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A case study of extractives and their effect on cooking performance.

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Cover:
Photograph of a twig of eucalyptus (left), black liquor (middle) and the development from eucalyptus wood chips to pulp (right). The development shows the pulp from different time intervals in the Kraft cook.

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Abstract

There is a growing interest for Eucalyptus within short fiber pulp production in Brazil. Due to the rapid growth and good pulp properties Eucalyptus represents a cheap and versatile raw material. Many of the Eucalyptus pulp mills in Brazil and other parts of South America are new and highly optimized which makes them sensitive to changes in wood composition of the wood feed stock. It is believed that the extractive content in the wood affects the cooking performance with a higher extractive content leading to higher alkali consumption. Since this may become a bottleneck for these highly optimized mills it is of interest to investigate further how these changes in composition affect the cooking performance.

In this project it is done by quantifying and characterizing extractives of 15 samples of Brazilian *Eucalyptus Urograndis* by GC/MS- GC/FID, GPC and NMR. In order to relate the extractives to cooking performance a batch Kraft cooking serie have been performed on selected samples. The black liquor and pulp obtained were then further analyzed by residual alkali, pulp yield, Klason lignin and carbohydrate analysis.

The results indicate that the extractive content varies significantly between the different samples and especially between clones. No correlation could be found between extractive content and region of plantation or age. Regarding the cooking performance, the results imply that the extractive content does not affect the alkali consumption nor the yield. However, some samples deviate more than others in cooking performance, indicating that other aspects of the wood composition might have a greater impact.

Keywords: Kraft pulping, *Eucalyptus Urograndis*, Extractives

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1. Introduction

Eucalyptus is a tropical tree that is very productive since it grows quickly and thrives in short rotation plantations. This, in combination with its good pulp properties, makes it at present the most important short fiber source within the pulp and paper production in Brazil [Silvério et al. 2007, 533-540].

There are large variations in the chemical composition between different eucalyptus species as well as eucalyptus grown in different geographical areas [Silvério et al. 2007, 533-540]. These variations are something that needs to be taken into consideration when converting the wood into products. Fluctuating amounts of some components might cause problems in one or more parts of the process. Studies have shown that the amount and composition of extractives in the wood differ depending on species, age, site, wood storage and seasonality [Morais & Pereira 2011, 704-719]. It is known that content and composition of extractives are important parameters in the wood processing for pulp and paper production. They can form pitch deposits (giving rise to colored specks in bleached pulp and paper) and contribute to the consumption of bleaching chemicals [Silvério et al. 2007, 533-540]. An increased extractive content in the wood is also found to contribute to a higher effective alkali demand in the cooking process [Da Silva Magaton et al. 2009]. From an economical point of view this is of course undesirable and a deeper knowledge of how the extractives in the wood affect the pulping process is essential.

1.1 Objective

The objective of this master thesis is to evaluate impact of genetic and environmental factors related to cooking behavior of *Eucalyptus Urograndis*. The focus will be on extractives as these are expected to reflect variation in environment and genotype.

The questions this report aims to answer are:

- Will genetic and environmental variations within the breeding program give effects on cooking behavior of eucalyptus?
- Can these variations be related to the content and composition of extractives? Which fraction is most significant in the cooking process?

1.2 Thesis outline

The thesis starts with a theoretical background where information is provided on the wood structure and morphology with special emphasis on eucalyptus. There is also a section on Kraft pulping. Thereafter experimental background is described where different methods and analyses are defined and explained in some detail for better understanding of how they work and their limitations. In the experimental method section there are descriptions of the laboratory approach. The experiments performed are explained in a way so they could be repeated.

Thereafter, the achieved results are presented and discussed. This includes a compilation of the extractive contents of the different samples, the results from GC/MS, GPC and NMR analysis of the extractives, the yield and residual alkali levels from the cooks and results from lignin and carbohydrates analyses. In the final section the conclusions drawn from the results are presented.

2. Theoretical background

In this section selected aspects of wood structure are explained including morphology and descriptions of the woods main constituents, with focus on the eucalyptus tree. Thereafter the Kraft process is described with all main steps starting with wood handling and continuing with cooking chemicals, steaming and impregnation, chemical reactions, cooking parameters and chemical recovery.

2.1 Wood Structure

When producing pulp, it is important to choose the right fiber resource to fit the desired product. The most common fiber resource in papermaking is wood. Wood from different tree species normally have different anatomies and are divided into two main groups, softwood and hardwood. Softwoods have a simpler morphology and are evergreen conifers Hardwood is genetically more evolved with a more complex morphology and its cells are more specialized. They are typically flowering trees [Henriksson, Brännvall & Lennholm 2009, 14-44]. This thesis work will focus on hardwood, in particular eucalyptus.

2.1.1 Morphology

The wood stem provides transport of water and nutrients between the roots and the leaves and also helps to expose the leaves to sunlight. When looking at a transverse section of a wood trunk different parts of the wood are visible. From the outside towards the center there are bark, inner bark, cambium, sapwood, heartwood and pith, each of them providing a mechanical support and more specialized functions The phloem (inner bark) provides liquid transport downwards of photosynthesis products and hormones. The cambium is where the growth takes place i.e. the cell division. Sapwood provides transport of water and nutrients upwards toward the leaves. The heartwood contains more extractives than sapwood and has a darker color. It consists only of dead cells and contributes mainly to the mechanical support of the tree [Henriksson, Brännvall & Lennholm 2009, 14-44].

In hardwood different cell types exist with specialized functions. Two of these are vessels and tracheids that provide transport of water and minerals in the tree. Other cell types are fibers that gives support and parenchyma cells that provide storage of extractives and starch. Between the wood cells there are pits, opening between the cells, which facilitate transport of water and nutrients. The wood morphology is important for processing of the wood since it influences how available the different components are to the chemicals [Daniel 2009, 45-70].

2.1.2 Wood cell wall structure and ultra structure

Wood cell walls consist mainly of three components called lignin, cellulose and hemicelluloses. The cellulose forms the skeletal matrix and it is surrounded by hemicelluloses and lignin. These different components will be described later in this section. It the cell wall they are arranged in a number of layers: primary (one layer) and secondary cell wall (2-3 layers).

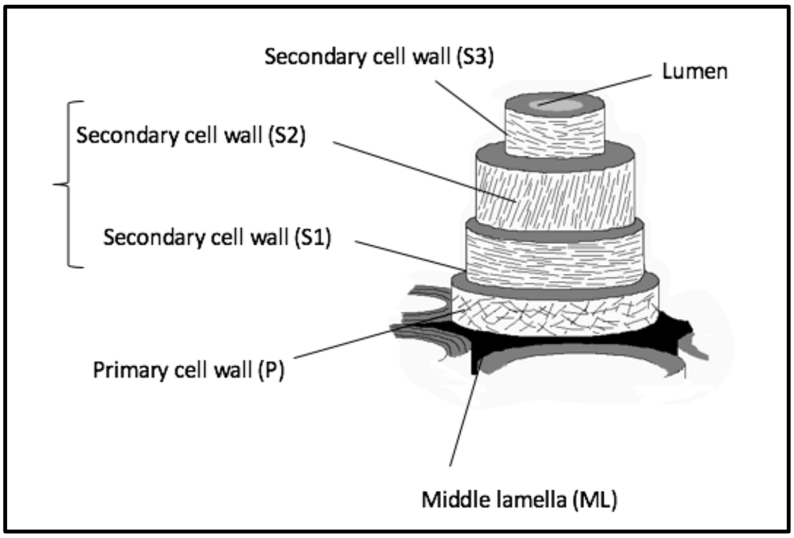

Figure 1. Ultra structure of a wood cell.

A typical ultra structure of a wood cell can be seen in Figure 1. The middle lamella (ML) that glues the individual cells together is a lignin rich region. However, only about 25-29 % of the total lignin is found in this region. The outer layer of a cell wall is called the primary cell (P) wall and it consist of randomly oriented cellulose microfibrils (these are explained in the next section). Inside the primary cell wall, the secondary cell walls (S1, S2 and S3) are found and the thickness of these layers varies between the cell types. The middle layer S2 forms the major part of the wood cell both in softwood and hardwood. The orientation of cellulose microfibrils is different in different layers. They wind around the axis in different directions and this orientation determines the physical properties of the wood cell. As seen in Figure 1 the S1 layer has almost horizontally oriented fibrils as in S3 while the S2 layer has almost vertically oriented fibrils [Daniel 2009, 60-65]. The S2 layer is of greatest importance due to its thickness and it is the main factor affecting the physical properties of the wood. The cellulose orientation in this layer is determined using a term called mirofibril angle (MFA).

This is the angle between the cellulose microfibrils in the secondary cell wall and the longitudinal cell axis [Barnett and Bonham, 2004]. The MFA can have significant variations between early and late wood (early wood is formed in the spring and late wood in the fall), juvenile or mature wood and between different clones of the same specie.
The chemical structure of the cell wall layers varies between different cell types and there are also considerable differences between hardwoods and softwoods. However, the content of hemicellulose and lignin is highest in the primary wall and is significantly lower in the S-layers (especially S2), where cellulose is the dominating component [Daniel 2009, 60-65].

2.1.3 Molecular structure

In hardwood approximately 45 % of the wood consist of cellulose, 30 % of hemicelluloses, 21 % of lignin and 4 % are extractives [Henriksson, Brännvall & Lennholm 2009, 14-44].

2.1.3.1 Cellulose

Cellulose is a linear polymer of glucose monomers linked together with β-1,4-glycosidic bonds forming a cellulose chain. Wood cellulose has an average degree of polymerization (DP) around 8 000. When biosynthesis of cellulose in wood takes place the cellulose is polymerized and aggregated, forming cellulose microfibrils. In these microfibrils t the cellulose chains form sheets that are held together by hydrogen bonds. These sheets are then further layered on top of each other by van der Waals bond and hydrophobic interactions [Henriksson & Lennholm 2009, 71-100].

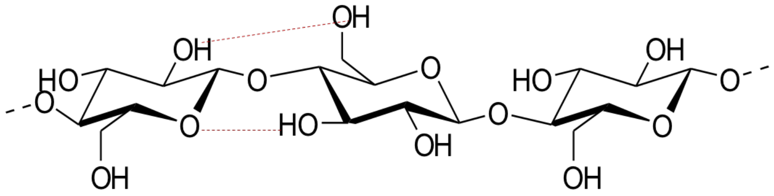

Figure 2. Cellobiose structure which consist of two anhydrous glucose units

2.1.3.2 Hemicelluloses

Hemicelluloses are heterogeneous, branched polymers built up of different kinds of sugars. They are like cellulose structural carbohydrates and they form the bulk of the trees supporting structure. Hemicellulose are however more easily degraded than cellulose during pulping. The polymers are compared to cellulose very short with only about 100 - 200 units. The composition of hemicelluloses is different in softwood and hardwood. The most important hemicelluloses are xylan, glucomannan and xyloglucan [Teleman 2009, 101-120].

Glucomannan is dominating in the cell walls in softwood and its main chain is built up by glucose and mannose monomers. In hardwood the glucose: mannose ratio varies between 1:2 and 1:1 depending on wood specie. The monomers are linked together with β-1,4-glycosidic as in cellulose, however it is acetylated and has side groups of galactose. In softwood the ratio of galactose to glucose to mannose units of 0.1:1:3-4 while in hardwood galactose units are very infrequent or absent. The acetyl groups are easily cleaved under alkaline conditions and the acetate formed in Kraft pulping predominantly originates from these groups. There is typically one acetyl group for every 3-6 backbone hexose units. Glucomannans undergoes extensive peeling reactions during Kraft pulping. [Teleman 2009, 101-120].

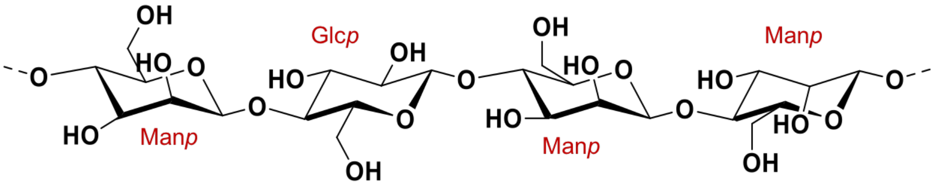

Figure 3. Glucomannan structure with mannose monomers (Manp) and glucose monomers (Glcp).

Xylans has a backbone of xylose monomers and side groups of methylglucuronic acids. Softwood xylans are more acidic than the xylans in hardwood since there is a higher content of methylglucuronic acid. Softwood consist of about 5-10 % of arabinoglucuronoxylan. In this xylan there is on average one methylglucouronic acid side group per 5-6 xylose units. This xylan is also substituted with a α-L-arabinofuranose. Hardwood xylan on the other hand has acetyl groups. In its xylan there is there is on average one methylglucouronic acid side group per 8-20 xylopyranosyl units and approximately 4-7 acetyl groups per 10 xylopyranosyl units. The acetate groups are easily cleaved off and the acetic acid formed in Kraft pulping mainly originates from these groups. During Kraft pulping the peeling reaction on the reducing end groups is the most significant carbohydrate reaction at alkaline conditions but in xylan the side groups stabilize against peeling. The dissolved xylan can also readsorb onto the fibers at lower alkali without being degraded. Therefore, xylan is relatively resistant to the Kraft process and it remains to a high extent in chemical pulps, where the xylan may have a significant impact on the pulp properties [Teleman 2009, 101-120].

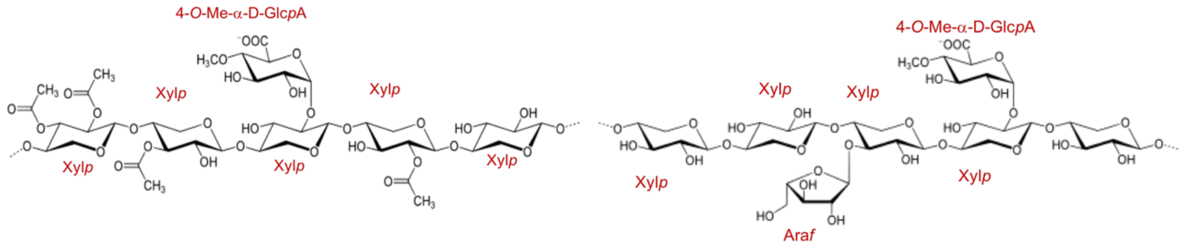

Figure 4. To the left: Glucuronoxylan fount in hardwood with xylose residues (Xylp), acetate side groups and methylglucuronic acids (4-O-Me-α-D-GlcpA). To the right: Arabinoglucuronoxylan found in softwood with xylose residues, arabinose side groups (Araf) and methylglucouronic acid (4-O-Me-α-D-GlcpA).

Xyloglucan is dominating in the primary walls of most plants. The molecular structure is similar to that of cellulose with a glucose backbone of 1,4 β-glucosidic bonds but with side chains of xylose, galactose and fucose monomers. It is easily soluble in water and creates strong bonds with cellulose [Teleman 2009, 101-120].

2.1.3.3 Lignin

Lignin is an irregular, branched phenolic polymer and it functions as a "glue" that binds the wood fibers and the cellulose fibrils together into woody tissues. Lignin provides stiffness to the cell walls, makes the cell walls hydrophobic and protects against microbial degradation. Lignin is polymerized from three monomers called monolignols. These are phenolic alcohols differing in the number of methoxy-groups that are attached to the ring. The content of these monolignols are different between softwood, hardwood and grass lignin. The total amount of lignin also differs between the different categories (15-35 % for softwood and around 20 % for hardwood) [Henriksson 2009, 121-146].

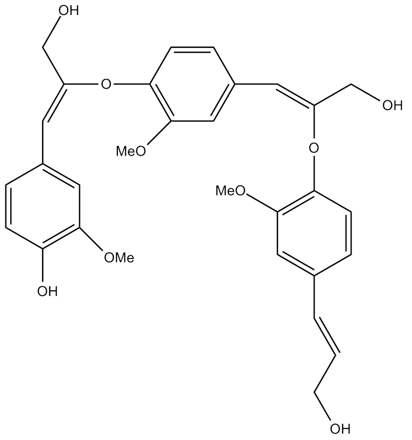

Figure 5. Three monolignols linked together with the most frequent lignin bond, the β-O-4 ether bond (figure drawn by Jonas Wetterling).

2.1.3.4 Extractives

Wood extractives are compounds with lower molecular weight that can be extracted from the wood with organic solvents or water. They have different functions in the wood such as protection against fungi and insects, plant hormones or act as an energy source. Extractives usually only represent a small fraction of the wood. However, it can be larger in parts like the bark and branches and it is higher in heartwood than in sapwood. The extractive content also normally increases in wounded wood. There are large variations in structure and composition between wood of different species, wood grown at different sites and in different parts of the wood. Water soluble (hydrophilic) extractives normally occur in small amounts. Lipophilic extractives are divided into three groups; Terpenes and terpenoids, fats and fatty acids and phenolic extractives [Björklund, Jansson & Nilvebrant 2009, 147-172].

Terpenes and terpenoids are present in resin canals and parenchyma cells. They are all built up of isoprene units with 5 carbons and the main groups are monoterpenes (C10), sesquisterpenes (C15), diterpenes (C20) and triterpenes (C30). Oxygen containing terpenes are often called terpenoids. Sterols and sitosterols comprise a special group with a tetracyclic ring system. In wood there is a clear difference in terpene composition between hardwood and softwood. Softwoods terpenes include both monoterpenes, sesquiterpenes, diterpenes and sterols. Hardwoods contain mainly sterols, triterpenoids and higher terpenes [Björklund, Jansson & Nilvebrant 2009, 147-172].

Fats and fatty acids exist predominantly in parenchyma cells and represent a significant part of the extractives in wood. The dominating fatty acids in most wood species have even chain lengths of C16-C24, but acids from C10 to C28 can be found. Some branched chain fatty acids such as anteisoheptadecanoic acid are also often present. The unsaturated C18 fatty acids such as oleic, linoleic and linolenic acid are normally the main constituents [Björklund, Jansson & Nilvebrant 2009, 147-172].

Phenolic extractives exist mainly in heartwood and bark. It contributes to the color of wood and has a fungicide effect. Since these compounds are water soluble they are dissolved during cooking. However, they can be found in acetone extracts of wood and mechanical pulps. Examples of phenolic extractives are lignans, stilbenes, flavonoids and tannins [Björklund, Jansson & Nilvebrant 2009, 147-172].

2.2 Eucalyptus

Most eucalyptus species originate from Australia but have been cultivated in tropical and temperate areas. In most areas the cultivation has been successful and eucalyptus is widely planted for its rapid growth and rotation abilities. This makes it suitable for various uses such as for fuel, construction material and pulp wood. It is especially interesting within short fiber pulp production due to various characteristics that leads to good paper and pulp quality [Silvério et al. 2007, 533-540]. The specific properties eucalyptus fibers give to paper are bulk, opacity, porosity, softness, smoothness, formation, absorbency and dimensional stability. This pulp requires less energy to reach the same tensile strength and therefore porosity and volume are improved. Eucalyptus pulps are rich in fines, fiber debris and intra-fiber capillaries. Fines are important for bonding which creates a stronger paper [Holland 2009].

Eucalyptus Urograndis is the main species for pulp production in Brazil. It is a hybrid of *Eucalyptus Grandis* and *Eucalyptus Urophylla*. It was developed aiming at combining the wood quality of *E. Grandis* with the higher canker (a tree disease) resistance and wood density of *E. Urophylla* [Gominho et al. 2001].

Studies by Gomide et al. (2005) have shown that the composition of Brazilian eucalyptus is approximately 43.9-49.7 % cellulose, 18.6-23.2 % hemicellulose, 27.5-31.7 % lignin and 1.76-4.13 % extractives. As mentioned earlier the amount of extractives in heartwood are larger than in sapwood. For *E. Urograndis* it has shown to be twice as large in heartwood compared to sapwood (7.6 % vs 3.7 %). The heartwood content is related to tree age and the heartwood formation starts at about five to eight years of age [Gominho et al. 2001]. Other studies have shown that 0.35 % of dry wood basis in *E. Urograndis* are lipophilic extractives. This is higher than *Eucalyptus Globulus* (0.26 %) but lower than other hardwoods for example *Acacia Mangium* (1.32 %). Sterols are the major lipophilic compounds in eucalyptus wood, particularly after hydrolysis, but fatty acids, long chained aliphatic alcohols and aromatic compounds are also main components of the lipophilic fraction. For other hardwoods sterols also occur but not to the same extent as in eucalyptus wood [Freire et al. 2006, 3-17].

2.2 Kraft pulping

Today Kraft pulping (also known as sulfate pulping) is the dominating pulping process. The use of sulfide ions gives selectivity to the delignification which is necessary to produce strong pulp. The Kraft process can be found all over the world and the pulps are used for a large variety of products. A typical outline of a Kraft pulp mill can be seen in Figure 6 [Gellerstedt 2009a, 92]

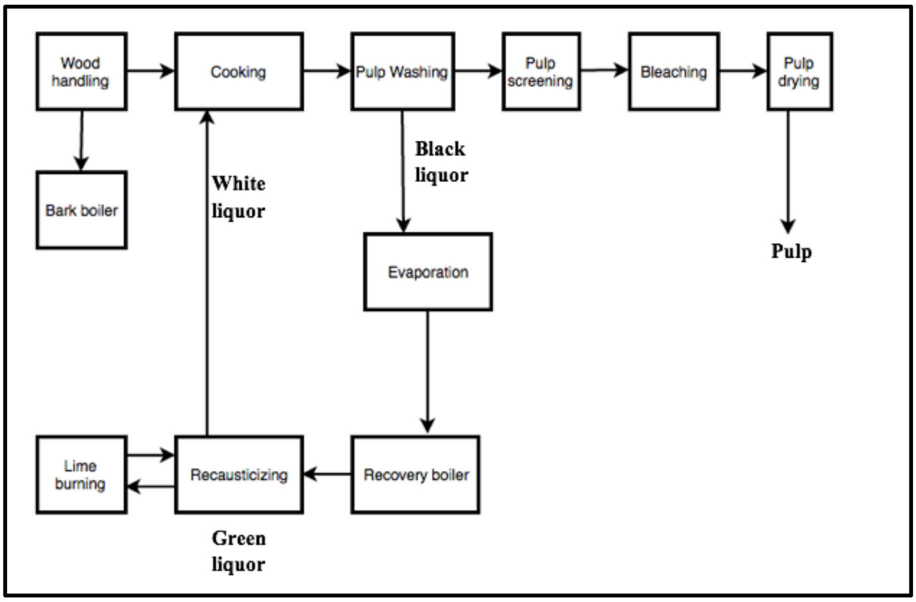

Figure 6. Schematic picture of the Kraft cooking process.

2.2.1 Wood handling

The first step in wood handling is the debarking. There are several reasons to remove the bark. First of all, there is a low fiber proportion in the bark and during chemical pulping only about 20 % of these can be retrieved. The second reason is that the extractive content is high in the bark and these will consume chemicals both in the cooking and bleaching steps. Further the bark may also contain dirt and sand which can cause damage to the process equipment. If not degraded during the cooking and bleaching it can also lead to unwanted spots in the paper. Different species of wood needs different amount of force to be debarked. The species of interest in this study, eucalyptus, is in the group of tropical hardwoods and is relatively easy to debark.

After debarking the wood need to be chipped. It is desired that the chips have a uniform geometry to make sure that they are evenly cooked. If the chips are small, it will make the shive content of the pulp lower. A shive is a part of a wood chip that has not been fully cooked. However, with small chips there is a higher risk for fiber damage which can result in reduced pulp strength. The reason is that the damaged parts in the fibers are more accessible for cooking chemicals and this will make the reactions take place much faster in these areas. The last step of the wood handling is storage. The storage has several purposes. First of all, it gives the mill a buffer of raw material. The second purpose involves both oxidative and enzymatic decomposition of different components in the wood, especially the extractives. To make sure that the size distributions of the chips are in the right range and not varying, a screening of the wood chips takes place after the chipping. If this range varies to much it can cause an uneven quality of the pulp [Gellerstedt 2009b, 13-34].

2.2.3 Cooking chemicals

In this section the active cooking chemicals in the Kraft process will be described together with formulas to calculate the amount that should be charged to the cooking process.

In the Kraft process the cooking liquor, called white liquor, consists mainly of sodium hydroxide (NaOH) and sodium sulfide (Na_2S) dissolved in water The active cooking chemicals in this solution are the hydroxide (OH^-) ions and the hydrogen sulfide (HS^-) ions. The amount of chemicals that needs to be charged is expressed as effective alkali (EA) since the total amount of OH^- cannot be expressed as the amount of NaOH. The reason for this is that the Na_2S is hydrolyzed into both OH^- and HS^- according to the following equilibrium reaction:

$$S^{2-} + H_2O \Leftrightarrow OH^- + HS^- \qquad (1)$$

Worth mentioning is that the HS^- can be further hydrolyzed, as shown below:

$$HS^- + H_2O \Leftrightarrow H_2S\,(aq) + OH^- \qquad (2)$$

This means that the S^{2-} can be present as either S^{2-}, HS^- or H_2S in solution. However, since the cooking takes place under alkaline conditions the equilibrium in Eq. 1 is pushed towards the right meaning that it will be predominantly present as HS^-. This leads to the following expressions for the EA.

$$EA(mol) = n_{NaOH} + n_{Na_2S} \tag{3}$$

$$EA\left(\frac{mol}{l}\right) = [OH^-] \tag{4}$$

The amount of sulfide that needs to be added is instead expressed as sulfidity which is related to the amount of alkali added. The amount of this depend on the recovery system of the chemicals and the equation for the sulfidity looks as follows, when expressed using the ions:

$$Sulfidity\,(\%) = 100\,x\,\frac{2[HS^-]}{[HS^-]+[OH^-]} \tag{5}$$

The most convenient way to calculate the amount of chemicals that needs to be added in a cook is to express the effective alkali as a percentage on the basis of dry wood.

$$EA(\%) = 100\,x\,\frac{m_{NaOH}+\frac{1}{2}m_{Na_2S*}}{m_{wood}} \tag{6}$$

Notice that the mass of Na_2S* in Eq. 6 is expressed in mass of Na_sS that is equivalent to NaOH. The expression for this can be seen in Eq. 7. Important to mention is that in North America the Na_2S and NaOH are instead expressed as the amount of Na_2O [Brännvall 2009, 134-138].

$$m_{Na_2S*} = \frac{M_{Na_2S}}{2M_{NaOH}}\,x\,m_{Na_2S} \tag{7}$$

As seen in Figure 6 the liquor after the cooking section is called black liquor and contains the residual alkali, organic material and water.

2.2.5 Steaming and impregnation

This is the first step of the actual cooking process. Both steaming and impregnation are important to make sure that the woodchips get an equal amount of chemicals during the same cooking time and temperature. The purposes with the pre-steaming of the wood chips before impregnation are both to heat up the wood chips but also to remove the air within the lumen (cavity) of the wood cells so that the chemicals later can penetrate more easily. The air is removed with different mechanisms and the first one is thermal expansion. This means that when the steam is heating up the air it expands and it is thereafter displaced. The second mechanism can be described with vapor pressure. When the moisture inside the wood chips is heated the pressure will increase and the moisture will then be pushed out. The third mechanism is the partial pressure gradient that causes air to diffuse out from the wood chips since the environment outside is saturated with water vapor.

After the pre-steaming the next step is impregnation where the white liquor is mixed with the wood to transport the cooking chemicals into the chips. There are two known mechanisms that describe the distribution of the cooking liquor within the wood chips.

The primary penetration of the liquid occurs through advection. As mentioned earlier hardwood libriform cells have pits and the vessels have different kind of pores and lumen, where liquid is transported. However, the transport is about 50 - 200 times slower in the tangential and radial direction compared to the longitudinal direction. There are important differences between sapwood and heartwood that may give a lower degree of penetration for the latter. The first one is that heartwood cells are filled with extractives and the second is the moisture content. This is since the pits in heartwood and dried wood may have been closed meaning that there may be more air in this volume. This highlights the importance of steaming and removing of air within the lumen to have good penetration of the liquid. Higher pressure and temperature as well as increased time of steaming results in better removal of air. Hence a better penetration can be achieved

The secondary penetration is caused by diffusion. This step is similarly to the primary penetration also faster in the longitudinal direction, since the available surface area is larger in this direction. However, this evens out during the course of the cook. The available surface area is one of the parameters for diffusion according to Fick’s law. However, Fick’s law also depends on the concentration gradient together with the size of the ions. The diffusion will also depend on the degree of the delignification that has taken place since the more lignin that is removed the more porous is the cell wall. This will reduce the differences in surface area available between the different directions. Two other variables affecting the diffusion are the amount of EA and the pH value that is related to the amount of EA left in the liquor [Brännvall 2009, 139-141].

2.2.6 Chemical reactions during Kraft pulping

The main purpose of pulping is to liberate the fibers from the wood matrix by removal of lignin. This is done by chemical fragmentation of lignin and introduction of charged groups, which leads to an introduction of ionizable hydrophilic groups. This is achieved by cooking of the wood with white liquor under certain conditions. During the cook all chemical building blocks of the wood cell wall will be affected but to different extents.

Delignification

The most important delignifying reaction is the breakage of aryl glycerol-β-aryl ether structures (β-O-4 bond) between the phenylpropane units in the lignin structure which fragments the lignin. There are two types of these structures, phenolic and non-phenolic. The phenolic β-O-4 structure is broken due to the action of the hydrogen sulfide ions. This reaction is made possible due to the alkaline conditions in the cook which forms a quinone methide from the phenolic benzyl alcohol structure as seen in Figure 7. Due to the presence of the hydrogen sulfide ions it will form an equilibrium with a benzyl thioalcohol structure. It is in the next step that the β-O-4 bond is broken through a nucleophilic attack of the thiol on the β-C and forms a new phenolic end group and an episulfide.

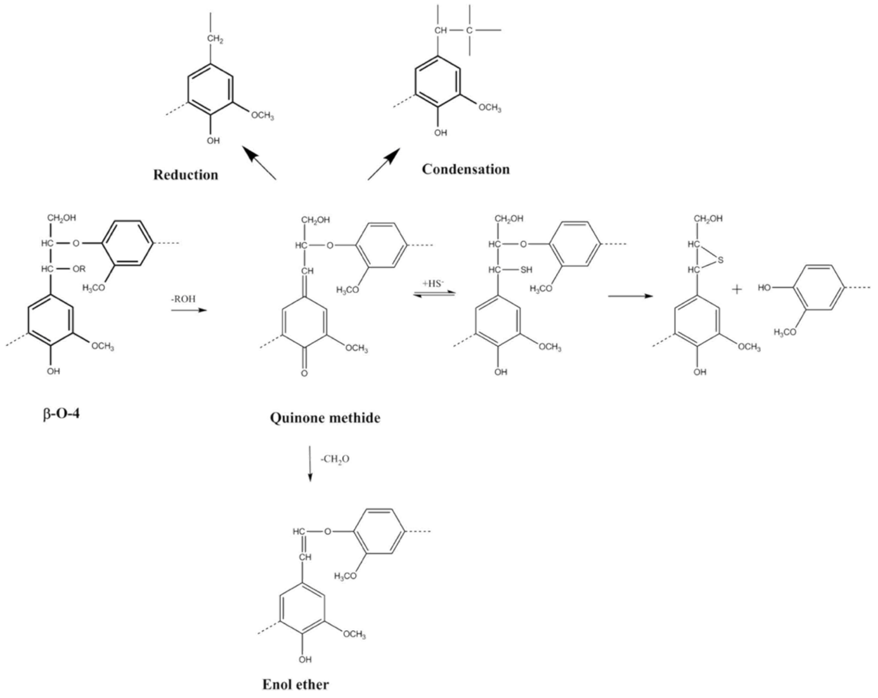

Figure 7. Reaction scheme for the cleavage of phenolic β-O-4 structures in lignin. Redrawn from Gellerstedt (2009).

The latter is not stable and will in turn lose elemental sulfur that will form polysulfides in the cooking liquor. Since Kraft cooking is done under alkaline conditions these will latter disproportionate and form hydrosulfide and thiosulfate ions. As seen in the reaction path in

Figure 6 there are also competing reactions taking place at the quinone methide intermediate and one is the loss of the γ-hydroxymethyl group which will form a stable enol ether without the β-O-4 bond being cleaved. This will slow down the delignification. Other reactions that might take place are the condensation and reduction reactions.

During the Kraft cook there is also cleavage of non-phenolic β-O-4 structure as seen in Figure 8. Instead of depending on the hydrosulfide ion to be cleaved as for the phenolic structure, this mechanism depend on the presence of α-hydroxyl group. This can be ionized during the alkaline Kraft cook and as such perform a nucleophilic attack on the β-C leading to cleavage of the β-O-4 linkage [Gellerstedt 2009a, 97-106].

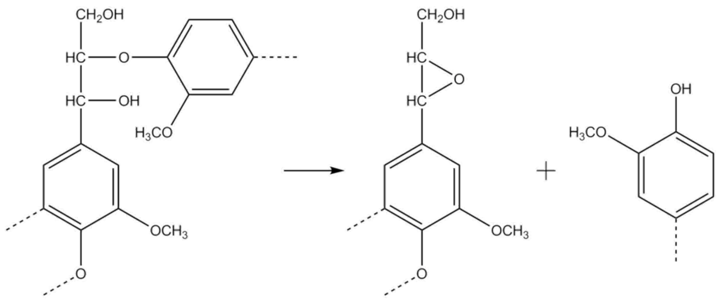

Figure 8. Reaction mechanism for the cleavage of the non-phenolic β-O-4 structures in lignin. Redrawn from Gellerstedt (2009).

On way to describe the delignification process is to divide it into three different phases. These can be obtained by plotting the decrease of lignin content towards the time of the cooking:

- Initial phase – In this phase the extractable lignin will be dissolved. This process proceeds fast and take place below 140°C
- Bulk phase – This is the most selective delignification phase and where most of the degradation and dissolution of lignin take place. In this phase the degradation of carbohydrates is low.
- Residual phase – This phase should be kept as short as possible since the selectivity for degradation of lignin is low.

However, there is a debate about whether it should be described in this way or not. It is important to understand that the delignification is a complex matter and that it is hard to describe.

Carbohydrate reactions

Except for the delignification there are also some side reactions with the other wood components. During the first part of the cook (impregnation and heating up period) the acetyl groups in the hemicelluloses will be hydrolyzed and thereafter split off. Temperatures around 100 °C are enough for the peeling reaction seen in Figure 9, to start. This means that the reducing end group on the carbohydrate chain will go through rearrangement and latter be eliminated which creates new reducing end groups.

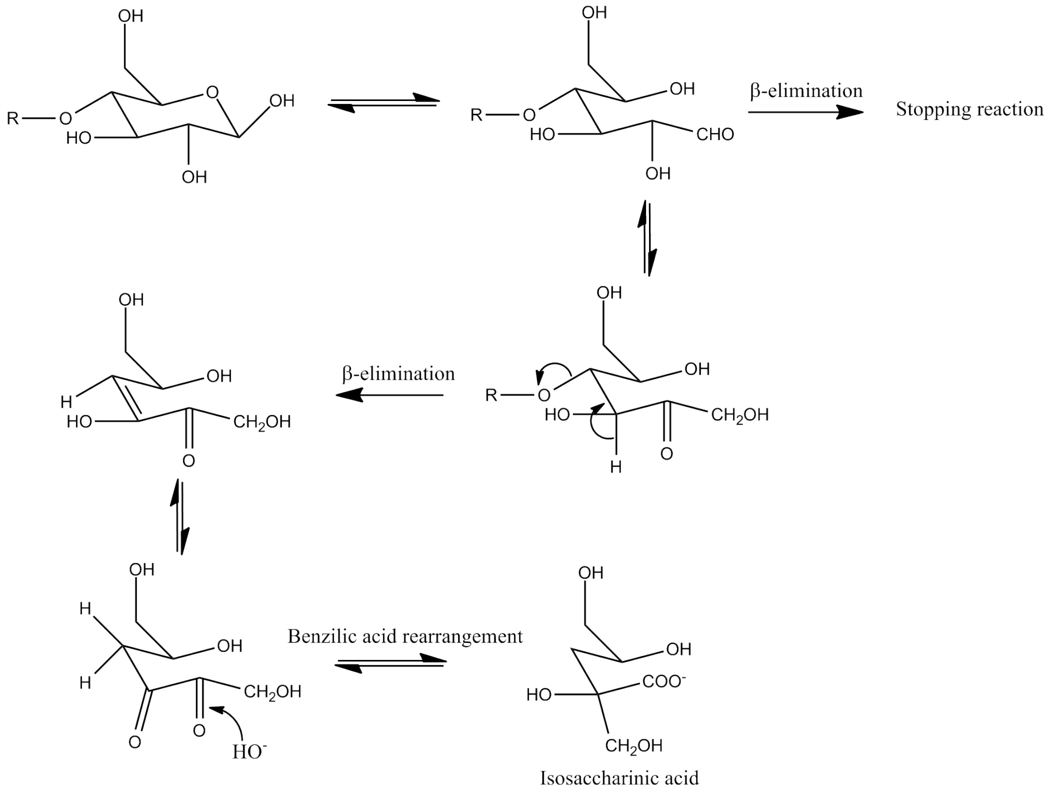

Figure 9. Peeling reaction (end-wise degradation) on a cellulose or glucomannan chain. Figure drawn by Jonas Wetterling.

This will continue until a stopping reaction occurs after approximately 50-100 monomers have been eliminated [Gellerstedt 2009, 105]. This reaction stabilizes the end groups by creating an alkali stable structure. At temperatures reaching above 130 °C alkaline hydrolysis will start to have an impact on the carbohydrates and as the temperature increases so does the speed of the reaction. Alkaline hydrolysis attacks random bonds between the carbohydrate monomers on the polymeric chain and creates new reducing ends which are subjected to secondary peeling until a stopping reaction occurs.

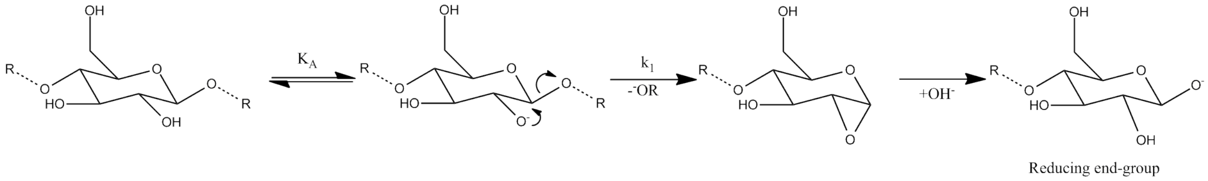

Figure 10. The reaction mechanism of alkaline hydrolysis. Figure drawn by Jonas Wetterling.

During the cook approximately 40 % of the carbohydrates are degraded and dissolved but this varies depending on cooking conditions. The main loss is due to the degradation and dissolution of the hemicelluloses [Brännvall 2009, 142-143].

2.2.7 Influences of cooking parameters and kinetics.

There are several variables affecting the cooking process. One of these is the temperature, which is gradually increased from the pre-steaming step until the final cooking temperature is reached. Other variables are the concentrations of the active cooking chemicals, HS^- and OH^-. The hydroxide is consumed during the cooking process. It neutralizes the acid groups and reacts with the alkali sensitive structures in the carbohydrates, acts on the reactive ether bonds in lignin (fragmentation) and keeps the dissolved lignin in solution. The hydrogen sulfide ion is responsible for the main part of the delignification and the reason why it goes much faster compared to cooking with only hydroxide ions. Therefore, is has a positive effect on the carbohydrate degradation. If the cook can terminate earlier, it will be less degraded. How fast the delignification proceeds is strongly dependent on the alkali concentration. With increased alkali the rate will increase as well.

As mentioned, the most abundant hemicellulose in hardwoods are xylans and the dissolution of these follows the dissolution of lignin, with respect to rate. There are small losses below 130 °C and these consist mainly of soluble xylan but as the temperature is increased the peeling reactions becomes more substantial, which leads to higher losses. However, some of the xylans will be dissolved and readsorbed on fibers at lower alkali concentrations without being degraded. The significant yield loss at higher alkali depend partly on the higher dissolution but also on that less of the dissolved xylan is readsorbed. Increased alkali concentration also degrades cellulose to a higher degree. This leads to shorter polymeric chains and therefore a lower pulp strength [Brännvall 2009, 144-147].

2.2.8 The effects of extractives during Kraft pulping – Problems associated with increased extractive content.

The type of extractives and the amount in the raw material affects the pulping in many ways. One of the effects may be increased consumption of cooking chemicals (Morais & Perreia 2011). Even though much of the chemicals can be recovered there is a limitation of how much of these that can be handled and still make the recovery both efficient and economical. This means that the pulping yield will be affected when there are larger amounts of extractives that react rapidly with the chemicals. Examples of extractives that will react rapidly with sodium hydroxide are the acidic and polyphenolic extractives. This will reduce the amount of alkali available for the delignification, which will lower the pulping yield [Hillis 1962, 375].

However, it is not only the amount of chemicals that are affected, the extractives will also influence the penetrability of the liquor into the wood. As mentioned earlier the heartwood is harder to penetrate due to that there might have been closures of the pits. However, it might also be due to that it has been covered with extractives. The extractives seem to accumulate in parts of the tree that are used for primary penetration, which in hardwood are the vessels where the Tyloses reduce the penetrability. Tyloses are are outgrowths on parenchyma cells surrounding the vessels. Another problem is that when the cooking liquor moves through the wood chip it will react with the extractives in its path. This means that when the cooking liquor reaches the fiber cell wall it might have been weakened, and this will therefore affect the delignification rate negatively [Rowe 1989, 885-887].

A consequence that especially regards the lipophilic extractives are that they can cause problems as they deposit on equipment and give rise to dark spots on the paper. The surface-active extractives may affect the surface properties of the paper [Björklund-Larson & Nilvebrant, 2009, 147-172]. However, it is important to understand that it is not only the content of lipid extractives that are important but also the composition. It is therefore important to further investigate what kind of lipophilic extractives are present [Prinsen et al. 2012].

2.2.4 Recovery cycle

This is the part within the pulp mill where the used chemicals in the black liquor are converted back into new white liquor that can be used in the digester. It also utilizes the latent heat in the dissolved organics. When the black liquor is burned in the recovery boiler a smelt is formed. This smelt goes into the recovery cycle outlined in Figure 11. The smelt consists mainly of sodium carbonate ($NaCO_3$) and sodium sulfite (Na_2S). When being dissolved in weak white wash, green liquor is formed. This green liquor goes through the slaker and into the causticization vessel where sodium hydroxide (NaOH) and new white liquor is obtained [Theliander 2009, 297-298].

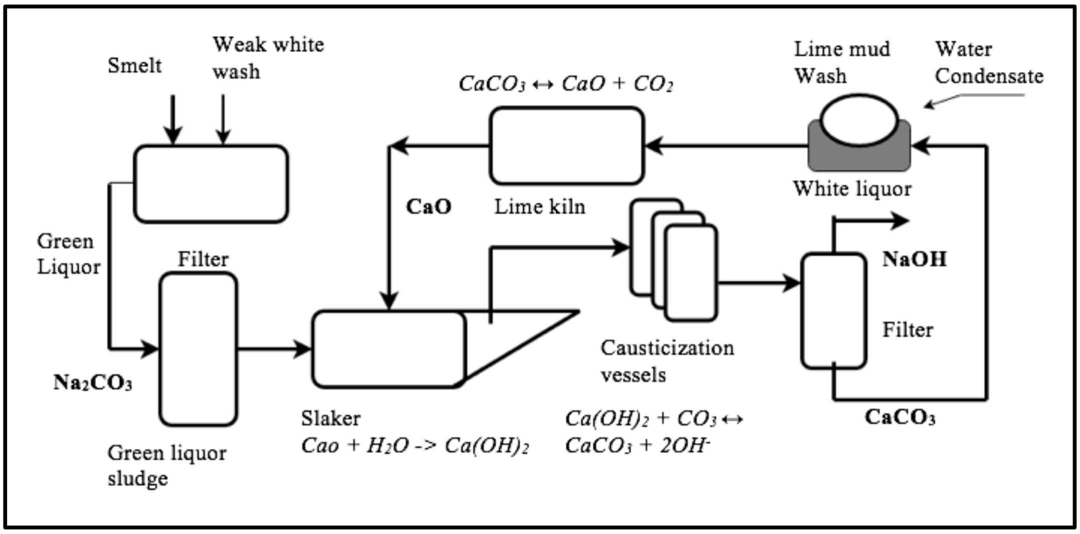

Figure 11. The recovery cycle and all reactions taking place.

Apart from the active cooking chemicals, the white liquor from the recovery cycle also contains other compounds. Some of these are the counter ions (Na^+, Ca^+ and K^+) and sodium carbonate ($NaCO_3$) that originates from the recovery system shown above. It is formed due to incomplete conversion of sodium carbonate to hydroxide. Further there may be thiosulfate and other sulfuric compounds present. In addition to these examples there may be many other compounds present in some processes. These are referred to as ballast. It is important to monitor these since they give contributions to the ionic strength of the liquor which affects the solubility in the cook [Brännvall 2009, 134-135].

3. Experimental background

This section contains short theoretical backgrounds to the analytical methods and experiments used in the project.

3.1 Extraction of extractives

A Soxhlet apparatus is an automated batch extractor. It has three main parts, a percolator (boiler and reflux) circulating the solvent, an extraction chamber where the solid sample is placed in a thimble (typically made of thick filter paper), and a siphon mechanism which periodically empties the thimble. On top of the Soxhlet apparatus a cooling unit with circulating water is placed to condensate the vapor formed when the solvent is heated up.

During a typical Soxhlet extraction the solvent is heated until boiling and the vapor then goes through a distillation arm. When it reaches the top of the thimble it is condensed by the cooling unit and drips into the thimble containing the sample. The extraction chamber will slowly be filled up by the solvent that extracts the desired compound from the sample. When it is full the siphon mechanism will empty the chamber into the distillation flask and it will start to fill up again with fresh solvent. This mechanism will make sure the concentration gradient in the solvent is kept low during the extraction period, thus making the extraction more efficient. After a specified number of cycles, the desired compound is concentrated in the distillation flask and the solvent can be removed. What will be extracted from the solid sample depend on the solvent used [Jensen 2007, Lugue de Castro & García-Ayuso 1998].

3.2 Gas Chromatography

In gas chromatography the sample is volatilized and brought through a coated glass capillary column by an inert carrier gas (mobile phase). The stationary phase is the coating inside the column and the time it takes for a substance to pass is called its retention time. This is specific for different compounds and can thus be used to determine which substances are present in the sample by comparing with a reference.

Gas chromatography mass spectrometry (MS) is a method that combines gas chromatography with mass spectrometry to identify different substances within one sample. It even allows for analysis and detection of low amounts of the substance. In GC/MS the substances leaving the GC are fragmented by electron impact. Subsequently the fragments are detected and the spectrum obtained can be used to identify the molecules. In order for a compound to be determined by GC/MS it has to be sufficiently volatile and thermally stable [Sparkman, Penton & Kitson 2011].

Flame iodization detector (FID) is the most widely and successfully used gas chromatographic detector for volatile hydrocarbons and many carbon containing compounds. It passes sample and carrier gas from the column through a hydrogen-air flame. When an organic compound is burned there is an increase in ions produced by the flame. A polarizing voltage attracts these ions to a collector located near the flame. The current across this collector is proportional to the rate of ionization which in turn depends upon the concentration of hydrocarbons in the sample. This current is sensed by an electrometer, converted to digital form and sent to an output device [Harris 2010, 581].

Generally, polar compounds are derivatized prior to GC analysis to enhance/enable vaporization. Compounds can be derivatized if they contain reactive functional groups such as hydroxyl, carboxyl etc. These functional groups are then converted into various ethers and esters. Since extractives may contain a significant amount of polar compounds it was necessary to add a derivatizing reagent into the vials before running the samples on the GC/MS [Sparkman, Penton & Kitson, 2011].

3.3 Gel permeation chromatography, GPC

Gel permeation chromatography is a type of size exclusion chromatography. It separates the analytes based on molar weight or hydrodynamic volume. The separation is achieved by porous beads packed in a column. This porous packaging material is the gel and it is used as the stationary phase. The mobile phase should be a good solvent for the sample, wet the packaging material and permit high detector response. Smaller molecules enter the pores more easily, making the distance they travel longer and leading to a longer retention time. The biggest molecules will exit the column first and the smallest molecules will exit last. All columns have a range of molecular weights that can be separated. GPC is often used to determine the molecular weight of polymers or molecular weight distributions [Determann, 1969].

3.4 Nuclear magnetic resonance spectroscopy, NMR

Nuclear magnetic resonance (NMR) spectroscopy is an analysis method that exploits the magnetic properties of certain atomic nuclei. Many nuclei have spin and all nuclei are electrically charged. If an external magnetic field is applied an energy transfer is possible, exciting the nuclei to a higher energy level. The energy transfer takes place at wavelengths corresponding to radio frequencies and when the spin returns to its base level energy is emitted at the same frequency. The signal that matches this transfer is measured and processed in order to yield a NMR spectrum for the nucleus concerned. It provides information about the chemical environment of the nuclei, which in turn provides structural information [Günther 2014].

3.5 Klason lignin/Carbohydrates

Klason lignin is an acid hydrolysis method where sugars and other acid soluble compounds are solubilized by sulfuric acid in a series of steps at different conditions. The undissolved lignin (Klason lignin) is filtered off, dried and quantified gravimetrically. The carbohydrates and other solubles are found in the filtrate which can be further analyzed. The sugar monomers are quantified by HPLC and the so called acid soluble lignin is quantified by UV/vis. In this method Klason lignin is defined as wood- or pulp constituent insoluble in 72 % sulfuric acid [Tappi T222 om-02].

3.6 UV/vis

According to Lambert Beers an absorbance of a solution is proportional to the concentration of the dissolved substance as described below:

$$A = \varepsilon * l * c \tag{9}$$

Where A is absorbance, ε is the molar extinction coefficient, l is the path length of 1 cm and c is the concentration.

The more light that the molecules in the sample absorbs the weaker will the intensity of outgoing beam be. When performing spectroscopy, a beam with a certain wave length will be sent towards the sample. A detector will measure the intensity of the outgoing beam. These values will be used by the instrument to calculate the absorbance using Eq. (9) [Radojevic & Bashkin, 2006].

3.7 High performance liquid chromatography, HPLC

High performance liquid chromatography (HPLC) is a technique to separate, identify and quantify components in a sample. The principle is that a pressurized liquid solvent (eluent) containing the sample is pumped through a column filled with solid adsorbent material. Each substance in the sample interacts with the adsorbent material differently, causing different retention times to pass through the column, thus leading to a separation of the components. The substances are then detected through chromatography. The adsorbent material inside the column is usually a granular material of solid particles of silica or polymers. This is called the stationary phase and can be polar or non-polar. The eluent is usually a mixture of different solvents such as water, acetone or methanol and it is together with the sample referred to as the mobile phase [Hanai 1999].

3.8 Residual alkali

The amount of residual alkali in the black liquor after the cook is the same as the remaining hydroxyl ions in solution after the cook. This is one of the most important variables to assess the course of the cook. It will also have a great influence on many processes within the pulping such as the combustibility of the black liquor solids. If it is a strong black liquor it may also affect the viscosity [Milanova & Dorris 1994]. Since the main focus of this thesis is to monitor the alkali consumption it is of large interest to measure this parameter to investigate if there is a difference between the wood samples.

3.9 Kappa number

Kappa number is an indication of the residual lignin content in chemical pulps.
Lignin can cause brown or yellow discoloration of pulp and paper and affect the mechanical performance, it is therefore undesirable. The Kappa number is consequently also an indication of the pulps bleach ability and it is used to determine the amount of bleaching chemicals that needs to be added during bleaching.

The kappa number for chemical pulps ranges from 1 to 100. For bleachable pulps the number has a range between 25 - 30 after the cook, and pulps for unbleached liner normally has a higher range between 60 - 90. The kappa number is proportional to lignin content. As an estimation the following relation can be used:

$$Kappa\ no. \ = k * \ lignin\ content\ (\%) \qquad (10)$$

where k is approximately 6.57. The constant k is however dependent on process conditions and wood species [ISO302:2015, Tappi T236 cm-85].

The Kappa number is determined by a standardized method where potassium permanganate is used to oxidize the lignin in the sample during a specified period of time. The Kappa number is determined by the milliliters of 0.02 mole/l potassium permanganate solution that is consumed by 1 g of dry pulp [ISO302:2015]. The measurement is inflated by the presence of hexenuronic acids in the pulp since their structure is sensitive to oxidation by permanganate. These compounds are formed from the hemicelluloses during the chemical pulping process [Li & Gellerstedt 1997]. More specific it is generated by conversion of the side group methylglucouronic acid and methyliduronic acid from xylan. These are converted into hexenuronic acid by β-elimination of methanol during Kraft cooking [Teleman 2009, 101-120].

3.10 Ion chromatography

Ion chromatography is a form of liquid chromatography. It measures concentrations of ionic species by separating them based on their interaction with the charged sites bound to the stationary phase. It can be used for almost any kind of soluble charged molecule. Sample solutions pass through a pressurized column where ions form ionic bonds and absorb to a stationary phase. As an ion extraction liquid (eluent) runs through the column, the absorbed ions begin separating from the stationary phase. The retention time of different species determines the ionic concentrations in the sample. The two types of ion chromatography are cation-exchange and anion-exchange. Cation exchangers have covalently bound, negatively charged sites on the stationary phase that attract solute cations. Anion exchangers contain positively charged groups which attract solute anions [Harris 2010, 642].

4. Experimental methods

The experimental methods and procedures for the different experiments and analyses are described in this section.

4.1 Sampling and preparation of wood for experiments and analysis

The wood samples investigated were collected from plantations in different regions of Brazil and provided by Stora Enso. They were comprised of three different clones of *E. Urograndis* and the age of the trees were between 3.2 and 8.8 years. The detailed specification of each sample can be seen in table (1) below.

Table 1 Information for the different samples investigated.

Sample no.	Region	Age (years)	Clone	Mean Annual Rainfall (mm/m^3)
1	South	5.9	A	1300
2	South	5.9	B	1300
3	Central A	5.9	B	1250
4	Central A	5.9	A	1250
5	Central A	3.2	B	1250
6	Central A	3.2	A	1250
7	Central A	8.8	B	1200
8	West	6.0	A	1000
9	West	5.9	B	1050
10	North	5.5	A	1350
11	North	5.5	B	1350
12	Central B	8.2	A	1450
13	Central A	5.4	B	1250
14	Central A	5.4	A	1250
15	Central A	5.4	C	1250

4.1.1 Collection and preparation of wood samples

The sampling of the wood was made by a cooperating mill in Brazil. For trees older than 5.9 years eight trees were used for each sample. For trees younger than 5.5 years five trees were used for each sample. Each tree was divided into five trunks (base, 25 %, 50 %, 75 % 100 % of commercial height) each being 1m. These trunks were chopped into chips and thereafter mixed. The wood chips for analysis was screened manually prior to all experiments and milling. They were selected to be homogeneous within in the range of 0.8 - 3.5 cm and to avoid dirt, knots and bark. For the extractions and Klason lignin analyses of the the wood, air-dried woodchips were milled to pass through a 1 mm sieve by a Wiley-type mill.

4.1.2 Determination of moisture content

The moisture content of wood chips, milled wood chips and pulp samples was determined by TAPPI T 258 om-85. 10 ± 0.5 g of sample was placed into dry beakers with known weight. For pulp samples 5 - 6 g of samples was used. The beakers with wet samples were oven dried at 105 ± 3 °C until the mass was constant, typically 24 hr. Analysis of the wood chips were performed in triplicates, the milled wood chips and pulp samples were investigated in duplicates.

4.2 Soxhlet extraction of extractives

The collected and milled wood samples were extracted with acetone using a Soxhlet apparatus for 6 h. The procedure was carried out according to TAPPI T 204 cm-97 but due to the hazardous nature of the suggested solvents acetone was used as a substitute as proposed by TAPPI. The air-dried milled wood samples (10 g) were placed into a Soxhlet thimble and 400 ml of solvent was used. The amount of sample and solvent were scaled up from the TAPPI procedure for practical reasons. To remove the solvent from the extractives, rotary evaporation was performed under vacuum. The total weight of the extractives was determined and expressed as percent of dry wood. All extractions were initially done in duplicates and thereafter some samples of particular interest were extracted again.

To isolate the lipophilic fraction, a known amount of the acetone extract was re-dissolved in dichloromethane. The dissolved phase was thereafter separated from the un-dissolved phase before it was evaporated under reduced pressure and weighed. Note that what is referred to as the lipophilic fraction is the extractives soluble in dichloromethane.

4.3 GC-MS analysis

GC/MS analysis was used to analyze the extractives obtained from the different samples of eucalyptus. The dichloromethane fraction was studied both before and after alkaline hydrolysis to determine if there were any difference in composition of the compounds found.

4.3.1 Sample preparation

4.3.1.1 Alkaline hydrolysis

Many of the extractives that are anticipated in the Eucalyptus tree are fatty acids and some might have large molecular weigh. The alkaline hydrolysis was done to liberate the fatty acids bound in triglycerides and make them detectible by the the GC/MS analysis of the lipophilic fraction.

40 mg of the acetone extract was weight into a 5 ml vial. 1.8 ml of 0.3M potassium hydroxide (KOH (aq)) was then added together with 1 ml of ethanol. The vial was then placed into a reaction block where the hydrolysis reaction was carried out during 4 h under constant stirring and at approximately 70 °C. The sample was then left to cool down to room temperature before it was acidified with concentrated hydrochloric acid (HCl) to approximately pH 2. The sample was washed with dichloromethane (3x2ml) and the lipophilic fraction was separated and put into a new vial. The solvent from the lipophilic fraction was then removed by rotary evaporation at reduced pressure. A couple of drops of dry ethanol was added to fully dry the sample and it was thereafter also removed by evaporation

4.3.1.2 Derivatization

The alkaline hydrolyzed samples and the samples of the lipophilic fraction were prepared in the same way. A known amount was placed into a vial together with a standard (200 µl of 1 mg/ml heptadecanoic acid methyl esther in dichloromethane) for semi-quantitative analysis. The samples were then derivatized by adding 300 µl of bis(trimethylsilyl)trifluoroacetamide (BSTFA) in each sample. To add volume to the vials for practical reasons, an appropriate amount of dichloromethane was added.

4.4.2 Method and Analysis

The analysis was performed on a chromatograph (Agilent technologies 7890A) connected to a mass spectrometer (Agilent 5975C) equipped with parallel flame ionization detection (FID) and mass spectrometer detection (MS) operating in an electron ionization mode. The MS detector is used for identification of the peaks and finding the specific compound while the FID detector was used for semi-quantitative analysis on these compounds since the FID technology is more linear in relationship to the amount of carbon atoms.

The analytes were separated in dual HP-5MS capillary columns (30 m x 250 µm x 0.25 µm), and using helium as carrier gas (1 ml/min in MS column and 0.56 ml/min in FID column). The chromatographic conditions were as follows: injector temperature 300 °C, injection volume 1 µl, oven initial temperature 50 °C hold for 2.25 min; temperature rate 2 °C/min, final temperature 300 °C hold for 30 min. The temperature into the FID was 250 °C and a split ratio of 10:1 was used. The mass detector was operated at electron impact mode (70 eV) with scan range m/z 30 to 800. For semi quantitative analysis an internal standard was added (Heptadecanoic acid methyl ester). One sample was first run without internal standard to check that the internal standard was not already present in the sample. The given spectrums from the analysis were analyzed with the software Enhanced ChemStation (MSD ChemStation E.02.02.1431 by Agilent) that was equipped with the NIST Mass Spectral Search Program (V. 2.0).

4.5 GPC - Determination of molecular weight

GPC was run with a PL-GPC 50 plus integrated system connected with RI and UV detectors (280 nm, Polymer Laboratories, Varian Inc.) Two series coupled PolarGel-M column and a guard column (300x75 mm and 50x7.5 mm, 8 µm) with DMSO/LiBr (0.01 mole/dm^3) as a mobile phase (500 mm^3/min) vas used. A 10-point calibration curve with Pulluan standards was used to determine the M_W and polydispercity index (PD). Data analysis was performed using Cirrus GPC software Version 3.2. Samples were dissolved in mobile phase and filtered through a syringe filter (GHP, Acro-disc, d=13mm, 0.2 µm GHP membrane).

4.6 2D-NMR analysis

When dissolving the acetone fraction in dichloromethane as described in Section (4.2) there where material that could not be dissolved. To determine what these insolubles consisted of 2D NMR was carried out at Swedish NMR center in Gothenburg. The insoluble material where dissolved in deuterated DMSO and analyzed with high field NMR (800 MHz).

4.7 Cooking and preparation of cooking chemicals

The cooking was performed on six samples of two different clones with varying extractive content. Of the 15 samples that were used in this study three samples of each clone (A and B) was chosen for the cooking study. The third clone (C) was not included since it was not of interest for the cooking serie and since there was only one sample provided from this clone.

This choice was based on the results from the Soxhlet extractions and the amount of extractives present in the sample (low, medium and high extractive content). These samples and their region, age and clone can be seen in Table (2).

Table 2. Samples chosen for the Kraft cooking serie. The names of the samples are based on region (CA=Central A; N=North; W=West), age (years) and clone.

Sample no.	Sample Name	Region	Age (yr)	Clone
14	CA5.4(A)	Central A	5.4	A
10	N5.5(A)	North	5.5	A
8	W6.0(A)	West	6.0	A
13	CA5.4(B)	Central A	5.4	B
5	CA3.2(B)	Central A	3.2	B
9	W5.9(B)	West	5.9	B

4.7.1 Cooking

The cooking was performed in autoclave batch cooking in a 270 l bath of Polyethylene glycol (PEG) using the following parameters. The dry wood was in the shape of wood chips with uniform size.

Table 3. Cooking parameters

Parameter	Value
Sulfidity (%)	33
Liquor: wood	4:1
Mass of dry wood (g)	50
Effective alkali (%)	16 (Determined experimentally according to section 4.5.2)
Moisture content (%)	88 - 90 (Determined experimentally for each sample according to section 4.1.2)

To simulate the impregnation, the autoclaves were pressurized to 5 bars with nitrogen gas for 3 - 5 min after the wood chips and chemicals were charged. Further the autoclaves were also left to be pre-heated at 80 °C for 20 min before the heating up period started. In this study four different autoclaves with a volume of 1.2 l were used, which made it possible to take out samples after several different cooking times. These time intervals were based on the assumed cooking behavior of extractives. Below 130 °C only hemicellulose and extractives are believed to react so the time intervals are closer in the beginning. The last time intervals are investigated in order to determine the performance of the cook and draw conclusions whether the samples will cause problems in the commercial cooking. These intervals can be seen in Figure 12, showing the temperature profile of the cook.

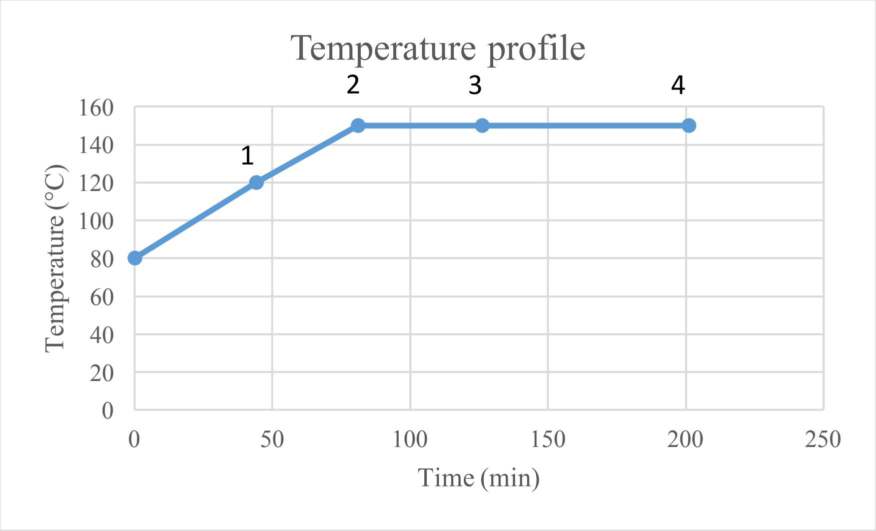

Figure 12. The temperature profile of the cook and the time intervals for discharge. The first being at 120 °C, the second at 150°C, the third 45 minutes into the cook and the fourth at the end of the cook.

After discharge from the oil bath the autoclaves were immediately cooled down in a cold water bath. The pulp samples where then separated from the black liquor using vacuum filtration and were re-filtered once. After the black liquor was retrieved the pulp was washed with 15 l of distilled water. It was thereafter disintegrated in a laboratory disintegrator. After this the pulp was washed with an additional 5 l of distilled water, weighed and stored cold for further analysis.

4.7.2 Alkali charge determination

The alkali charge was determined experimentally to reach a kappa number around 18.5. This was done by keeping all other parameters constant and only varying the alkali charge. For this analysis the same wood sample was used for all experiments, Sample (1). Based on the combined results from Kappa number determination and Klason lignin an effective alkali of 16 % was selected.

4.7.3 Preparation of cooking chemicals

The white liquor was prepared before it was added to the autoclaves. The sodium sulfite solution, sodium hydroxide and water were mixed according to calculations for the determined effective alkali of 16 %. For full calculations see Appendix A. Industrially there is also sodium carbonate present that is generated in the recovery cycle. This is important to take into consideration since it affects the solubility of the cook. An experimental error in this study was that sodium carbonate was not added. However, it is not believed to affect the results since the samples in the cooking serie are only compared with each other.

The concentration of the sodium sulfite solution needs to be known in order to calculate the amount to be added in the white liquor. To determine the concentration of the mixed sodium sulfite solution an ABC titration according to the method described by Wilson (1971) was performed. First, 20 g of the solution was put into a beaker, thereafter 30 ml of barium chloride (BaCl, 200 g/kg) and 50 ml of deionized water was added. Potentiometric titration was performed using hydrochloric acid (HCl, 1M) and for each step the amount of acid was noted. The first step was to titrate down to pH 11 and the second to pH 9. At this point 5 ml of 35 % formaldehyde neutralized with sodium hydroxide (NaOH, 1M) was added. It was left to be mixed for 30 seconds before a titration down to pH 9 was performed. The amount of acid in the last step corresponds to the amount of hydroxide ions in the solution and these are related to the amount of hydrosulfite ions. From this the concentration of the solution was determined.

4.8 Kappa number determination

For this analysis TAPPI T 236 om-99 with some modifications were used.
For all analysis 30 % of the given volumes were used. Instead of using Tappi T 550 for determination of the moisture content of the pulp this was carried out on a Sartorius MA 30, Moisture analyzer.

4.9 Yield

The yield was determined by weighting 5 - 6 g of the moist pulp. The samples were oven dried at 105 °C until constant weight was achieved, typically after 2 - 3 days. This analysis was performed in duplicates.

4.10 Residual alkali analysis

The standard used for these analysis was SCAN-N 33:94 which is based on potentiometric titration with 1M hydrochloric acid (HCl). When preparing the samples 10 ml of black liquor, 10 ml of sodium carbonate ($NaCO_3$) and 10 ml of water were added to a plastic beaker. The sodium carbonate was added to get a better inflection point and to buffer the solution. If the initial pH of the sample would have been above 11.0 but below 12.5 a known amount of 1M sodium hydroxide (NaOH) should have been added before titration. However, all samples had a higher initial pH than this. The analysis was performed with some modifications. In the SCAN method the solution should be titrated down to the first inflection point. Since no obvious inflection point was found the analysis was made by acid titration down to pH 11.5 (as suggested by SCAN) under constant stirring. The content of residual alkali was calculated from the consumption of hydrochloric acid at pH 11.5. To get comparable values for the initial white liquor this titration was also performed on the original alkali mix (white liquor). Analysis for all liquor samples was performed in duplicates [SCAN-N 33:94, 1994].

4.11 Klason lignin

The method used was first developed by Theander and Westerlund (1986). This method was used with some modifications in execution according to Tappi T222 om-02. 200 mg of the oven dried sample was weighted and mixed with 3 ml of sulfuric acid (H_2SO_4, 72 %). The samples where then evacuated for 15 min and put into a 30 °C water bath for 1 hour. 84 g of ionized water was added to the samples before they were placed into an autoclave at 125 °C for 1 hour. After the hydrolysis the samples where filtered by suction filtration and pre weighted filters with the insoluble Klason lignin where put into an oven at 105 °C over night to dry. The hydrolyzate from the filtration is saved for further analysis of acid-soluble lignin according to section 4.12 and to section 4.13 for carbohydrate analysis.

4.12 Acid-soluble lignin

The hydrolyzate from section 4.9 contains the acid-soluble lignin. To measure the concentration of lignin the absorbance was determined using UV-vis at 205 nm. These values were then compared to a calibration curve. The measurements were carried out on a Specord 205, Analytic Jena. The absorption constant used was 110 $dm^3\ g^{-1}\ cm^{-1}$ [Zhu 2013, 24]

4.13 Carbohydrate analysis

The carbohydrates dissolved in the Klason lignin hydrolyzate were analyzed by HPLC.
The hydrolyzate from Section (4.11) was diluted (1:10 and 1:50) with deionized water and an internal standard, in this case fucose (200 mg/ml) was added. Before injection to the HPLC the diluted solutions were filtered through a 0.45 µm PVDF filter.

The analysis of monomeric sugars was performed using the Dionex ICS-5000 HPLC system equipped with CarboPac PA1 columns and run using NaOH, NaOH/NaAc (0.2 M) as eluents. An Electrochemical Detector was used for detection measurements and the software used was Chromeleon 7, Chromatography Data System, version 7.1.3.2425.

4.14 Ion chromatography – determination of acetyl groups on xylan

The amounts of acetic acid in the hydrolyzates were determined by ion chromatography with conductivity detector. A Dionex ICS-2000 with a Dionex IonPac AG15 column (with a precolumn) and potassium hydroxide (KOH (aq)) was used as eluent.

5. Results and discussion

In this section the results obtained from the different analyses will be presented and discussed. Initially the focus was on the content and composition of extractives as these are expected to influence the cooking performance. Later on the work was expended to the content and composition of carbohydrates.

5.1 Extractives

The extractive contents and GC-MS/GC-FID analysis together with results from GPC and NMR studies are presented in this section.

5.1.1 Total Extractive content

The extraction results show that there was a variation of extractives content between the 15 samples and it ranged from 1.80 - 4.73 % on dry wood basis. All values for total extractives content and lipophilic extractives content can be seen in Table (4).

Table 4. The average total extractive content and lipophilic extractive content of all wood samples. The samples in bold text are the ones that were cooked in the Kraft cooking series.

Sample	Extractive content (% on dry Wood basis)	Lipophilic extractive content (% on dry wood basis)	Clone
1	2.61	0.36	A
2	3.21	0.46	B
3	3.91	0.43	B
4	3.10	0.37	A
5	**4.08**	**0.32**	**B**
6	3.52	0.31	A
7	4.73	0.48	B
8	**3.93**	**0.25**	**A**
9	**4.02**	**0.42**	**B**
10	**2.72**	**0.31**	**A**
11	4.19	0.39	B
12	2.58	0.11	A
13	**3.45**	**0.38**	**B**
14	**1.80**	**0.49**	**A**
15	2.30	0.49	C
Average clone A	2.89	0.31	
Average clone B	3.94	0.41	

Selection of clone B samples for the cooking serie was based on early extraction studies that can be seen in Appendix B and resulted in a somewhat narrow range of samples. Ideally Sample 7 with an extractive content of 4.75 % should have been chosen as the high extractive sample for clone B instead of Sample 5 with an extractive content of 4.08 %.

As mentioned in the experimental section for the extraction, the lipophilic fraction is considered to contain all extractives that are soluble in dichloromethane. This includes both fatty acids and other dichloromethane soluble extractives. Attempts were made to separate the fatty acids after alkaline hydrolysis to quantify this fraction as well. However, difficulties during the execution resulted in values that were not accurate enough to compare with. However, the results for the dichloromethane fraction indicates that this fraction is very small, as can be seen in Table 4. These results are comparable to literature values of approximately 0.35 % by Freire et al. (2006).

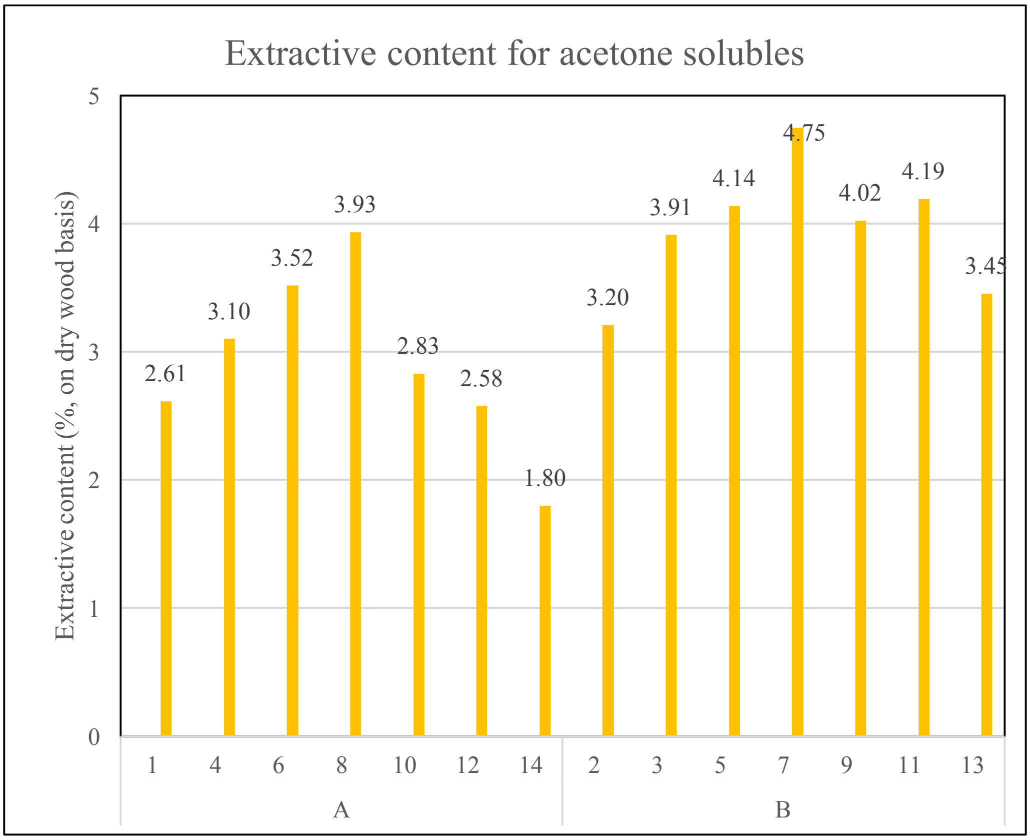

Figure 13. Chart of extractive content for all samples within clone A and B. It is presented as weight percent on dry wood basis.

In Figure 13 the distribution of extractive content between all samples from clone A and B can be seen. It is obvious that both clones had a wide variation but that clone B had slightly higher absolute values. When comparing these data with literature values the extractive content in this study seemed to be similar or slightly higher. According to Prinsen et al. the fraction of acetone solubles is 2.1 % and in another study by Silviero et al. (2007b) it was in a range of 1.32 - 3.97 %.

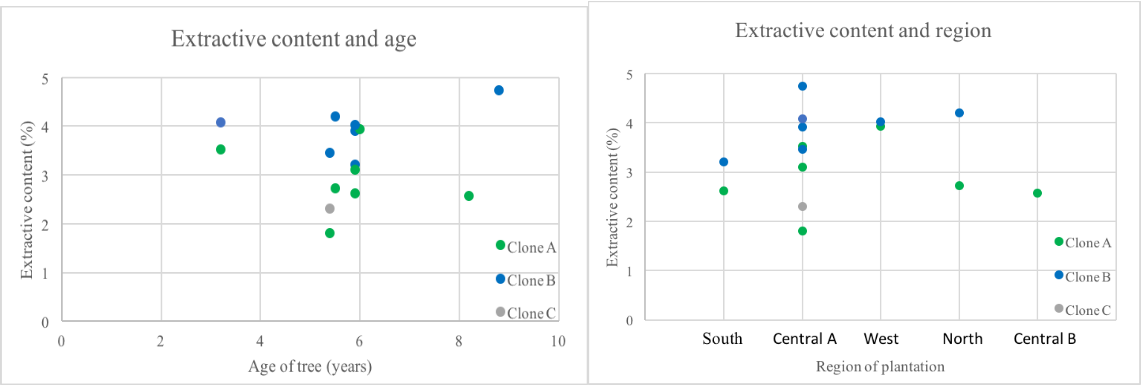

Figure 14.a) To the left: Extractive content plotted against three age. 14.b) To the right: Extractive content plotted against region of plantation.

From the information obtained there are no indications of correlations between region of plantation or age and extractive content. This can be seen in Figures 14.a, b. It was surprising that there was no clear correlation between extractive content and age in Figure 14.a. Considering that studies by Morais & Pereira (2011) have shown a strong relation between heartwood formation and extractives it would be expected that older trees with more heartwood would have a higher extractive content. It was also believed that the region in which the trees were planted would be of interest. However, in Figure 14.b no obvious correlation can be seen. The region West seemed to have high extractive content but this could not be verified since there were not enough data points for that region. Central A had the highest number of data points but also the largest variation in extractive content, thus the region of plantation probably does not affect the extractive content. The results from Central A also showed that clone B had higher extractive content as previously seen in Figure 13. Since the extractive content varied significantly within the region Central A it is possible that other factors such as micro climate had a more substantial effect on the wood composition.

5.1.2 Composition of extractives

In this section the results from the semi-quantitative analysis of the lipophilic extractive fraction, their abundance and molecular weight will be presented as well as the results from the NMR analysis. The identified compounds are visible in the GC-MS chromatograms before and after alkaline hydrolysis, that can be seen in Figures 15 and 16 respectively. The fraction basically consisted of sterols and fatty acids.

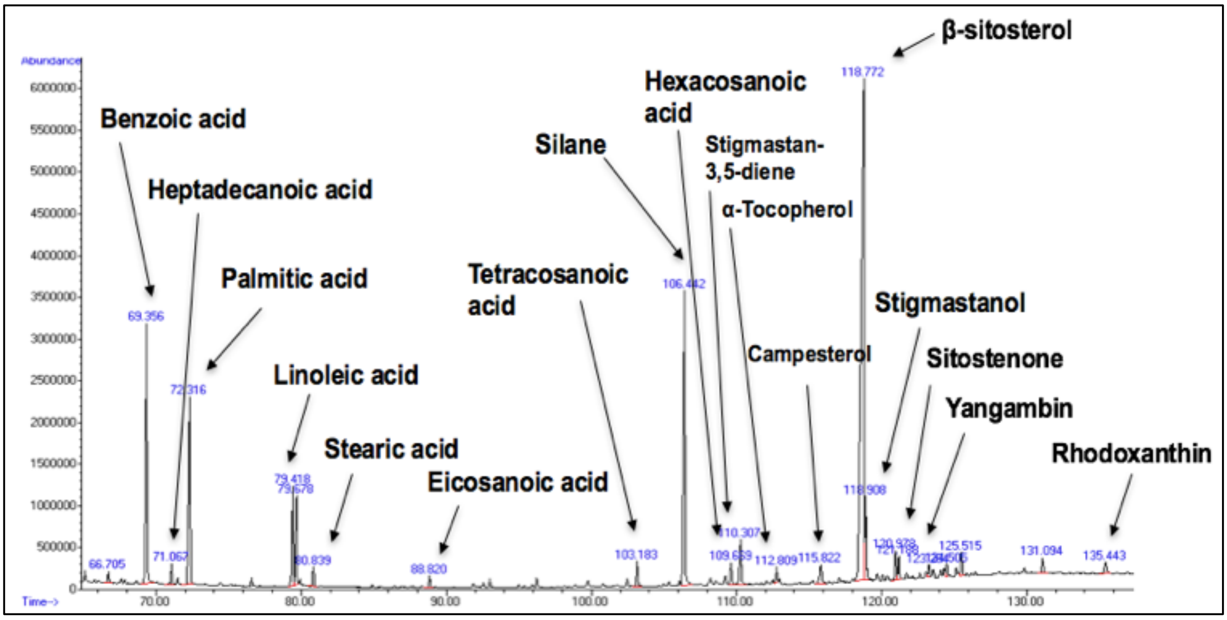

Figure 15. The GC-MS chromatogram of the dichloromethane fraction and the identified compounds

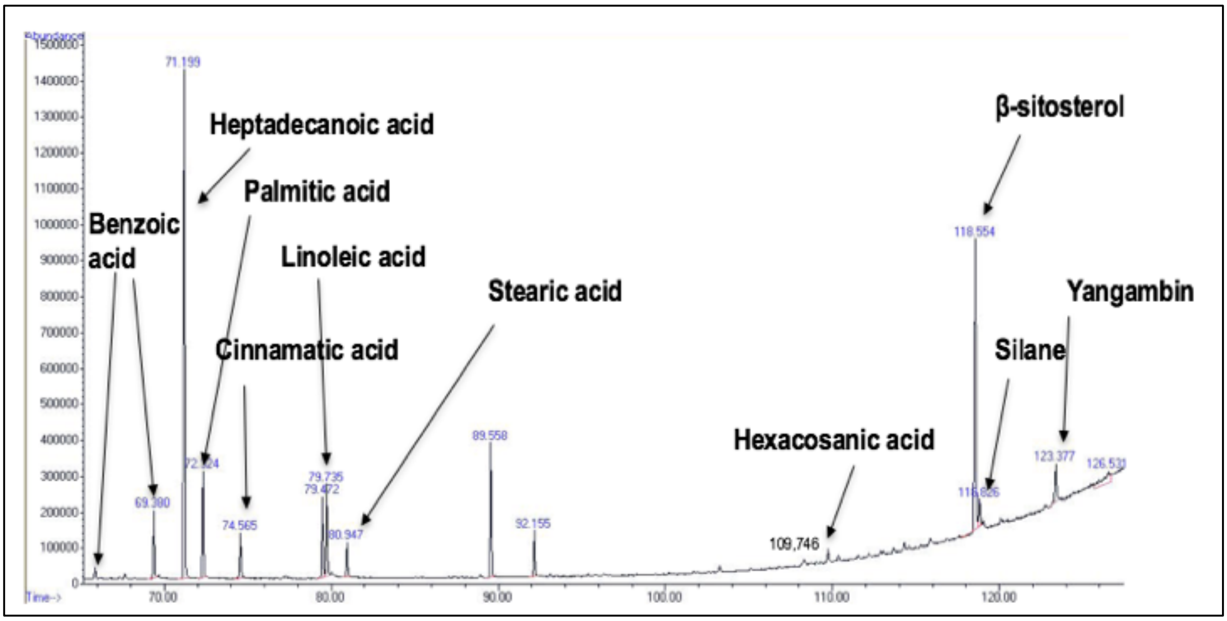

Figure 16. The GC-MS chromatogram of the dichloromethane fraction after alkaline hydrolysis and the identified compounds.

In Table 5 one sample from each of the clones and their strongest signals are reported. Results for other samples can be seen Appendix C.

Table 5. Shows both the lipophilic and hydrolyzed lipophilic compounds from the largest peaks found in the GC-MS/GC-FID analysis and respectively mass fraction

	Semi-quantitative analysis of GC-MS results - largest peaks and mass fraction (%)			
	Lipophilic fraction		Lipophilic fraction after alkaline hydrolysis	
Sample	Compound	Mass fraction (%)	Compound	Mass fraction (%)
CA3.2(B)	β-Sitosterol	6.39	Benzoic acid	5.60
	Hexadecanoic acid	1.65	β-Sitosterol	4.08
	Oleic acid	1.61	Linoleic acid	2.18
	Linoleic acid	0.85	Hexadecanoic acid	1.85
	Stigmastanol	0.46	Yangambin	0.89
	Stigmast-4-en-3-one	0.43	Cinnamic acid	0.76
	(+)-α-Tocopherol	0.35	Stigmastanol	0.46
W6.0(A)	β-Sitosterol	7.83	β-Sitosterol	6.62
	Hexadecanoic acid	2.72	Benzoic acid	3.30
	Linoleic acid	1.43	Hexadecanoic acid	2.77
	Stigmastanol	0.64	Cinnamic acid	1.74
	(+)-α-Tocopherol	0.50	Stigmastanol	0.90
	Stigmast-4-en-3-one	0.41	Silane	0.88
			Hexacosanoic acid	0.68
			Yangambin	0.66

Looking at Sample CA3.3B and W6.0A it was obvious that there seems to be roughly the same compounds were present in the two samples. The amount of these were also in the same range. This was true also for the samples presented in Appendix C. Further, there was a change in the mass fraction before and after alkaline hydrolysis. However, in the work presented by Silvéro et al. (2007) the amounts of the fatty acids and sterols were increasing after the hydrolysis and in this study they were decreasing. It is believed that this is due to difficulties regarding the experimental method. The amount presented in this work should only be considered to be semi-quantitative and to be used for comparison within this study. The difficulties involved problems with solubility and the separation of the different phases during sample preparation and will be discussed later in this section.

It is clear that there were new peaks (compounds) such as Yangambin, Benzoic and Cinnamic acid identified after the alkaline hydrolysis.

The results of the GPC analysis investigating molecular weight are shown in Table 6.

Table 6. Weight average molecular weights of the extractives for the samples cooked.

Sample	**Molecular weight M_w (kDa)**	
	UV	**RI**
CA3.2(B)	14.8	15.1
W6.0(A)	14.1	14.5
W5.9(B)	12.6	13.0
N5.5(A)	13.8	14.0
CA5.4(B)	13.2	13.7
CA5.4(A)	13.1	13.5

The UV-detector detects aromatic compounds at 280 nm. This means it only shows phenolic extractives and lignin which are based on aromatic structures. The RI detector detects sugars, extractives and lignin. The peaks for the UV and the RI-measurements coincide which indicates that the compounds present co-elute and possibly form large networks. These fragments with a large molecular weight around 12.5 - 15 kDa hampered the redissolution of acetone solubles in dichloromethane to retrieve the lipophilic fraction. It was also a problem to separate this fraction from salts and precipitates after the alkaline hydrolysis to obtain the hydrolyzed lipophilic fraction. Therefore, it is possible that the content of lipophilic compounds in reality was higher and that a part of non-detected material was enclosed within the networks not soluble in dichloromethane.

The results from the NMR analysis of the insoluble extractive fraction after redissolution in dichloromethane can be seen in Figure 17.

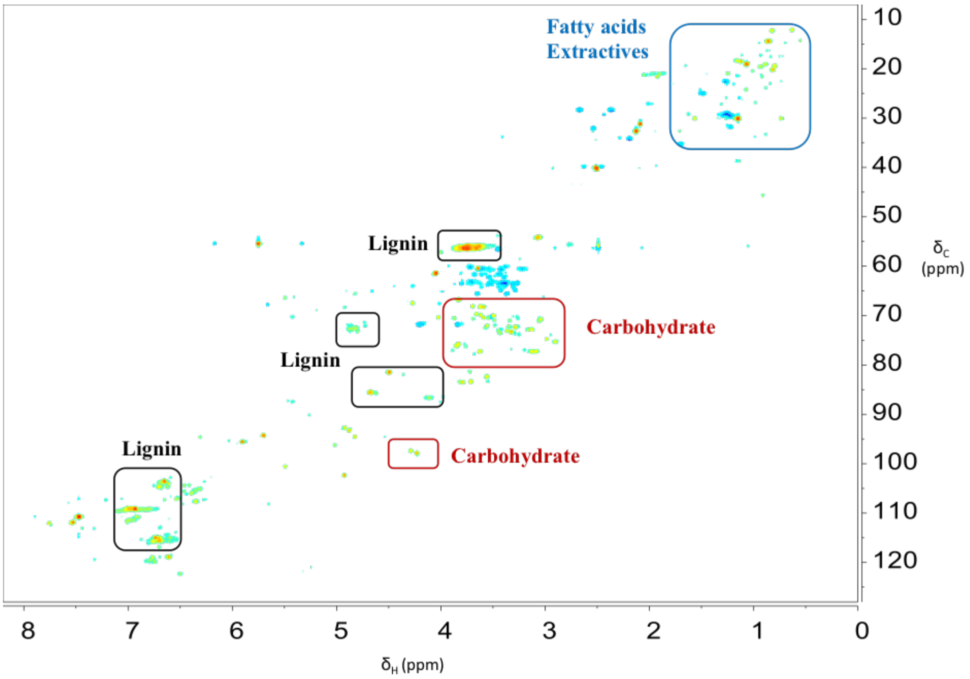

Figure 17. 2D- NMR spectrum of the dichloromethane insoluble fraction of extractives.

By 2D NMR it is possible to gain structural information of the various CH, CH_2 and CH_3 structures within the dichloromethane insoluble material. The 2D NMR gave further indications that the material insoluble in dichloromethane after separating the lipophilic fraction did not only contain extractives. Figure 17 shows typical areas of lignins, carbohydrates and extractives (fatty acids). This is a verification that also carbohydrate and lignin structures were extracted with acetone. This further implies that parts of the lipophilic extractives (fatty acids) where trapped inside the carbohydrate/lignin networks and not as easily dissolved in the dichloromethane when separating the different fractions. These networks may have been broken during the alkaline hydrolysis, thus liberating new extractives detected after the hydrolysis.

This can also mean that the extractive content after Soxhlet extraction were overestimated since the mass fraction also contained traces of carbohydrates and lignin.

5.2 Cooking performance

From the cooking experiments black liquor and pulp was obtained. These were further analyzed in order to determine the cooking performance and the results from these analyses are found in the following section.

An important notice is that the cooking serie performed in this study deviates from a typical practice used within cellulose technology. This study employed the same effective alkali and execution for all samples. Normally, a number of cooking experiments are performed to reach different kappa numbers and values for the yield. Then the yield or other properties are compared to the kappa number by interpolation, to characterize small differences.

5.2.1 Unscreened Yield

In this section all results related to the achieved yield will be presented and discussed.

Table 7. Unscreened yield for the different time steps for 6 samples of eucalyptus

	Yield (g/g)				**Achieved pulp (kg)**
	Time (min)				
Sample	**44**	**81**	**126**	**201**	
W6.0(A)	0.77	0.64	0.54	0.52	0.026
N5.5(A)	0.91	0.73	0.56	0.52	0.026
CA5.4(A)	0.80	0.75	0.55	0.52	0.026
CA3.2(B)	0.86	0.65	0.53	0.50	0.025
CA5.4(B)	0.72	0.66	0.54	0.51	0.025
W5.9(B)	0.83	0.70	0.54	0.53	0.026

As seen in Table 7 the pulp yield was approximately 50 % at the end of the last time interval for each of the cooked samples. The first two time intervals had more varying results but are still considered to be similar. This because it was more difficult to retrieve all fibers from the filtration step during these time intervals. Figure 18 shows yield over time during the cooking for the different samples.

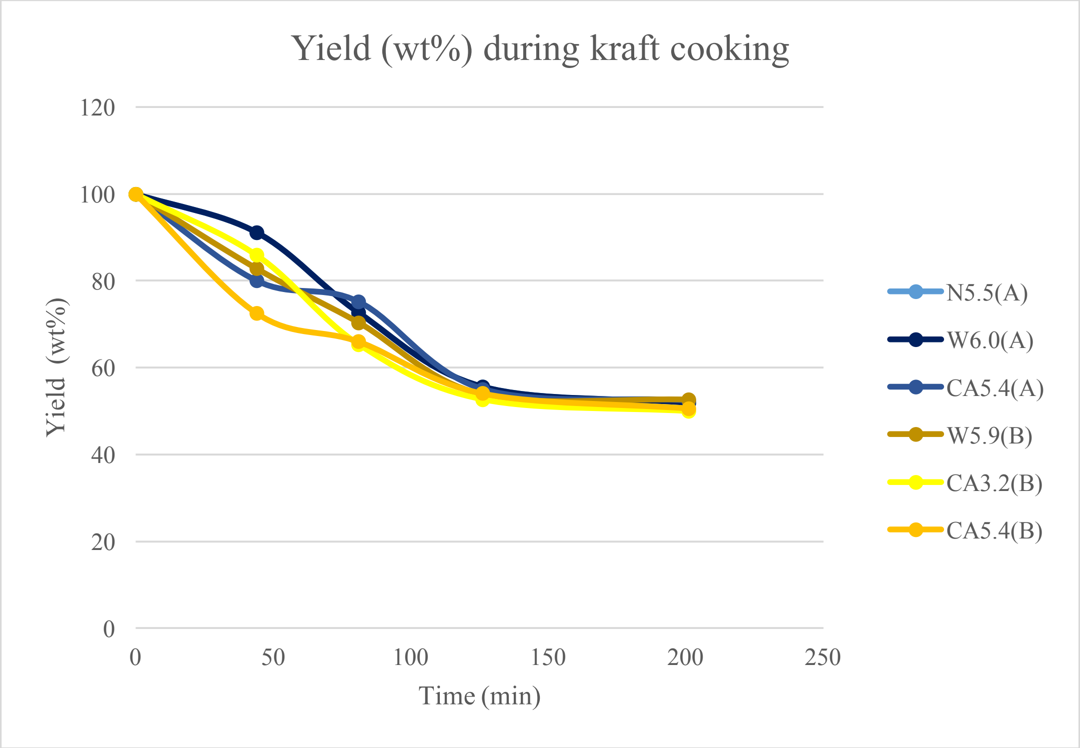

Figure 18. Cooking yield over the time intervals in the cook, presented as weight percent on dry wood basis.

The pulp yield results were considered reasonable since a value around 50 % was expected from previous studies by Martino et al. (2013). Although the yield was evaluated on unscreened pulp it was not considered to have a great impact on the results compared to screened pulp since the pulp obtained did not contain any dark spots or visible shives.

5.2.2 Residual alkali

The results from the residual alkali analysis showed a very small variation in residual alkali between the samples from the clone A and a larger variation within the clone B. The residual alkali for each sample and the corresponding time intervals are shown in Table 8 and the percentage of the original residual alkali left at each time interval in Figure 19.

Table 8. Residual alkali for the six samples cooked and their respective time interval together with the total consumption of sodium hydroxide (NaOH). The time intervals can be seen in figure (9).

	Residual alkali NaOH (g/l)				
	Time (min)				
Sample	**0**	**44**	**81**	**126**	**201**
W6.0(A)	47.8	25.4	18.9	10.7	9.21
N5.5(A)	48.2	25.2	20.4	11.7	9.40
CA5.4(A)	48.2	25.4	19.3	11.5	8.83
CA3.2(B)	47.0	22.5	15.5	9.20	6.36
CA5.4(B)	43.2	21.2	12.4	7.88	5.22
W5.9(B)	48.5	24.1	17.9	11.1	9.21

Initially there did not appear to be any large differences between the samples regarding the residual alkali levels at the varied time intervals. One sample that stood out was Sample CA5.4B, that had lower values for all time intervals as can be seen in Table 8. However, comparing this result with Table 7 showing the yield it seemed to be in the same range as the others and even among the lowest, indicating the lower consumption of alkali does not affect the cooking performance. Regardless of the lower values, Sample CA5.4B was following the same trends in alkali consumption compared with the other samples. This can be seen in Figure 19.

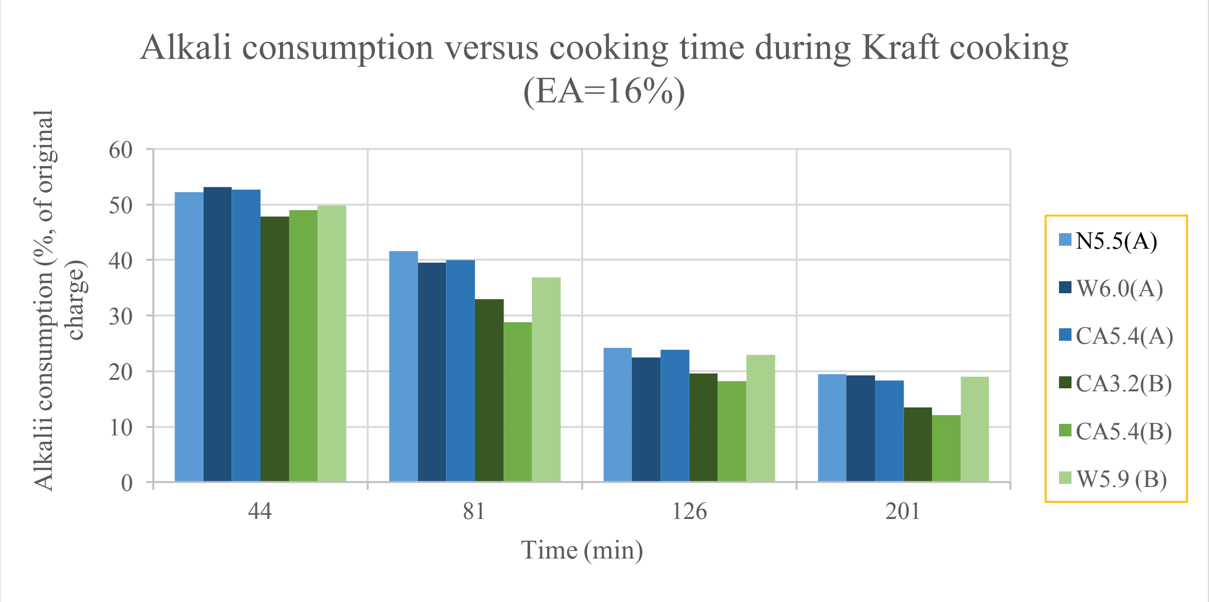

Figure 19. Alkali consumption over the different time steps in the cook.

The trends that could be observed from the cooking series were that the largest percentage of the alkali charge was consumed until the first time interval (≈50 %). When comparing these results with previous work made by Pettersson et al. (2002) the alkali consumption was around the same value as the one reported for *E. Grandis*.

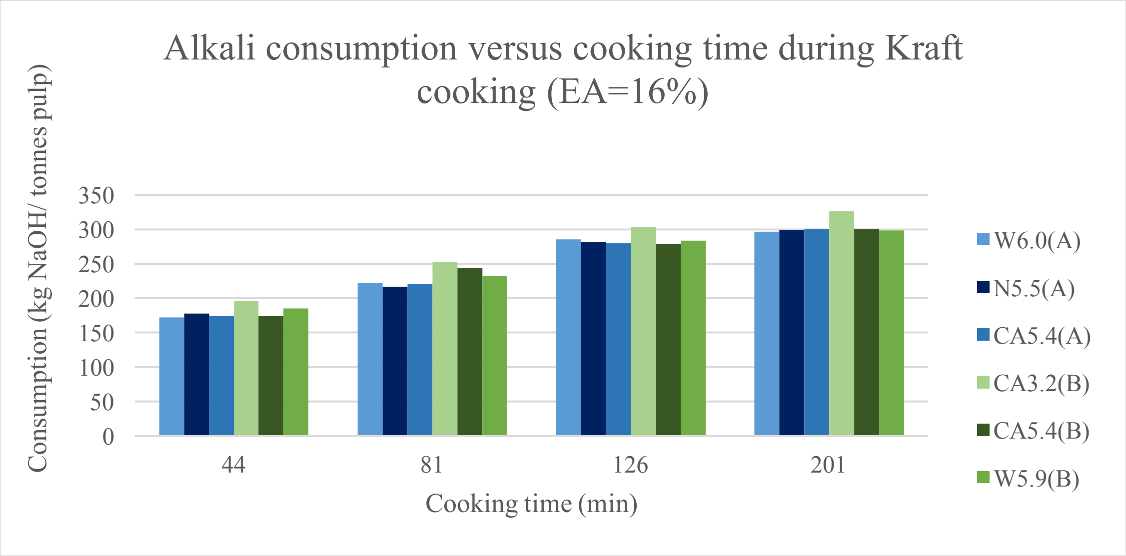

Figure 20. Shows the alkali consumption of NaOH (kg) per tonnes of pulp for each sample (clone) versus cooking time (min).

In Figure 20 the chemical consumption is based on how much sodium hydroxide (NaOH) that is consumed per tonne of pulp. This further emphasizes the very small variations seen in clone A. It also highlights the fact that Sample CA3.2B had a larger consumption than the other samples for all time intervals.

5.2.3 Cooking performance related to extractive content.

In this section the yield and alkali consumption are further related to the extractive content of the selected samples.

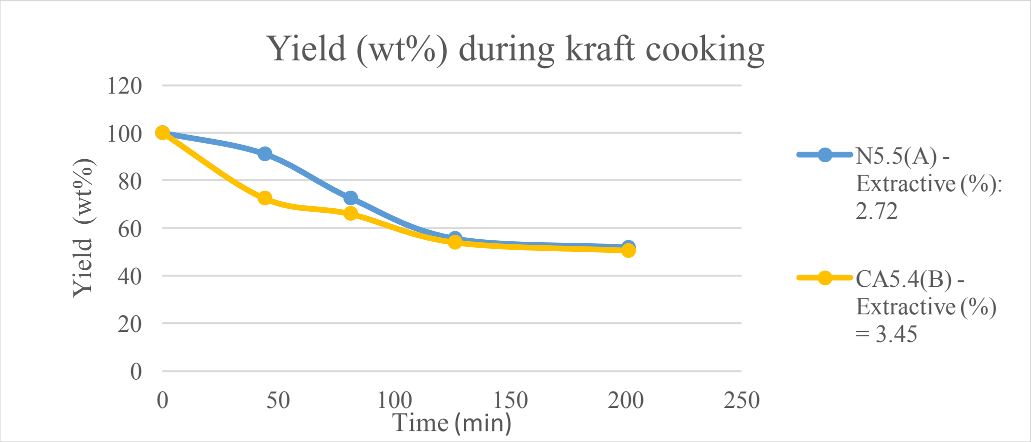

Figure 21. Shows the yield (%) versus cooking time for the two samples that deviated the most from each other at the first time interval and their respective extractive content.

From Figure 21 it is interesting to note that Sample CA5.4B that had the highest extractive content also had a much lower yield at the first time interval (44 min) comparing to Sample N5.5A that had a lower extractive content.

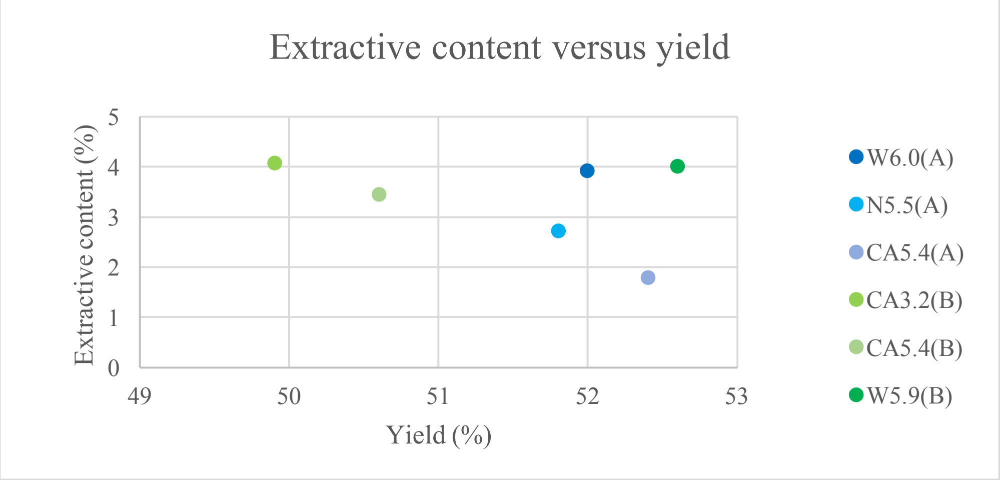

Figure 22. Extractive content versus yield for all samples.

Studies by Gomide et al. (2005) have shown that a higher extractive content leads to a lower pulp yield. Looking at Figure 22 no such conclusions could be drawn. Indeed, the sample with highest extractive content showed the lowest pulp yield, however the sample with second highest extractive content had the highest pulp yield. However, to draw accurate conclusions the yield would have to be compared at the same kappa number of the samples and in this project the lignin content (kappa number) differs in the pulp for the different samples. The number of data points were low and additional experiments are also necessary to draw confident conclusions.

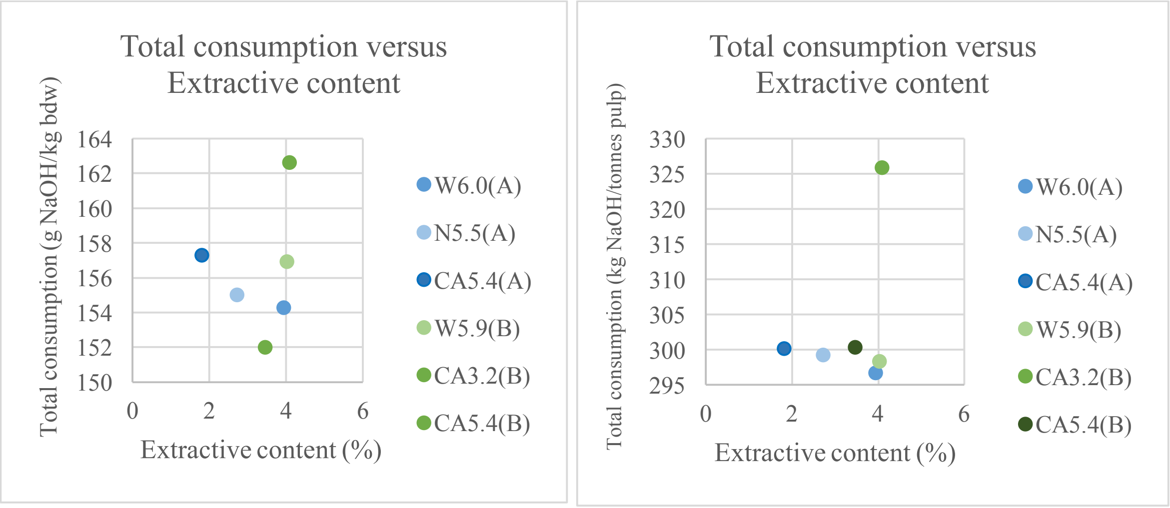

Figure 23.a) The total consumption of NaOH (g) per kg of bone dry wood versus the extractive content in percent on dry wood basis for each sample. Figure 23.b) The total consumption of NaOH (kg) per tonnes of pulp versus the extractive content in percent on dry wood basis for each sample.

In Figure 23.a the total consumption of sodium hydroxide (on bone dry wood basis) versus the extractive content can be seen. As in Figure 19 and 20 it is clear that there was less variation in clone A. This is also highlighted in Figure 23.b where the consumption is on pulp basis. Another interesting fact is that Sample CA3.2B and W5.9B, which had similar extractive content, showed a large difference regarding the consumption.

To summarize this section there was no indication that the extractives were affecting the cook. However, it could be concluded that there was more variation regarding both yield and the alkali consumption in clone B. Important to note is that the cooking results are only initial and that this study had limited time to refine the cooking experiments to draw more confident conclusions. Since no obvious correlation could be established from these parameters the focus was shifted to the main wood components, which are lignin and carbohydrates.

5.3 Cooking performance as a function of main components

This section will handle the variation within the main wood components and how they vary between the samples during cooking.

5.3.1 Klason lignin

The analyses of Klason lignin and acid insoluble lignin were made to determine the amount of lignin in the starting material for comparison. Further, the analyses were also performed to ensure that the same quality of the cook was achieved for all samples.

Table 9. Klason lignin and acid soluble lignin for wood and pulp.

	Sample (Clone)											
	CA3.2(B)		W5.9 (B)		CA5.4(B)		W6.0(A)		N5.5(A)		CA5.4(A)	
Component (%, on dry Wood basis)	**Wood**	**Pulp**	**Wood**	**Pulp**	**Wood**	**Pulp**	**Wood**	**Pulp**	**Wood**	**Pulp**	**Wood**	**Pulp**
Klason lignin	29.8	1.15	28.5	1.31	28.0	0.88	31.5	1.17	29.4	1.55	30.0	1.18
Soluble lignin	3.99	0.65	3.97	0.70	4.06	0.62	3.17	0.62	3.14	0.58	2.94	0.59
Total lignin	33.7	1.80	32.5	2.02	32.1	1.50	34.6	1.79	32.6	2.13	32.9	1.77

The results from the Klason analyses can be seen in Table 9 and Figure 24. These showed that the variation in lignin content between the wood samples was low. However, the amount of lignin was in general higher in the wood samples for clone A. Looking at the lignin in the pulp the variation was lower, indicating that the quality of the Kraft cooking was consistent and that the same delignification was achieved.

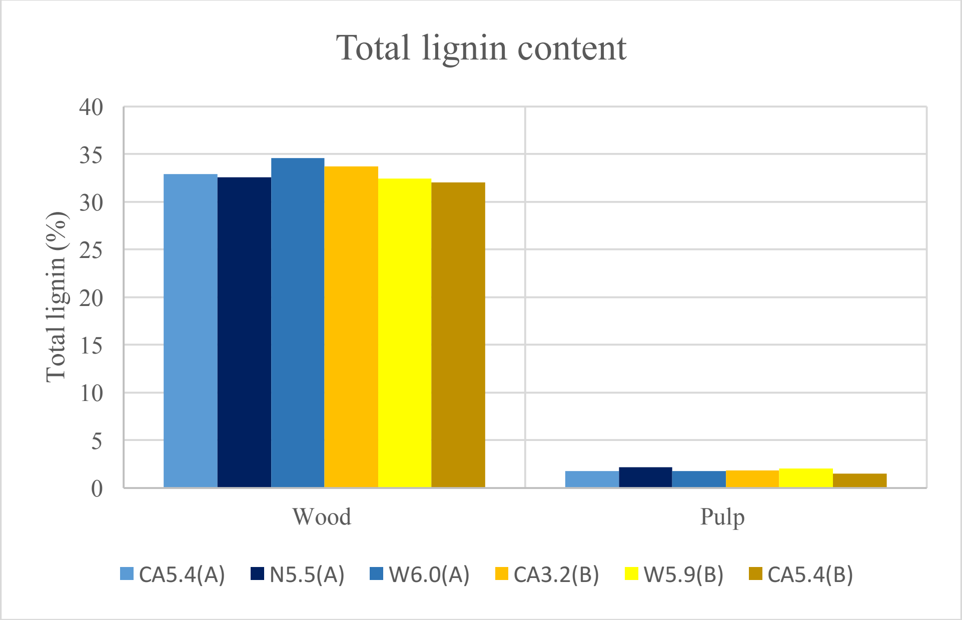

Figure 24. Total lignin content of wood and pulp.

Based on earlier work made by Gomide et al. (2005) a lignin content in the range of 27.5 - 31.7 % should be expected for Brazilian eucalyptus. Another study by Martino et al. (2013) of *E. Urograndis* gave total lignin values of 29.5 %. These higher values of lignin are not typical for hardwood and in this sense eucalyptus is more similar to the composition in softwood. This project showed values that were within the given range of these previous works or slightly higher. A source of error in this analysis could be that extractive free wood was not used for the analysis.

Table 10. Kappa number for all pulp samples.

	Sample (Clone)					
	CA3.2(B)	**W5.9(B)**	**CA5.4(B)**	**W6.0(A)**	**N5.5(A)**	**CA5.4(A)**
Kappa no.	15.3	16.7	11.7	15.0	20.0	15.0

Kappa number is the most common parameter for measuring the lignin content in pulp used in industry. Therefore, it was estimated using the relation in Eq. 10 together with the Klason lignin in Table 9. As can be seen in Table 10 the Kappa number varied between 15 - 20 with an outlier Sample CA5.4B. These were relatively large variations comparing to the kappa numbers seen in industry. However, since these values were estimated from Klason lignin they can have more errors than the ones obtained in industry. The large variations in kappa number could also affect results from other analyses and this will have to be considered when comparing the samples.

5.3.2 Carbohydrates

The carbohydrate analyses were made on both the wood samples and the pulp to be able to follow the changes in wood composition during the Kraft cook.

Table 11. Carbohydrate composition (% on wood dry basis) of the studied samples.

	Wood Components content (% on dry wood basis)							
	Cellulose		**Xylan**		**Glucomannan**		**Acetyl groups**	
Sample	**Wood**	**Pulp**	**Wood**	**Pulp**	**Wood**	**Pulp**	**Wood**	**Pulp**
CA5.4(A)	44.2	39.8	12.0	7.21	3.19	0.62	3.19	0.02
N5.5(A)	42.8	36.8	12.2	7.36	3.35	0.60	3.06	0.02
W6.0(A)	43.0	35.5	11.6	7.24	2.95	0.15	2.97	0.02
CA3.2(B)	42.6	37.8	14.0	8.88	2.97	0.61	3.38	0.02
W5.9(B)	44.8	37.2	13.2	8.32	3.10	0.18	3.16	0.02
CA5.4(B)	45.8	37.1	13.3	7.76	3.19	0.61	3.22	0.02

The amounts of cellulose, xylan, glucomannan and acetyl groups can be seen in Table 11. The content of these wood components was calculated from the sugar monomers using the relations described in Appendix D.

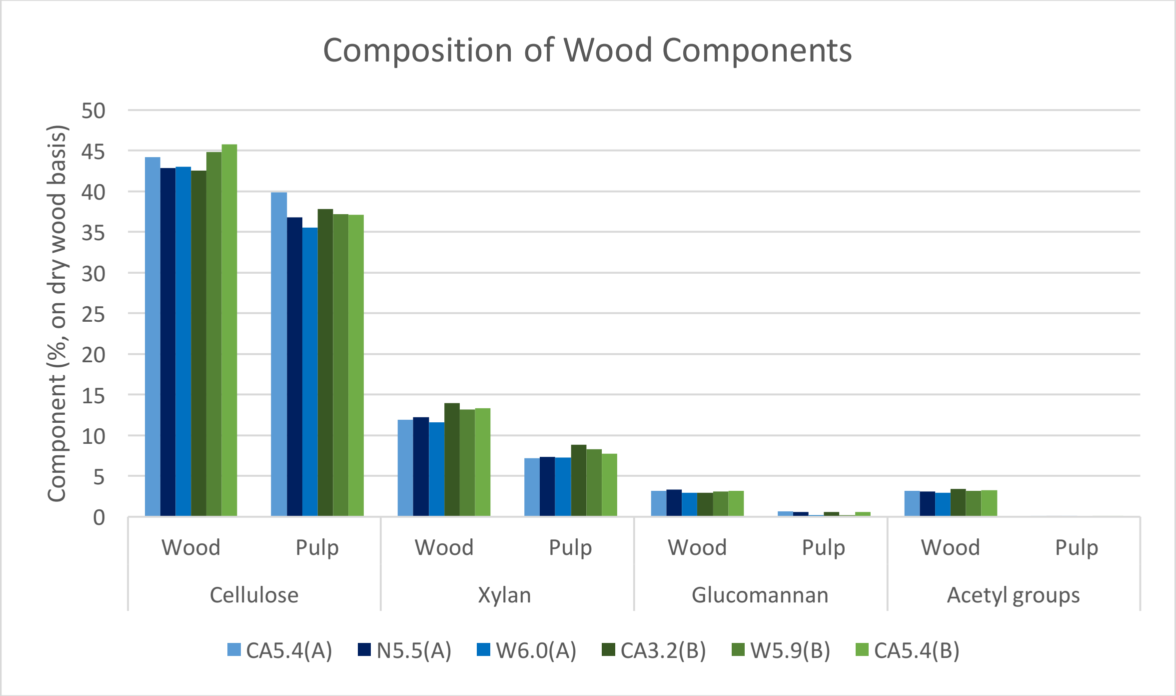

Figure 25. Carbohydrate components for wood and pulp (% on dry wood basis).

An initial look at Figure 25 gives a picture of a quite constant trend between the samples when it comes to carbohydrate composition. However, looking in Table 11 the component that varied the most was the cellulose which had a range between 42.5 - 45.8 %. There were variations for the wood samples within both clones but it was larger for clone B. An interesting fact when considering the pulp, was that the variation for clone B was low (37 %). This indicate a rather consistent cooking performance within clone B.

The xylan content in the wood had low variations within respective clone (<1 %) but the wood samples for clone B had about 1 – 2 % higher xylan content. This was also true for the pulp samples which indicates a similar degradation between the clones.

The glucomannan content in the wood was very low, which is typical for eucalyptus. Most of it was as expected degraded during the cook. The same is true for the acetyl groups. They ranged between 3.0 - 3.4 %. The amount for the wood samples are slightly higher than presented by Martino et al. (2013) that were 2.0 - 2.2 %.

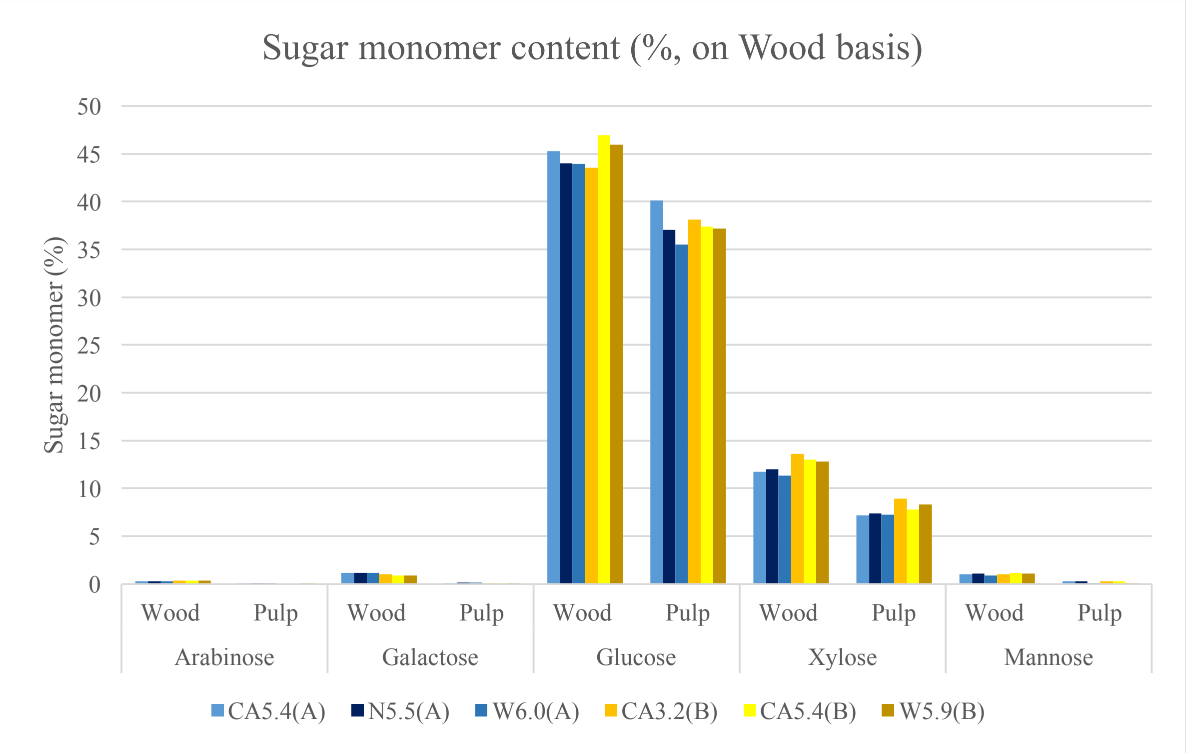

Figure 26. Distribution of the different sugar monomers present in the wood and pulp (%, on dry wood basis). The sugars are reported as anhydrous sugars.

In Figure 26 the distribution of the carbohydrates can be seen. This figure together with the full values from Appendix D gives the amounts of the different anhydrous sugar monomers. These results can be related to values achieved by Martino et al. (2013) for *E. Urograndis*. Another study by Gomide et al. (2006) also showed similar values for their clones of Brazilian eucalyptus.

Comparing the amount of hemicelluloses in Table 11 that were achieved (≈ 16 %) with values from the literature, there are some differences. Relating these values to the previously mentioned studies by Martino et al. (2013) and Gomide et al. (2006) gave values for the hemicelluloses at 21.1 - 21.5 %. However, these also included the Uronic acids (4.0 %). If excluding, these the amounts of hemicelluloses were similar to this study or slightly higher.

To conclude these results, the values in this study seemed to be reasonable when comparing with other studies on the same wood types. As expected most of the glucomannan and basically all acetyl groups were degraded, a significant part of the xylan was still present and the cellulose was only slightly affected.

5.4.1 Mass balance

To evaluate the total composition of the wood and pulp samples a mass balance was made over 50 g of bone dry wood. For this the amounts of carbohydrates, lignin and extractives needed to be known. These values can be found in Table 17, 18, 19 and 20 in Appendix E and the result of the mass balance can be seen in Table 12.

Table 12. The total mass balance and the amount of the different components (g/50 g bone dry wood). This is made on the average values through all samples.

	Amount (g/50 g bone dry wood)	
Component	**Wood**	**Pulp**
Carbohydrates	31.5	22.8
Lignin	16.5	0.47
Extractives	1.67	-
Total	49.7	23.3

From this it was concluded that there was approximately 0.35 g (0.7 %) missing in the wood samples and 2.45 g (9.2 %) missing in the pulp samples that can not be accounted for. This could be due to losses during analysis but it could also consist of uronic acids and/or inorganic material. Note that this is only a quantitative analysis and that there might be experimental errors. The pulp samples had a larger fraction missing. A reason for this might be that the values were calculated using an average of the yield, which can cause more errors than in the wood samples. There might also be extractives left in the pulp samples but this has not been analyzed in this study.

5.5 Summary of results

In this section the results from the different analyses will be discussed together to connect the different parts of the results.

Table 13. Summary of Kraft cooking results. All results are based on weight percent if not stated otherwise.

Sample	Average Extractive content (%)	Time interval	Residual alkali (%) of initial charge	Yield (%)	Klason lignin (%)	Carbohydrates (%)
CA5.4(B)	3.45	0	100	100	28.0	62.3
		1	49.0	72.6		
		2	28.8	66.0		
		3	18.2	54.1		
		4	12.1	50.6	1.75	89.9
W5.9(B)	4.02	0	100	100	28.5	61.1
		1	49.8	82.8		
		2	36.9	70.4		
		3	22.9	53.8		
		4	19.0	52.6	2.50	86.9
CA3.2(B)	4.14	0	100	100	29.8	59.5
		1	47.9	85.9		
		2	32.9	65.4		
		3	19.6	52.7		
		4	13.5	49.9	2.30	94.7
CA5.4(A)	1.80	0	100	100	30.0	59.3
		1	52.7	80.0		
		2	40.0	75.2		
		3	23.9	55.1		
		4	18.3	52.4	2.25	91.0
N5.5(A)	2.83	0	100	100	29.4	58.4
		1	52.3	91.1		
		2	41.6	72.7		
		3	24.3	55.6		
		4	19.5	51.84	3.00	86.3
W6.0(A)	3.93	0	100	100.0	31.5	57.5
		1	53.1	77.27		
		2	39.6	63.72		
		3	22.5	54.45		
		4	19.3	51.99	2.25	82.5

What can be concluded from the analyses performed in this work is that eucalyptus is a heterogeneous species with a varying composition. Even among samples taken out from one clone there were differences. These were differences regarding both the content of different wood components such as lignin, carbohydrates and extractives, but also how they behave during cooking. This however, is a trend that have been seen in other studies as well [Pettersson, 2002] and is expected since wood is a product of the nature. Even though significant variations were seen in the extractive content they had similar compositions. It could also be concluded that the amounts of extractives were overestimated. This since not only extractives were extracted but also small amounts of carbohydrates and lignin.

Although there was variation in composition among the samples their performance during cooking was very similar and there were only small differences. However, the samples can only be compared between each other since no reference with a known industrial pulping performance was analyzed. An interesting deviation to note was that two samples within clone B, both with a low yield compared to the other samples (≈ 50 %), had large variations regarding the alkali consumption. Sample CA3.2B had the highest alkali consumption of all samples and Sample CA5.4B had the lowest alkali consumption. This indicates that some other structures in CA3.2B gave rise to higher alkali consumption or that Sample CA5.4B was easier to delignify. Another deviation within clone B was between Sample CA3.2B and W5.9B. Both had similar extractive content but Sample CA3.2B had a higher alkali consumption. This indicate that the extractive content did not influence the cooking performance. This study could also conclude that there was only a relatively small content of lipophilic extractives present and that these should not have an extensive effect of cooking performance.

Throughout the discussed results it can be concluded that the results regarding the composition of the wood were similar to literature on Brazilian eucalyptus and especially *E. Urograndis.* Especially the extractives did not seem to be much larger than has been seen before. To fully understand the cooking behavior for the wood components it would be important to analyze changes in wood composition for all the time intervals since there were larger variations in residual alkali for time intervals 2 and 3 as can be seen in Table 8.

6. Conclusion

In this section the conclusions from this thesis will be presented and related to the objectives of this study.

- The content of the lipophilic extractives in the studied samples was very low. According to literature these extractives are responsible for chemical consumption.
- The compounds present in the lipophilic extracts of the different clones were similar for all samples.
- There were no indication that age or region of plantation would affects the extractive content.
- When performing extraction with acetone small amounts of other wood components such as lignin and carbohydrates were also extracted.
- The cooking showed an expected degradation of the wood components.
- No correlation between alkali consumption and extractive content could be seen.
- There was no indication that a higher extractive content lead to a lower yield.
- The consumption of cooking chemicals was possibly more influenced by composition and cooking behavior of the main components.

7. Looking Forward

In this section suggestions on how to continue this project will be presented. These are based on the results that were achieved in this study and what could have been done if there was more time.

For more confident conclusions a more thorough cooking method would have to be developed. This could be done with several experimental cooks to determine cooking parameters for each sample to reach the same kappa number. The results could then be interpolated to be able to detect even small differences in cooking performance, that would make significant differences in the mill.

The Kraft cooking studies should be continued on additional samples. This should be done both for statistics but also on wood samples that are considered to have good performance within the pulp mills as reference to be able to compare the results. It could also be done on wood samples that are known to perform badly in the mills causing problems with chemical consumption. To be able to monitor the cooking performance in more detail, the analyses should be done for all time intervals.

Another suggestion when looking forward on this issue is to investigate variations in lignin structure among the samples and its effect on the cooking performance. The lignin structure should also be related to the structural variations in hemicelluloses, celluloses and extractives to see if there is a combined effect.

8. References

Barnett, J. and Bonham, V. (2004). Cellulose microfibril angle in the cell wall of wood fibres. *Biological Reviews*, 79(2), pp.461-472.

Björklund Jansson, M. and Nilvebrant, N. (2009). Wood Extractives. In: M. Ek, G. Gellerstedt and G. Henriksson, ed., *Pulp and Paper Chemistry and Technology - Wood Chemistry and Wood Biotechnology*, 1st ed. Berlin: Walter de Gruyter, pp.147-172.

Brännvall, E. (2009). Pulping Technology. In: M. Ek, G. Gellerstedt and G. Henriksson, ed., *Pulping Chemistry and Technology*, 1st ed. Berlin: Walter de Gruyter, pp.121-148.

Christopher, L., Yao, B. and Ji, Y. (2014). Lignin Biodegradation with Laccase-Mediator Systems. *Frontiers in Energy Research*, 2, pp.2.

Da Silva Magaton, A., Luiz Colodette, J., De Fátima Gomes Gouvêa, A., Lívio Gomide, J., Coelho Dos Santos Muguet, M. and Pedrazzi, C. (2009). Eucalyptus wood quality and its impact on Kraft pulp production and use. *Tappi Journal,* 8 (8), pp.32-39.

Magaton, A.D. *et al.* (2009) 'Eucalyptus wood quality and its impact on Kraft pulp production and use'. *Tappi Journal,* 8 (8), pp. 32-39.

Daniel, G. (2009). Wood and Fibre Morphology. In: M. Ek, G. Gellerstedt and G. Henriksson, ed., *Pulp and Paper Chemistry and Technology - Wood Chemistry and Wood Biotechnology*, 1st ed. Berlin: Walter de Gruyter, pp.45-70.

Determann, H. (1969). *Gel Chromatography. Gel Filtration, Gel Permeation, Molecular Sieves. a Laboratory Handbook. (Translated by Erhard Gross and John M. Harkin)*. 1st ed. New York: Springer.

Gellerstedt, G. (2009a). Chemistry of Chemical Pulping. In: M. Ek, G. Gellerstedt and G. Henriksson, ed., *Pulping Chemistry and Technology*, 1st ed. Berlin: Walter de Gruyter, pp.92-120.

Gellerstedt, G. (2009b). Wood Handling. In: M. Ek, G. Gellerstedt and G. Henriksson, ed., *Pulping Chemistry and Technology*, 1st ed. Berlin: Walter de Gruyter, pp. 13-34.

Gomide, J., Colodette, J., Oliviera, R. and Mudado, C. (2005). Technological Characterization of the New Generation of Brazilian Eucalyptus Clones. In: Tappi Pulping Conference. Philadelphia.

Gominho, J., Figueira, J., Rodrigues, J. and Pereira, H. (2001). Within-tree variation of heartwood, extractives and wood density in the eucalypt hybrid Urograndis (Eucalyptus Grandis x E. Urophylla). *Wood and Fiber Science*, 33(1).

Günther, H. (2014). NMR spectroscopy. 3rd ed. [Place of publication not identified]: Wiley-VCH.].

Hanai, T. (1999). *HPLC: A Practical Guide*. 1st ed. Cambridge: Royal Society of Chemistry.

Harris, D. (2010). Quantitative chemical analysis. 8th ed. New York: Freeman, p.581-642.

Henriksson, G. (2009). Lignin. In: M. Ek, G. Gellerstedt and G. Henriksson, ed., *Pulp and Paper Chemistry and Technology - Wood Chemistry and Wood Biotechnology*, 1st ed. Berlin: Walter de Gruyter, pp.121-146.

Henriksson, G., Brännvall, E. and Lennholm, H. (2009). The Trees. In: M. Ek, G. Gellerstedt and G. Henriksson, ed., *Pulp and Paper Chemistry and Technology - Wood Chemistry and Wood Biotechnology*, 1st ed. Berlin: Walter de Gruyter, pp.13-44.

Henriksson, G. and Lennholm, H. (2017). Cellulose and Carbohydrate Chemistry. In: M. Ek, G. Gellerstedt and G. Henriksson, ed., *Pulp and Paper Chemistry and Technology - Wood Chemistry and Wood Biotechnology*, 1st ed. Berlin: Walter de Gruyter, pp.71-100.

Hillis, W. E., & ScienceDirect Archives (e-book collection). (1962;2014;). *Wood extractives: And their significance to the pulp and paper industries*. New York, New York; London, England; Academic Press.

Holland, P. (2009). *The Pros and Cons of Eucalyptus*. [online] Pulp & Paper. Available at: http://www.pulppapernews.com/2009/04/the-pros-and-cons-of-eucalyptus [Accessed 8 May 2017].

ISO302:2015. *Pulps – Determination of Kappa Number.* 3rd ed. International Organization for Standardization.

Jensen, W. (2007). The Origin of the Soxhlet Extractor. *Journal of Chemical Education*, 84(12), p.1913.

Li, J. and Gellerstedt, G. (1997). The contribution to kappa number from hexauronic acid groups in pulp xylan. *Carbohydrate Research*, 302(3-4), pp.213-218.

Luque de Castro, M. and García-Ayuso, L. (1998). Soxhlet extraction of solid materials: an outdated technique with a promising innovative future. *Analytica Chimica Acta*, 369(1-2), pp.1-10.

Martino, D., Colodette, J., Silva, T., Júnior, D., De Paula, D. and Azevedo, M. (2013). Factors Affecting Bleachability of Eucalypt Pulp. *BioResources*, 8(1).

Milanova (1994). On the determination of residual alkali in black liquors. *Nordic Pulp and Paper Research Journal*, 09(01), pp.4-9.

Milanova, E., Dorris, G. M., Tech Assoc, Pulp, & Paper, I. N. D. (1991, Nov 03-07). ON THE DETERMINATION OF RESIDUAL ALKALI IN BLACK LIQUORS. Paper presented at the 1991 Pulping Conf, Orlando, Fl.

Morais, M. and Pereira, H. (2011). Variation of Extractives Content in Heartwood and Sapwood of Eucalyptus Globulus Trees. *Wood Science and Technology*, 46(4), pp.709-719.

Pettersson, E., Ragnar, M. and Lindström, M. (2002). Kraft cooking characteristics and hexenuronic acid concentration of pulps from Eucalypt and other hardwood species. Nordic Pulp and Paper Research Journal, 17(03), pp.222-227.

Prinsen, P., Gutiérrez, A., Rencoret, J., Nieto, L., Jiménez-Barbero, J., Burnet, A., Petit-Conil, M., Colodette, J., Martínez, Á. and del Río, J. (2012). Morphological characteristics and composition of lipophilic extractives and lignin in Brazilian woods from different eucalypt hybrids. *Industrial Crops and Products*, 36(1), pp.572-583.

Radojevic, M. and Bashkin, V. (2006). *Practical Environmental Analysis*. 2nd ed. Royal Society of Chemistry, p.412.

Rowe, J.W. (1989). Natural products of woody plants. Springer-Verlag Berlin Heidelberg.

SCAN-N 33:94. (1994). Residual alkali (Hydroxide ion content). Scandinavian pulp and paper board.

Silvério, F., Barbosa, L., Silvestre, A., Piló-Veloso, D. and Gomide, J. (2007). Comparative Study on the Chemical Composition of Lipophilic Fractions from Three Wood Tissues of Eucalyptus Species by Gas Chromatography-Mass Spectrometry Analysis. *Journal of Wood Science*, 53(6), pp.533-540.

Silviéro, F., Barbosa, L., Maltha, C., Silvestre, A., Pilo-Veloso, D. and Gomide, J. (2007). Characterization of Lipophilic Wood Extractives from Clones of Eucalyptus Urograndis Cultivate in Brazil. BioResources, 2(2), pp.157-168.

Sparkman, O., Penton, Z. and Kitson, F. (2011). *Gas chromatography and mass spectrometry*. 2nd ed. Amsterdam: Elsevier.

S. R. Freire, C., C. R. Pinto, P., S. Santiago, A., J. D. Silvestre, A., V. Evtuguin, D. and Neto, C. (2006). Comparative Study of Lipophilic Extractives of Hardwoods and Corresponding ECF Bleached Kraft Pulps. *BioResources*, 1(1), pp.3-17.

Tappi T 222 om-02. *Acid insoluble lignin in wood and pulp*. Tappi Standard.

Tappi T 236 cm-85. *Kappa Number of Pulp*. Tappi Standard.

Teleman, A. (2017). Hemicelluloses and Pectins. In: M. Ek, G. Gellerstedt and G. Henriksson, ed., *Pulp and Paper Chemistry and Technology - Wood Chemistry and Wood Biotechnology*, 1st ed. Berlin: Walter de Gruyter, pp.101-120.

Theander, O. and Westerlund, E. (1986). Studies on dietary fiber. 3. Improved procedures for analysis of dietary fiber. *Journal of Agricultural and Food Chemistry*, 34(2), pp.330-336.

Theliander, H. (2009). Recovery of Cooking Chemicals: The Treatment and Burning of Black Liquor. In: M. Ek, G. Gellerstedt and G. Henriksson, ed., *Pulping Chemistry and Technology*, 1st ed. Berlin: Walter de Gruyter, pp. 297-334.

Wilson, K. (1971). Bestämning av effektivt alkali i svartlut. Svensk Papperstidning, pp.446-447.

Zhu, W. (2013). Precipitation of Kraft Lignin Yield and Equilibrium. Ph.D. Chalmers University of Technology

Appendix A – Effective alkali calculation

Example calculation of white liquor:

Parameters:

Sulfidity (%)	S
Effective alkali (%)	EA
Dry content wood (%)	DC
Mass wood chips dry (g)	m_{wood}
Mass liquor (g)	m_{liquor}
Conc. Na_2S solution (g/kg)	$[Na_2S]$

To be calculated:

Amount of NaOH (g)	NaOH
Amount of Na_2S solution (g)	Na_2S (solution)
Amount of moist wood chips (g)	$m_{wood,wet}$
Amount of water (g)	H_2O

$$Na_2\mathrm{S}\ (\text{as NaOH}) = \frac{S * EA * m_{wood}}{(1 - 0.5 * S)}$$

$$\mathrm{NaOH} = \mathrm{EA} * \mathrm{m} - 0.5 * Na_2\mathrm{S}\ (\text{as NaOH})$$

$$Na_2\mathrm{S} = Na_2\mathrm{S}\ (\text{as NaOH}) * \left(\frac{78}{80}\right)$$

$$Na_2\mathrm{S}\ (solution) = \frac{Na_2S}{[Na_2S] * 1000}$$

$$\mathrm{m}_{wood,wet} = \frac{m_{wood}}{DC}$$

$$H_2O_{wood} = m_{wood,wet} - m_{wood}$$

$$H_2\mathrm{O} = m_{liquor} - NaOH - Na_2S\ (solution) - H_2O_{wood}$$

Appendix B – Extractives

Table 14. Extractive content in percent on dry wood basis. Within each sample the independent duplicates are where two values form an average. An exception is sample 5 where the highest values of 5,97 is considered to be an outliner and it is not included in this average. In the bottom the averages for each clone and a total average can also be seen.

Sample no.	Extractive content w%	Average of duplicates w%	Total average w%
1	2.64	2.61	2.61
	2.59		
2	3.18	3.21	3.21
	3.23		
3	3.92	3.91	3.91
	3.90		
4	3.04	3.10	3.10
	3.16		
5	6.17	5.97	4.14
	5.77		
	4.34	4.14	
	3.95		
	4.01	4.13	
	4.25		
6	3.43	3.52	3.52
	3.60		
7	4.72	4.73	4.75
	4.74		
	4.65	4.76	
	4.87		
8	4.04	3.96	3.93
	3.89		
	3.70	3.90	
	4.10		
9	4.29	4.18	4.02
	4.07		
	3.87	3.87	
10	2.69	2.83	2.83
	2.97		
	2.87	2.83	
	2.79		
11	4.13	4.19	4.19
	4.25		
12	2.43	2.58	2.58
	2.72		
13	3.03	3.11	3.45
	3.20		
	3.59	3.79	
	4.00		
14	1.87	1.68	1.80
	1.49		
	2.03	1.92	
	1.82		
15	2.39	2.40	2.30
	2.42		
	2.20	2.20	
	2.20		
Average clone A	2.91		
Average clone B	3.95		
Total average	3.43		

Appendix C - GC-MS results

Table 15. Semi-quantitative results from the GC-MS/GC-FID analysis. Shows five of the samples most abundant compounds and the mass factions.

GC-MS results - largest peaks and mass fractions (%)

	Lipophilic fraction		**Lipophilic fraction after alkaline hydrolysis**	
Sample	Compound	Mass fraction (%)	Compound	Mass fraction (%)
CA5.4(B)	β-Sitosterol	13.21	β-Sitosterol	4.643
	Linoleic acid	2.701	Benzoic acid	1.636
	Stearic acid	0.915	Linoleic acid	1.318
	Stigmastanol	0.705	Hexadecanoic acid	0.987
	Stigmastan-3,5-diene	0.485	Cinnamic acid	0.871
	Stigmast-4-en-3-one	0.446	Yangambin	0.748
	(+)-α-Tocopherol	0.415	Stigmastanol	0.465
W5.9(B)	β-Sitosterol	10.801	β-Sitosterol	4.973
	Hexadecanoic acid	2.743	Benzoic acid	2.116
	Linoleic acid	2.059	Yangambin	1.026
	Benzoic acid	0.533	Linoleic acid	0.977
	Stigmastanol	0.511	Cinnamic acid	0.848
	(+)-α-Tocopherol	0.498	Hexadecanoic acid	0.742
	Stigmastan-3,5-diene	0.403	Stigmastanol	0.489
CA3.2(B)	β-Sitosterol	6.391	Benzoic acid	5.598
	Hexadecanoic acid	1.650	β-Sitosterol	4.077
	Oleic acid	1.614	Linoleic acid	2.183
	Linoleic acid	0.852	Hexadecanoic acid	1.852
	Stigmastanol	0.458	Yangambin	0.888
	Stigmast-4-en-3-one	0.428	Cinnamic acid	0.756
	(+)-α-Tocopherol	0.345	Stigmastanol	0.464
W6.0(A)	β-Sitosterol	7.825	β-Sitosterol	6.615
	Hexadecanoic acid	2.715	Benzoic acid	3.299
	Linoleic acid	1.432	Hexadecanoic acid	2.768
	Stigmastanol	0.638	Cinnamic acid	1.740
	(+)-α-Tocopherol	0.501	Stigmastanol	0.899
	Stigmast-4-en-3-one	0.414	Silane	0.884
			Yangambin	0.657
CA3.2(A)	β-Sitosterol	6.343	β-Sitosterol	4.149
	Hexadecanoic acid	2.072	Linoleic acid	1.697
	Linoleic acid	0.980	Benzoic acid	1.640
	Catechine	0.661	Hexadecanoic acid	1.282
	Stigmastan-3,5-diene	0.581	Phenolic derivative	0.679
	Stigmastanol	0.444	Stigmastanol	0.565
	Stigmast-4-en-3-one	0.433	Cinnamic acid	0.433

Appendix D – Carbohydrate results

Table 16. The results from the carbohydrate analysis showing the content of all sugar monomers (%, on dry wood basis). The number in parenthesis gives the number of the experimental sample.

Neutral anhydrous monosaccharides		**Wood Composition (% on dry wood basis)**					
Sample	**Clone**	**Arabinose**	**Rhamnose**	**Galactose**	**Glucose**	**Xylose**	**Mannose**
14(1)	A	0.25	0.00	1.15	46.0	11.9	1.02
14(2)		0.25	0.00	1.14	44.5	11.5	1.03
10(1)		0.27	0.00	1.18	45.0	12.4	1.17
10(2)		0.26	0.00	1.15	43.0	11.5	1.03
8(2)		0.27	0.00	1.15	44.3	11.4	0.80
8(2)		0.27	0.00	1.15	43.6	11.2	1.00
5(1)	B	0.37	0.00	0.97	42.9	13.4	0.97
5(2)		0.37	0.00	1.02	44.2	13.9	1.00
13(1)		0.31	0.00	0.87	47.0	12.9	1.15
13(2)		0.32	0.00	0.88	46.9	13.1	1.17
9(1)		0.31	0.00	0.88	45.4	12.5	1.09
9(2)		0.32	0.00	0.90	46.5	13.1	1.12
		Pulp Composition (% on dry wood basis)					
		Arabinose	**Rhamnose**	**Galactose**	**Glucose**	**Xylose**	**Mannose**
14(1)	A	0.03	0.00	0.10	40.0	7.39	0.27
14(2)		0.00	0.00	0.09	40.2	7.01	0.26
10(1)		0.00	0.00	0.10	39.6	6.96	0.24
10(2)		0.03	0.00	0.13	34.5	7.74	0.26
8(2)		0.02	0.00	0.13	36.5	7.51	0.04
8(2)		0.00	0.00	0.12	34.5	6.94	0.00
5(1)	B	0.00	0.00	0.08	39.3	8.62	0.30
5(2)		0.00	0.00	0.09	36.9	9.16	0.23
13(1)		0.00	0.00	0.10	38.4	7.47	0.19
13(2)		0.00	0.00	0.11	36.4	8.08	0.32
9(1)		0.02	0.00	0.09	37.6	8.36	0.05
9(2)		0.00	0.00	0.09	36.9	8.27	0.05

In the calculation of the sugar monomers in Table 16 above the amounts was corrected for the acid hydrolysis yield. The sugars are also presented as anhydrous sugars (withdrawal of water). The pentoses are multiplied with 0.88 and the hexoses with 0.90. The acetyl groups are multiplied with 0.73 and uses the same correction factor for the acid hydrolysis yield as xylose.

Calculations of wood component content from the sugar monomers in Table (16):

$$Xylan = Xylose + Arabinose$$

$$Cellulose = Glucose - \left(\frac{1}{1}\right) * Mannose$$

$$Glucomannan = Galactose + (1 + \left(\frac{1}{1}\right)) * Mannose$$

These calculations are based on the molar ratio between Galactose and Mannose in Glucomannan which are 1:1 in eucalyptus.

Figure 27. Cellulose content in the wood and pulp (% on dry wood basis).

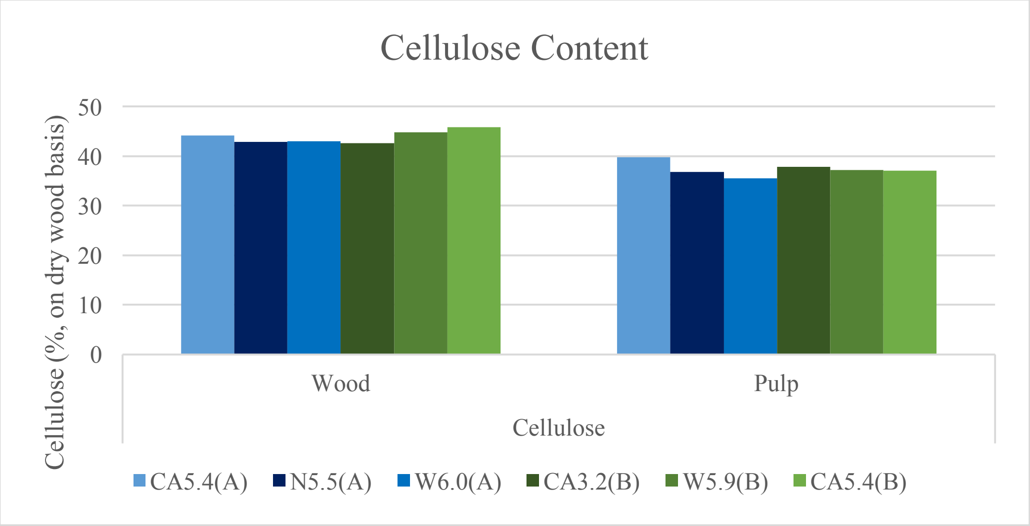

Figure 28. Xylan content in the wood and pulp (% on dry wood basis).

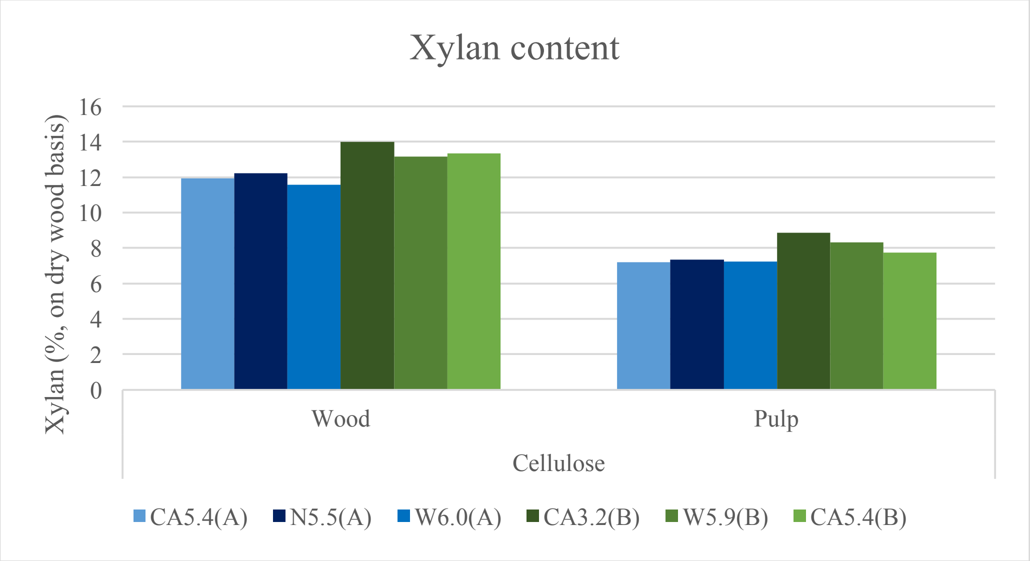

Table 17. Amount of cellulose, hemicellulose and holocellulose (cellulose + hemicellulose) of the wood samples (% on dry Wood basis).

	Component (% on dry wood basis)					
	Hemicellulose		Cellulose		Holocellulose	
Sample	**Wood**	**Pulp**	**Wood**	**Pulp**	**Wood**	**Pulp**
CA5.4(A)	18.3	7.85	44.2	39.8	62.5	47.7
N5.5(A)	18.6	7.98	42.8	36.8	61.5	44.8
W6.0(A)	17.5	7.41	43.0	35.5	60.5	42.9
CA3.2(B)	20.3	9.51	42.6	37.8	62.9	47.3
W5.9(B)	19.4	8.52	44.8	37.2	64.2	45.7
CA5.4(B)	19.7	8.39	45.8	37.1	65.5	45.5

Appendix E – Results from mass balance calculations

Table 18. Amounts of different carbohydrates in the wood and pulp samples for the cooking Kraft cooking series.

	Carbohydrate content in wood samples (g/50 g bone dry wood)						
Sample	**Arabinose**	**Rhamnose**	**Galactose**	**Glucose**	**Xylose**	**Mannose**	**Total (g)**
CA5.4(A)	0.126	0.000	0.573	22.6	5.86	0.511	29.7
N5.5(A)	0.134	0.000	0.582	22.0	5.98	0.549	29.3
W6.0(A)	0.137	0.000	0.576	22.0	5.66	0.451	28.8
CA3.2(B)	0.185	0.000	0.498	21.8	6.81	0.493	29.8
CA5.4(B)	0.158	0.000	0.437	23.5	6.51	0.579	31.2
W5.9(B)	0.158	0.000	0.443	23.0	6.42	0.553	30.5
						Average	**29.9**

	Carbohydrate content in pulp samples (g/50 g bone dry wood)						
	Arabinose	**Rhamnose**	**Galactose**	**Glucose**	**Xylose**	Mannose	Total (g)
CA5.4(A)	0.008	0.000	0.048	20.1	3.60	0.132	23.8
N5.5(A)	0.008	0.000	0.058	18.5	3.67	0.125	22.4
W6.0(A)	0.006	0.000	0.062	17.8	3.61	0.006	21.5
CA3.2(B)	0.000	0.000	0.041	19.0	4.44	0.131	23.7
CA5.4(B)	0.000	0.000	0.053	18.7	3.88	0.127	22.8
W5.9(B)	0.005	0.000	0.043	18.6	4.16	0.023	22.8
						Average	22.8

Table 19. Amounts of acetyl groups in the wood and pulp samples for the cooking Kraft cooking series.

	Acetyl groups (g/50 g bone dry wood)	
Sample	**Wood**	**Pulp**
CA5.4(A)	1.60	0.005
N5.5(A)	1.53	0.005
W6.0(A)	1.49	0.005
CA3.2(B)	1.69	0.005
W5.9(B)	1.58	0.005
CA5.4(B)	1.61	0.005
Average	1.58	0.005

Table 20. Amount of lignin and extractives in the wood samples for the Kraft cooking series. For lignin the amount in the pulp can also be seen.

	Total lignin content (g)		**Extractives content (g)**
Sample	Wood	Pulp	Wood
CA5.4(A)	16.5	0.46	2.04
N5.5(A)	16.3	0.55	1.97
W6.0(A)	17.3	0.46	2.01
CA3.2(B)	16.9	0.45	1.36
CA5.4(B)	16.0	0.38	1.73
W5.9(B)	16.2	0.53	0.90
Average	16.5	0.47	1.67