acid, inducing lignin precipitation.

Here, inside the reactor is very important the control of the precipitation temperature for the separation properties of the precipitated lignin.

After precipitation, the solid lignin is separated and purified further by washing with acidified water (normally with pH between 1 and 4) in several steps to remove contaminants from the black liquor. Filtrate and wash water are returned to the recovery system to avoid a loss of pulping chemicals and to recovery energy from the remaining organic compounds.

2.5 LignoBoost process

The LignoBoost process consists in three steps: precipitation, filtration and washing. This is shown in figure 6.

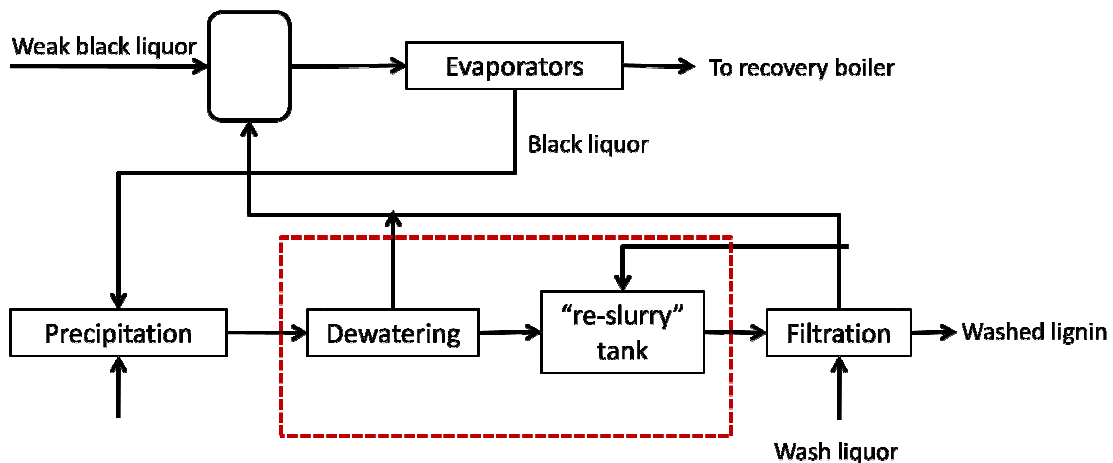


Figure 6: The modified method of washing lignin precipitated from black liquor

The lignin is precipitated by acidification in the precipitation reactor and filtered in the following filtration step. Instead of washing the lignin directly after filtration, however the filter cake is re-dispersed in water at low pH (pH 1- 4). The new slurry is filtered again, and finally, washed by displacement washing with acidified wash water. If the filter cake is dispersed in liquor where the pH and temperature are controlled until the final wash liquor, the pH gradients during the washing step will be small. Gradients in ionic strength still exist, but depending on the degree of dilution in the re-slurrying stage, these can also be smaller than for the case with direct displacement washing.

Most of the changes that happen in the lignin particles take place in the re-suspension stage instead of in the filter cake during the washing.

3 Materials and methods

The methods that were put to use in this study are treated in this chapter. The experimental methods used in the laboratory are described, followed by the analytical methods.

3.1 Black liquor used

Softwood black liquor from Swedish pulp mill was used in all of the experiments. It should be mentioned here that the black liquors (samples) were taken from the same mill but at different times.

3.2 Laboratory-scale experiments

3.2.1 Precipitation

In this experimental work, the experiments were made in plastic bottles with fitting lids and the temperature was controlled by placing the bottles in water baths.

The experiments were performed according to the following steps: weight 200 g of black liquor in a bottle and placed the sample in the water bath to equilibrate the temperature. Dissolve a certain amount of sodium sulphate in the black liquor and place the bottle in the water bath again. When the target temperature was reached, added the amount of 6M sulphuric acid to the bottle and shaken before being put back into the water bath. The bottle was shaken every 5 minutes. After 60 minutes, the bottle was taken of the bath. It's proved that 60 minutes is more than sufficient to complete reaction and formation of the precipitated.

The following table lists the conditions investigated in this experience.

Table 4: The process parameters investigated

Dry content (%)	Temperature (°C)	Na content	pH
45	45	Original + 5%	11.0
	55		10.3
	65		9.5
	75		

3.2.2 Precipitated lignin – Washing

Lignin suspension was prepared by precipitating lignin from black liquor according to procedure described in 3.2.1. The suspension was filtered using a Büchner-hopper and filter paper. The filtration equipment was placed on a vacuum flask and vacuum was applied. When the filtration was concluded, the filtrate was removed and a sample taken from it for further analysis.

The filter cakes were washed continuously with wash water having a pH 3 and other were washed with wash water having a pH of 1. This water wash is made by mixing deionized water with H₂SO₄ to adjust the pH to the desired value. The experiment was stopped when the pH was reached. The lignin filter cake was removed and dried in an oven (125°C), after was crushed and stored for further analysis (Klason lignin, acid soluble lignin and carbohydrates).

3.3 Analytical methods

The lignin concentration of black liquor and filtrates (lignin-lean black liquor after precipitation) were determined by UV light absorption using a Hitachi UV-3200 spectrophotometer: the wavelength was 280 nm. The following equation is used to calculate the lignin concentration of black liquor and filtrates. The absorption constant (ϵ) used for all was $24.6 \text{ dm}^3/(\text{g}\cdot\text{cm})$ and “b” was the covet spread ($b=1\text{cm}$).

$$A(280\text{nm}) = C \times \epsilon \times b \quad (3.1)$$

Klason lignin, acid soluble lignin and carbohydrates were analysed after acid hydrolysis of the samples (Theander and Westerlund 1986). Acid hydrolysis was performed by adding 3.0 ml of 72% sulphuric acid to approximately 200 mg of dry sample or 1.2 g of liquid samples. The mixture was stirred carefully and evacuated after 15 minutes before being placed in water bath (30°C) for 60 minutes. The sample was then diluted with 84 g of deionised water and mixture transferred to an autoclave where it was kept at 125°C for 1 hour.

The solid residue was filtered and washed with a small amount of hot water. The solid residue that remained after washing (Klason lignin) was determined gravimetrically according to TAPPI T222 cm-00. Klason lignin was calculated according to the following equation.

$$Klason (\%) = \frac{W_{lignin}}{W_{sample}} \times 100 \quad (3.2)$$

Equation 3.2 shows that the klason lignin is defined as the ration between the quantity of lignin obtained after acid hydrolysis and the quantity of wood residue used for hydrolysis.

The filtrate was transferred to a flask, 2.0 ml of fucose was added and the sample was diluted to 100 ml with deionised water. Acid-soluble lignin was determined by measuring the absorbance of the solution at 205 nm (using an absorption coefficient (ϵ) of 110 g/(l.cm)).

$$\text{Acid – soluble lignin (\%)} = \frac{\frac{A}{\epsilon}}{W_{\text{sample}}} \times 100 \quad (3.3)$$

The solubilised monosaccharides were quantified using Ion Chromatography.

After acid hydrolysis, the monosaccharides detected are therefore assumed to be originated from polysaccharides. High-performance anion-exchange chromatography, coupled with pulsed amperometric detection (HPAEC-PAD) using an ED40 electrochemical detector (Dionex, Sunnyvale, CA, USA) was used to analyse the monomeric sugars.

The chromatograph was equipped with a gradient pump (GP40), an autosampler (AS50), a Carbo Pac PA1 guard and a PA10 analytical column (Dionex). Millipore water with 2 nM NaOH was used as eluent at a flow rate of 1 ml/min, with an injection, volume of 10 μ l. D-mannose, D-glucose, D-galactose, D-xylose and L-arabinose were used as standards.

3.4 HPLC calibration

The calibration of the HPLC was performed using four standard samples. The standard samples were used to obtain the calibration curves for glucose, arabinose, galactose, xylose and mannose. The following table presents the concentrations of the standard solutions:

Table 5: Concentrations of the different standard samples used for the calibration of the HPLC

Sample	Concentration (mg/l)					
	Fucose	Arabinose	Galactose	Glucose	Xylose	Mannose
1	40	2.2	3.2	0.8	4	0.4
2	40	5.5	8	2	10	1
3	40	11	16	4	20	2
4	40	16.5	24	6	30	3

Since the fucose was used as an internal standard, its concentration was fixed. Thus, for each chromatogram resulting from each analyzed sample, the areas of the peaks of the others monomers were divided by the area of the fucose peak. These values and their corresponding concentrations (table 5) were plotted and linearly adjusted in order to obtain the calibration curves for each monomer. This procedur was repeated for each series of measurements. The following figures show the calibration curves obtained for one of these series.

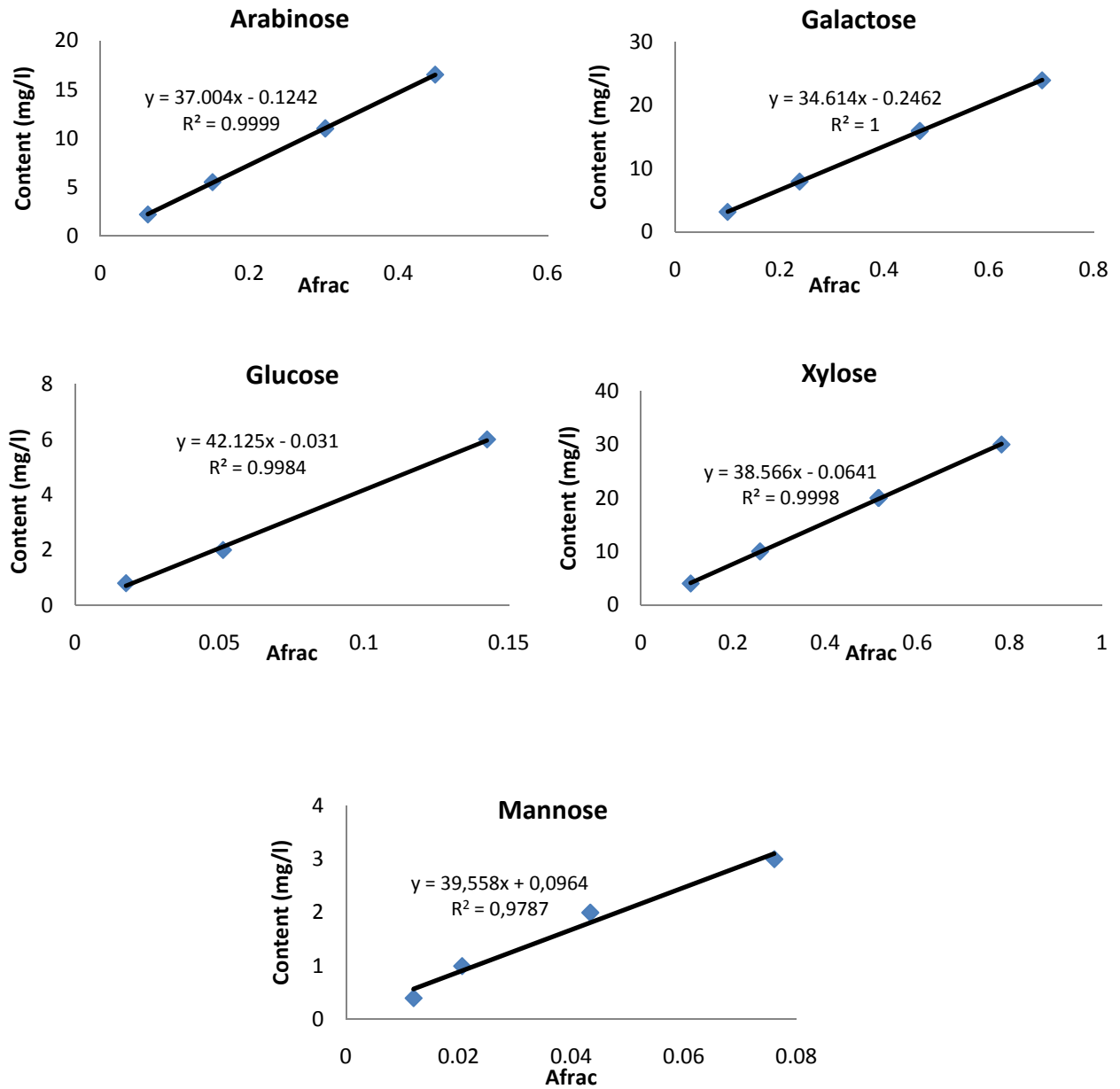


Figure 7: Arabinose, Galactose, Glucose, Xylose and Mannose calibration curves

These calibration curves were used to determine the concentration of the different monomers in the solutions prepared after separation of Klason lignin from the carbohydrate content.

3.5 Determination of carbohydrate percentages on wood

The concentrations of the monomers in the solutions prepared after hydrolysis were determined using the areas of the peaks that resulted from the analysis of the vials on HPLC and the calibration curves of each monomer.

After that calculation, the amount of anhydrous sugars (i.e. Arabian, galactan, glucan, xylan and mannan) was determined by the following equations:

$$\mathbf{Arabian} = \frac{[\mathbf{Arabinose}] \times V_{sol} \times a}{c} \quad (3.4)$$

$$\mathbf{Galactan} = \frac{[\mathbf{Galactose}] \times V_{sol} \times a}{c} \quad (3.5)$$

$$\mathbf{Glucan} = \frac{[\mathbf{Glucose}] \times V_{sol} \times a}{c} \quad (3.6)$$

$$\mathbf{Xylan} = \frac{[\mathbf{Xylose}] \times V_{sol} \times a}{c} \quad (3.7)$$

$$\mathbf{Mannan} = \frac{[\mathbf{Mannose}] \times V_{sol} \times a}{c} \quad (3.8)$$

In these equations, “a” is a parameter that results from the fact that when two monomer units are linked to each other a molecule of water is lost and “c” is a correction factor for the fact that some monomers are further degraded during the acid hydrolysis procedure. The following table shows the values of the parameters “a” and “c” from the different monomers.

Table 6: Values of the parameters “a” and “c”

	a	c
Arabinose	0.88	0.944
Xylose		0.899
Glucose		0.952
Galactose	0.90	0.974
Mannose		0.926

Following, the equations used for determining the amount of carbohydrates (i.e. Cellulose, Glucomannan and xylan) were shown:

$$\mathbf{Cellulose = Glucan - \frac{1}{3.5} \times Mannan} \quad \mathbf{(3.9)}$$

$$\mathbf{Glucomannan = Galactan + \left(1 + \frac{1}{3.5}\right) \times Mannan} \quad \mathbf{(3.10)}$$

$$\mathbf{Xylan = Arabian + Xylan} \quad \mathbf{(3.11)}$$

4 Results and discussion

4.1 Properties of the black liquor used

In all the experiments, softwood kraft black liquor was used.

The following table shows the most important characteristics of the black liquor used.

Table 7: The properties measured of the black liquor investigated

	DC (%)	Na (g/kg liq.)	K (g/kg liq.)	NaOH (g/kg liq.)	Na ₂ S (g/kg liq.)
Liquor	44.8	88.0	9.1	18.3	20.9

	Lignin UV (g/kg liq.)	Lignin Klason (g/kg liq.)	Acid sol. Lignin (g/kg liq.)
Liquor	163	140	34

4.2 Precipitation

Different conditions, temperature and pH, were used in order to obtain the best parameters to compare. It was difficult to obtain the same pH in the experiments; normally they differ by 0.1 or 0.2 pH.

The lignin concentration of the black liquor was measured as UV lignin and Klason lignin with different temperatures and pH, and the same ion strength (5% extra). This is present in a chart where the lignin concentration is plotted versus the temperature at different pH.

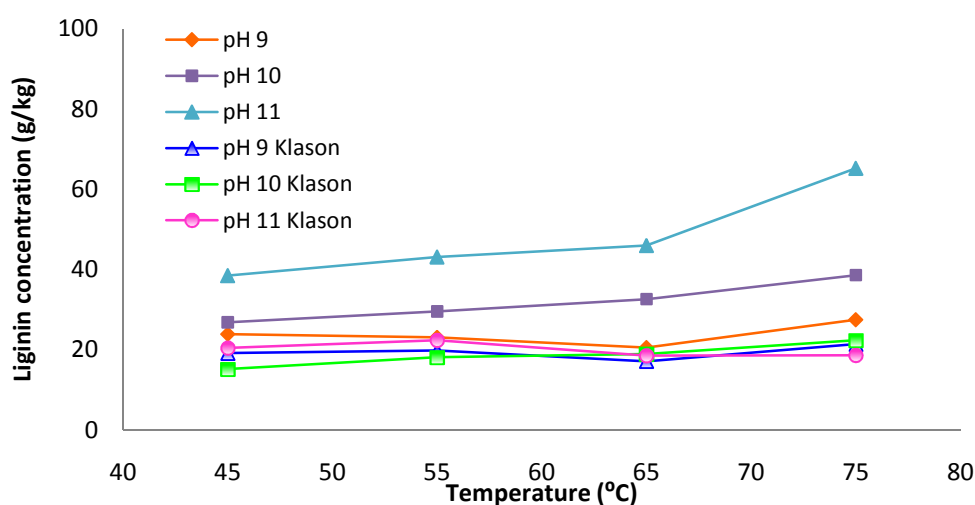


Figure 8: Concentration of lignin in the liquor (measured as UV and Klason lignin) versus temperature at different pH values

This figure shows that when the pH and the temperature decrease more lignin precipitates, which was in accordance with earlier studies.

This figure also shows there is a difference when the lignin concentration is measured using Klason method or the UV method with the standard absorption constants. In this work the standard absorption constant ($24.6 \text{ dm}^3/\text{g}\cdot\text{cm}$) was used, but this constant varies with the relative concentration of components that are absorbed at wavelengths around 280 nm. So, if a correct absorption constant has not been used, lignin-lean black liquor gives a wrong result what makes the Klason method preferred.

However, the Klason method has a higher consumption of time, and to monitor a process, the UV method may be faster and more practical. So, is important to determine an adequate numerical value of the absorption constant for the different conditions.

4.3 Yield

The precipitation yield was calculated as the difference in UV absorvancy or Klason lignin between the original black liquor and the filtrate. So, the yield is plotted versus the temperature at different pH, and with the same ion strength in the following figure:

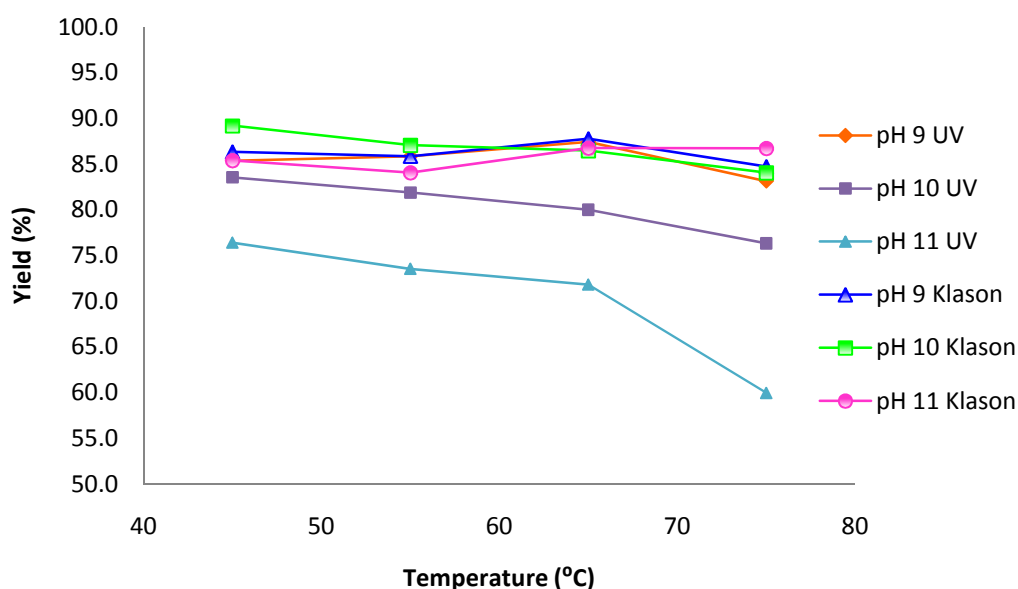


Figure 9: Yield (based on both UV and Klason lignin) versus temperature at different pH values

This chart shows that the yield in this precipitation step is influenced by some important process conditions, mainly by pH and temperature. When the pH is decreased, the influence of the other parameters seems to decrease.

It's also possible to see in this plot why is important to measure the lignin content correctly. When UV lignin was used with standard absorption constants, the yield is underestimated. And this fact, leads to a wrong optimization of the process, and as a consequence, increases in the cost for process chemicals.

4.4 Characterization of filtrates and precipitated lignin

Further analyses of the organic phase of filtrates and precipitated lignin, i.e. the determination of Klason lignin, acid soluble lignin and total carbohydrate content are shown in table 8.

Table 8: Klason lignin, acid soluble Klason and carbohydrate content of the filtrate and filter cakes

Denotation	Klason	Acid sol. Klason	Carbohydrates	Sum
(%w of DS)				
Filtrate	1.5	1.5	0.31	3.3
Filter cake				
pH 3	89.1	3.8	1.1	94.1
pH 1	90.5	4.1	0.63	95.2

The amount of the organic material is reduced considerably in the filtrates, where the Klason lignin content in particular is much lower. The amount of Klason lignin is of course high in the lignin filter cakes.

Analyzing only the filter cakes, is possible to observe through the values that the Klason lignin and acid soluble lignin are lower, and the carbohydrates (the sum of monosaccharides) is higher, at pH 1 than at pH 3.

The table 9 shown the composition of the carbohydrate fraction of the filtrate and filter cakes.

Table 9: Composition of the carbohydrate fraction in the filtrate and filter cakes.

Denotation	Arabian	Galactan	Glucan	Xylan	Mannan
(%w of carbohydrate fraction)					
Filtrate	25.6	37.1	9.4	22.5	5.5
Filter cake					
pH 3	13.0	29.2	26.1	28.7	3.1
pH 1	9.7	33.9	30.8	21.5	4.0

Observing the table, the fact of the concentration of glucan is higher in the filter cakes, and the concentration of arabian is higher in the filtrate is easy detected.

Analyzing only the filter cakes, between filter cakes pH 3 and pH 1, it's possible to see a small difference in the composition. The concentration of arabian and xylan are higher in the filter cake with pH 3.

5 Conclusions

The main propose of this thesis was study the precipitation step during the extraction of lignin from kraft black liquor when LignoBoost process is used, in terms of lignin concentration, yield and composition of the filter cakes and filtrates.

Regarding to the first subject, the most important conclusion in this part of the work was the difference found between the results obtained from measuring the lignin concentration using UV method and those obtained using the Klason method (with “standard” absorption constants). The best method for these experiments is Klason method. The used of the UV method with “standard” absorption constants underestimates the yield, which may lead to erroneous optimizations of the process and, as a consequence, a higher cost for process chemicals.

Furthermore, it was found that the yield in the precipitation step is influenced by: pH and temperature. Moreover, when the pH and the temperature decrease, more lignin is precipitated.

The composition of the precipitated solid was almost independent of the conditions in the precipitation and in the separation stage. The composition was almost constant and had a high content of Klason lignin (90%), some acid-soluble lignin (4%) and a low content of carbohydrates (0.8%). It was found an enrichment of glucan in the filter cakes.

6 Final assessment and future work

In this work has been initiated a studied about the precipitation operation of extracting lignin from black kraft liquor using the LignoBoost process: how the concentration of lignin after precipitation and the yield are influenced by some important process conditions (pH and temperature).

Some future work in this field is suggested below:

- Most of the research and development work related to LignoBoost process has so far been related to the filtration and washing of the lignin. It would be interesting to continue the research in the precipitation step.
- This work was focused on softwood kraft black liquor. More work is needed on different types of black liquor.

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Appendix 1– High-Performance Liquid Chromatography (HPLC)

The following figure is one example of the chromatograms obtained from the HPLC analysis. Each peak represents one of the monomer.

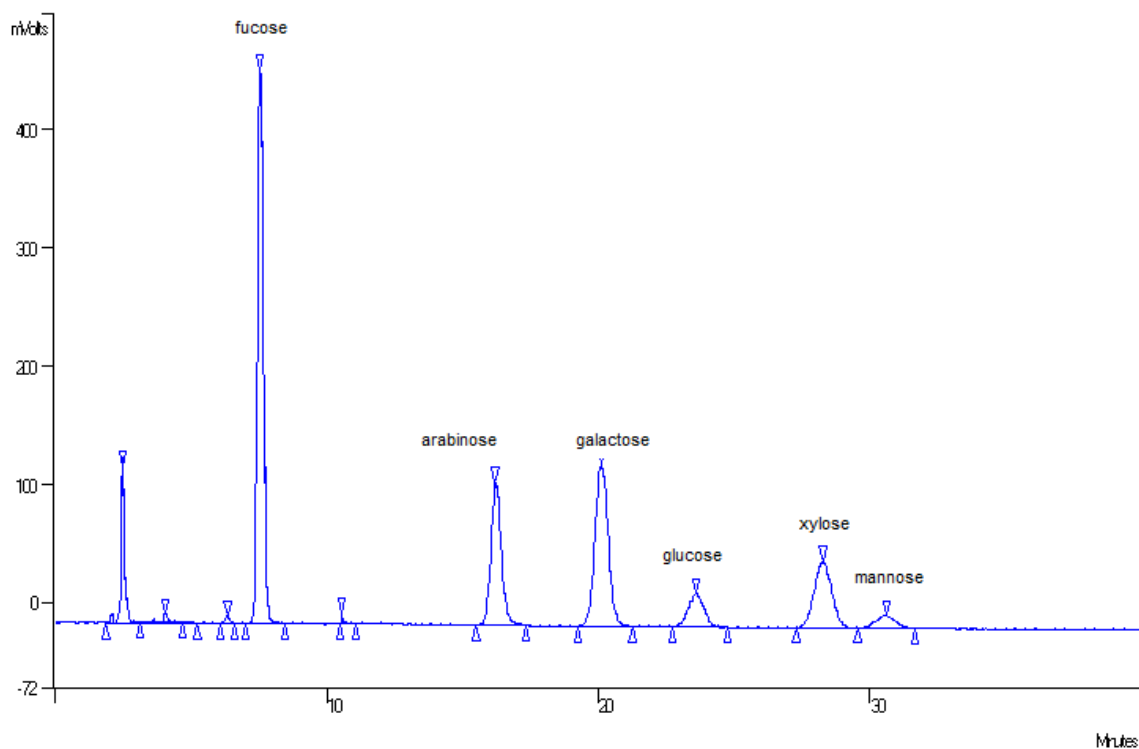


Figure 10: Example of HPLC image

Moreover, the HPLC analysis gives the exact area of each peak. That is shown in table 10.

Table 10: HPLC data

Peak no.	Ret. Time (min)	Area (counts)
1- fucose	7.540	6985283
2- arabinose	16.220	3221417
3- galactose	20.100	4627088
4- glucose	23.607	1086288
5- xylose	28.260	2486233
6- mannose	30.593	521376