Hardwood delignification

Investigating Kraft Cooking of Hardwood Chips of different Sizes

Master's thesis in Innovative and Sustainable Chemical Engineering

EBBA SUNDQUIST

DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING
CHALMERS UNIVERSITY OF TECHNOLOGY
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Abstract

The Kraft process is the dominating method for producing paper pulp. During the chipping process, preceding the pulping, pin chips are being generated. There is today limited knowledge about how these finer fractions behave during delignification. The most commonly used wood type in northern Europe has over the years been softwood, but during the recent years the interest in using hardwoods has increased. Hardwood has specialized conductive cells, so called vessels, that allows for an effective liquid transportation within the wood. The purpose of this study was to investigate how chip size affect delignification and also to compare this between two hardwood species since there are significantly morphological differences between hardwood species. The species investigated in this study were aspen and birch and the investigated chip sizes were accepted chips, small accepted chips and pin chips. The chips were cooked with an effective alkali of 20 % and a sulfidity of 30 % at a temperature of 160 °C. The delignification of the chips was ended at different times to be able to follow the delignification rate. Both the lignin content and the content of different carbohydrates were measured, including molecular weight distribution of lignin for selected samples. The effect of the liquor to wood ratio was also studied, by applying both low and high concentrations of cooking chemicals.

When the wood chips were cooked with a low concentration of cooking chemicals the difference between the wood chip sizes were larger than when cooking at higher concentration. At higher concentration of cooking chemicals the wood was effectively delignifed and the differences between the species were limited. The accepted chips seems to be unevenly delignified in contrast to pin chips even tough having very similar Klason lignin content. The method does not consider the local content of lignin, hence local variations in residual lignin content visible in accepts can not be captured. An extension of this work would be needed to be able to fully understand the local delignification rates. The overall trend found that the diffusion distance, related to the wood chip size, and the diffusion resistance, related to the wood structure had the highest impact on the delignification rate in the initial delignification phase. When comparing the delignification rates between the species it was seen that aspen was easier delignified than birch, and that the differences between the chip sizes were smaller compared to birch. The reason for this was believed to be a more porous wood structure of aspen that allows for easier transportation of chemicals and lignin fragments. The results from the molecular weight distribution measurements indicated that there was a difference between the pin chips and the accepts, where the lignin transported out from the pin chips was shifted towards larger molecular weights.

Keywords: Hardwood, Pin chips, Delignification, Kraft process, Chip sizes

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Ebba Sundquist, Gothenburg, June 2024

List of Acronyms

Below is the list of acronyms that have been used throughout this thesis listed in alphabetical order:

ASL	Acid Soluble Lignin
DMSO	dimethyl sulphoxide
DP	Degree of Polymerisation
EA	Effective Alkali
LCC	Lignin carbohydrate Complex
l/w	liquor to wood ratio
MWD	Molecular Weight Distribution
PEG	Polyethylene glycol
S	Sulfidity

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1
Introduction

The world is now facing an environmental crisis. In the foreseeable future the fossil resources will be depleted. From these resources products that are of high importance and those that could be taken for granted are obtained. To be able to still get access to these products the fossil resources must be replaced with renewable resources. The forest industry could be one of the ways out, with pulp mills having the ability to provide raw material for a broad range of products, like packaging and textiles, they could lead the transition to a more circular and bio-based society. However, even though the forest and its resources are renewable it doesn't mean that they are endless. Therefore, it is important to have a sustainable forest industry that utilizes the wood in a resource-efficient way.

The Kraft process is the dominating process for making pulp and providing a separation of wood components. One of the first steps in the process is to cut the wood into smaller pieces. In this step there are fractions generated that are outside the targeted size range. These are often separated to be used as energy, pulped separately or added to the process in small amounts.

Hardwood, leafy trees, will probably be used even more in the future to produce pulp, due to the increasing demand for non-fossil products. There is very limited research about how the finer fractions of hardwood behave during the delignification to produce pulp. With a better understanding of this, it would be possible to tune the processes and better control the properties of the pulp obtained from these fractions.

1.1 Aim

The aim is to bring an understanding of the behavior of different size fractions of hardwood chips during Kraft cooking to be able to fine tune the process for increasing yield and pulp uniformity, leading to a more resource efficient process.

1.1.1 Specification - Research Questions

How does the rate of delignification differ between pin chips, small accepts and accepts? What are some of the relevant mechanisms influencing the delignification of each fraction?

How do cooking conditions similar to the ones applied in industry affect the delignification profile and pulp yield of pin chips?

How does the molecular weight distribution of the dissolved Kraft lignin vary between the species and fractions and why are these differences observed?

What differences could be observed between aspen and birch chips? Do the delignification behaviour, yield and molecular weight distribution differ?

1.1.2 Limitations

Only hardwood is investigated, and limited to birch and aspen.

Three size fractions are considered, accepts, smaller accepts and pin chips. Other dimensions will not be considered.

All cooking experiments were conducted under the same conditions (e.g., temperature, EA and S). The only difference between the high concentration case and the low concentration case was the liquor to wood ratio utilized.

In the study there will be no large focus on minor components in the wood such as extractives and ash, the main focus will be on the lignin and polysaccharides as their behaviour closely interferes with delignification.

2
Theory

2.1 Wood structure

Trees could be dived into softwoods or hardwoods, depending on if they are gymnosperms or angiosperms. Softwoods belongs to the gymnosperms and hardwoods to the angiosperms [1]. A gymnosperm creates a naked seed, while the angiosperm created seeds enclosed within fruit developed from a flower. All trees are perennial, meaning that they live for several years. Wood consists of stems with xylem and phloem tissues. Xylem constitute the main part of the wood, while pholem is referred to as the inner bark. Both of these consists of conducting cells that conduct nutrients and photosynthetic products or give mechanical support [3]. The cells are mostly oriented in the longitudinal direction of the stem and are connected with each other through pits. In the xylem structural variations could be seen as annual growth rings. The inner part of the xylem consists of heartwood, while the outer parts consists of sapwood. In some cases, they can be differentiated by color, with heartwood presenting a darker shade than sapwood. Heartwood is composed of sealed cells and usually presents lower porosity due to deposits of resins while sapwood is responsible for the transportation of sap of conducting cells, living or dead. The radial growth of the tree takes place in the area between the xylem and phloem, called the cambial zone [1].

2.1.1 Tree growth

The trees grow through cell division and usually grow most intensively during the spring. Over the years the trees grow continuously but with a slower rate at the end of its life. The longitudinal growth proceeds at the end of the stems, branches or the roots. The radial growth begins in the cambial zone, where the cells divide and produces daughter cells that could be further divided. More cells are produced towards the xylem than the phloem, hence the wood is thicker than the bark. Each of the cells that have been divided encloses itself with a thin wall consisted of cellulose, lignin, hemicellulose and other minor components. This thin wall is referred to as the primary wall. The cell will expand to its full size and deposits additional sublayers (S1, S2 and S3) with a specific orientation of cellulose microfibrils in each of them. The middle layer (S2) is the thickest one and is also where the main part of the cellulose, hemicellulose and lignin is located [1].

2.1.2 Hardwood Cells

Wood cells could be divided into prosenchyma and parenchyma cells. A prosenchyma cell are a longer and thinner cell with narrow ends while a parenchyma cell are shorter and rectangular with more rounded ends. Depending on their functions the cells could also be divided into three different groups, conducting cells, supporting cells and storage cells. In hardwoods, the conducting cells consist of vessels which are dead cells containing cavities. The vessels are placed on top of each other to form a long tube, which could be several meters. The vessels in hardwood allow for a more effective water transport than exists in the softwood, which is important during the leafing, which requires a lot of water. In birch and aspen, the vessels occupies 25% of the stem volume. The supporting cells in hardwoods are fibers, mainly libriform cells. The storage cells are thin parenchyma cells which function as long as they are in the sapwood. In birch, the libriform cells and the fiber tracheids constitute almost 70 % of the volume of the stem [1].

2.1.3 Ultrastructure

The cell wall is built up of cellulose, hemicellulose and lignin arranged in a complex matrix. The length of a cellulose molecule can be up to 10 000 glucose units, and they are connected by hydrogen and van der Waals bonds into microfibrils. These are then combined to larger fibrils. The hemicelluloses are amorphous, while cellulose have a more ordered structure. The cell wall is built up by several layers consisted of cellulose fibrils embedded in a hemicellulose and lignin matrix. The cell walls are connected through the middle lamella (M) and the layers in the cell wall are the primary wall (P), secondary wall, that has three layers (S1, S2, S3) and sometimes there also exists a warty layer (W), a schematic drawing is shown in Figure 2.1. In these layers, the direction of the microfibrils differs, resulting in physical differences between them. The middle lamella is located between cells and is binding the cells together and has a high content of lignin. The primary wall is thin, and here the cellulose fibrils have a random orientation. The inner and outer layers of the secondary wall are thin, while the middle one is thick. In S2 the cellulose fibrils form a relatively small angle with the fiber axis, which also strongly affects the stiffness of the cell wall. The thickness of the S2 layer varies depending on when during the growth season the cell is formed. The warty layer is thin and amorphous and contains deposits with mostly unknown composition [1].

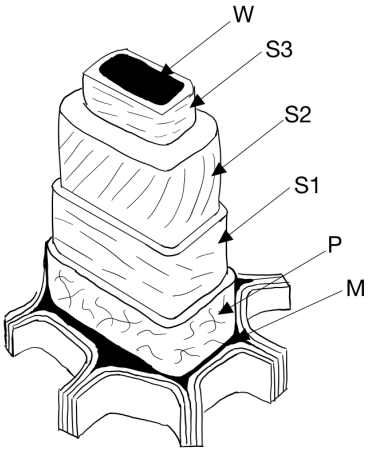


Figure 2.1: Ultrastructure of wood, picture edited from [1]

2.1.4 Aspen and Birch

Aspen (*Populus tremula*) is the species also commonly named Eurasian aspen and is a fast-growing tree that could be found in Europe and Asia. The wood is mainly used as matches, veneer or to produce pulp. Today there also exists several hybrids to maximize the desired yield. In the Nordics the hybrid Populus tremula x tremuloides is often planted for the purpose of pulp fibre production. Aspen is one of the most most widely distributed trees in the world. Due to its wide distribution over the globe, the morphology could differ depending on where the tree is grown. The wood of aspen is not as dense as others in the poplar family [4].

There exists several subspecies of Birch (*Betula pendula, Betula pubescens*). *Betula pendula* and *Betula pubescens* occur throughout most of Europe and are particularly common in the northern regions. *Betula pubescens* are more northern and easterly distributed than *Betula pendula* which can reach southern regions such as Italy or Greece. Birch trees are the dominating hardwood source in the northern Europe and *Betula pubscens* is the one mostly used for pulping [5].

Aspen (*Populus tremula*) and Birch (*Betula sp.*) share some common features but do also have some differences. Some of the differences that might affect the outcome of the delignification could be related to how effective the transport in the wood is. What could be seen is that aspen has some vessels that are of a bigger size compared to what is found in birch, between 80-130 micrometer and birch has vessels of smaller size than 80. Birch does also have fewer rays, around 5-12 rays/mm while aspen has more than 12/mm [6].

Previous studies, [7], have shown that the lignin content is higher in birch than in aspen. Meanwhile, the amount of carbohydrates is higher in aspen. The overall composition found in the study, [7] is summarized in Table 2.1.

Table 2.1: Raw material Composition

Component	Birch	Aspen
Carbohydrates	63.6 ± 0.6	65.8 ± 0.4
- Glucan	39.1 ± 0.4	44.8 ± 0.2
- Xylan	21.9 ± 0.1	17.2 ± 0.2
- Mannan	1.6 ± 0.0	2.9 ± 0.0
- Arabinan	0.3 ± 0.0	0.3 ± 0.0
- Galactan	0.7 ± 0.0	0.6 ± 0.0
Klason Lignin	19.6 ± 0.2	19.0 ± 0.2
Acid soluble lignin	5.0 ± 0.1	4.7 ± 0.1
Total	88.2 ± 0.7	89.5 ± 0.3

2.2 Lignin

Wood contains a significant amount of lignin, softwood has around 15-35 % of lignin and hardwood around 20 %. Lignin is a hydrophobic polymer and has a complex structure that forms an intricate three-dimensional web. The chemical pulping is mainly based on reactions to degrade the lignin, why its structure and properties are of importance for the field [8].

Lignins are polymerized from monolignols, which are propylphenol derivatives with different number of attached methoxy groups. These could be of three different kinds: p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. Softwood lignin consists almost exclusively of coniferyl alcohol, while hardwood lignin contain both coniferyl and sinapyl alcohols [8].

Lignin has different functions in the woody plants. It provides stiffness to the cell wall, glues different cells together in tissues, introduces hydrophobicity to the cell wall and protects the wood from microbial degradation. Lignin appears in close relation to the polysaccharides in wood, cellulose, hemicellulose and pectin. The network and close connection makes it difficult to isolate the lignin polymer in its native form. This makes it almost impossible to determine the molecular weight of the intact lignin in the wood. It has been found that lignin has many different carbon-carbon and ether bonds. The most frequent bond between the monolignols is the $\beta - O - 4'$ linkage, it is therefore critical for the reactions during pulping. The carbon-carbon bonds are more resistant and these often withstand the chemical pulping. The covalent bonds between the monolignols are formed due to radical couplings. Lignin-carbohydrate complexes, LCC, are structures where the lignin and hemicelluloses are linked with covalent bonds. Sinapyl alcohol, which is more present in hardwood than softwood, can not couple in the carbon 5 position [8].

The concentration and structure of lignin varies through wood morphology and ultrastructure. In hardwood, the composition of monomers also differ between different cell types. The ray parenchyma cells and the vessels have a higher content of coniferyl alcohols than the fibers. The cell wall consists of three different layers and the deposition is therefore done in three steps. When each layer is formed,

different lignin concentration and structures are deposited. In the first step, the corners of the primary wall and the middle lamella are formed. The second step is when cellulose and hemicellulose has been deposited in the S2 layer. The S3 layer and the middle lamella have a higher lignin content than the S2 layer, both for hardwood and softwood. However, since the S2 layer is thicker the total amount of lignin is highest in the S2. The lignin in the middle lamella of hardwood has a more branched structure than the lignin in the S2. The reason for this is that it contains more coniferyl alcohols, which results in a higher content of carbon-carbon bonds [8].

2.3 Cellulose

Cellulose is the main component in the cell walls of plants. It is the most common biopolymer on earth and belongs to the group of carbohydrates. A polysaccharide is a carbohydrate that has more than 10 monosaccharide units. The monosaccharides in plant cells are almost only pentoses or hexoses. Pentoses, and those with more carbons, have a strong tendency for forming cyclic structures. The pyranose ring can take several conformations and are never flat. The chair form is the dominating, and is also found in cellulose. Glucose is the monosaccharide that is building up the cellulose chain. The glycosidic bond formed by condensation connects a monosaccharide to another. When multiple monosaccharides are connected, a polysaccharide is formed. The polysaccharide could be linear, branched or cross-linked, depending on if it has side groups or not, or if several chains are connected. The glycosidic bond in cellulose is the $\beta - 1 \rightarrow 4$ connecting the glucose units into linear unbranched chains [9].

The structure of cellulose could be divided into the primary structure and the secondary structure. The primary structure is its covalent bond pattern, which consists of a linear and unbranched polymer connected with $\beta - 1 \rightarrow 4$ glycosidic bonds, as could be seen in Figure 2.2. The DP of cellulose is very high, often up to 15 000 monomers, which makes it the longest known polysaccharide. The secondary structure of cellulose gives it its biological and technical characteristics. Two intramolecular hydrogen bonds stabilize the glycosidic bond and make the structure stiff by hindering any rotation around the glycosidic bond.

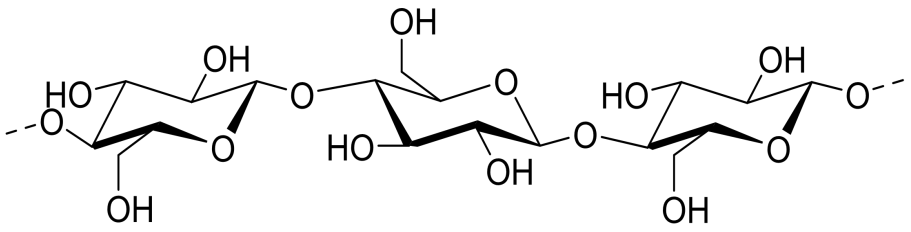


Figure 2.2: Primary structure of cellulose

There are also hydrogen bonds between adjacent cellulose chains which are forming a sheet, one of these bonds is located between C6 in one chain and C3 in the other. These cellulose sheets are then stacked on top of each other and being subjected to van der Waals interactions. These long and narrow sheets form bundles called fibrils. The number of chains each fibril contains is still under debate. The cellulose chains are just a few μm long, but they overlap, leading to at least 40 μm fibrils [9].

Cellulose chains are arranged in fibrils and deposited under a certain orientation during the biosynthesis. The cellulose is insoluble in water due to its high DP and crystalline structure and could therefore not be synthesized and then later transported to the cell wall, but instead need to be synthesized outside the cell membrane where the cell wall is being deposited. In woody plants, the theory is that the cellulose fibrils are extruded from enzyme complexes called rosettes. During the biosynthesis, several cellulose chains are synthesized in parallel from these rosettes. The cellulose fibrils have different angles in different parts of the cell wall, as previous discussed. This angle is believed to be controlled by a network of protein fibers which direct the complex in some way [9].

Some of the characteristics of cellulose is that it is a very strong material and is totally insoluble in water but can interact strongly with water. During drying of wet cellulose the fibers often get hard and inflexible, this is called hornification. Cellulose is also very resistant to chemical derivatization. The compound does also have a strong interaction with lignin. [9].

2.4 Hemicelluloses

Hemicelluloses constitute between 20 and 35 % of the dry mass of wood. They are found in the matrix in between the cellulose fibrils. The type and amount of hemicelluloses could differ widely between species but also the location and the growth conditions of the tree. The hemicelluloses in wood have been reported to have a DP of up to 200, which compared to cellulose is significantly lower. The chemical and thermal stability is lower for hemicellulose than cellulose due to their amorphous structure and side groups. The major hemicelluloses in softwood are galactoglucomannan, glucomannan and arabinoglucuronoxylan. The main hemicelluloses in hardwood are glucuronoxylan and glucomannan. Hemicelluloses may regulate the wall porosity and mechanical strength by serving as an interface between the lignin and cellulose and maintaining the spacing between the fibrils [10].

2.4.1 Xylan

Xylans are almost linear polysaccharides with a back bone of $\beta - (1 \rightarrow 4) - D - xylopyranosyl$ residues, some xylans could have side groups with single sugar residues. Xylans in wood also contain side groups of 4-O-methyl-D-glucoronic acid (MeGlcA) but the distribution of the side group differs between softwood xylan and hardwood xylan. A more regular distribution of MeGlcA is found in softwoods while they seem to be more irregularly distributed in hardwood xylans. Hardwood xylans do also contain acetyl groups [10].

2.4.1.1 Hardwood Xylan

The xylan in hardwood is glucuronoxylan and the full name is O-acetyl-(4-O-metylglucurono)xylan, due to the MeGlcA side group and the substitution with acetate groups. This side group is occurring every 8-20 xylopyranosyl residue, on average. The average DP of hardwood xylan is between 100 and 220. The xylan in birch has a higher polydispersity index, but still rather more narrow, than aspen. The index is 1.13 and 1.09 respectively. The amount of acetyl groups in hardwood xylans are between 9 and 17 % which corresponds to 4-7 acetylgroups per 10 residues [10].

2.4.2 Glucomannan

The glucomannans are linear chains of $(1 \rightarrow 4)$ linked β-D-mannopyranosyl and β-D-glucopyranosyl units. The ratio between these two could vary between 1:1 and 1:4. There are three kinds of (galacto)glucomannan that have been isolated from hardwoods and softwoods. Hardwood glucomannan, softwood glucomannan and galactoglucomannan. These differ by their galactose and acetate substitution as well as the mannose:glucose ratio.

2.4.2.1 Hardwood Glucomannan

Dry hardwood has a content of glucomannan between 3 and 5 %. The ratio between glucose and mannose is between 2:1 and 1:1 depending on the species. Galactose substituents are often infrequent or absent in hardwood glucomannan. The average degree of polymerisation for hardwood glucomannan is lower than for xylan, with a value between 60 and 70 [10].

2.5 Extractives

Extractives are non-structural wood constituents that are of both lipophilic and hydrophilic types. The composition of extractives differs strongly even between closely related wood species. The trees need diversified biological functions and for this a wide variety of extractives is needed. For example, fats are needed to store energy for the wood cells, resin acids and phenolic structures are needed to protect the wood against microbial degradation. Extractives usually constitute less than 10 % of the dry wood weight but could be higher for some species. The extractives could be seen as a valuable raw material to produce organic chemicals. The content of extractives is also important in the pulping and paper processes since they could disturb the processes or be valuable byproducts [11]. The extractives are considered to negatively influence the color and the bleachability of the pulp by contaminating it in form of dark spots and streaks. The extractives could also cause corrosion and lead to piping blockages [12].

2.6 The Kraft Process

The Kraft process is dominating the chemical pulping methods and the active cooking species used are OH^- and HS^-, the hydrogen sulphide is crucial for fragmentation of phenolic beta-O-4 structures. There is also other linkages in lignin that are broken due to the hydroxide ions, these also keeps the lignin fragments in solution. In the Kraft pulping process, the chemicals are recovered from the spent cooking liquor and used again in the digester. The liquid residue from the cooking is called black liquor and consists of both spent cooking liquor and dissolved organic materials. The organic materials are then used as an energy source to supply the process, or could be taken out, to a certain extent, and refined to higher value applications [13].

The main steps of the process are shown in Figure 2.3 and include wood handling, steaming and impregnation, delignification, chemical recovery and then there are also steps not considered in this report such as bleaching and washing of the final pulp product. In this study the steps after delignification are not considered when doing the experiments. The first step in the Kraft process is to prepare the wood to be suitable for going into the process, by removing bark and cutting it to pieces. The steaming and impregnation step are to prepare the wood so that the delignification can proceed uniformly throughout the whole chip. The delignification step is the main step and it start already during impregnation as the temperature is increased and delignification reactions starts so the lignin that holds the fibers together is removed and dissolved. The chemical recovery is a process were the used chemicals are recovered so they can be used again in the process, making the need of adding new chemicals very limited. In the following sections these steps will be explained in more detail [14].

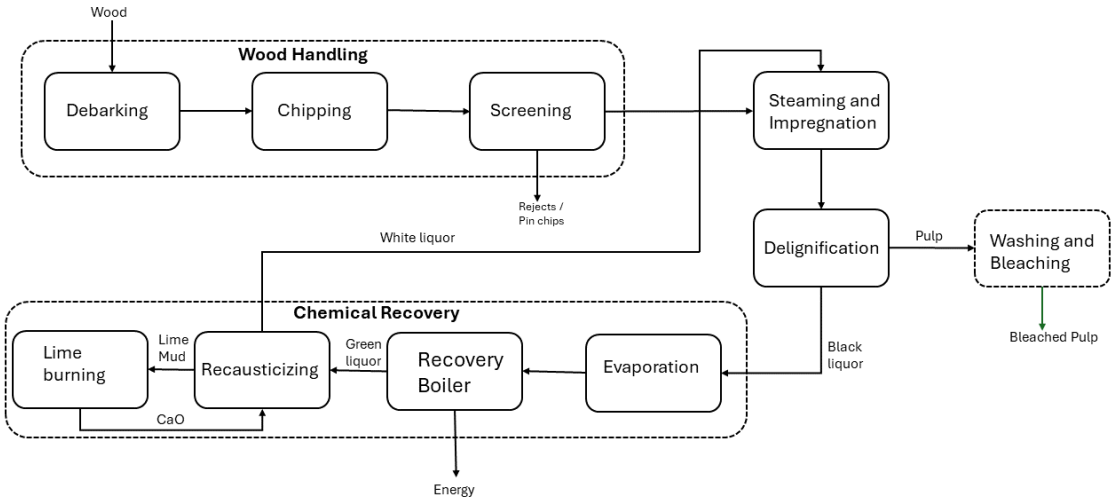


Figure 2.3: Schematic overview of the Kraft process

There are numerous variables that are important for the outcome of the Kraft pulping, some of them being the wood species, chip geometry, EA, S and liquor to wood ratio [15]. These concepts will also be described further in this section.

2.6.1 Wood Handling

The handling of the wood has a large impact on the quality of the pulp that is obtained in the end. If the wood chips are too small or damaged they will reduce the quality of the pulp. When having too small fractions the yield could be decreased due to degradation of carbohydrates. If the chips are to large, they could result in shives, undelignified wood, instead. Since the wood is the most costly part of the production it is of high importance that it is utilized to the most [14].

2.6.1.1 Debarking

The bark is undesired in the process since it contains high amount of extractives and non-process elements and has a low fibre proportion. The bark could also cause damage to the equipment and give dark impurities in the pulp or the final paper. The bark is often used for heat and power production at the pulp mills [14].

The debarking is often performed in rotary drum barkers which consist of a long cylinder. When the drum is spinning the logs are rubbed against each other or the walls causing the friction to remove the bark. If the wood is going to a sawmill the barking is performed by a one log barker which handles one log at the time. The log is held by spiked rolls and a debarking tool is rotating and shaving off the bark from the wood [14].

2.6.1.2 Chipping

Prior to impregnation and pulping, the wood needs to be chipped into pieces of suitable size to ensure appropriate delignification kinetics alongside with a certain pulp quality. The commercial chip size could vary depending on the conditions used and the desired outcome of the pulp. Normally a wood chip has a length between 20 and 30 mm a thickness between 3 and 8 mm and a width of 15-30 mm, a schematic drawing could be seen in Figure 2.4. The length of the chip is determined by the distance between the chipper disc and the knife. The edge of the knife is then pressed against the wood and the further the knife penetrates the higher the shearing force becomes and when it reaches a certain point a slice of wood will be shaved off. Hence, there is a relationship between the length and the thickness of the chips. The wood is chopped across the fiber, leading to a shortening of the average fiber length, which is the reason the length (and thus the thickness) need to be within a certain region to ensure only limited shortening of the fibers. The chips could also be cracked, and the ends damaged leading to the chip being more accessible to cooking chemicals. The width of the chips is determined when the chips are broken longitudinally while falling. The random breakage can also generate a fraction of very small wood pieces. The chips are often screened before going to the digester to make sure that they have a more uniform size [14].

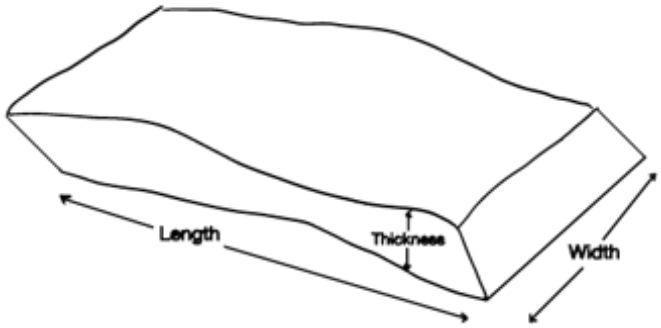


Figure 2.4: Wood Chip Dimensions

2.6.1.3 Screening

A uniform size of chips is desired for producing pulp. It avoids problem with low yields due to nonuniform cooking. The chips are therefore screened to separate the desired chips from the undesired. The screening equipment consists of several plates placed above each other, each one below having smaller openings. A rotating or vibrating motion shakes the chips, that are placed on the top, and the chips will fall down and be retained on the different plates depending on their size. The fractions obtained are called, in descending order, oversized chips, overthick chips, accepted chips, small accepted chips, pin chips and fines. There are other types of equipment that could be used to separate the different size fractions such as, disc screens, roll screens and bar screens [14].

2.6.1.4 Pin Chips

Pin chips are wood chips that have a size smaller than 7 mm and bigger than 3 mm in length and width. There are several reasons that pin chips are generated. A worn knife give the chips uneven surfaces and the chips tend to break more easily and gives rise to higher amounts of pin chips. Another thing that impacts the quality of the chips, and the amount of pin chips generated, is how the log is fed into the chipper. The log should be fixed and don't move around freely to minimize the production of pin chips. Another thing that could impact is the temperature of the wood, if frozen wood is used it often results in higher amount of pin chips. If the wood has a high dry content (>70%) or the timber logs are smaller, more pin chips and fines are usually produced. The pin chips are often added to the process in controlled amounts to not interfere the quality of the pulp too much. The pin chips could also affect the circulation in the digester since they could be clogging up and hinder sufficient mixing [14].

2.6.2 Steaming and Impregnation

Steaming is performed to remove the air that is entrapped within the lumen of the chips. The air prevents the cooking liquor from penetrating efficiently and by replacing the air with steam the transport will be through a liquid layer instead, allowing for an easier mass transportation. There are usually three phenomena contributing to steaming: first the steam heats the air inside the chip so that it expands and is displaced. Secondly the vapour pressure increases and forces the air out. Lastly, outside the chips there is saturated vapour creating a pressure gradient which causes the air to diffuse out from the fibres [16].

During the impregnation the steamed chips are submerged in the white cooking liquor. This stage involves penetration of chemicals into the cavities of the wood as well as diffusion of the chemicals. The rate of penetration is dependent on the pressure gradient, and is relatively fast. The diffusion on the other hand is dependent on concentration of the dissolved chemicals, and is often slower. The penetration will also be influenced by the wood structure, such as the pore size distribution and capillary forces, and the diffusion is more dependent on the overall area of the pores. An important factor is also that the chemicals will be consumed along the way due to the reactions with the wood components. The concentration will hence be lowered and a concentration gradient will be formed, which in some cases could lead to difficulties to impregnate the central parts of the chip. The chemicals diffuse from the lumen and through the cell wall layers and reach the middle lamella, to promote separation of fibers, as the delignification progresses. Although the most preferable case would have been to start delignifying the middle lamella, but this is not the case and the losses of polysaccharides in the cell wall cannot really be avoided [17].

2.6.2.1 Cooking Chemicals

The chemicals used in Kraft cooking are sodium hydroxide (NaOH) and sodium sulphide (Na_2S). The cooking chemicals used during the delignification are referred to as white liquor. There is also important to know some of the common terms used in the industry to describe the content of the liquor. The first being effective alkali (EA) expressed as g/l or % on dry wood, which is the sum of NaOH and half of the Na_2S, since one Na_2S gives rise to two sodium equivalents. The other is the sulfidity (S) which is expressed as: $Na_2S/(NaOH + Na_2S)$ [17]. These compounds gives rise to an equlibrium that could be seen in Equation 2.1 and 2.2. All the chemicals are calculated as sodium equivalents, meaning they are expressed as weight of NaOH or Na_2O. It is also important to know that the EA and S is a percentage on oven dried wood rather than a concentration in the liquor. This means that the concentration in the liquor is based both on the EA and S but also on the liquor to wood ratio (l/w).

$$S^{2-} + H_2O \rightleftharpoons HS^- + HO^- \tag{2.1}$$

$$HS^- + H_2O \rightleftharpoons H_2S + HO^- \tag{2.2}$$

The effective alkali is usually between 18-24 % on wood when producing pulp of bleached grade. When working with hardwood the lower values are often used, due to the lower lignin content in hardwood. The sulfidity is often between 24-28 % but does also depend a lot on the wood species. The sulfidity increases the delignification rate which occur by nucleophilic attack of the HS^- ion on quinone methide intermediates created in phenolic beta-O-4 structures, as will be discussed in the section below. The sulfidity could also lower the cooking time needed, resulting in less degradation of the carbohydrates. However if a too high sulfidity is used it could give rise to high sulfur emissions and could lead to corrosion in the recovery process [15].

The liquor to wood ratio, l/w, is often between 3 and 4 in industrial chemical pulping. The l/w should be as small as possible but at the same time allow for good liquor circulation inside the digester as well as an uniform cooking [15]. The liquor to wood ratio is calculated according to Equation 2.3.

$$\frac{liquor}{wood} = \frac{total\ white\ liquor\ mass}{dry\ wood\ mass} \tag{2.3}$$

2.6.3 Chemistry of Kraft delignification

A fragmentation of the lignin structure and/or introducing hydrophilic groups is necessary to dissolve and separate lignin from the cellulose/hemicellulose matrix. When targeting these reactions, other reactions affecting the carbohydrates are also initiated. In this section, the reactions occurring during Kraft pulping will be explained [2].

2.6.3.1 Lignin Reactions

The targeted bonds in lignin during Kraft pulping are the ether bonds connecting the lignin units, among which $\beta - O - 4'$ is the most common one. The reaction paths differ depending on if the structure is phenolic or non-phenolic. Due to the highly alkaline conditions, the phenolic alcohol structures in lignin form a quinone methide structure in equilibrium, see Figure 2.5. In Kraft pulping, the presence of hydrosulphide ions makes it possible to react this structure, that otherwise would form alkali stable enol ethers, to form a thiol that can attack the β-carbon in a nucleophilic reaction and form an episulphide and a new phenolic end group while cleaving the beta-O-4 linkage. It will release elementary sulphur that will form polysulfide in the cooking liquor. The targeted reaction and the reaction scheme is presented in Figure 2.5

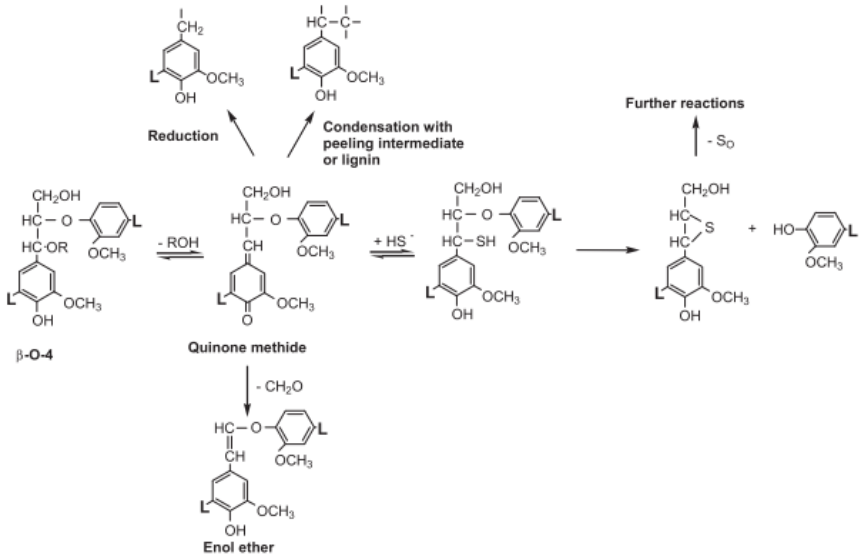


Figure 2.5: Reaction Scheme for the cleavage of phenolic $\beta - O - 4'$, [2]

The cleavage of the non-phenolic $\beta - O - 4'$ structures in lignin is dependent on the hydroxide ion concentration. These are cleaved more slowly in the later part of the cook due to their slower reaction rate. A nuclophilic attack of an alkoxide formed in alpha position on the β-carbon will cleave the $\beta - O - 4'$ bond and form an epoxide. Leading to a formation of a new phenolic structure [2].

Despite the efficiency of the $\beta - O - 4'$ cleavage reaction in Kraft pulping, competing reactions occur. The methide could react with other nucleophilic structures such as lignin and carbohydrates and then instead create new linkages in the complex. Condensation reactions of various types could occur both between lignin and between lignin and carbohydrate structures, which lower the dissolution ability of the lignin and makes it more difficult to separate [2].

2.6.3.2 Carbohydrate Reactions

As mentioned, hemicelluloses are more prone to degradation than cellulose due to their amorphous structure and accessibility in the cell wall. Peeling reactions, alkaline hydrolysis of the glycosidic bonds and deacetylation are the main reactions leading to the loss of carbohydrates [2].

The polysaccharides have reducing end groups present, which results in primary peeling. As a result of the alkaline conditions the aldehyde at the reducing end are easily subjected to rearrangments resulting in cleaving off monomers from the polysaccharide, starting at the end. The end group rearranges into a keto intermediate followed by a beta-alkoxy elimination. The last monosaccharide unit is cleaved off and rearranged to an isosaccharinic acid, and a new reducing end group is formed at the end of the polysaccharide chain starting a new rearrangement leading to elimination of another monosccharide, the reaction path are shown in Figure 2.6. Significant peeling reactions could occur already in the beginning of the delignification due to the low activation energy. The peeling reaction stops when the reducing end group is converted to metasaccharinic acid that can't undergo peeling reactions. This reaction is referred to as the stopping reaction [2].

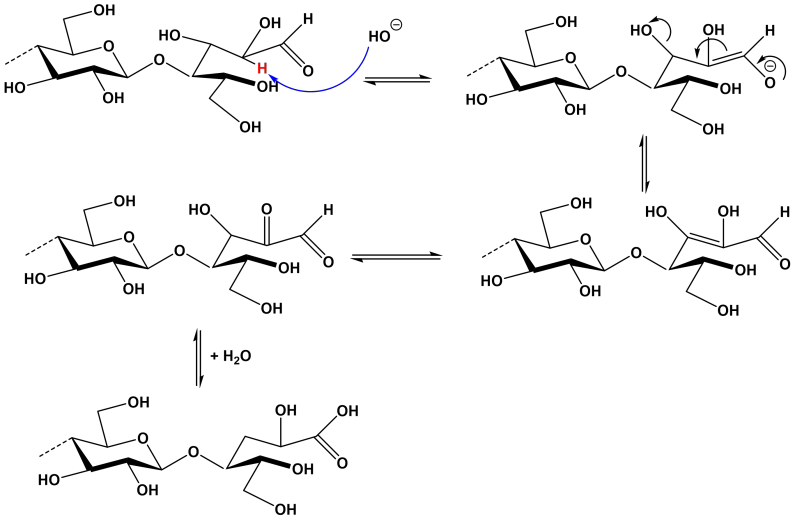


Figure 2.6: Peeling reaction in a polysaccharide chain

The glycodsidic bonds between the monosaccharide units can be broken by alkaline hydrolysis, cleaving the chain at different positions. The reaction is explained in Figure 2.7, where it could be seen how the hydroxide ion deprotonates the monosugar in the C2 position. The carbohydrate rearrange during high temperature which allows for a nucelophilic attack at the carbon in the glycosidic bond, and the bond is broken. When the glycosidic bond is cleaved, new reducing end groups are formed, which could undergo secondary peeling. The alkaline hydrolysis needs higher temperature to be initiated [17].

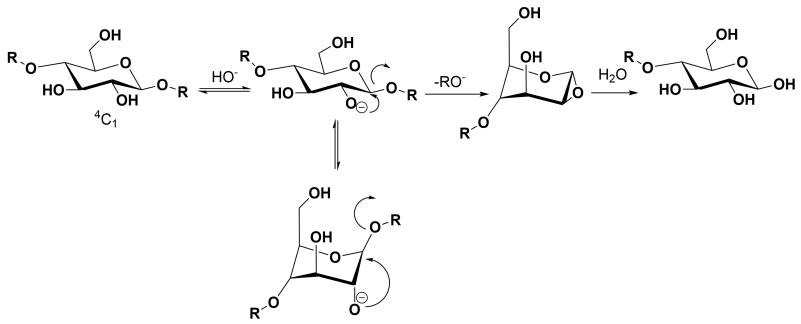


Figure 2.7: Alkaline hydrolysis of a polysaccharide

Deacetylation could occur already at temperatures around 70 $°C$. The deacetylation increases the solubility of the hemicelluloses and these would be partially dissolved already before the delignification starts. Xylan has side groups that provide some protection against peeling reaction and are hence not as degraded as the other hemicelluloses. Instead there are other mechanisms being important for xylan behaviour during pulping, which is the direct dissolution of xylan chains during the alkaline conditions [17].

2.6.4 Chemical Recovery

The liquor in the digester after delignification is called black liquor, due to its color. The black liquor consists of lignin and carbohydrate degradation products together with inorganic chemicals. The Kraft lignin, found in the black liquor, has a wide molecular weight distribution, is complex and could vary a lot in its structure and functional groups. Compared to native lignin, Kraft lignin is expected to contain more phenolic hydroxyl groups and carboxyl groups [17].

The black liquor is treated to be able to recycle the cooking chemicals and to generate energy from the organic materials. This is done by first partially evaporating the black liquor to increase its dry content to 50-70 % or even higher. After evaporation it is transported to a recovery boiler were the organic materials are burned to generate energy. The inorganic smelt that is remained at the bottom of the furnace consists of mainly sodium carbonate and sodium sulfide. The smelt is dissolved in water to what is called green liquor. By adding reburned lime (CaO) to the filtered green liquor the sodium carbonate is converted to sodium hydroxide in causticizing step, the reactions are shown in Equation 2.4 and 2.5.

$$CaO + H_2O \rightarrow Ca(OH)_2 \tag{2.4}$$

$$Ca(OH)_2 + NaCO_3 \rightleftharpoons NaOH + CaCO_3 \tag{2.5}$$

The calcium carbonate ($CaCO_3$), also called lime mud, is separated from the liquor and the remaining solution consists mostly of the desired chemicals, sodium sulfite and sodium hydroxide. The lime mud is washed and dried and then reburned to regenerate the calcium oxide in a rotary kiln in a process called calcination. With this method the chemicals are recycled in a closed loop and only minor amounts of new chemicals need to be added to compensate for losses [17].

2.7 Analytical Methods

In this section, the methods used to characterise and analyse wood components are presented. Analysis of wood could be challenging due to the complexity and heterogeneity of the material.

2.7.1 UV Spectroscopy

Ultraviolet spectroscopy could be used to quantify the concentration of molecules in solution. A specific amount of energy is needed to promote electrons in a substance to a higher energy state which could be detected as absorption. According to Lambert Beers law, see Equation 2.6, the absorbance is proportional to the concentration of the dissolved substance. The higher the concentration is in the sample, more of the in going light will be absorbed and less will be reflected to the detector. The intensity of this light will be used to calculate the concentration of the analyte.

$$A = \epsilon \cdot l \cdot C \tag{2.6}$$

Where ϵ is the molar extinction coefficient, l is the length of the vial (usually 1cm), C is the concentration and A is the absorbance. ϵ is characteristic for each substance in combination with the used solvent and the wavelength of the light absorbed.

Ultraviolet spectrophotometry is a useful and convenient method to analyse lignin in solution. This is due to the lignins aromatic structure, which absorbs ultraviolet light. Lignin will have a sharp peak at a wavelength between 200 and 210 nm. To keep in mind is that lignin structures isolated after Kraft cooking are complex, and their detailed structure are not known. Therefore, the absorbtivities of lignin compounds are only approximations of the true absorbtivity of lignin. The absorbtivity of softwood lignin has been thoroughly studied, which is not the case for hardwood lignin [18].

2.7.2 HPAEC-PAD

High Pressure Anion Exchange Chromatogrpahy is a type of liquid chromatography that is used to effectively separate and quantify carbohydrates [19]. The carbohydrates separate depending on their affinity to the column. The stationary phase is positively charged, which means that ions with stronger negative charge or other bonding affinity to the phase will be more strongly bound to the column and hence elute later.

With high-performance anion-exchange chromatography it is possible to detect neutral, uncharged, carbohydrates [19]. Carbohydrates are weak acids and at high pH they will ionize and could then be separated as anions. In HPAEC alkaline solutions are used as eluent to be able to transform the hydroxyl-groups of the carbohydrates to oxy-anions [20]. These hydroxyl groups have a slightly different Pka between the carbohydrates and this give rise to different retention times for the substances.

Several monosaccharides, which may not easily dissolve in neutral aqueous solutions, could be handled in an HPAEC due to the alkaline media, giving it an advantage compared to other HPLC equipment [20].

Pulsed amperometric detection, PAD, is a direct technique, which could detect carbohydrates without requiring them to undergo derivatization [19]. The carbohydrates are detected by measuring the electrical current generated by their oxidation. The most popular tool of detection is using a PAD with a gold electrode, which could go through a cleaning cycle so that the surface could be recovered and used over and over again [20].

2.7.3 Gel Permeation Chromatography

Gel permeation chromatography, GPC, or size exclusive chromatography, SEC is an analytical method used for determination of molecular size distribution of polymers, where the stationary phase is a gel. GPC could be used to analyse properties of both lignin and polysaccharides and give information about both the molecular size and the individual size distribution. The gel is a porous material and smaller molecules will enter the pores and travelling a longer path and hence elute later than the larger molecules. A GPC is often coupled with two different detectors, one UV detector and one refractive index detector. The first one could be used to quantify amount of lignin eluted in different fractions while the latter is useful when quantifying carbohydrates. No exact mass could be obtained by the GPC equipment used in this work but with a calibration of known standards the results could be compared between the mass and the elution time [21].

3
Methods

3.1 Screening of Wood Chips

Around 50 kg of birch and the same amount of aspen were collected from Södra Cell in Mörrum. These chips were collected after the chipping process and sent to Södra Cell in Värö where the screening was performed. The wet chips were screened in a Chip classifier of model JWIIA from Muototerä oy. The equipment has screen plates according to the SCAN-CM 40:1 standard. The chips are classified into 6 different fractions, according to Table 3.1.

Table 3.1: Screen Plates

Fractions	**Size (mm)**
Oversized Chips	>45 (hole)
Overthick Chips	>8 (slot)
Big Accepted Chips	>13 (hole)
Small Accepted Chips	>7 (hole)
Pin Chips	>3 (hole)

The damp chips were measured in a 10 L bucket and poured at the top of the chip classifier. The equipment shakes the plates for 10 minutes. Depending on the size of the chips they will stay on the corresponding plates and when the time is over the different fractions are sorted and could be taken out.

The size distribution within the different fractions was also investigated with an Andritz ScanChip analyzer. It uses image technology to analyze the chips and give information about the chip size distribution by measuring the dimensions. Samples of the sorted chips were added to the vibrating band which distributes a small amount to the analyzer where it records the dimensions of the chips. The chips that were collected for being analyzed were the big and small accepted chips as well as the pin chips.

3.2 Kraft Cooking

The chips were dried to a dry content above 90 %. They were also screened to remove pieces with a lot of bark or knots. First, the chips were impregnated with the cooking liquor (white liquor). The procedure was carried out inside autoclave vessels in which the chips were loaded together with the liquor. The autoclaves were closed and set under vacuum for 5 minutes. After this, the autoclaves were pressurised to 5 bars with nitrogen gas for 15 minutes. The pressure was released before the autoclaves were placed in the polyethyleneglucol (PEG) bath. A liquor to wood ratio of 20 was used for most of the cases, while some of the experiments were made with an industrial like ratio of 4. The temperature of the bath was set to 160 $°C$. The liquor contained sodium hydroxide and hydrogen sulphide so that the EA and the S were 20 and 30 % respectively. The amount of chips was 25 g for the liquor to wood ratio 20 and 100 g for the ratio 4. The reason for the higher amount of chips in the lower l/W is to not let the autoclave be too empty and to have comparable amounts in the autoclaves. The chips were cooked for different times between 10 and 120 minutes.

When the autoclave had been in the bath for the desired time, it was removed and cooled down in a water bath for 10 minutes, in order to terminate the delignification. The black liquor was then vacuum filtered off from the pulp and the filtrate was returned once before the pulp was washed with 4 liters of deionized water. It was then left in 4 l of water to be leached from any residual liquor. The samples were left for 1 week and the water was replaced every few days until neutral pH was achieved.

3.2.1 Yield

To be able to see how much delignified wood that was left after cooking, the wood was dried overnight in a 105 $°C$ oven. The dry samples were weighted and the result was divided by the initial mass of wood to obtain a yield, in percentage.

3.3 Klason Lignin

The dried pulp was milled into a fine powder in a Wiley mill and then sieved through a 1 mm sieve. The pulp was analyzed for Klason lignin in duplicates. 200 mg of milled pulp was weighted and to this 3 ml of 72 % sulfuric acid was added to initiate an acid hydrolysis and dissolve the carbohydrates. The samples were put under vacuum for 15 minutes and then placed in a 30 $°C$ water bath for 1 hour, stirring every 20 minutes. The content was then diluted with 84 g of deionized water. After this, the beakers were covered and placed in an autoclave cooker (CV-EL 125/140, CeroClav) at 125 $°C$ for one hour. The samples were then vacuum filtered while still hot to separate the lignin from the sugars. The filters containing the solid residues were dried and weighted in order to quantify the acid insoluble lignin, Klason lignin. The filtrate was collected and analyzed for acid soluble lignin and sugars. It is worth noticing that no extractives were removed prior to the Klason procedure, which could result in an overestimation of the lignin values.

3.4 Acid Soluble Lignin

The lignin that was dissolved during the acid hydrolysis was measured with an UV spectrophotometer (Specord 205, Analytik Jena). A 1 mm cuvette of quartz was used. Lignin is detected at a wavelength of 205 nm. The samples were diluted so that the absorbance were in the range of 0.2 and 0.7. The absorptivity constant was set to 110 $dm^3/g/cm$ in accordance with Dence, [22].

3.5 Carbohydrates

The filtrate from the Klason proceudre was diluted and utilized to quantify the content of carbohydrates. The carbohydrates, or the anhydrosugars, were detected via high pressure anion exchange chromatography (HPAEC-PAD Dionex ICS-5000, Thermo Fisher Scientific). The samples were added to vials and inserted in the instrument. The instrument is separating the components based on their affinity to the column, and they were then detected with pulsed amperometric detection. The columns used in the system were Dionex CarboPac PA1 columns, and a gold reference electrode was also connected to the system for the amperometric detection. The different conditions and eluents used in the system are described in Table 3.2.

The data were processed using the Chromeleon software to identify the different sugars. The concentration of the monosaccharides was corrected with the yield from the acid hydrolysis in the Klason procedure, [23], and the final results were expressed as anhydro sugars.

Table 3.2: HPAEC Conditions

Conditions	
Elution (Lower Pump)	0.26 mL/min
Elution (Upper Pump)	0.13 mL/min
Temperature	30 $°C$
Time	25 minutes (+13 min column wash)
Injection Volume	10 μL
Mobile Phase Elution	H2O/200 mM NaOH
Mobile Phase Washing	200 mM NaOH/200 mM NaOH + 170 mM sodium acetate

3.6 Lignin precipitation

After Kraft cooking, lignin from the wood is dissolved in the black liquor. To be able to characterize the structural motifs of the lignin, it is required to separate it from the liquor. To separate it, the lignin was precipitated following the procedure by Dang [24].

50 ml of black liquor were used and to the liquor sulfuric acid with a concentration of 72 % was added until the pH reached 3. This allowed the lignin in the samples to precipitate. The samples were then placed in an -18 $°C$ freezer overnight. The samples were thawed before being filtered through glass filters to separate the lignin. The solid residue was dried in an oven at 40$°C$ for three days. The lignin was precipitated from 6 samples, all from the industrial cases. The time point of 60 minutes was chosen. The motivation for the choice was that it was the middle time point and that a substantial amount of lignin had been removed from the chips at this point.

3.7 Molecular Weight Distribution

The dried acid precipitated lignin samples were analyzed by GPC to determine the molecular weight distirbution. First the samples were dissolved in DMSO (dimethyl sulphoxide) with 10 mM of LiBr. 10 mg of the dry lignin was dissolved in 1 ml solvent and was left over night to be fully dissolved. Then 100 μl of the solution was diluted with 4 ml of the DMSO with LiBr. Before adding this to the autosampler the solution was filtered through a 0.2 μm PTFE filter.

The GPC used was a PL-GPC 50 plus integrated GPC system from Polymer Laboratories, Varian INC and connected to an UV detector and an RI detector. The GPC used two coupled PolarGel-M column in series and an additional guard column (300x75 mm and 50x7.5 mm, 8 µm). The mobile phase consisted of DMSO with a concentration of LiBr of 0.01 mole/dm^3 and the flow were 500 mm^3/min and the temperature 50 $°C$.

4
Results

4.1 Raw Material

This section will present and discuss the results of the starting point, the aspen and birch wood chips. Both the sizes of the chips and the composition in the chips will be evaluated.

4.1.1 Size Distribution

The wood chips were screened, but to be able to see how effective the screening was the chips were also analyzed in the Andritz ChipAnalyzer. This resulted in average values for the thickness, length and width, which could be compared to the sizes according to the standards mentioned in Section 3.1 Screening of Wood Chips. The sizes obtained in the three different fractions could be seen in Table 4.1.

	Length (mm)	Width (mm)	Thickness (mm)
Birch Big Accepts	25.4	26.8	4.3
Aspen Big Accepts	25.8	27.3	4
Birch Small Accepts	20	11.5	2.7
Aspen Small Accepts	20.9	11.8	2.6
Birch Pin Chips	19.5	6.8	1.9
Aspen Pin Chips	21	8.1	2.1

Table 4.1: The average size of chips in the different fractions

When screening the chips the length was not directly regulated, leading to be the longest dimension. This is also the dimension being the most uniform between the chips. The thickness is only directly controlled by the second plate with the diameter of the opening of 8 mm. However, the average thickness of all fractions is well below 5 and even thinner for the smaller fractions. The width is the dimension that differs the most between all chip sizes.

The differences in size between aspen and birch are small. The length and width of the aspen chips are slightly larger than the ones for birch, with the biggest difference in the width of the pin chips. The same method was used for both species so a similar result between them was expected. However since they differ in their wood structure, the ability to break into smaller pieces might differ as well as how they

break into pieces. In literature, [25], it is found that denser hardwoods often tend to give thicker chips at identical lengths compared to softwoods. The density for birch and aspen is reported to be between 0.4 and 0.75 g/cm^3 [25], however since this is a quite broad range the density could still differ and be one of the reasons for the size differences.

Studies have shown, [26], that the transport in the longitudinal direction is faster than in the other two, implying also that there are significant concentration gradients along the transversal direction of the chip. In the longitudinal section the diffusion and liquor penetration are aided by vessels and lumen suggesting that the mass transport is more efficient along the length of the chips than in transversal direction. In this direction the diffusion is mainly aided by pits and cavities/porosity of the cell wall created as the delignification progresses. This would possibly imply that the thickness together with the width, which also are the dimensions varying the most, are the most important dimensions of the chips during delignification. A difference in the delignification rate and the lignin/carbohydrate content of the pulps obtained from the different size fractions could therefore be expected.

In figure 4.1 there is a picture of the size fractions after screening. From there it could be seen that there is a significant difference in the appearance between the pin chips and the big accepts.

(a) Big Accepts

(b) Small Accepts

(c) Pin Chips

Figure 4.1: Screened aspen chips

4.1.2 Composition

In this section the results for the composition of the raw material, aspen and birch chips of different sizes will be evaluated. It will begin with a comparison of the composition between aspen and birch and followed by comparison between the chips of different sizes.

4.1.2.1 Aspen and Birch

The composition of the raw material could be seen in Table 4.2. When comparing the results from this study with previous studies, [7], the carbohydrate content is a bit lower for birch and a bit higher for aspen. At the same time the Klason lignin content is higher for both. The explanation for this could be that the species could vary depending on where they are grown, and which part of the wood is used. The values, with their standard deviation, are although not too far from previously observed and could therefore be considered to be reliable.

The differences between aspen and birch do follow the same trends as in the mentioned literature, with aspen having a higher carbohydrate amount and a lower Klason lignin content than birch, just that the overall values are a bit higher. The xylan content is very similar compared to the literature for both species, where it could be seen that birch has higher xylan content compared to aspen.

The composition of aspen and birch, despite being somewhat similar present relevant differences in their content of lignin, hemicellulose and cellulose. The differences could result in different behaviour during delignification. At the same time, it is also important to remember that these two also will differ in their wood structure which could impact the delignification as well.

4.1.2.2 Chip Sizes

To be able to compare the delignification rate of the different chip sizes it is also of high interest to see if the composition of the raw material, which constitutes the pin chips, differ from the composition of the accepts. One could discuss if there is any reason some parts of the trees become pin chips during chipping and some not. Perhaps wood with certain characteristics or morphological origin might break more easily than wood that comes from a different part of the stem, with another morphology. This section will therefore evaluate the composition of the big accept fraction and the pin chip fraction to see if there is a significant difference in lignin content or carbohydrate content and composition.

As could be seen in Table 4.2 the pin chips have a slightly higher lignin content than the accepts, for both aspen and birch. When it comes to the overall carbohydrate content the pin chips have a somewhat lower carbohydrate content than the accepts. The pin chips are also showing a slightly lower content of xylan compared to the accepts, for both birch and aspen. One of the reasons the pin chips have a higher lignin content could be that there is more bark present in this fraction than in the accepts. Bark has been reported to have a higher lignin content and does also contain more extractives, that might also affect the delignification [27].

Table 4.2: Raw Material Composition. The values are from two replicates.

Component	Birch Accept	Aspen Accept	Birch Pin	Aspen Pin
Carbohydrates	62.4 ± 0.4	71.1 ± 0.1	60.4 ± 0.9	69.2 ± 0.8
- Glucan	36.9 ± 0.8	45.2 ± 0.2	35.7 ± 0.5	44.6 ± 1.0
- Xylan	22.0 ± 0.1	17.2 ± 0.1	20.7 ± 0.9	16.7 ± 0.8
- Mannan	1.8 ± 1.4	7.6 ± 0.5	2.23 ± 6.0	6.3 ± 0.3
- Arabinan	0.4 ± 0.4	0.3 ± 0.8	0.5 ± 0.6	0.6 ± 1.6
- Galactan	1.1 ± 3.1	0.5 ± 1.3	1.0 ± 0.6	0.7 ± 0.5
Klason Lignin	21.6 ± 1.2	19.8 ± 0.3	23.5 ± 2.5	21.0± 0.7
ASL	4.8 ± 0.2	4.4 ± 0.1	4.5 ± 0.5	4.7 ± 3.4
Total	88.8 ±0.5	95.3 ± 0.1	88.6 ±1.1	94.5 ± 1.5

To conclude, the pin chips show differences in the composition compared to the accepts. This would support the theory that the pin chips come from different type of wood structure than the accepts. Perhaps the pin chips could come from reaction wood, decaying wood, dry wood or similar. A more detailed study is needed to fully understand why pin chips are formed and the relation to the composition. The differences between the content in the pin chips and the accepted chips could have an impact on how they behave during delignification.

4.2 Pulp after Kraft cooking

The wood chips were cooked, and samples were taken out after 10, 20, 30, 60, 90 and 120 minutes. The degree of degradation of the wood structure differed between the samples, as could be seen in Figure 4.2. The difference between the pin chips and the accepts is more noticeable when cooking with low concentration of cooking chemicals compared to those cooked with higher concentration. There is a large difference in the appearance depending on if the wood has been cooked with higher or lower l/w ratio. The wood chips that have been cooked with higher concentration, lower l/w ratio, look more like a pulp compared to the pulp cooked at lower concentration. The EA and the S are the same in both cases, but the concentration of the cooking chemicals in the industrial case ends up being higher, which causes the large difference in the delignification rate between the cases. Further studies with a higher l/w, but with the same concentration, as in the high concentration case could be a great complement to this discussion.

(a) Accepts low concentration case

(b) Pin Chips low concentration case

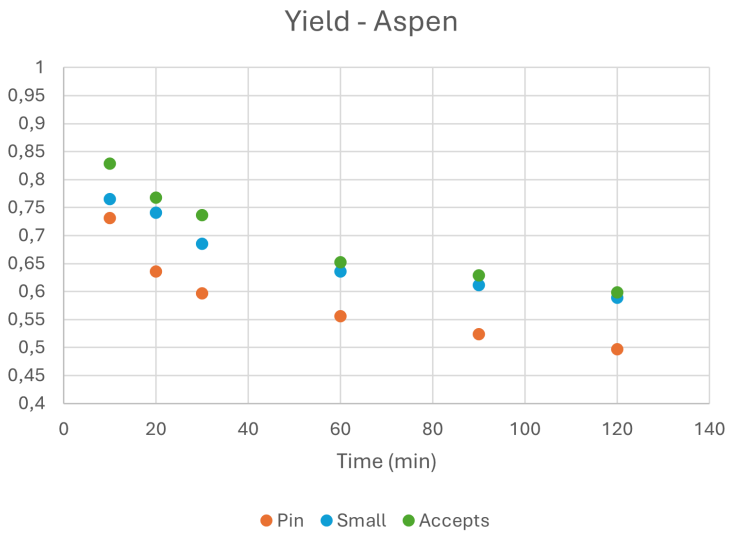
(c) Accepts high concentration case

(d) Pin Chips high concentration case

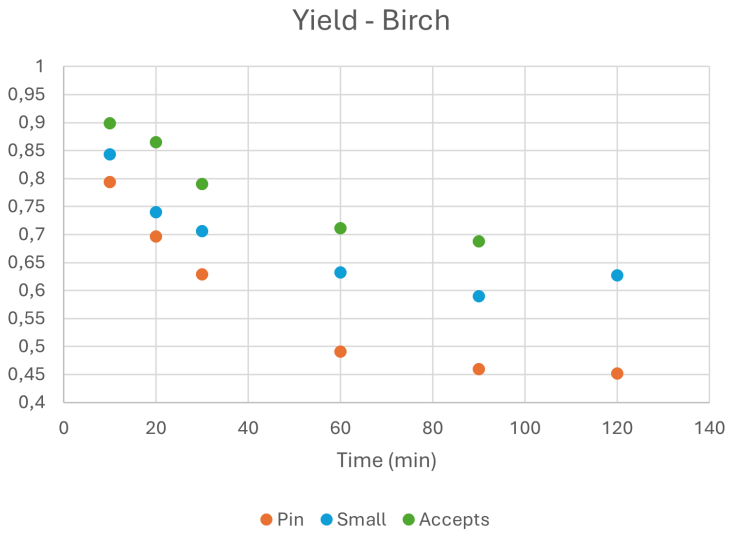
Figure 4.2: Pulp obtained after 120 minutes from aspen

4.3 Yield

The yield should decrease with time during the Kraft cooking, this is also the case, as could be seen in Figure 4.3. When cooking the wood chips, carbohydrates, lignin and other components are partly fragmented, degraded and dissolved in the black liquor, leaving less material in the pulp. The yield, amount of pulp or cooked chips obtained from the wood chips, should therefore be lower for the material being delignified for a longer time. At the same time the yield is much lower for the pin chips than the accepts. One explanation for the large difference is that the pin chips, since being so small, are broken down into small pieces. Even if the filtrate is being returned once, some materials are not being retained on the filter and thus being lost. In this case there is a loss of all components and not one individual.



(a) Aspen



(b) Birch

Figure 4.3: Yield of pulp from wood chips

As explained, material could have been lost during the experimental work, but a difference between the sizes was also expected, since there is a difference in the lignin and carbohydrate content between the wood material of different sizes. The difference could also be an effect of the pin chips being overcooked, so that the wood components are to a larger extent degraded and not detected at all during the normal analytical procedures, like Klason lignin and sugars analysis by HPAEC. The large difference observed in the yield is not really observed when looking at the individual components. The same pattern could also be seen when applying the industrial conditions, however here the losses were even larger. The values for the yield for the industrial case is provided in Appendix D.
Data is missing for birch accepts at 120 minutes due to an unreliable and unrealistic measurement of the yield. For this reason the experimental point are excluded.

4.4 Kraft Cooking with High Concentration

In this section the results from the delignification at the l/w of 4, meaning that the concentration of the active ions is high, are presented. The concentration is similar to what is applied in industry. These results were obtained for both aspen and birch for pin chips and accepts.

4.4.1 Delignification

Figure 4.5 and 4.6 show how the Klason lignin content decreases over time. Three time-points were studied, 20, 60 and 120 minutes. One could see that with high concentration the delignification rate is fast resulting in a relatively low residual Klason lignin content in the pulp.
It could be seen that the wood chips cooked under industrially relevant conditions after 120 minutes had been substantially broken down. By visual appearance it looked like the pulp obtained from the accepted chips were more unevenly delignified than the pulp obtained form the pin chips, this is illustrated in Figure 4.4.

(a) Pin Chips **(b)** Accepts

Figure 4.4: Pulp obtained after 120 minutes of Kraft delignification at high concentration

As could be seen in Figure 4.5 and 4.6 the differences in lignin content between the sizes are difficult to distinguish for both 60 and 120 minutes. Larger differences could be seen at 20 minutes, for both aspen and birch, with a larger difference for aspen.

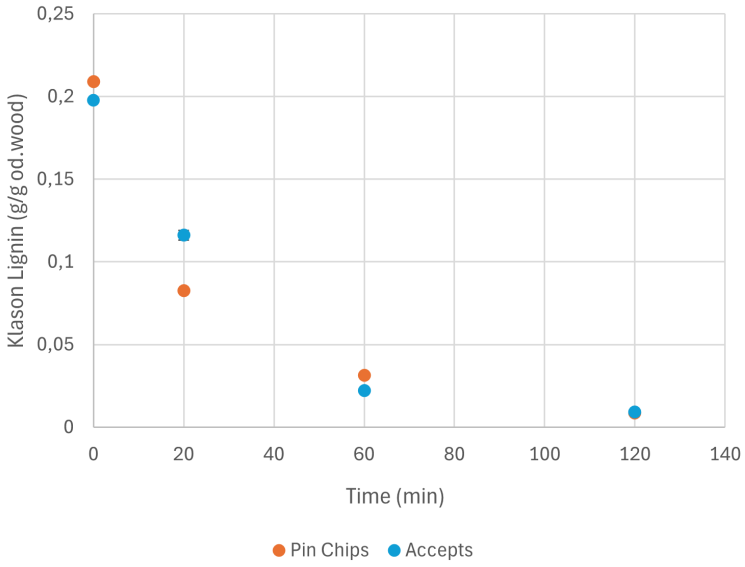


Figure 4.5: Klason lignin in aspen during high concentration cooking

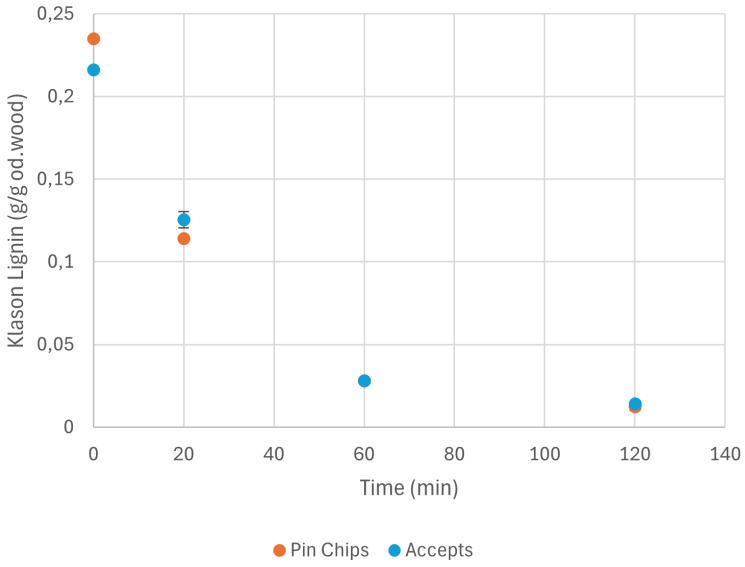


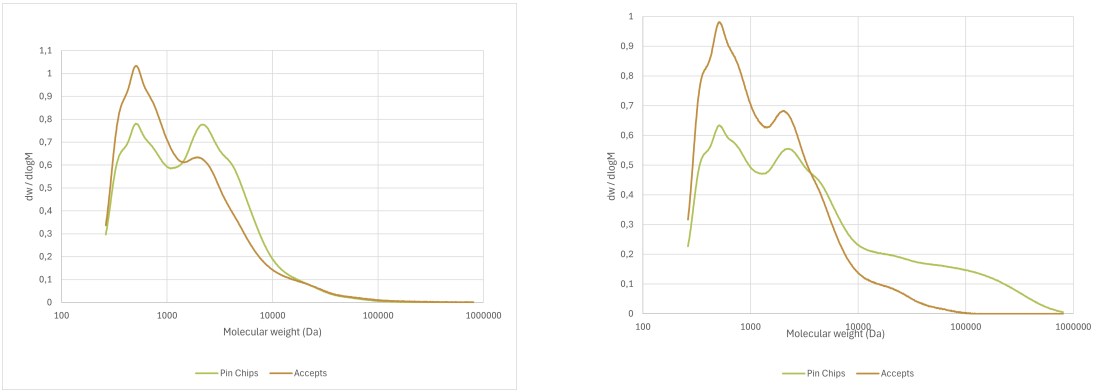
Figure 4.6: Klason lignin in birch during high concentration cooking

Early in the cooking, after 20 minutes, the mass transport is still hindered by the structure of the wood chips and fibers. As delignification proceeds, meaning a longer delignification time, the removal of lignin and the accompanying porosity increase make the transport resistance lower. At 20 minutes the determining factor might instead be the diffusion distances for the dissolved lignin, leading the pin chips to be faster to delignify than the accepted chips. In this initial phase the structure of the wood could also play a vital role, leading the lignin to be removed much faster in the aspen pin chips than in the other samples. Over time, the structure will be broken and the differences between the species will not influence the delignification rate as significantly as in the beginning.

What is interesting to see is that despite the similar amount of Klason lignin left after 120 minutes the pulps look a lot different from each other. There are therefore reasons to suspect that the delignification might have been preformed unevenly in the larger chips. The uneven delignification that could be suspected from the pulp's appearance could be a result of the mass transfer issues during delignification. Due to the long diffusion distances, and that the lignin might be of relatively large molecular weight, could hinder the lignin fragments from the center of the chip to diffuse out in the liquor. Instead, the outer parts of the chip are being subjected to efficient delignification. When measuring the lignin content after cooking Klason analysis was used. In this procedure a representative sample of the pulp is milled and analyzed and will hence not tell anything about the local lignin content in the wood chip/pulp after delignification. The determination of the defibration point and a more thorough analysis of local delignification rate would be needed to clarify if the size affects the delignification even after longer cooking periods.

4.4.2 Molecular Weight Distribution

In figure 4.7 the difference between the molecular weight distribution of lignin extracted from pin chips and accepts could be seen. From this it could be observed that there exists lignin fragments of higher molecular weight from the pin chips than from the accepts. This indicates that the larger lignin fractions are diffused faster in the pin chips than in the accepts. The Klason analysis indicated that the amount (g) of lignin left in the wood was very similar between the two fractions, but there is an evident difference in the size of the lignin fractions that have diffused into the black liquor. This indicates that the structure and the size of the pin chips has facilitated the diffusion, it could partially depend on that the distances are shorter but also that the cell wall have been swollen and loosened up due to a more extensive delignification. It would also have been interesting to see if the molecular weight of the lignin, from the beginning, in the chips differed between the accepts and pin chips. This could support the theory that the pin chips might come from a different part of the tree, parts with another morphology than the chips that are of bigger size.



(a) Aspen **(b)** Birch

Figure 4.7: Molecular weight distribution of aspen (a) and birch (b) lignin after 60 min cooking with high concentration.

The result could also support the fact that the pin chips are more evenly delignified while the accepts are more unevenly delignified. In the pin chips all lignin fractions in all parts of the chip have a better ability to diffuse while in the accepts the fibers are not broken down as substantially, causing the diffusion to be more difficult in the larger chips.

In Figure 4.8 the molecular weight distribution for all samples is compiled. From this it is possible to see some differences between aspen and birch. When looking at the accepted chips there is no larger difference in the molecular weight between the species. However, a larger difference could be observed between the pin chips. The lignin diffused from the birch pin chips seem to have more of very high molecular weight lignin, over 100 000 Da, which is not the case for the lignin from aspen.

The large difference could be due to different lignin structures between the species. Since native lignin is difficult to extract without degrading it, it is difficult to know the exact structure. However a comparison between the species would be of high interest and could be done as a future study to get a better understanding of the different behaviour of aspen and birch during delignification.

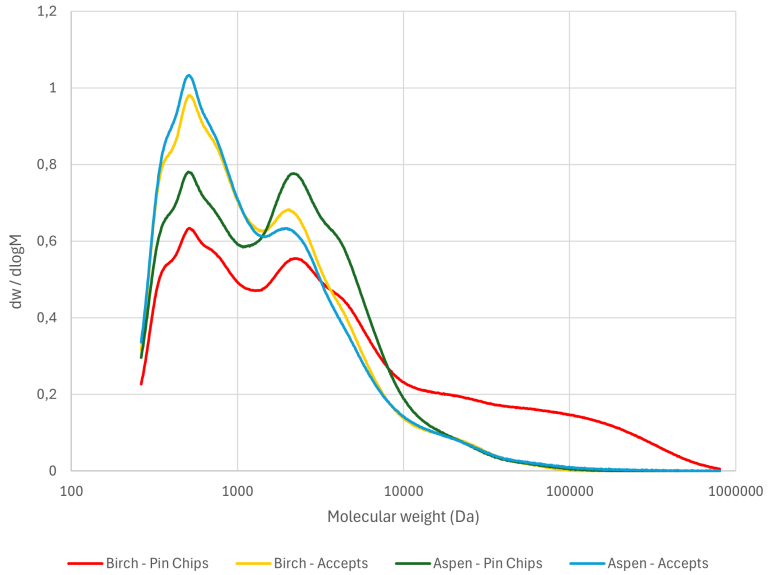
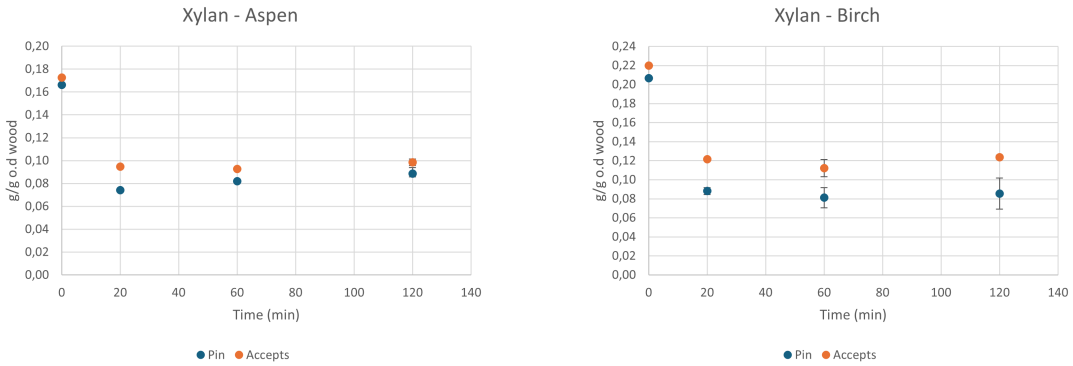


Figure 4.8: Molecular weight distribution of lignin after 60 min at industrial composition.

4.4.3 Carbohydrates

In Figure 4.9 and 4.10 a compilation of the glucose and xylan content during delignification for both aspen and birch could be distinguished. The overall result shows that there is a lower content of anhydro sugars in the pin chips compared to the accepted chips.

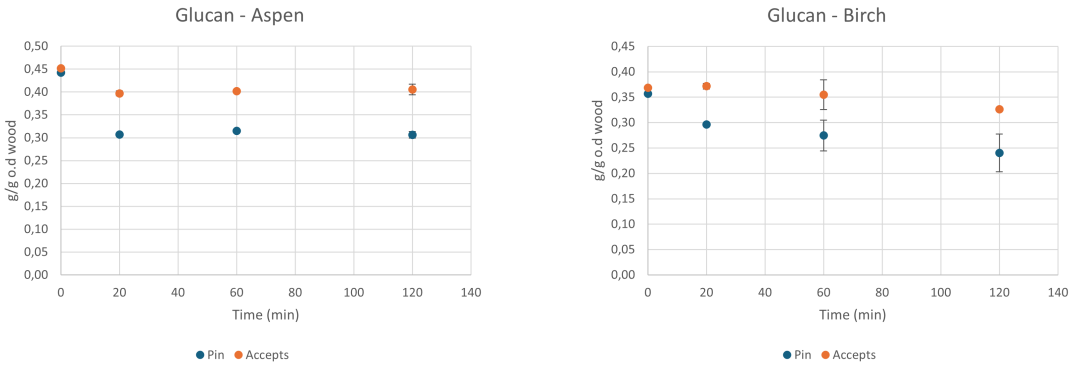


(a) Xylan in Aspen **(b)** Xylan in Birch

Figure 4.9: Xylan during delignification with high concentration of cooking chemicals

The xylan content drops fast in the beginning of the cooking time and then levels out. The content of xylan is governed by the extent of dissolution, delignification and also the extent of readsorption. At high extent of delignification accessibility for dissolution is not a problem and the losses of xylan will be substantial. When lignin is removed it might also at the same time remove xylan that might be connected to lignin. In accepts, where the delignification is not that substantial, the dissolution and the accompanying diffusion of xylan may be challenging. With this motivation it supports the result that the xylan should be removed faster in the beginning, when the structure is still intact, and faster in the pin chips, where the diffusion distances are shorter.

What could also be noticed is that the xylan content seems to drop to a certain level and then stay there, or perhaps even increase a bit in the end. The xylan that is left is probably too inaccessible to be degraded and diffused out, why the values stabilise. Another contributing factor could also be the ability for xylan to readsorb to cellulose fibers. After 2 hours the xylan content is higher for all samples than it was at 1 hour, which might be due to the readsorption of xylan on the cellulose fibers.



(a) Glucan in Aspen **(b)** Glucan in Birch

Figure 4.10: Glucan during delignification with high concentration of cooking chemicals

The glucan content in the delignified material, when using a high concentration of cooking chemicals in the white liquor, is significantly lower for the pin chips compared to the accepts, which again indicates a more extensive delignification and overcooking of the pin chips. Both fractions follow the same trends and the differences between the sizes are quite constant. For aspen it seems like it is almost stable over all 120 minutes, while there is a decrease of glucan for birch. There is although a faster loss of glucan for aspen, in the first 20 minutes, than for birch, this drop could be the glucan from the hemicellulose glucomannan that is easier degraded than the cellulose. The reason the drop is larger for aspen than birch could be due to a higher amount of glucomannan in aspen compared to birch. From Table 4.2 it could be seen that aspen has more mannan in the wood than birch, which could indicate the higher amount of glucomannan.

4.5 Kraft Cooking with Low Concentration

When cooking with a high liquor to wood ratio the concentration of the chemicals will be low and a constant composition of the cooking liquor could be assumed, due to the very high l/w. Even if the chemicals are consumed during the reactions, the concentration will remain quite stable. This could be important since the concentration and its change could impact the transportation rates. The EA and the S are the same as in the high concentration case, instead the amount of liquor, water, is increased.

4.5.1 Delignification

During delignification under low concentration aspen and birch were cooked for 6 different times between 10 minutes and 2 hours. By measuring the Klason lignin content for each time point a graph showing the delignification rate could be obtained. With a lower concentration the reaction rates are slower leading to the possibilities to observe trends that were not seen in the industrial case.

Figure 4.11 shows the delignification behaviour of chips from aspen during Kraft cooking. For each time point, duplicates were used to quantify the amount of Klason lignin. The overall trend is that the lignin content in the wood decreases with time, with a faster rate in the beginning of the cook. The differences between the sizes are larger in the beginning than in the end of the cooking. In the first 10 minutes the wood chips haven't reached the desired delignification temperature, hence no large degradation of lignin has started in any of the fractions. On the other hand, in the end of the cooking both the smaller and the larger chips have achieved a substantial delignification and the cell wall has been loosened up, and the lignin has had time to both be degraded and be transported out regardless of the diffusion distance. However it is also worth notice that the amount of lignin removed is much lower than in the case of cooking with a higher concentration. A higher concentration of cooking chemicals in the liquor will lead to both higher reaction rates and (to a certain extent) promoted dissolution, which leads to a more efficient lignin extraction. This could explain why there also is more noticeable differences between the sizes in the low concentration case.

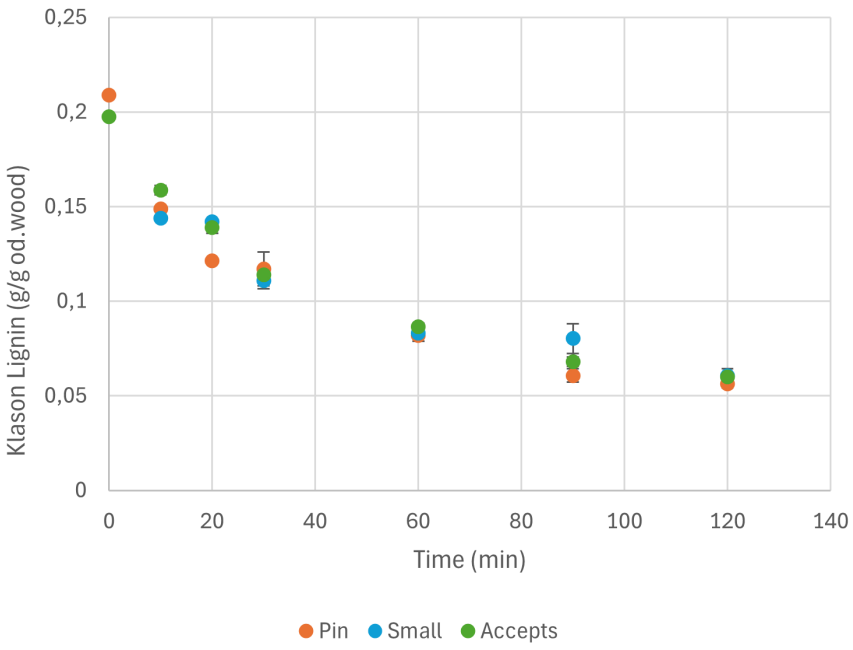


Figure 4.11: Klason lignin content in aspen during cooking with low concentration of cooking chemicals

When looking at the delignification of birch during the low concentration case, one could see a larger difference between the chip sizes, see Figure 4.12. There is also a more constant difference throughout the cook, with the smallest chips being fastest, and the largest slowest, to delignify compared to aspen.

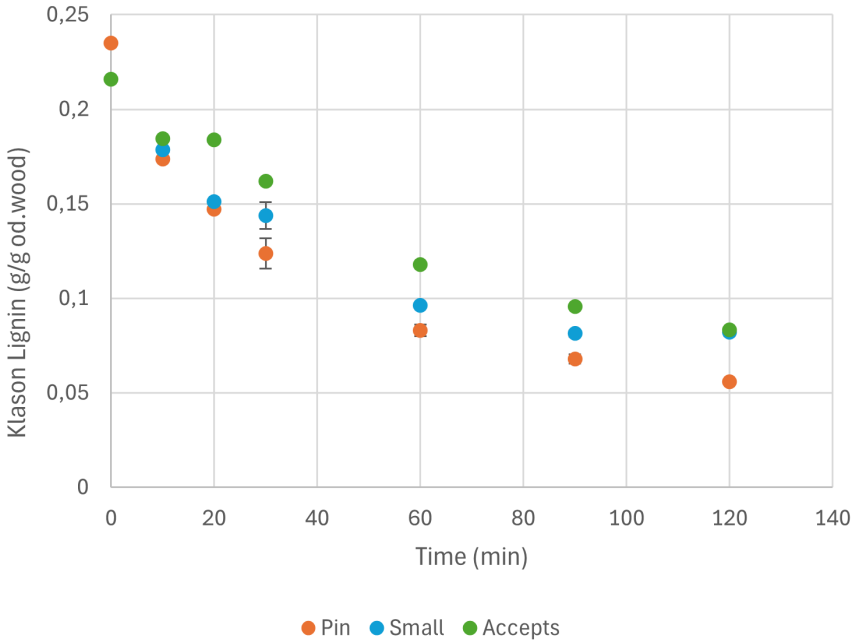


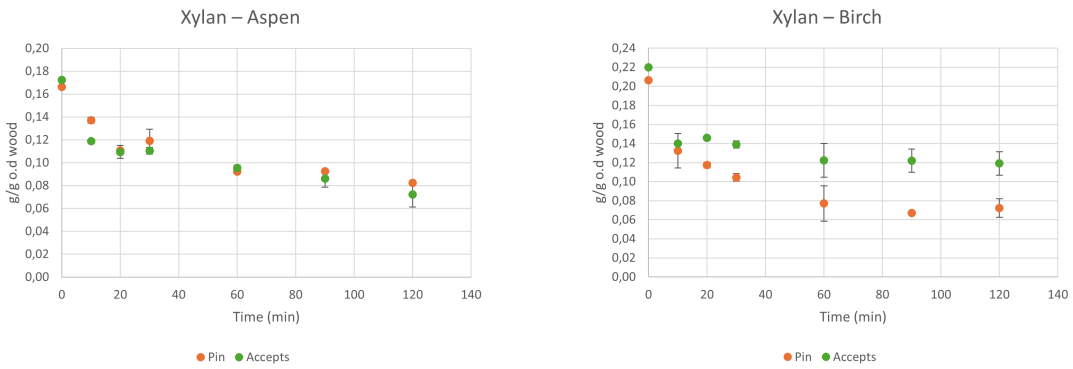
Figure 4.12: Klason lignin content in birch during cooking with low concentration of cooking chemicals

The fact that there are larger differences in birch than in aspen is probably due to the wood structure of aspen. The structure of aspen has a morphology which supports liquid transportation in the cells, which should indicate that aspen is easier to impregnate and facilitate the lignin fractions to diffuse. Aspen is known for being quite easily delignified due to its more porous structure, which has been reported and discussed in several studies, [28], [29]. In spite having a higher lignin content than birch aspen is delignifed faster. From this results it could tough be seen that the structure of the wood had a higher impact than the lignin content. A graph showing the delignification for both species can be found in Appendix A. The conclusion from this is that when having lower concentration of cooking chemicals, the wood structure is still intact and plays a vital role in the mass transport and hence the overall delignification rate. This also indicates that the wood species and their morphological peculiarity might have a higher impact than the diffusion distance, e.g the wood chip size.

4.5.2 Carbohydrates

In this section the evaluation of the anhydrosugars glucan and xylan in the chips during delignification at low concentration is presented. Some of the measurements from the HPAEC are excluded due to large experimental errors. In Appendix B the explanation for the missing points is provided. The values for the small accepts were disregarded since they were deviating a lot and a clear explanation from the results could not be drawn without a more thorough analysis and rerun of the samples. The graphs, with the results for the small accepts included, could be seen in Appendix C.

Figure 4.13 shows the xylan content in the aspen and birch chips over time. The content of xylan is governed by the extent of dissolution, delignification and the extent of the readsorption to cellulose surfaces. The xylan content drops a bit in the beginning but is then later levelling out around a value of 0.1. Xylan is expected to be decreasing quite fast in the beginning due to dissolution, but this is perhaps not that noticeable as it was for the high concentration case. The lower concentration does also lower the solubility for the xylan, which is why the xylan removal rate is lower. The xylan removal is largest and fastest in the pin chips, which could be expected since there are shorter distances and a more accessible structure in the pin chips than in the accepted chips.



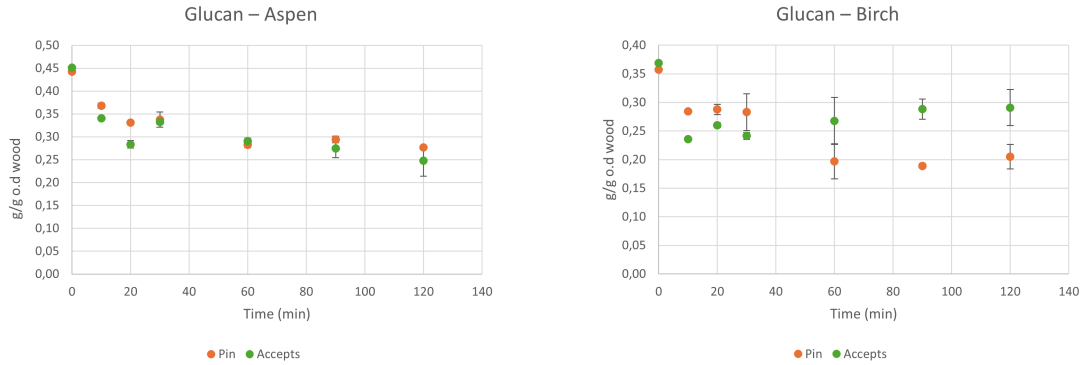
(a) Xylan in Aspen **(b)** Xylan in Birch

Figure 4.13: Xylan during delignification with low concentration of cooking chemicals

In aspen the difference between the content of xylan in chips of different sizes are not significant whereas a larger difference could be seen between the birch chips. This is aligning with the results for the delignification, where larger differences in the delignification rate was observed between the aspen chips. Since xylan has a close connection to lignin the behaviour of the removal of xylan seem to follow that of lignin.

There could perhaps be a noticeable increase of xylan at 120 minutes for birch pin chips, which could possibly be explained by the readsorption of xylan to cellulose. It is not that extensive as for the industrial case, it could be due to that the amount of lignin removed is lower, and hence also the delignified cellulose surfaces which xylan could readsorb onto.

The amount of glucan in the chips during delignification of aspen and birch could be studied in Figure 4.14. For aspen there seem to be a slow degradation of glucan, with a small difference between the chip sizes. The glucan that is being degraded in the beginning is probably mostly from glucomannan which is more available than the semicrystalline protected cellulose.



(a) Glucan in Aspen

(b) Glucan in Birch

Figure 4.14: Glucan during delignification with low concentration of cooking chemicals

One explanation to the lower glucan values in the birch accepts compared to the pin chips, in the beginning, could be that the data is from an average value of the delignified chip and does not show the true composition of the local content in the chip. The inner part of the wood chip probably contain more glucan, especially as the concentration of cooking chemicals is low, but the outer parts are more heavily affected and the glucan is more degraded in these parts. This makes the results difficult to analyze since there will also be dependent on which sample that was analysed, and where from the wood chip it was obtained. However further studies must be conducted to determine the reasoning behind the degradation of glucan during lower concentrations.

5
Conclusion

The study has shown that size of wood chips affects both early delignification rate and the overall outcome of the process, with differences among the studied species.

What could be seen is that if the concentration of cooking chemicals is low there is a larger difference in the delignification rate of the different chip sizes, where pin chips were delignifying faster than the larger chips. When applying higher concentration of chemicals, there is less difference in the lignin content both between the chip sizes and the wood species. However the pulp from the accepted chips appeared to be more unevenly delignifies after 2 hours than the pulp from the pin chips. This could be a result of the diffusion distance making it more difficult to delignify the central parts of the chips, leading to unevenly delignified accepted chips. During the initial phase of the delignification the dependence on the chip size and the wood specie were larger and seem to be decreasing as the delignification proceeds.

When comparing the delignification behaviour of the species, it could be seen that aspen was delignified faster and that there where smaller differences between the chip sizes than for birch. The main reason for this is believed to be the wood structure of aspen, which is facilitating the transportation in all the chip sizes. This also tells that both the diffusion distances, coming from the chip size, and the diffusion resistances, coming from the wood structure, are of high importance when looking at the mechanisms influencing the delignification behaviour.

The results from the MWD indicate that there are differences in the lignin that is being dissolved into the black liquor, between the size fractions. The pin chips with their shorter diffusion distances allow for a faster diffusion of comparably larger lignin structures then the larger accepts. This is possibly also the main reason, but there is also a possibility that the native lignin structure is different in the wood of different wood chip sizes, due to different chipping behaviour of different wood structures. A more detailed study of this would be needed to be able to draw any more conclusion, and would be an interesting topic for an extension of this work.

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A

Delignification of Aspen vs Birch

In the report the focus has been on investigating the differences in delignification of different chip sizes. During the work it was also seen that there were variations between how different species were delignified. In the following graphs the differences between the species are easier illustrated.

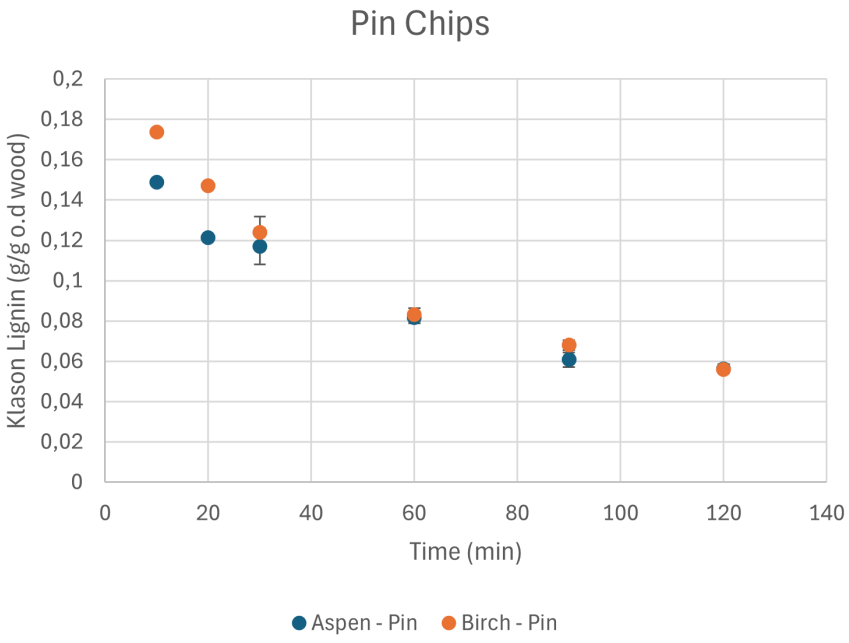


Figure A.1: The differences between aspen and birch pin chips during delignification

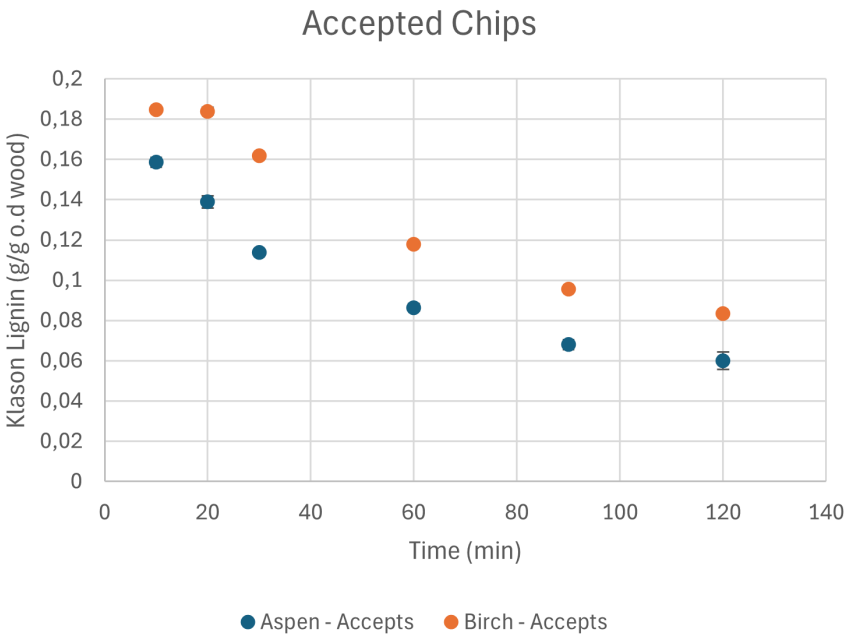


Figure A.2: The differences between aspen and birch accepts during delignification at constant composition

As could be seen there is a larger difference between the species when looking at the larger accepts than for the pin chips. The transport of chemicals and lignin is faster for aspen than for birch, which is more noticeable when there are larger distances, as in the accepts. This is further explained in the Section 4.5.1 and 4.4.

B

Experimental Errors

The results for the anhydrosugars measured in the HPAEC showed some unexpected values. With a further look into the values it was found that some values might were deviating. Each sample contained a fixed amount of fucose, to be able to use as reference. This peak are supposed to be of equal size within the same run. If the value were higher or lower it may be a problem with the injection volume to the column, leading to errors in the values. For each time point, two replicates were inserted. In the below tables, Table B.1 and B.2, the average values of the height of the fucose peak in nC are presented. The cells are marked either yellow or red depending on if the values are deviation with on or two standard deviations from the average value.

Table B.1: Fucose standard injections - Aspen

	Asp Accepts	Asp Small	Asp Pin
10-1	68	104	96
10-2	75	99	93
20-1	56	94	98
20-2	53	93	87
30-1	61	95	93
30-2	64	104	96
60-1	60	95	81
60-2	58	93	77
90-1	57	98	80
90-2	58	93	79
120-1	57	95	80
120-2	51	94	73

Table B.2: Fucose standard injections - Birch

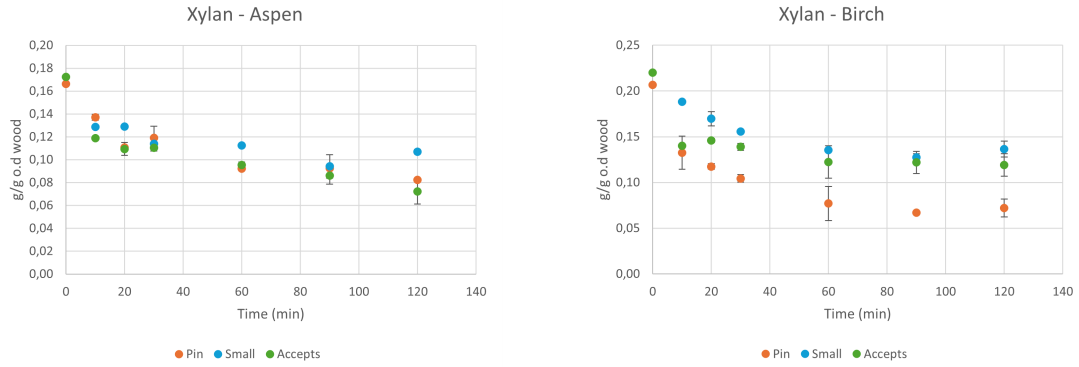
	Birch Accepts	Birch Small	Birch Pin
10-1	49	126	140
10-2	55	145	141
20-1	54	127	140
20-2	52	122	142
30-1	53	121	149
30-2	52	122	126
60-1	63	154	130
60-2	76	121	118
90-1	70	125	110
90-2	69	126	116
120-1	73	124	113
120-2	66	111	124

Some values were also deviating despite having a good injection volume. The three samples that were disregarded were one for aspen pin chips at 20 min, one for birch accepted chips at 10 min and one for birch small accepts at 10 min. The fact that the total anhydro sugar content deviated so much from the other values could be due to an error in the experimental work, diluting etc or some error in that measurement in the HPAEC.

C

Carbohydrate Content

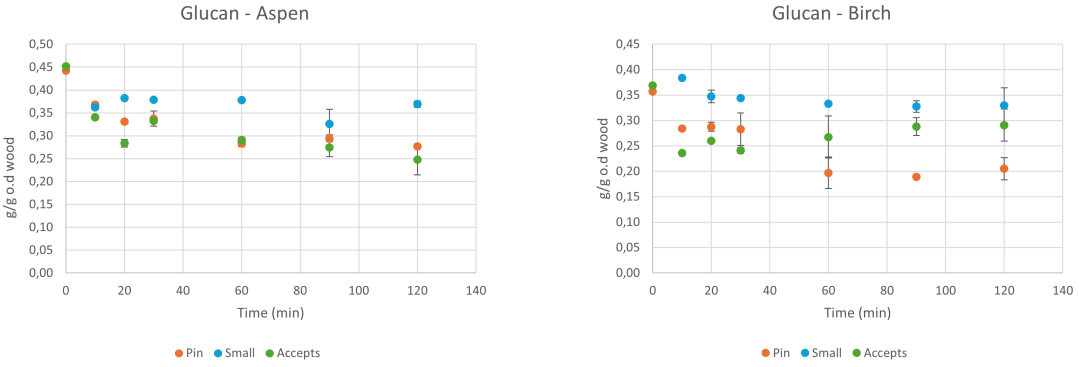
In this section the xylan and glucan results are included in the graphs, see Figure C.1 and C.2. The reasoning for the deviation is not fully understood. One explanation could be that the content of the carbohydrates differed from the beginning in the small wood chips. Since the composition of the small accepts never where measured further analysis must be done to be able to explain the behaviours.



(a) Xylan in Aspen

(b) Xylan in Birch

Figure C.1: Xylan content of all size fractions



(a) Glucan in Aspen

(b) Glucan in Birch

Figure C.2: Glucan content of all size fractions

D

Yield Industrial Delignification

The amount of pulp obtained after Kraft cooking were caluclated based on the amount of wood chips used and are presented as a yield in Table D.1

Table D.1: The yield after Kraft cooking at industrial conditions

	20 min	60 min	120 min
Birch Accepts	67.5 %	51.2 %	49.1 %
Aspen Accepts	67.4 %	54.6 %	51.5 %
Birch Pin Chips	57.9 %	43.6 %	44.6 %
Aspen Pin Chips	55.4 %	46.7 %	42.7 %

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