Impact of pulp chemical composition and fiber morphology on hygroexpansion and strength properties of kraftliner

Master of chemical engineering

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During the autumn of 2022, the project was conducted at RISE (Research institution of Sweden) in Stockholm. The primary objective of the study was to determine the impact of hemicellulose on the hygroexpansion of kraftliner. Additionally, other properties, such as the tensile and compressive strength of kraftliner were also examined. I am grateful for the support of my co-supervisor, Galya Simoneova, who helped me throughout the project. I would like to express my appreciation for being given the opportunity to work on this interesting and rewarding project. I would like to thank my supervisor Christian Hulteberg for his support, and Mats Galbe for being my examiner at Lund University. I would also like to extend my gratitude to Lars Norberg, Lars Granlöf, Katarina Prestjan, and all workers at RISE for their assistance during the laboratory parts and for providing access to equipment.

Abstract

Kraftliner is the unbleached pulp used in the outermost layer of corrugated cardboard. Like other types of paper, it is produced from wood chips as a raw material. Kraftliner is known for its high tensile strength, tear resistance, compressive strength, etc., making it suitable for packaging material for heavy objects. When paper is exposed to moisture, there is usually a dimensional change within the fiber structure as it is a porous material. Thus, paper can absorb water from the environment and swell, called hygro-expansion. When exposed to moisture, corrugated cardboard boxes used for high-quality boxes, packaging, and protective layers in transport packaging suffer as well. By boiling wood chips to different kappa numbers (lignin content) and reducing the hemicellulose content in some of the pulp samples, the influence of the chemical composition on the tensile strength, compressive strength, and hygroexpansion of the number of produced sheets was experimentally determined. A fiber test was also performed to compare fiber properties and identify any relationships between them. Tensile strength, compressive strength, and hygroexpansion were found to increase with increased sheet density. Removal of hemicellulose was shown to decrease tensile strength by up to 72% and increase hygroexpansion by up to 17%, but did not significantly affect compressive strength. Finally, the effect of lignin's chromophore groups on the brightness of the sheets was also studied, which resulted in a significant decrease of about 15-18% when removing the chromophores.

Sammanfattning (swedish)

Efterfrågan på hållbarhet ökar ständigt, inte minst inom förpackning och wellpappkartong. Kraftliner är den oblekta pappersmassan som används i det yttersta lagret på wellpappkartong, som precis som andra papperstyper produceras av träflis som råvara. Trä som råvara har varit av enormt intresse, bland annat för att det är förnybart, återvinningsbart, biologisk nedbrytbart och billigt. Den vanligaste träsorten som använts för pappersproduktion är barrved(gran), som består av 33-42% av cellulosa, 22-40% hemicellulosa, 27-32% lignin, men även små mängder av extraktivämnen. Massan framställs i den traditionella kraftprocessen, där stora mängder träflis får koka i starka alkaliska kok-kemikalier (vitlut) bestående av framförallt NaOH (kaustiksoda) och Na_2S. Kokningen sker vid höga temperaturer på ca 160-170 ^oC, och på så vis möjliggörs nedbrytningen av ligninet i träflisen och separationen av cellulosafibrerna. För att reducera vitlutkonsumtionen brukar oftast träflisen förbehandlas med svartlut som är "begagnat" vitlut. Genom att mäta kappatal för en pappersmassa så kan kokningsgraden bestämmas, där ett lågt kappatal innebär en mer omfattande delignifiering. För att bibehålla fiber strukturen och egenskaperna kokas kraftlinermassan oftast till ett kappatal på ca 90, d.v.s.till ganska högt kappatal. Detta medför att kraftlinermassan fortfarande innehåller mycket lignin och inga ytterligare blekningssteg genomförs på massan. Kraftliner är känd för sin höga dragstyrka, rivmotstånd, kompressionsstyrka, etc. som på så vis gör den lämplig för bland annat förpackningsmaterial för tunga föremål.

När papper utsätts för fukt brukar det ske dimensionsförändringar i fiberstrukturen då papper är ett poröst material. Papper kan alltså absorbera vatten från omgivningen och svälla, vilket benämns som hygroexpansion. Hygroexpansion är ett stort problem bland annat vid tryck och utskrift, vilket gör att papper skrynklar ihop sig och ändrar form. Wellpappkartonger som bland annat används för högkvalitativa kartonger, lådor, förpackningar och skyddande lager i transportemballage lider också av samma problem. Detta påträffas dagligen inom transportsektorn, där lådor och förpackningar av kraftliner som lagrats i fuktiga miljöer ska lastas och transporteras. När fuktnivån stiger i omgivningen och hygroexpansion sker till en viss grad, så sker även en oönskad förändring i de mekaniska egenskaperna som dragstyrka, kompressionsstyrka och rivmotstånd. Genom att producera kraftliner och wellpappkartonger under optimerade förhållanden, så kan hygroexpansionen reduceras och de mekaniska egenskaperna som drag- och kompressionsstyrka bibehållas.

I detta arbete kokades träflis till olika kappatal (ligninhalt) och hemicellulosahalten minskades i några av massorna, och på så vis kunde inflytandet av den kemiska sammansättningen på dragstyrkan, kompressionsstyrkan och hygroexpansionen bestämmas för ett antal producerade ark. Ett fibertest genomfördes även för att jämföra fiberegenskaperna och se eventuella samband med de mekaniska egenskaperna. Dragstyrkan, kompressionsstyrkan och hygroexpansionen visade sig öka med ökad arkdensitet, med riktningskoffecienterna 28.5, 9.9 och 0.46. Borttagning av hemicellulosa minskade dragstyrkan, ökade hygroexpansionen men påverkade inte kompressionstyrkan. Slutligen studerades även hur mycket ligninets kromoforgrupper påverkade arkens ljushet. Det visade sig att kromoforgrupperna påverkade ljusheten av arken markant, med ca 15-18%.

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List of abbreviations

EIC - Extended Impregnation Kraft Cooking
DP - Degree of polymerisation
TMP - Thermo-mechanical pulp
LCC - Lignin carbohydrate complex
MRA - Multiple regression analysis
EA - Effective alkali
PEG - Polyethylene glycol
SR - Schopper riegler
SW - Sprout waldron
stdev - Standard deviation
GMM - Glucomannan
PH - Pre-hydrolyzed
R - Reference
O - Oxygen delignified
(O+X) - Oxygen delignified and further enzyme treated samples
HEX - Hygroexpansion
Ts - Tensile strength index
Cs - Compressive strength
Csi - Compressive strength index
HexA - Hexenuronic acid

1 Background

Wood-based paper and kraftliner can exhibit different chemical and mechanical properties, resulting in divergent behaviors despite similar manufacturing processes. High levels of moisture in the surrounding environment can cause the paper to expand and contract, leading to a loss of functionality of the paper. For example, when humidity increases, corrugated boxes made of kraftliner become unsuitable for storage, while printed paper may curl and buckle, making it useless. The main focus of this project is to investigate how hemicellulose affects the hygroexpansion (moisture-induced expansion) and the tensile and compressive strength of kraftliner.

Kraftliner is a renewable and environment-friendly paperboard, is very durable, and has very high strength properties. It is commonly used in packaging applications to hold heavy loads and resist tearing [72,73]. To produce kraftliner, wood chips, typically from softwood (spruce and pine), are cooked in the traditional kraft process, where an alkaline white liquor (NaOH and Na_2S) is used as a cooking chemical. Wood consists mainly of three components cellulose, hemicellulose, and lignin. To reduce the consumption of white liquor chemicals, a pre-impregnation step is usually performed with reused white liquor called black liquor (BL) [41,42]. A pre-steaming step is usually necessary to enhance the impregnation of the cooking chemicals and eliminate the entrapped air in the wood [37]. The cellulose microfibrils and the hemicellulose are held together by the lignin, i.e., the abbreviation LCC (lignin carbohydrate complex) [62]. The kraft process is performed under high temperatures and pressure to break down the LCC and impurities in the wood and retain the carbohydrates, mainly the cellulose microfibrils. However, lignin removal is very limited in kraftliner pulps to preserve the fiber properties, and no further bleaching steps are added. Therefore, the kraftliner has a very high kappa number compared to other papers, which measures how much lignin the pulp contains[63]. After the kraft cooking (delignification process), the pulp is washed and mechanically refined before being formed into sheets to ensure that the fibers are uniform and, at the same time, improve the strength properties of the pulp [77].

Unbleached pulp masses for packaging make up a large proportion of the total pulp production nowadays, and kraftliner production is expected to considerably growth in the future due to increasing packaging demand. A lot of research and investments are made to maintain the high strength properties of the kraftliner, such as the tensile and compressive strength. Recently, there have been much speculation and research about how to improve hygroexpansion, i.e., the swelling of fibers in humid environments. When kraftliner or papers are exposed to high humidity levels, they swell and undergo dimensional changes due to the separation of the fibers when water molecules enter the structure. This expansion can be annoying, especially when printing (buckle of the paper) or preserving stuff outdoors in corrugated boxes. Many factors and parameters are involved when investigating the strength properties and hygroexpansion of kraftliner. Some essential and crucial parameters are inter-fiber bonding, microfibril angle, fiber morphology, and other fiber properties, as well as the chemical composition of the pulp, such as the carbohydrate and lignin content [58]. Fiber properties such as fiber length, width, and shape

factor are also important. To reduce the binding capability of water to the fibers, a pre-hydrolysis step is a method to get rid of the hemicelluloses before the cooking steps. In this way, the hemicelluloses and the hydrophilic groups disappear, and the water absorption decreases [78].

1.1 Purpose of the work

The project aims to investigate the impact of chemical components such as hemicellulose and lignin on the hygroexpansion profile of kraftliner. In addition to the hygroexpansion, the impact on tensile and compressive strength is also investigated. By removing hemicelluloses from the wood chips, the contribution of the hemicellulose can be eliminated. This is possible by performing different cooks at different kappa numbers, with and without a pre-hydrolysis step.

The intention is also to investigate if parameters such as the fiber shape, width & length, number of kinks per fiber, and other fiber properties affect the hygroexpansion & mechanical properties of the kraftliner. Furthermore, the impact of the degree of refining and sheet density is also investigated. Another purpose of the work is to investigate the extended impregnation cook (EIC) technique, primarily to see if inline refining could be avoided by cooking at lower temperatures for longer periods and avoiding using a mechanical disc refiner.

The following research questions will be explored:

- How do the hemicellulose and lignin content affect the hygroexpansion, tensile strength, and compressive strength of kraftliner?
- How is the sheet density affecting the hygroexpansion, tensile strength, and compressive strength of kraftliner?
- Can the kraftliner be made through EIC (extended impregnation cooking) without an inline refiner?
- Is there any other parameter such as fiber length, fiber width, fiber shape factor, and the number of kinks per fiber that significantly impacts the mechanical properties of the kraftliner?
- How is the brightness of the pulp affected during the cook, and to what extent do the chromophoric groups affect the brightness?
- How are the pulp properties being affected by pfi (papperindustrins forskningsinstitut) refining?

2 Theory

This section describes the reactions in the kraft process in detail and how kraftliners and corrugated boards are made. The wood composition, interactions between the different compositions, and the fiber morphology & properties are also explained. In addition to the kraft process, oxygen delignification and pre-hydrolysis are explained in detail. Finally, there is a small paragraph about multiple regression analysis because it was used to compare different parameters in the result.

2.1 Wood composition

Biomass, such as wood, is an interconnected network of cellulose, hemicellulose, lignin, and minor amounts of extractives. There are two types of wood, softwood (gymnosperms) and hardwood (angiosperms) [1]. To distinguish between the wood types, the wood morphology and the species concentrations in the wood can be observed according to table 1. For instance, the softwoods are relatively homogenous and consist mainly of two cell types, i.e., the longitudinal tracheids and the ray cells. At the same time, the hardwoods are heterogeneous. They comprise more complex and diverse xylem cells, including tracheids and vessel elements, making water transport more efficient [2]. Softwood is the primary material for industrial kraftliner production. The combination of cellulose and hemicellulose, i.e., holo celluloses, accounts for 65-70% of the dry weight of wood. The fraction of the different components varies depending on wood type and environmental factors [3]

***Table 1**: The amount of the different wood species in dry hardwood and softwood in percentage [T1].*

	Cellulose	Hemicellulose	Lignin	Extractives
Hardwood	38-51	17-38	21-31	3
Softwood	33-42	22-40	27-32	2-3.5

Extractives are low molecular weight compounds found in the wood. They can be divided into water-soluble products such as sugar and phenolics and non-water-soluble products such as wood resins and lipophilic compounds. The extractives are typically found in the barks and branches [52].

2.1.1 Cellulose

Cellulose is the most abundant organic chemical on the face of the earth. It consists of D-glucopyranose units linked by β-(1-4)-glucosidic bonds in long homopolymers. The building block is called cellobiose since the repeating unit is two glucose molecules. The DP, i.e., the average number of molecules linked together of native cellulose, is about 10,000 glucose units. In bleached kraft pulps, the DP is merely about 1000 [4]. In its native form, cellulose is called cellulose-I, which forms two allomorphs, i.e., triclinic cellulose α and monoclinic cellulose β [5]. Cellulose I comprises parallel chains, while cellulose II comprises antiparallel chains. Cellulose II is the most stable among the two forms and, with its high density and supramolecular

structure, has a reduced swelling capacity [58]. Cellulose molecules can form intra and intermolecular hydrogen bonds due to the hydroxyl groups at carbon 2, 3, and 6 on the glucose units, as depicted in figure 1 [6].

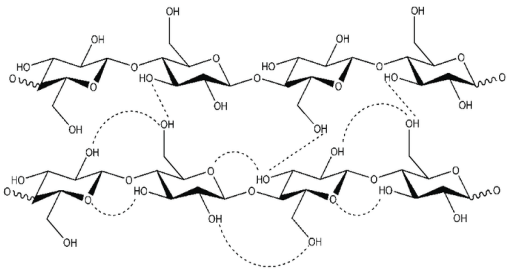

Figure 1: *The cellulose molecule and the different inter/ intramolecular bonds [F1].*

The polymer chains appear in crystalline and non-crystalline (amorphous) forms depending on the density and orientation of the polymer chains. Crystalline regions are formed when straight cellulose polymer chains are densely packed. Wood contains as much as 65% crystalline regions [7]. As mentioned, hydrogen bonds and van der Waal interactions hold the polymer chains of glucose molecule units, making up fibrils with 3-5 nm in diameter. The microfibrils can be up to 20 nm in diameter. Besides, microfibrils can make up larger macro fibrils or be split into elementary fibrils with only 40 cellulose chains [58]. There are also intramolecular hydrogen bonds of adjacent atoms in the glucose polymer chains [8]. The microfibrils are embedded in a hemicellulose and pectin matrix and encrusted with lignin to form the robust framework of the cell wall.

The cellulose molecules in the wood are arranged in a specific direction and are divided into accessible and non-accessible cellulose. The division of these two arrangements depends on the availability of water, microorganisms, and minor constituents to enter and reach the cellulose molecules. For example, in crystalline cellulose, the outer surface of the crystal is accessible, and the rest is non-accessible. In contrast, in amorphous cellulose, all the cellulose is accessible except the high lignin and hemicellulose-covered parts [7].

2.1.2 Hemicellulose

Hemicellulose consists of heteropolysaccharide molecules of pentoses and hexoses and is much shorter in the polymer chain length than cellulose. The DP of hemicellulose molecules is around 100-200. Hemicelluloses are built up of several different sugar monomers, mainly d-glucopyranose, d-xylopyranose, d-galactopyranose, d-mannopyranose, l-arabinopyranose, and d-glucopyranosyl uronic acid. The xylan molecules, for example, consist of a β-1-4-linked backbone of xylopyranose molecules and are branched with monomers from carbon 2, 3, or 6. The hemicelluloses thus have an amorphous non-crystalline structure, although some can also form crystalline structures [9]. The hemicelluloses are named depending on the involved sugar monomers, such as glucuronoxylan, arabinoglucuronoxylan, arabinogalactan, galactoglucomannan, glucomannan, and so on.

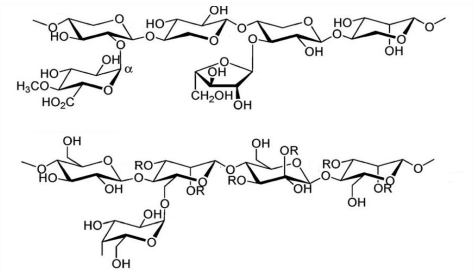

***Figure 2**: Two common hemicelluloses, xylan (up) and glucomannan (down) [F2].*

Hemicellulose in softwood is mainly made of galactoglucomannan and mannose, while hemicellulose in hardwood is made of glucuronoxylan and xylose [9]. The hemicellulose also contains substituted carboxyl, acetyl, and methyl groups. Galactoglucomannan contains acetyl groups linked on carbon 2 and 3 on every 3-5 hexoses. Xylans also carry acetyl groups, but glucuronic acid groups such as O-methyl-α-D glucuronic acid are more common in xylans [10]. When the glucuronic acids on the glucuronoxylan are removed, the ability of the xylan polymers to combine with the cellulose in a more ordered structure increases, especially after kraft pulping. Glucomannan is more sensitive than xylans during kraft cooking, dissolves faster, and is more accessible [11]. It has been shown that xylan is more associated with lignin compared to glucomannan, which shows more tendency to link to glucose. Therefore, hemicellulose is an interfacial coupling agent between the polar cellulose fibrils and the less polar lignin molecules [4].

2.1.3 Lignin

Lignin has an amorphous complex structure consisting of aromatic units of mainly phenylpropanoid polymers. The three-dimensional structure of lignin is due to the C-C and C-O linkages between the molecules. The main monolignols of lignin are p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. These alcohols comprise the backbone of the lignin molecules by forming the building blocks p-hydroxyphenyl, guaiacyl, and syringyl monomers shown in figure 3 [12].

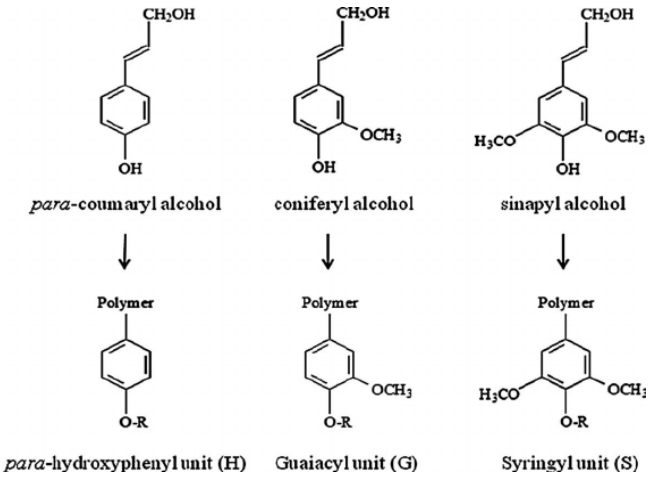

***Figure 3**: The monolignols p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol turning into p-hydroxyphenyl, guaiacyl, and syringyl monomers [F3].*

These lignin monomers are synthesized in the cell's cytosol, transported to the cell wall, and radically polymerized by different oxidative coupling reactions [26,14]. Various functional groups of the monomer units, such as carbonyl, aromatic methoxy, and primary & secondary aliphatic hydroxyl groups, are the reason for the C-O-C and C-C linkages in the lignin molecule. However, the most frequent bond is the β-O-4 ether bond, together with the β-β, 5-5, and β-5 bonds shown in figure 4 [13]. In addition, lignin has acidic groups that can form stable catechol complexes, i.e., forming bonds with multivalent metal cations [14].

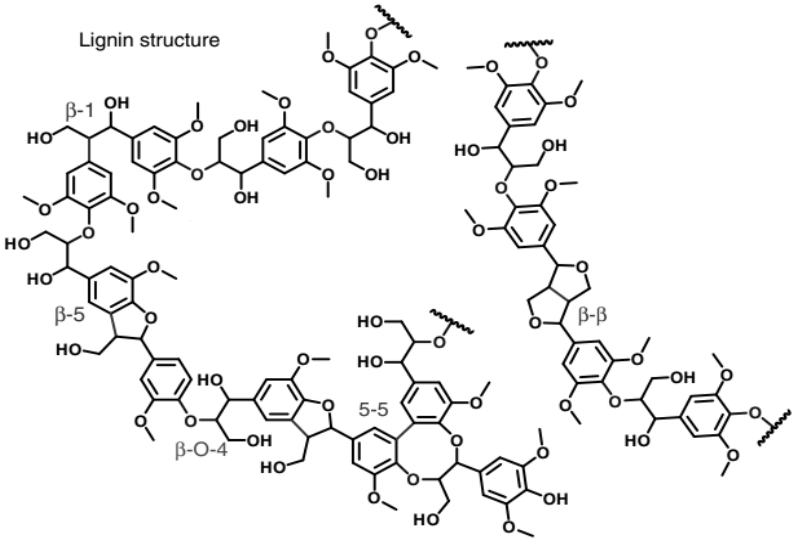

Figure 4*: Most common bonds in lignin [F4].*

Softwood lignin is usually a polymer of guaiacyl monomers, while hardwood lignin is a syringyl-guaiacyl copolymer with excess syringyl units. The lignin content in softwood varies from 27-32%, which is slightly higher than the lignin content in hardwood, which is about 21-31%. The methoxyl content is about 15-20% in softwood and 20-21% in hardwood [15]. The phenylpropane can be substituted at the α, β, or γ positions into combinations by ether and carbon-carbon bonds. More than two third of the linkages in lignin are typically ether bonds [16].

Lignin is a crucial chemical component in the cell walls and provides strength and stiffness to the cell. It enables the transport of water and solutes through the wood cell and protects the wood against external factors [26]. Functional groups in lignin, such as α-carbonyl, biphenyl, and ring-conjugated double bonds, are known to absorb UV light and form chromophoric groups. Quinone and conjugated carbonyl groups are the main chromophoric groups in lignin, and their maximal absorption wavelengths are shown in figure 5. The absorption maxima can be altered in a lignocellulosic material, as shown in substituted ortho/para quinone, which absorbs much more UV light in a lignin-rich pulp [66]. Chromophores are also derived from carbohydrates during the kraft process, which specific oxidation reactions, such as the conventional bleaching process with chlorine dioxide, etc., can easily destroy. However, the quinones found in the lignin affect the pulp color significantly. It is possible to precipitate and hydrolyze the charged chromophoric groups and increase the brightness of the pulp. This can easily be done by adding a strong acid

such as sulfuric acid (H_2SO_4). The groups will mostly be the dissolved lignin chromophores, such as the quinone methids, quinone, catechols, cinnamyl aldehydes, etc. It should be kept in mind that acid treatment is not without drawbacks, and strong acids are often hazardous and generate a certain amount of waste, and can also impact the strength properties of the pulp [67].

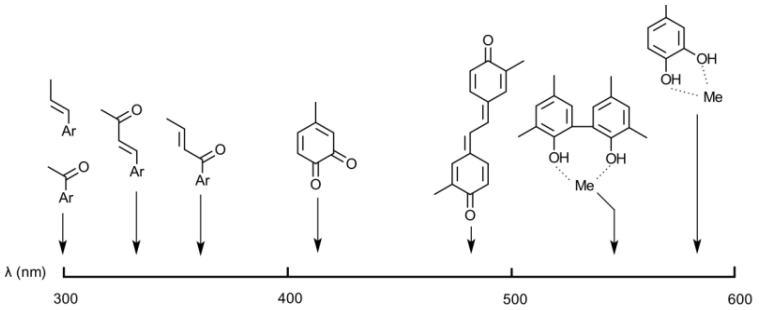

Figure 5: *Typical chromophores found in lignin and their maxima absorption wavelengths [F5].*

2.1.4 Pectins

Pectins are hydrophilic polysaccharides with very complex structures, primarily found in the middle lamella and the primary cell walls of the wood. Pectins are divided into groups, i.e., galacturonan, arabinans, galactans, and arabinogalactans. Characteristic glycosyl residues in pectin molecules are galacturonosyl, rhamnosyl, arabinosyl, galactosyl residues. Galacturonans are primarily acidic, while arabinans, galactans, and arabinogalactans are neutral polysaccharides. Like most pectins, the galacturonans can exist in two forms, i.e., methyl esterified or non-esterified, with the most abundant methyl esterified [68,69].

2.2 Lignin carbohydrate complex

Lignin works as a glue in the wood and holds the wood fibers together, i.e., the abbreviation LCC. It can be considered a filing agent in the cavities between the cellulose microfibrils in the cell wall, aiding the rigidity of the cell wall [62]. LCC is the primary key to understanding the fractionation of biomass. According to the literature, the primary LCC bonds are the phenyl glycosides, benzyl ethers/ethers, and some hemiacetal or acetal linkages [17]. The lignin is covalently bound to hemicellulose through the acetylated groups on the hemicelluloses, which have a more hydrophilic character.

In contrast, the hydroxylated side groups are turned towards the cellulose molecules. No clear, detailed evidence exists about how lignin is associated with cellulose [18,19]. The benzyl ester bonds are usually through the uronic acid of the hemicellulose and hydroxyl groups of lignin. Benzyl ether and phenyl glycosidic bonds link the glycosyl and mannosyl residues of the hemicelluloses to the phenolic and hydroxyl groups of the lignin molecules. The acetal bond links the carbonyl groups of lignin and the hydroxyl groups of carbohydrates together [20].

2.3 Wood fiber morphology

Different types of wood cells exist, such as pointed, elongated, and closed in the ends as tubes. These types of wood cells are found in softwood called tracheid fibers. In hardwood, the corresponding fibers are called the libriform cells[65]. The tracheids are connected through each other through bordered pits. Such bordered pits are circular, with a hole in the middle where water diffusion occurs [21]. On the other hand, there are also ray cells in softwood and ray cells and vessels in hardwood. Other important cells are the parenchyma cells, with open ends and varying sizes and shapes [22]. Vessels exhibit inter-vessel pitting, which has been shown to facilitate long-distance water transport. The cell walls of hardwood fibers have a greater thickness than those found in softwood earlywood because they do not conduct water[26].

The cell wall of wood fibers consists of repeated crystalline structures of cellulose chains in the form of microfibrils surrounded by a matrix of hemicellulose, pectins, and lignin [23]. The wood fibers are held together in the 0.2-1 μm thick middle lamella consisting of approximately 70-80% lignin by weight with a high concentration of pectins at an early growth stage [65]. The lignin works as an adhesive and, at the same time, provides rigidity to the cell wall. The wood cell consists of several wall layers with wall S2 dominating, located between walls S1 and S3. The three S cell walls belong to the group secondary cell walls, which are covered with a primary cell wall P, as depicted in figure 6 [24,26].

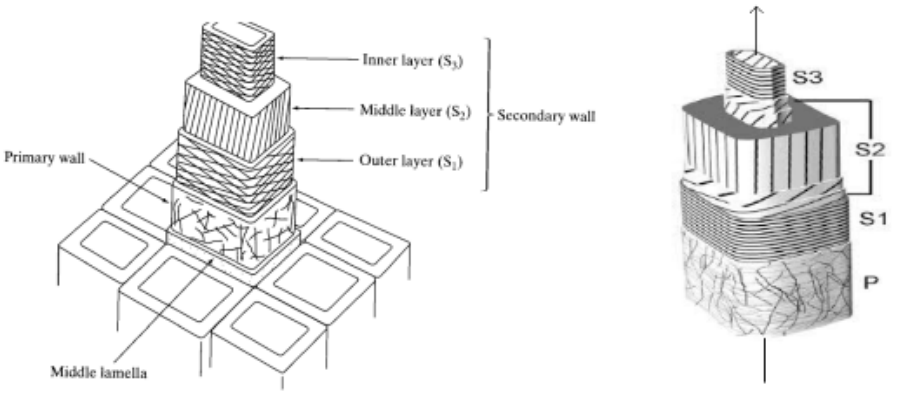

Figure 6: *The different layers, i.e., the cell walls and the fiber structure of a typical fiber [F6].*

The S1 and S3 cell walls are about 0.1-0.2 μm thick and consist of a single lamella composed of cellulose, hemicellulose, lignin, pectins, and proteins [65]. The cellulose microfibrils are oriented almost perpendicular ~ 70-90^{o} to the axis in these lamellas. However, the fibril angles can vary between 30-90^{o} in the S3 cell wall. More transverse strength is gained when the fibrils are oriented perpendicular to the axis, i.e., affecting the elastic modulus in the transverse direction. The S2 wall varies between 1-5 μm in thickness depending on whether it is earlywood or latewood and forms the central portion of the cell wall. Latewood has the thickest wall. The S2 fibers are aligned mainly parallel to each other with varying angles between 0-30^{o} to the axis

in a Z-helix. This indicates that the S2 layer primarily contributes to the mechanical strength in the longitudinal direction. The S2 layer consists of many lamellae with closely packed microfibers where the space between them is occupied by lignin. S1 and S3 wind generally in the opposite direction of S2, i.e., in an S-helix. Latewood tends to have a slightly lower mean angle of the fibers [24]. The approximate weight fractions of the S1/S2/S3 layers polymers are 30/33/36% hemicellulose and 27/47/50% cellulose [58,62]. The P cell wall is the first created cell wall and consists of microfibrils with a random orientation that allows expansion during cell growth [24]. By beating the fibers, the MFA can increase up to 30º, while drying further can increase it by up to 15º [58].

The hemicellulose xylan shows to be more associated with lignin, while the glucomannan shows to be more associated with cellulose. Therefore, some of the glucomannan surrounding the fibers in the S2 cell wall aggregates the fibers into larger macrofibers. The lumen in the cell is mainly empty, thus making the wood a relatively porous material [25,24].

2.4 Industrial Kraft process

A typical block diagram of the kraft process is shown in figure 7. When the wood logs arrive at the pulp mill, they go through a debarking step and then cut into small chips. The debarking is essential from many points of view, for instance, to eliminate all metal ions in the bark [40]. The next step is the pre-steaming step at around 120 ºC, followed by an impregnation step [43]. Next, the delignification is done in the digester at an elevated temperature of approximately 170 ºC with white liquor, i.e., mainly NaOH and Na_2S. During the cooking, parts of the Na_2S are oxidized to Na_2SO_4, while NaOH is oxidized to Na_2CO_3 [40]. After the pulp separation, the remaining liquor is called weak black liquor and consists of lignin, acids, carbohydrates, inorganics, and other valuable chemicals [41][42]. When the delignification is done, the separated pulp is washed and extensively bleached with strong chemicals such as hydrogen peroxide, ozone, and chlorine reagents. The bleaching process is either done to remove the remaining lignin and obtain higher pulp brightess, or removing the chromophores in the pulp using oxygen [44]. However, the bleaching steps are not included when producing kraftliner or other high kappa pulps for corrugated boards.

The weak black liquor obtained from the delignification process is sent to the recovery line to increase the feasibility of the pulping process from an economic aspect. The black liquor is concentrated in a series of evaporators, i.e., multiple-effect evaporators. This is done to increase the steam economy. The most commonly used evaporators are the rising film and the falling film evaporators. However, calculations have shown that the falling film evaporators could be better scaled than the rising film evaporators [45].

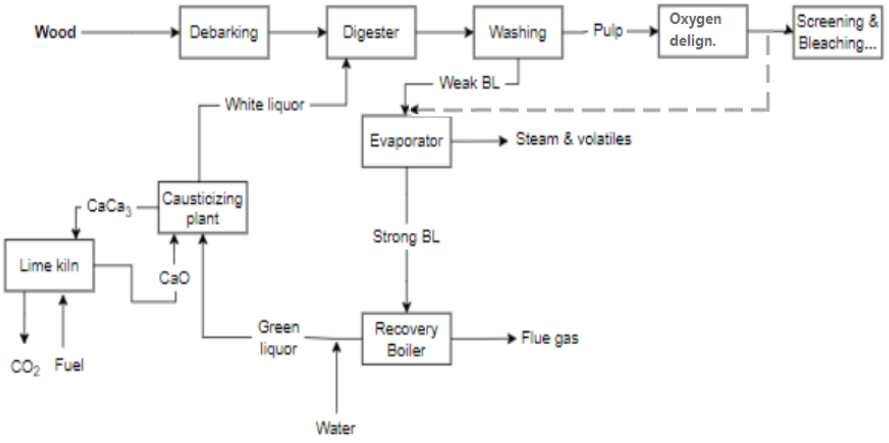

Figure 7: *Typical Block diagram of the kraft process [F9].*

When the weak black liquor is evaporated in the multiple effect evaporators, the solid concentration increases from 15-20% to around 65-86% [46]. The flue gas formed during evaporation has a high steam content and is therefore utilized in the form of condensed water, i.e., reducing the need for freshwater [47]. The more viscous black liquor is now called strong black liquor and contains many organic compounds, making it an adequate fuel. The strong black liquor continues into the recovery boiler and is burned at 1100 ºC [48]. Modern kraft pulp mills are generally self-sufficient when it comes to energy consumption. Nevertheless, it is important to note that there are some integrated pulp and paper mills that are not net exporters of energy. This includes mills situated in areas with restricted access to renewable energy sources, mills that use outdated and less efficient equipment, or mills that produce other energy-intensive products like chemicals or biofuels. Sometimes The recovery boiler typically has an electrostatic precipitator to capture and recycle the dust from the flue gas, mainly Na_2SO_4 [49].

When the combustible compounds in the black liquor have been burned in the recovery boiler, the hot smelt in the bottom containing salts such as sodium carbonate (Na_2CO_3) and sodium sulfide (Na_2SO_4) are now dissolved in water or weak white liquor and called green liquor. The green liquor is further delivered to the re-causticizing plant for the preparation of new white liquor. Lime is burnt at 1100-1250 ºC in the lime kiln to form burnt lime. The burnt lime reacts with the water in the green liquor to form calcium hydroxide, which further reacts further with sodium carbonate and forms sodium hydroxide and lime. The lime is recycled back to the lime kiln.

2.4.1 Impregnation

Impregnating the alkaline chemicals into the wood fibers is essential during the delignification. During this step, diffusion and advection of the cooking chemicals into the wood chips occur. The impregnation of the chemicals into the wood fibers is affected by several factors. Wood morphology is one crucial factor that depends on which type of wood is used. Earlywood and latewood have different types of pores in the fiber walls but also different numbers of bordered pits where the transport of the cooking liquor occurs. The tracheids in earlywood have about 200

bordered pits compared to the latewood, with only about 10-50 [36,37]. The cooking chemicals transportation in the fibers longitudinal direction is up to 200 times faster than the transportation across the fiber direction due to the greater surface area of the lumen in the wood cell [39].

To enhance the penetration of the cooking chemicals and make it as even as possible, a pre-steaming step is normally necessary to get rid of the entrapped air. In the pre-steaming step, the steam enters the pores and lumen through diffusion and condensates inside the pores. When the temperature increases, the condensate evaporates, and the pressure inside the pores expels the air out. In this way, it enables more alkali chemicals to diffuse into the wood fibers [37]. However, no pre-steaming was not carried out in this experiment.

A high liquid-to-wood (L:W) ratio, in combination with a long impregnation time, results in a more homogenous delignification [38]. An implemented method is the pre-cooking used in this experiment, where the wood chips are cooked with black liquor (used white liquor) as a pre-step. This is done to increase the yield, get as even an alkali profile as possible throughout the wood chips during the delignification process, and avoid unnecessary consumption of the white liquor. In addition, hydrogen sulfide ions (HS^-) diffuse into the saturated wood faster than the hydroxide ions (OH^-), possibly because they are not entering some of the pores in the wood chips. Therefore, high hydrogen sulfide concentration early in the cooking increases the selectivity toward lignin degradation [36]. One indication of an inhomogeneous delignification is the existence of shives after the cook. These shives have a high residual lignin content, meaning that the active chemicals have not reached the core of the wood chips. To obtain fewer shives, certain factors such as chip size, L:W ratio, temperature, and impregnation time can be varied and optimized [38,39].

***Table** 2: The approximate weight percentage of the four substances in white liquor in the industry [T2].*

NaOH	Na_2S	Na_2CO_3	Na_2SO_4
50-60	25-30	15-20	< 5

2.4.2 Wood delignification (cooking)

The delignification process of wood is a reaction mechanism to remove the embedded lignin in the cell wall of wood and facilitates the separation of the fibers. The predominantly delignification process is the Kraft process. A mixture of mainly sodium hydroxide (NaOH) and sodium sulfide (Na_2S) is used as cooking chemicals, as listed in table 2, also named white liquor. In addition to the most frequently used Kraft process, other methods include acidic delignification, reductive catalytic fraction, and other lignification techniques. A rule of thumb is that during kraft cooking, about 50% of the hemicelluloses, 80% of the lignin, and 10% of the cellulose molecules are dissolved [27]. Na_2S is hydrolyzed in water according to reaction 1, and the active chemicals, which are hydroxide ions (OH^-) and hydrogen sulfide ions (HS^-), are formed according to reaction 2-3 [32].

$$Na_2S \rightleftharpoons 2\,Na^+ + S^{2-} \quad (1)$$
$$S^{2-} + H_2O \rightleftharpoons HS^- + OH^- \quad (2)$$
$$HS^- + H_2O \rightleftharpoons H_2S + OH^- \quad (3)$$
$$NaOH \rightarrow OH^- + Na^+ \quad (4)$$

These ions are making nucleophilic attacks on the lignin molecules [31]. Reaction 2 shows that the sulfide ions contribute to both the hydroxide ions and the hydrogen sulfide ions, making it very difficult to determine the hydroxide ion concentration solely based on the concentration of the sodium hydroxide in reaction 4. Therefore, a variable EA (effective alkali) in eq 1 is introduced, which collects the hydroxide ions obtained from both sodium sulfide and the sodium hydroxide.

$$EA = EAv\,x\,m(tved)/(100x40) \quad \text{eq. 1}$$

$$HS = sulf.\,x\,EA\,/\,(200 - sulph.) \quad \text{eq. 2}$$

m(tved) is the dry mass of wood chip, 40 stands for the molar mass of NaOH, EAv is the effective alkali in mol, sulf. is the sulfidity in%, 200 stands for the factor 2 x 100%, and HS is the amount of HS- ions.

The kraft cooking reactions start at a temperature of approximately 135-175 ºC [27]. Depending on the cooking conditions, the cooking time varies a lot. A slow temperature increase is favorable to get an evenly distributed concentration gradient of the cooking chemicals in the wood, generally during about 1.5h [29]. The reaction rate is very temperature dependent, i.e., very low under 140 ºC, and increases rapidly as the temperature increases [37]. To obtain good results, several parameters such as EA, sulfidity, amount of wood, which type of wood, L:W ratio, and cooking time & temperature should be kept as optimal as possible [39]. To obtain the desired sulfidity and EA, the volume of the stock solutions NaOH and Na_2S can be calculated by taking eq 1 and eq 2 into account and using eq 3 and eq 5.

$$b = EA - (a\,x\,C(OH)/d) \quad \text{eq. 3}$$

$$a = HS/C(HS) \quad \text{eq. 4}$$

Where b is the volume of NaOH stock solution needed, d is the OH^- concentration in NaOH stock solution (mol/L), C(OH) is the OH^- concentration in Na_2S stock solution, a is the volume of Na_2S stock solution needed, HS is the amount of HS^- ions, and C(HS) is HS^- concentration in the Na_2S stock solution (mol/L).

The process occurs in three phases. The first phase is called the initiation phase and occurs during the temperature increase, i.e., slightly under 140 ºC. During this phase, mainly hemicelluloses are degraded, followed by lignin degradation when the phenolic ether bonds break [29]. In the initiation phase, the smaller parts and the extractable lignin dissolve fast, and

approximately 20% of the lignin becomes dissolved. The second phase is the bulk phase, the most selective delignification phase regarding the lignin dissolution. During this phase, lignin primarily degrades due to the cleavage of phenolic ether bonds and non-phenolic bonds. The bulk phase is slower than the initiation phase [36,37]. The last phase is called the residual phase; during this phase, the carbohydrates are degraded slowly with a small amount of lignin [30,31]. During the delignification of the wood, the wood porosity increase, enabling more and more fragments to diffuse out to the solution [36].

The alkali liquor is consumed in five different ways during the cooking, i.e., reaction with the lignin, reaction with the resins, neutralization of organic acids, dissolution of the carbohydrates, and adsorption by the fibers. The most alkali-consuming step is during the neutralization of the organic acids, accounting for about 60-70% of the alkali consumption, whereas the lignin dissolution accounts for only about 20-30%.
High temperatures will consume the active chemicals faster than they are diffused into the center of the wood, leading to uneven cooking. Therefore, the most optimal condition is not to exceed a temperature of 170 °C to maintain a high enough alkali concentration. The most alleged problem with a low temperature is that the center of the wood chips will have a deficit of active cooking chemicals due to the lowered diffusion rate [38].

The H-factor is a variable based on the Arrhenius equation as shown in eq 5, where the reaction temperature and time are combined in a single variable. The lignin content is denoted by the kappa number (K), which is inversely related to the H-factor. For instance, a high cooking temperature requires a shorter reaction time to achieve a certain kappa number and vice versa. The H-factor is a helpful variable to produce a pulp with an equivalent lignin content to another pulp mass on different occasions. The disadvantage of this correlation is that the influence of the chemicals is neglected, which means that the same amount and concentrations of the chemicals need to be used if different pulp masses are going to be compared [27,33]. With a known lignin percentage of the pulp, the kappa number can easily be calculated using equation 6 [64].

$$H = \int_{t0}^{t} e^{(43.2-16113/T)} dt \qquad \text{eq. 5}$$

$$K = 6.57 * lignin\,(\%) \qquad \text{eq. 6}$$

2.4.2.1 Carbohydrate dissolution

The inevitable carbohydrate degradation starts at the reducing end groups of the polysaccharides and is called the peeling reaction, shown in figure 8. The only attacking chemical on the carbohydrate molecules is the hydroxide ions OH^-, not the hydrogen sulfide ions HS^-. The OH^- concentration is calculated as the previously explained parameter EA in equation 1. Even before the peeling reactions, the acetyl groups on the hemicelluloses undergo a deacetylation reaction, contributing to an enormous alkali consumption. This means the hemicelluloses acetic acid

groups are split off below 100 ºC, especially on the soluble glucomannan molecules [37,39]. 4-O-methyl glucuronic acid attached to the xylan backbone reacts with the cooking chemicals, primarily with OH^- at high temperatures, forming hexenuronic acid (HexA). The reaction is a typical β-elimination of the methoxy groups on the 4-O-methyl glucuronoxylan. It reduces the brightness of the pulp and contributes to a higher kappa number due to the consumption of potassium permanganate ($KMnO_4$) used during the determination of the kappa number [50,56]. HexA can be removed from the pulp by alkaline hydrolysis but also by acidic hydrolysis being attacked by electrophilic oxidants [57]. Therefore, considerations should be taken to the amount of HexA in the pulp while determining the degree of delignification by the kappa number.

As mentioned before, a pre-cooking step with black liquor could be crucial to reduce white liquor consumption during the deacetylation of carbohydrates. During the deacetylation, the accessibility of the cell wall is increased, which leads to improved ion transport [39].
About 70% of the glucomannan content is dissolved during cooking [37]. The peeling reactions dominate on glucomannan at a temperature of about 100-130 ºC, and on xylan above 130 ºC. The peeling reactions are interrupted due to the transformation of the reducing end groups of the carbohydrates into more alkali-resistant acid groups [33,34]. These reactions are also called stopping reactions. Acids such as formic, lactic, and acetic acid are formed during the peeling reactions and are neutralized by the alkalis. This results in an enormous consumption of alkalis [32]. At higher temperatures above 150 ºC, alkaline hydrolysis randomly cleaves the polysaccharide chains into smaller fractions at the glycosidic bonds, increasing the possibility of peeling reactions [35]. The peeling and alkaline hydrolysis mainly affects the amorphous part of the cellulose chains. These types of reactions are also decreasing the yield of the pulp. When the alkaline charge has decreased, the dissolved but not degraded hemicelluloses can reabsorb on the fibers at the end of the delignification process [37].

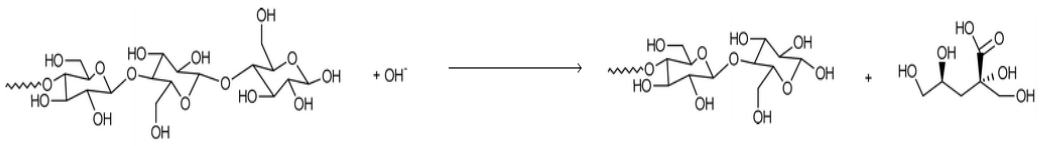

Figure 8: *A typical peeling reaction where the reducing end of the polysaccharide chain is cleaved off [F6].*

2.4.2.2 Lignin dissolution

The desired reaction is lignin degradation. During the cook, the porosity of the wood increases, and more and more lignin becomes dissolved [28]. The cleavage of the different aryl bonds, such as the most dominant β-O-4 ether bond shown in figure 4, liberates new soluble hydroxyl and carboxyl groups, as shown in figure 9. These groups will be ionized due to the alkaline environment, and the lignin molecules will become negatively charged and repel each other [31]. The C-C bonds are more stable than the C-O-C bonds, i.e., the C-O-C bonds are the most frequently broken, especially at the beginning of the cook [27].

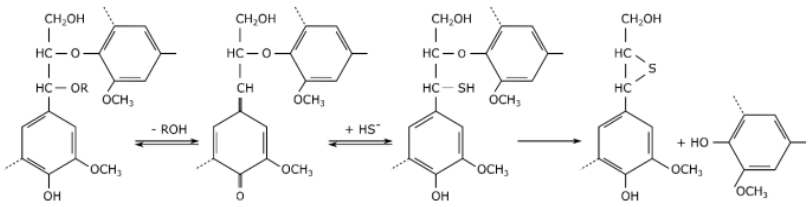

Figure 9: *A typical Cleavage mechanism of β-O-4 ether bond in lignin molecules during kraft cooking [F9].*

If the hydrogen sulfide concentration is low, lignin can be preceded by unwanted condensation reactions and start to re-build up [27]. By keeping the hydrogen sulfide concentration as high as possible, carbohydrate degradation can be avoided, and the lignin selectivity can be increased. This can be done mainly at the beginning of the process. Higher sulfidity increases the delignification rate and protects the carbohydrates from degradation [37]. Another undesired reaction is the demethylation reaction of the non-phenolic lignin, which occurs in the presence of hydrogen sulfide and methyl mercaptide ions forming methyl mercaptan and di-methyl sulfide [31].

2.4.2.3 Pre-hydrolysis

Pre-hydrolysis using hot water is an environmentally friendly process to extract and dissolve hemicelluloses from wood, generally before kraft cooking. During the process, a small amount of acid-soluble lignin and extractives will also dissolve, affecting the structure of the wood, such as the cellulose crystallinity and wood porosity [50]. The dissolved lignin can, however, condense and obstacle the delignification process. The pre-hydrolysis is conducted under high temperatures whereby certain acids, such as acetic and formic acid, are formed during the deacetylation reactions. Hemicellulose polymers are further degraded into smaller mono and oligosaccharides and dissolved in the hydrolysis liquor, consisting mainly of pentoses and hexoses [51]. The pre-hydrolysis rate increases proportionally as the solution acidity increases, which also means that adding mineral acids will significantly increase the solubility of the hemicelluloses [52].

The pre-hydrolysis is affected by factors such as the L:W ratio, wood type, temperature, and time. The temperature and time dependency are measured as the P-factor according to eq. 7 by similar to the H-factor in the delignification step [52].

$$P = \int_{t0}^{t} e^{(40.48-15106/T)} dt \qquad \text{eq. 7}$$

The hydrolysate liquor usually has a pH of 3-4 due to the formation of acetic and formic acid during the hydrolysis reactions [52].

2.4.2.4 Oxygen delignification

The oxygen delignification process is one of the most well-proven existing bleaching processes. It is often the first bleaching step after the kraft cooking to avoid later usage of non-environmentally bleaching chemicals. Oxygen gas is supplied at high temperatures and pressure to eliminate the lignin in the pulp. This is an environmentally friendly and cost-effective process. It can reduce up to 30-50% of the lignin from unbleached pulp without diminishing the pulp strength and other vital properties. The temperature and pressure must be elevated to about 80-120 ^{o}C and 6-8 bars to make the oxygen reactive. If the temperature and pressure are too high, the yield and fiber strength may be reduced significantly, making the oxygen delignification a non-selective process. This is due to the peeling reaction and the random chain cleavage of the carbohydrates. The pH value should be above 10, which is usually achieved by adding NaOH. Oxygen delignification has some crucial advantages, such as low chemical cost, reduced lignin condensation, reduced carbohydrate degradation, and improved bleachability of the pulp [55].

The oxygen atom contains two unpaired electrons, which have an affinity to the opposite spin of other electrons, i.e., making it a free radical. Oxygen will react with organic compounds if the temperature and pH are high enough. The hydroxide ions will deprotonate the lignin molecules and form phenolate ions, which further react with the oxygen to form resonance-stabilized phenoxy radicals and superoxide anions. These anions can further react with other oxygen radicals such as hydroxyl (HO•), hydroperoxy(HOO•), and other superoxide ions (O_2•$^{-}$) to form organic acids [53]. Hydroxyl radicals are more prone to oxidations but are less selective than superoxide anions. Transition metals such as Cu, Mn, and Fe are typically found in the pulp, which can catalyze the decomposition of the peroxides into non-selective radicals such as hydroxyl radicals. To hinder the negative impact of the transition metals, magnesium sulfate $MgSO_4$ is added to protect the carbohydrates and preserve the pulp strength by forming complexes with the transition metals. The uncondensed phenolic lignin molecules tend to be the most degradable compounds compared to the condensed phenolic or the non-phenolic molecules that are almost unaffected during oxygen delignification [55].

Mass transfer is another limitation because gas-to-liquid and liquid-to-solid oxygen transfer are necessary to oxidize the lignin molecules [54]. One-step oxidation was the first method implemented during the 70s. However, later investigations have shown that the process can be carried out in two phases, i.e., an initial rapid phase and a slow final phase. In the latter two-phase oxidation, the delignification yield can be as much as 70% [55].

2.5 Kraftliner used for corrugated boards and packaging

The kraftliner process is a method to produce high-strength paperboards, which are called kraftliner. Usually, the kraftliner is used in packaging applications & corrugated boards. After that impurities and lignin, the binding glue-like substance, have been removed by the kraft process, the pulp is refined and fed into a paper machine. Kraftliner pulp masses are cooked during shorter times and not bleached, i.e., they contain a high amount of lignin and have a high kappa number at around 90. The paperboards are dried and sometimes coated with starch,

making the sheets more durable, improving strength properties, etc. The final product is rolled into large reels, which are further shaped into various forms depending on the area of use [70,71].

Due to the unique properties of kraftliner, they are primarily used in corrugated boards and packaging applications. It is ideal for packaging applications due to its flexible fibers and high-strength properties, and it is an excellent material to enclose and protect products for storage. It is also crucial in preserving the quality and safety of goods during transport. Packaging material made from three layers of paper, i.e., an outer layer, a fluted layer (wavy paper sheet), and an inner layer, provides structural rigidity such as during transports and is called a corrugated board or cardboard. Corrugated board is highly versatile and is used in many applications, such as in the food and beverage industry and electronics. Another vital characteristic of kraftliner is that it is very printable, lightweight, and can be assembled into various shapes and sizes. Kraftliner is also more moisture-resistant than other paper types and can be stored in relatively high-humidity environments. Finally, kraftliner is also highly cost-effective, recyclable, and has no significant negative impact on the environment [72-74].

2.6 Hygroexpansion

Hygroexpansion (HEX) is a fundamental property and should be considered when producing kraftliner and other paper types. Moisture sensitivity, especially irreversible sensitivity, is a huge problem nowadays. This means a paper going through an expansion when exposed to moisture should at least return to its normal dimension when it dries and shrinks, and the paper should not curl in the out-of-plane direction. This is especially encountered during printing applications [59,63]. When relative humidity fluctuations occur in the surrounding air, a dimensional change of the paper due to a change in moisture content is always witnessed. Consequently, tensile strength, compressive strength, and other mechanical properties are being deteriorated [62]. HEX is thus responsible for the deformation of paper, i.e., plane deformations, cockling, and curls[59]. As pulp and paper are a network of individual fibers, the HEX depends on the fiber morphology and the polymers making up the fibers. Measurements of the HEX can, in general, be divided into two types of measurement techniques, i.e., optical such as atomic force microscopy (AFM) or light microscopy (LM), and mechanical techniques, such as by the Nee-nah type hygroexpansiometer [58].

Optical imaging is a better method to calculate the HEX for the measurement of single fibers to acquire fiber dimensions under varying humidity. Consequently, the fiber orientation is exciting because fibers typically are aligned anisotropically. The alignment of fibers in the machine direction (MD) is less prone to expansion in that direction and vice versa. Apart from this, considerations should be taken to the dimension change in the out-of-plane direction [58,59]. However, measuring the exact HEX behavior is challenging due to the enormous kinematic freedom, the release of dry in strain, bending, and translation [60].

By taking different sources into account, the moisture content in the fiber can be divided between cellulose, hemicellulose, and lignin with an approximate ratio of 0:2.6:1. The

hemicellulose is claimed to influence the elastic properties of the fibers mostly. In contrast, lignin and cellulose only have a moderate effect. Highly covalently bonded polymers in the fibers lead to higher stiffness, whereas a high concentration of hydrogen bonds creates more swelling capacity. The swelling of polymers is related to the solubility of the polymers in a solvent. About 70% of the cellulose is normally in crystalline form, which makes the cellulose unlikely to expand compared to lignin and hemicellulose. Nevertheless, the amorphous part of the cellulose makes it impressionable by water. Hydroxyl group, number 2 and 6 on the cellulose monomers, are the first being hydrated at low humidities, and at very high humidities, hydroxyl number 3 and the acetal groups are also affected [58].

There are various theories about how the fibers absorb water, such as solid solution theory, capillary condensation theory, two-phase mechanism, and the pore size distribution mechanism. Important factors that affect the sorption mechanism are the wood type, temperature, pH, electrolyte concentration, the valency of counter ions, fiber density, pore size distribution, presence of sulfonated lignin, morphological factors, cell wall thickness, etc. [58,63]. The dimensional changes due to expansion or contraction also depend on micromechanical constituents, i.e., free and bonded fiber segments which in turn depend on the distribution of the fibers, orientation, density [59]. Specific investigations have been made to determine the difference between free or bonded fiber segments during constrained and free drying. Even if the observations were restricted to the surface fibers, it was clear that the deformations taking place were mostly in the bonded segments [61]. The impact of lignin on the HEX has not been dealt with that much due to the usually extensive removal of lignin during the cooking and bleaching processes [63].

The fibers microfibril angle (MFA) also tends to impact the HEX. Around 90% of the fiber mass is concentrated in the S2 layer, which also defines the swelling properties of the fibers to a significant degree. However, research studies have shown that the S1 and S3 layers also impact the HEX, where a double thickness of the S1 layer increases the transverse elastic modulus by around 20%. A rule of thumb is that higher MFA leads to a higher degree of HEX in the longitudinal direction but decreased HEX in the transversal direction [58].

2.7 Multiple regression analysis

Multiple regression analysis (MRA) is a statistical tool to determine the relationship between independent and dependent variables. For example, the length, width, and shape factor (independent variables) and the tensile strength (dependent variable). In this thesis, the regression data analyzer in excel is utilized. The output of the regression analysis can be used to interpret the obtained results, such as the following outputs:

Multiple R (correlation coefficient): The degree of linear relationship among the chosen variables, where 1 means strong positive relationship, 0 means no relationship, and -1 means strong negative relationship.

Adjusted R^2: The goodness of fit, i.e., how the different data fit with the regression line. The adjusted R^2 is more appropriate than the standard R^2 when more than one independent variable is involved. It can reach a maximum value of 1, and the higher the R^2, the more the variation of the dependent variable can be explained by the independent variables.

The coefficients: The strength and direction of the relationship between each independent variable and the dependent variable.

P-value: The probability that the relationship between the independent and the dependent variable occurred by chance, i.e., lower p-value means better results. If the p-value is lower than the significance level, the relationship should not be rejected.

F-test: Provides the overall importance of the regression model for the null hypothesis. It is a tool to observe the difference between two or more data sets by their variances. The higher the F-test value, the better the result. The F-test often confirms that two or more groups are unequal by rejecting the null hypothesis. This is often also referred to as the significance F value (p-value of the F-test), indicating whether the model is statistically significant or not. When the significance F-value is lower than the significance level, the null hypothesis can be rejected, and the variance is confirmed to be unequal between the data sets [75-76].

3 Experimental

This chapter will provide an explanation of the experimental part. Initially, a detailed account of the materials and equipment used will be given, including how they were utilized. Subsequently, the steps involved in the different cookings will be outlined. As the impregnation and delignification processes were carried out consistently in all cookings, the overall implementation and delignification steps will be explained first. Following that, in each part section, the specific temperatures, times, and quantities of different cooking solutions will be stated.

The experiment has three parts (I, II, and III). Softwood chips with a length of 2-3 cm and a width of 1-2 cm were used in all three parts. Small portions of the wood chips were taken and oven-dried overnight at a temperature of 105 ^{o}C to determine the dryness of the wood chips. The dryness of the wood chips was determined to be 66.5 wt%, according to Appendix A. No pre-streaming step was conducted.

The pre-impregnation and delignification steps were conducted using four 2.5 L identical metallic autoclaves, each with 250 g of dry wood chips and the desired amount of cooking liquor. The pre-impregnation and delignification steps were conducted by rotating the autoclaves in a heated PEG (Polyethylene Glycol) bath at the desired temperature. Withdrawal of the autoclaves was done continuously from the PEG bath at different times during the delignification step and cooled down in a large tank supplied with circulating cold water. This procedure was done to terminate the ongoing reactions and obtain different kappa numbers of the samples. Instead of comparing the kappa numbers or the H-factors, the lignin content was directly measured and compared according to the standard method SCAN-SN 71.

Part I consists of a pre-impregnation step followed by a delignification step. After the delignification step, two samples with different H-factors were further oxygen delignified due to the unsuccessful disintegration of the fibers. The oxygen-delignified samples were then split into two halves, where each half was further treated with xylanase enzymes. Part II and III consist of a pre-impregnation step followed by a delignification step in the same way as in part I but without further treatment. The distinction between parts II and III is that part II also consists of a pre-hydrolysis step to remove the hemicelluloses before the cooking step. All three parts (I, II, III) were performed with four samples each.

The EA and HS concentrations of the black liquor used in the pre-impregnation steps are shown in table 3. To measure the EA and HS concentrations of the black liquor, titration was conducted with a 685 dosimat according to the standard methods SCAN:N 31:94 and SCAN:N 30:85. The dry solid content of the black liquor was measured to 33.1 wt%, according to Appendix A. EA and sulfidity were adjusted to 17.5% and 50% during the pre-impregnation and delignification steps in all parts. The temperature elevation was always conducted at a rate of 3 ^{o}C/min.

***Table 3**: The EA and the HS^- concentration of the black liquor used in the pre-impregnation step in the three parts.*

Black liquor :	Part I	Part II & III
EA (mol/L)	0.59	0.58
HS (mol/L)	0.43	0.38

The pre-hydrolysis and the pre-impregnation steps were carried out with a L:W ratio of 7. In contrast, the delignification steps were carried out with a L:W ratio of 4, based on the dry weight of the wood. Since no pre-steaming was performed before the pre-impregnation steps, the wood chips were allowed to rest in deionized water overnight to enhance the diffusion rate.

3.1 Pre-Impregnation

Due to the water absorption of the wood chips, the weights of the wood chips increased overnight. The wood chips were weighted, and the new weights were listed in the tables as wet weights. To be able to adjust the L:W ratios, the absorbed water must be measured and taken into account. After the wood samples had been drained, they were inserted into the autoclaves. The calculated amount of water, black liquor, and stock solutions were added to obtain the desired sulfidity and EA, according to Appendix B. The concentrations of the stock solutions are 9.2030 M (OH^-) from NaOH and 1.6885 M (HS^-) in addition to 1.4165 M (OH^-) from Na_2S.

By the use of lids, the autoclaves were sealed. The lids were screwed on by using an automatic nut driver to isolate the inside of the autoclaves from the outside. The PEG bath was then prepared by increasing the temperature to the desired insertion temperature. The four autoclaves were immersed in the PEG bath at the desired temperature, and the temperature was further increased to the desired pre-impregnation temperature. When the impregnation time was up, the autoclaves were removed from the PEG bath and cooled down in the water tank. The lids were opened up, and the black liquor was poured off by the use of a strainer. Small bottles were prepared, and the black liquor was collected and further titrated with the same standard methods as before, i.e., SCAN:N 31:94 and SCAN:N 30:85. The HS^- and OH^- concentrations are necessary to know to be able to calculate the amount of white liquor needed for the following delignification step.

3.2 Delignification

The wood chips were inserted back into their respective autoclave after being drained. According to Appendix B, the calculated amount of white liquor was prepared and added. All four autoclaves were sealed with their respective lids in the same way and immersed into the PEG bath. The bath temperature was now increased to the desired delignification (cooking) temperature. The H-factor will be slightly affected during the temperature increase, which should be considered. When the delignification time was up, the wood chips were again separated from the white liquor using a strainer. The white liquor has now turned into black liquor. The delignified wood chips were always washed overnight with deionized water.

3.3 Part I

Part I was carried out differently than parts II and III. Lower delignification temperatures for longer periods (EIC - extended impregnation kraft cooking) were conducted. Approximately 2L of deionized water was added to a mechanical disintegrator with 1000 x 10 revolutions to defibrate the fibers. Afterwards, the samples were centrifuged to get as high dryness as possible and eliminate the excess water. This defibration step was performed after the delignification process, i.e., before the oxygen and enzymatic treatment. Due to unsuccessful defibration directly after the delignification, where many shives were still present, the samples were instead further oxygen and enzyme-treated. The oxygen-delignified samples are abbreviated with (O), while the oxygen-delignified and further enzyme treated samples are abbreviated with (O+X).

3.3.1 Part I Impregnation

The amount of black liquor, distilled water, and stock solutions (NaOH and Na_2S) needed to get the desired L:W, EA, and sulfidity in the impregnation step are listed in table 4.

Table 4*: The dry/wet weights of the wood chips, the added amount of Water, BL, NaOH, and Na_2S into the autoclaves.*

Samples:	sample 1	sample 2	sample 3	sample 4
Wet weight (g)	615.3	632.7	617	623.7
Dry weight (g)	250	250	250	250
Water added (ml)	446.5	429.1	444.8	438.1
BL added (ml)	875	875	875	875
NaOH (ml)	63	63	63	63
Na_2S (ml)	0	0	0	0

The PEG bath was prepared by increasing the temperature to 90 ºC. When the desired temperature was reached, the four autoclaves were immersed in the bath, and the bath temperature was further increased to 120 ºC. The temperature increase from 90 to 120 ºC took 10 min, and the wood chips were impregnated for 40 min.

Table 5 contains the withdrawn amount of black liquor and the measured concentrations of OH^- and HS^- ions after the impregnation step, according to Appendix B. Average concentrations of OH^- and HS^- were 0,303 M and 0,21 M.

***Table 5**: The withdrawn amount of black liquor after the impregnation step and concentrations of HS^- and OH^-.*

Samples:	sample 1	sample 2	sample 3	sample 4
Withdrawn (ml)	1476	1475	1483	1480
[HS^-] M	0.226	0.220	0.2047	0.2019
[OH^-] M	0.3060	0.2988	0.3052	0.3018

3.3.2 Part I Delignification

Water and stock solutions were prepared according to table 6 for the delignification step.

***Table 6**: The amount of the different stock solutions needed when preparing the white liquors.*

Samples:	sample 1	sample 2	sample 3	sample 4
H_2O (ml)	466	465.2	472	469.4
NaOH (ml)	82.4	82.4	82.5	82.5
Na_2S (ml)	178	177	179	178

The temperature was increased from 120 ºC to 140 ºC, and the H-factors obtained at the different reaction times are listed in table 15 under the results.

3.3.3 Oxygen delignification

Samples two and four were chosen to further go through an oxygen delignification step. Both samples were thus split into halves according to figure 10, introduced into four autoclaves with the dry weights according to table 7. These teflonized autoclaves used for the oxygen delignification hold a maximum weight of 80 g (dry weight) of wood.

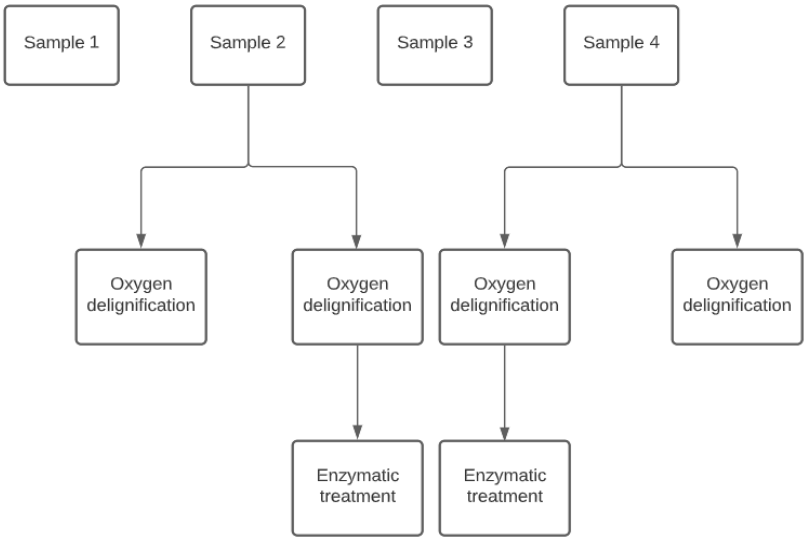

Figure 10: *Block diagram where samples 2 and 4 go through the oxygen delignification step followed by an enzymatic treatment step.*

In addition to the oxygen gas, deionized water, magnesium sulfate ($MgSO_4$), and sodium hydroxide (NaOH) were added according to table 7. When the lids were screwed on and the autoclaves isolated, the oxygen gas was supplied from a pressurized oxygen tube. This increased the pressure inside the autoclaves to 0,7 bar. The oxygen delignification was conducted in the PEG bath at a temperature of 100 ^{o}C for 75 min. The autoclaves were then taken out and cooled down in the water tank when the reaction time was up. The pressure was checked before the gas release to observe any gas leakage. As shown in table 7, the pressures had slightly decreased, probably due to gas leakages through the valves.

Because of the small portions of liquors used during the oxygen delignification, the liquors were sucked out from the pulps by vacuum suction after the process. A calibrated pH electrode was used to measure the pH of the liquors, which is listed in table 7 as well. The pulps were washed three times with 1,5 L of deionized water under vacuum suction and stored in small isolated plastic bags.

***Table** 7: Dry and wet weights of the samples, the amount of added chemicals, and the measured pressure.*

Samples (x 2 of each sample):	sample 2	sample 4
Dry sample weight (g)	76.28	76.9
Wet sample weight (g)	269	266
NaOH, 2M (ml)	38.1	38.4
$MgSO_4$, 100g/L (ml)	1.5	1.5
H_2O (ml)	331.28	334.6
Pressure (bar)	0.65	0.60
pH	10.625	10.9

3.3.4 Enzymatic treatment

One of each oxygen-delignified sample was treated with commercial xylanase enzymes. This experiment was carried out to demonstrate how the removal of xylan molecules affects the pulp properties after an oxygen delignification process. According to the instructions, the enzyme dosage should be between 25-75 grams per metric ton of oven-dry fiber, the temperature should be in the range of 40-90 ºC, the pH in the range of 5-10, and the retention time should be + 20 min.

Both samples were prepared in small plastic bags. The chosen enzyme dosage was 50 g/ton of dry wood. Sample weights, dosages, retention times, and pH values (after treatment) are listed in table 8. The enzymes received as a liquid was added to 1 L of deionized water using an automatic pipette. A dilution of the enzymes was necessary to get as even a distribution as possible of the enzymes over the fibers. However, the enzyme concentration was mistakenly only diluted 1000 times, i.e., g/L instead of mg/L. Nevertheless, due to the overflow of enzymes, this is not going to affect the result negatively in any way.

***Table 8:** Sample weight, enzyme dosage, retention, and reaction time during the enzyme treatment step.*

Samples	sample 2	sample 4
Dry sample weight	64.25	63.17
Enzyme added (ml)	3.2	3.16
Retention time (min)	45	45
Reaction temperature (ºC)	70	70
pH (after)	8.7	8.33

The two bags were carefully welded and kneaded before being immersed in a hot water bath. After the retention time was up, the bags were removed from the hot bath. The fibers were washed three times with 1.5 L of deionized water (two times with boiling water).

3.4 Part II & III:

In the following two parts, a similar H-factor was supposed to be obtained as much as possible but with different contents of hemicellulose. This was possible by conducting a pre-hydrolysis step only in part II before the pre-impregnation and the delignification steps. Thus, identical steps were performed in parts II and III regarding the pre-impregnation and delignification steps. In this way, similar lignin content was obtained in both parts, and the hemicelluloses were easily removed in part II using only boiling water. After the delignification process in parts II and III, the wood chips were washed and refined using the sprout waldron (SW). As the wood chips are introduced into the refiner, they undergo a process of high-pressure and high-speed blade rotation, resulting in their breakdown into individual fibers. After the refining step, the fibers were centrifuged to eliminate the excess water. The pre-hydrolyzed samples are abbreviated with PH, while the reference samples are abbreviated with R.

3.4.1 Part II Pre-hydrolysis

The temperature was increased to the insertion temperature, i.e. 90 ºC. The amount of deionized water added to the autoclaves and the wood weights are shown in table 9.

***Table 9**: The weights of the wood inserted into the autoclaves, and the amount of deionized water added.*

Samples:	PH 1	PH 2	PH 3	PH 4
Wet weight (g)	375.2	375.2	375.1	375.4
Dry weight (g)	250	250	250	250
Water added (ml)	1624.8	1624.8	1624.9	1624.6

The autoclaves were sealed with their lids and immersed in the PEG bath, and the temperature was increased to 110 ºC. The pre-hydrolysis was carried out for 120 min. When the time was up, the autoclaves were taken out and cooled down before the lids were opened. Approximately 1.4 L of hydrolysate was poured off from each autoclave. The average pH of the hydrolysates was measured to 3.55 by the use of a calibrated pH electrode.

3.4.2 Part II & III Impregnation

The amount of black liquor, deionized water, and stock solutions (NaOH and Na_2S) added to get the desired L:W, EA, and sulfidity during the pre-impregnation step of the PH and R samples are shown in table 10.

Table 10: *The weights of the dry/wet wood, the amount of Water, BL, NaOH, and Na_2S added to the autoclaves.*

Samples:	PH 1	PH 2	PH 3	PH 4	R1	R2	R3	R4
Wet weight (g)	606.7	608.2	608.8	603.3	655.5	648.7	648.2	639.1
Dry weight (g)	250	250	250	250	250	250	250	250
Water added (ml)	455.1	453.6	453	458.5	406.3	413.1	413.6	422.7
BL added (ml)	875	875	875	875	875	875	875	875
NaOH (ml)	64	64	64	64	64	64	64	64
Na_2S (ml)	0	0	0	0	0	0	0	0

The PEG bath was stabilized at the insertion temperature of 90 ºC before the immersion of the autoclaves. After the wood chips and the liquors, according to table 10 had been added to the autoclaves, the temperature was further increased to the pre-impregnation temperature of 110 ºC. The pre-impregnation of the wood chips was accomplished after 120 min, and the BL was poured off. According to Appendix B, the withdrawn average OH^- and HS^- concentrations were measured to 0.197 and 0.218 for the PH and 0.210 and 0.238 for the R samples.

3.4.3 Part II & III Delignification

Water and stock solutions were added according to table 11 in preparation for the delignification process.

Table 11: *The amount of stock solutions needed when preparing the white liquors for the (PH) and (R) samples.*

Samples:	PH 1	PH 2	PH 3	PH 4	R1	R2	R3	R4
Water added (ml)	299	299	290.3	290.3	346.3	346.3	346.3	337.7
NaOH (ml)	83.8	83.8	83.7	83.7	83.6	83.6	83.6	83.6
Na_2S (ml)	157	157	156	156	160	160	160	159

The temperature was increased from 110 ºC to 160 ºC and the H-factors obtained at the different reaction times are listed in table 15 under the results.

3.5 Sheet making & Schopper riegler (SR) determination

To create sheets out of the prepared fibers, the dryness of the pulps must be determined. The dryness of the samples was calculated according to Appendix B, by drying small portions (~10g) of the fibers overnight at 105 ºC. As mentioned, the oxygen-delignified samples are abbreviated with (O), while the oxygen-delignified and further enzyme-treated samples are abbreviated with (O+X). These samples originated from part I, where samples 2 and 4 were chosen to be further treated. Portions of samples R1 and R4 from the reference samples in part III were also refined with 10,000 pfi to investigate how the degree of refining affects the pulp properties. The wood

chips are loaded into the pfi refiner, and the discs are rotated at high speed to apply shear forces to the chips. The refining process is conducted under controlled conditions, including the pulp consistency, the gap between the discs, and the rotational speed.

***Table 12**: The calculated dryness of each pulp sample.*

Samples:	PH1	PH2	PH3	PH4	R1	R2	R3
Dryness (%)	25.2	17.4	19.2	22.9	20.4	23.9	22.2
Samples:	R4	2 (O)	4 (O)	2 (O+X)	4 (O+X)	R1 refined	R4 refined
Dryness (%)	22.0	25.7	26.0	24.9	26.2	20.4	22.0

The sheets are supposed to be square-shaped with a side length of 155 mm. A margin of 10 mm is good enough for punching the sheets. Thus, sheets with a side length of 165 mm were made with the standard dry weights of 140 g/m^2, equivalent to 3.81 g/sheet. Since the samples have different dry contents according to table 12, 50 g (dry weight) was divided by the dryness of the samples to get the desired sample weights (wet weight) needed. The calculated wet weights were mixed with 15 L of deionized water in large buckets to obtain a fiber concentration of roughly 3-4 g/L. The mixture was constantly agitated to obtain a uniform distribution of the fibers inside the bucket.

Before each sheeting moment, the exact fiber concentration of the sample mixtures must be determined to create sheets with an accurate weight of 3.81g. Therefore, a small portion of the mixture was weighed with a jug. The fibers in the jug were collected on filter paper using vacuum suction. By folding and drying the filter paper with the fibers on it, the fiber concentration in g/L of the prepared mixture could be determined. This could thus be calculated by knowing the weight of the filter paper with the dry fibers and the amount of mixture taken. The procedure was done twice on each sample to avoid measurement errors, and an average concentration was always estimated. The amount of sample mixture needed to make sheets with the dry weight of 3.81g was now easily calculated by dividing the desired sheet weight by the measured mixture concentration. A dry fiber weight of 2g is always used to determine the SR value according to the standard method in table 14. The calculated concentrations and the amount of mixture needed, according to Appendix C, are listed in table 13. The sheets were easily made using a pulp hand sheet machine. Approximately 10 sheets were made of each sample mixture. After being dried overnight, the sheets were punched to the side length of 155 mm and stored at a humidity level of 50% and a temperature of 25 ^{o}C.

***Table 13**: Concentrations of the different sample mixtures, amount of mixture needed for making the sheets & measuring the SR.*

Samples:	PH1	PH4	R1	R2	R3	R4
Conc. (g/l)	3.44	3.17	3.27	3.53	3.35	3.55
Sheet sol. (g)	1108	1201	1166	1078	1137	1058
SR sol. (g)	581	630	612	566	596	556
Samples:	2 (O)	4 (O)	2 (O+X)	4 (O+X)	R1 refined	R4 refined
Conc. (g/l)	3.11	3.38	3.28	3.34	2.30	2.92
Sheet sol. (g)	1225	1129	1161	1141	1657	1305
SR sol. (g)	643	593	610	599	870	685

The pre-hydrolyzed samples PH2 and PH3 were wasted and not included in the tables due to being overrefined in the SW. Extremely high SR value due to over-refining makes the sample worthless.

3.6 Pulp & sheets tests

A series of tests were carried out on the pulps and the created sheets according to the standard methods used by Rise, listed in table 14.

***Table 14:** A summary of all conducted tests and the methods used by Rise.*

Test:	Iso-brightness	Chemical composition/ lignin content	Fiber-tests	Dryness
Std method:	ISO 2470	SCAN-SN 71	SCAN-P 88:1	SCAN-N 22
Test:	Tensile strength	Compressive strength	Hygroexpansion	Schopper riegler (SR)
Std method:	ISO 1924-3	ISO 9895	ISO 8226-1	ISO 5267-1

Depending on the tests, they were either carried out on the pulp masses, sample mixtures, or the sheets themselves. First, the dryness and chemical composition were measured on the pulp masses, where a small portion of the fibers was taken. The chemical composition of the lignin and carbohydrate content of the pulps was carried out using the standard method SCAN-SN 71,

according to table 14. Then, the compressive strength (Cs), tensile strength (Ts), and hygroexpansion (HEX) tests were carried out on the sheets, which were cut into small strips according to the standard methods. Finally, the fiber tests were carried out on the sample mixtures, according to the standard method SCAN-P 88:1. Fiber length, width, shape factor, and number of kinks (deformations) per fiber were all measured and investigated.

Ts was carried out, so the sheet stips were pulled horizontally until they broke, and the required force was measured. During the Cs test, the sheet strips were instead compressed vertically. The brightness of the sheets was also measured, both with and without pH adjustment, to investigate how the chromophores in the lignin affect the brightness of the sheet. This was possible by measuring the brightness of the original sheets followed by measurements on sheets where the pH was lowered to about 5, using sulfuric acid (H_2SO_4). The HEX measurement was carried out so that all the sheet stips were simultaneously exposed to moisture in an isolated climate chamber, where the humidity varied between 33-50-66%. The HEX measurement was performed in two sets to ensure that the obtained values or at least the obtained trend were correct. The measurement was carried out in the first round without a preconditioning step at 20% humidity. The 50% humidity level was complemented afterwarda with short-level maintenance, according to Appendix D. This is not according to the standard method in table 14. Therefore a second measurement was necessary, this time according to the standard method ISO 8226-1. Due to the preconditioning step performed during the second measurement, the equilibrium was achieved before the humidity level of 20%. The obtained trendlines were very similar for both measurements, and only the results for the second and the most accurate measurement are presented under the results. In this experiment, a mechanical method was utilized, where the sheet strips were fixed between two movable clamps, and the contraction and expansion of the strips were measured in this way. The movement is generally monitored via a micrometer, linear variable differential transformer, or a scanning laser. In this experiment, a scanning laser was used. A specific load is applied on the clamps to keep the strips in place, and it should be kept in mind that if the load is too high, a false result may be obtained.

The system used during the HEX measurements is a typical mechanical system, where the sheet strips are fixed between two movable clamps. When the strips between the clamps expand or contract, a displacement of the clamps occurs, and the monitor registers the dimension change with a laser. The cycle was carried out twice for each measurement to obtain an average result.

4 Results and discussion

The results are divided, so parts II and III are compared in one graph while part I is plotted individually. Tensile strength (Ts), compressive strength index (Csi), Hygroexpansion (HEX), iso-brightness, schopper riegler (SR), and carbohydrate composition were all measured and investigated. In addition, fiber tests such as length, width, shape factor, and number of kinks per fiber were also analyzed. As mentioned, the pre-hydrolyzed samples are abbreviated with PH, reference samples with R, oxygen delignified samples with (O), oxygen delignified and further enzyme-treated samples with (O+X), and finally, the refined samples with R1 & R4 PFI.

The obtained H-factors for the samples are listed in table 15. The H-factor will deviate slightly between the PH and the R samples even though they have the same cooking time. These deviations depend on the contributions during the temperature elevations. However, the deviations are insignificant and can thus be neglected. The S abbreviation is for the samples in part I, i.e., where S2 and S4 were the only chosen samples to be further oxygen delignified and treated with xylanase enzymes. It should be noted that the H-factors for the S samples in table 15 are achieved after the alkaline cooking, and the oxygen and enzyme treatment is not included here.

Table 15*: The obtained H-factors during the delignification process of all the samples R1-R4, PH1-PH4, S1-S4.*

Samples:	PH 1	PH 2	PH 3	PH 4	R1	R2	R3	R4	S1	S2	S3	S4
HF	300	375	450	500	300	376	449	506	235	256	279	301
Time (h)	0.58	1.10	1.21	1.28	0.57	1.08	1.19	1.28	3.2	3.4	4.0	4.2

Tables 16 and 17 list the chemical compositions of each sample in percentage, based on an average of duplicate samples. Upon treatment with xylanase enzymes, samples 2(O+X) and 4(O+X) showed a reduction of approximately 40% in xylose and arabinose content. Galactose and mannose have not been affected by the enzymes, which is reasonable because the xylanase enzymes only attack the xylans. Comparing the pre-hydrolyzed samples PH1 and PH4 with the corresponding reference samples R1 and R4, all the hemicelluloses have been drastically reduced. However, the lignin remains relatively high after the pre-hydrolysis step, which is expected.

***Table 16**: Carbohydrate composition in (%) of the R1-R4, PH1 & PH4, and (O) & (O+X) samples.*

Samples:	PH 1	PH 4	R1	R2	R3	R4	2(O)	4(O)	2(O+X)	4(O+X)
Xylose	3.6	3.6	7.7	7.6	7.6	7.5	9.1	8.9	5.3	5.3
Arabinose	0.1	0	1.3	1.1	1.0	1.0	1.6	1.4	0.9	0.8
Galactose	0.1	0.1	1.2	1.0	0.9	0.8	1.0	0.9	0.9	0.9
Mannose	2.0	2.0	7.2	7.5	7.0	7.2	7.7	7.6	7.8	7.8
Glucose	94.3	94.4	82.6	82.8	83.5	83.5	80.6	81.1	85.1	85.3

The lignin, cellulose, GMM (glucomannan), and xylan content in (%) are listed in table 17. The lignin proportion in each sample is determined by dividing the sum of the acid-soluble and acid-insoluble lignin residues by the total amount of carbohydrate + lignin, as shown in Appendix F. The percentage of the carbohydrates in table 16 and 17 was calculated according to an article written by Jan Janson[79]. The calculations are based on the values in table 16, calculated as 50% mixture of spruce and pine. As assumed, the lignin content decreases from R1 to R4, PH4 to PH1, and 2(O) to 4(O), i.e., with increased cooking time. The aim was to achieve a similar lignin content between samples PH1-R1 and PH4-R4. Despite the challenge posed by the two separate cookings, the results are satisfactory and fall within the same range. There is a slight decrease in the lignin content of the (O) samples after treatment with xylanase enzymes. This can be attributed to the breaking of LCC bonds, which releases lignin and is a reasonable explanation for the decrease.

***Table 17**: Lignin, cellulose, xylan, and glucomannan (GMM) content in (%) of the R1-R4, PH1 & PH4, and (O) & (O+X) samples.*

Samples:	PH 1	PH 4	R1	R2	R3	R4	2(O)	4(O)	2(O+X)	4(O+X)
Cellulose	74.4	84.3	65.9	67.7	71.1	71.4	69.6	69.4	71.2	73.3
GMM	2.1	2.2	8.3	8.6	8.4	8.5	8.9	9	9.1	9.2
Xylan	3	3.3	7.5	7.5	7.7	7.6	9.7	9	5.4	5.5
Lignin	20.7	10.3	18.4	16.3	12.9	12.6	15	12.3	14.3	12

4.1 Schopper riegler

A key property to take into account when comparing individual sheets is the degree of refining measured as schopper riegler (SR), as shown in figure 11.

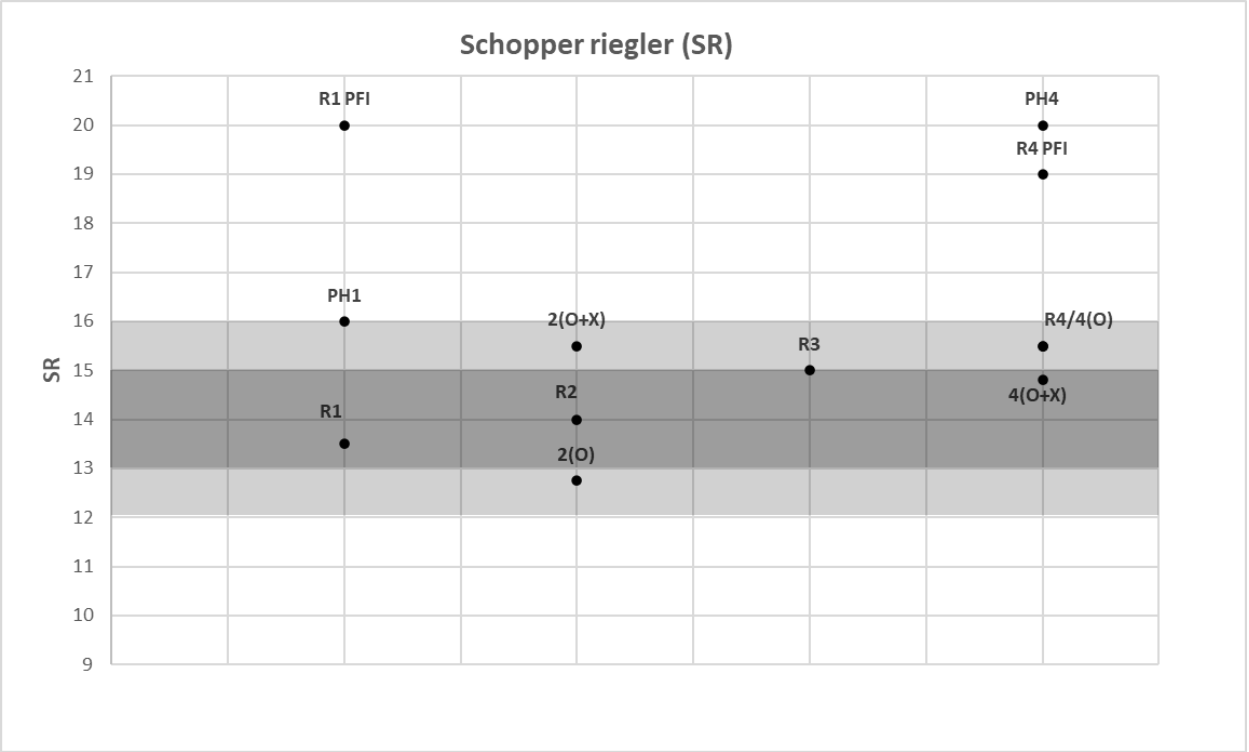

Figure 11: *The degree of refining of the samples measured as Schopper riegler (SR).*

The sample's degree of refining (SR) is widely distributed, as shown in figure 11. The desirable distribution of the SR values is in the dark grey area between 13-15. Unfortunately, many samples are in the light grey area. It is reasonable to expect that the pfi refined samples would have a much higher SR than the other samples, as they have undergone more extensive refinement. Sample PH4 is, however, unfavorably high, at the same level as the pfi refined samples, which indicates that this sample has been slightly overrefined in the SW. Samples with a high SR value tend to also have a high density because the fibers are more fibrillated and can thus be packed more densely. The SR differs between the samples because the SW was adjusted by hand, i.e., the plates were tightened by hand during the refining process.

4.2 Fibre test

Investigations were made to determine the dimensions of the fibers in each sheet mixture by the standard method SCAN-P 88:1. In this experiment, the mean values were not relevant because there was no reversal stream of the fibers, which led to varying amounts of fines in the sheets. Figure 12, 13, and 14 show the distribution of the fibers length, width, and shape factor in each sample mixture. The number of kinks (deformations) per fiber was also investigated, as shown in figure 15. Finally, the brightness of the sheets was measured by the standard method ISO 2470, shown in figure 25. Sheets having high pH values correspond to the actual sheets, while the pH-adjusted sheets were only made for the brightness analysis. The brightness analysis was conducted to determine to what extent the chromophoric groups in the lignin affect the brightness of the sheets. It is worth mentioning that even though the R and PH samples were refined in the SW, the fibers were not cut according to the mean lengths in figure 12.

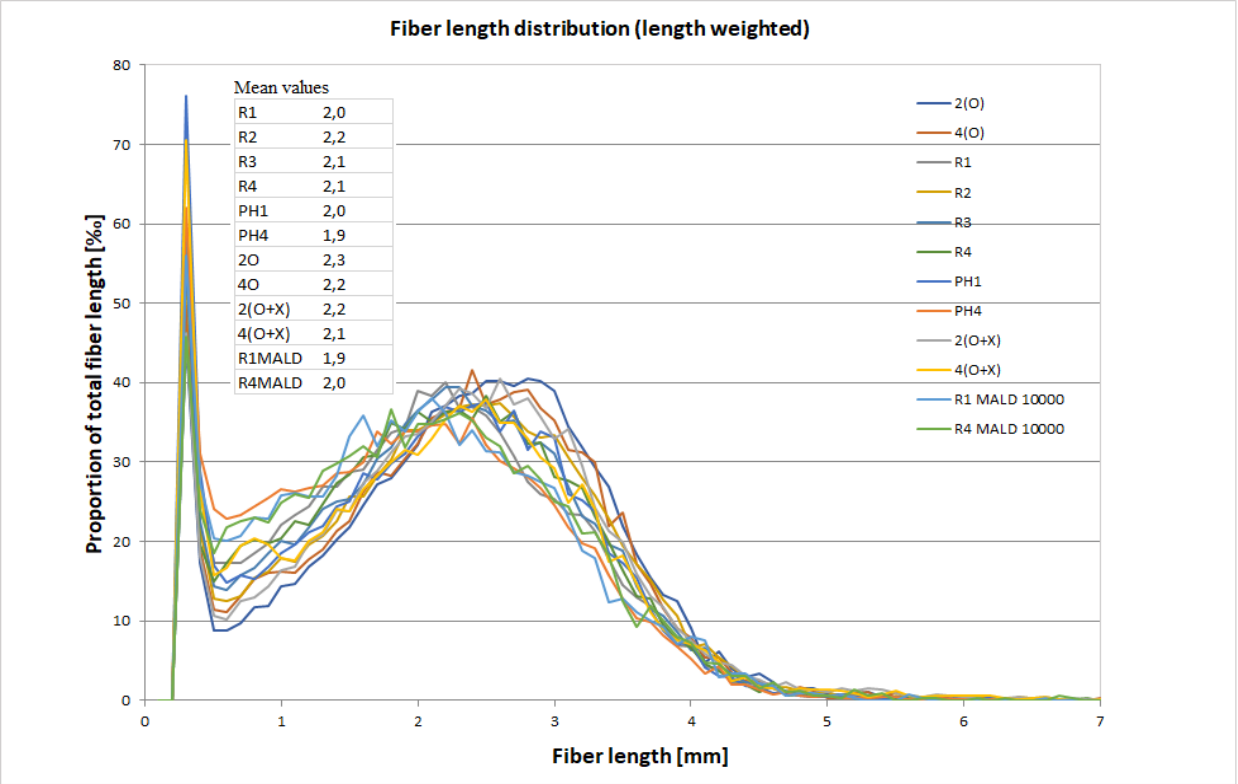

Figure 12: *Fiber length distribution (mm) of the fibers in each sample mixture, with the mean values in the upper left corner.*

Two peaks are observed in figure 12, one at a very short fiber length and one close to the average mean value of approximately 2 mm. The reason is that all fibers are not involved in the sheets, and only a small amount of the fines are probably present, while the rest are flushed away during the sheet making. As a result, the mean fiber lengths in the sheets are expected to be slightly longer than the mean values displayed in the upper left corner. Additionally, the first peak indicates that fiber lengths below 0.5-0.7 mm should be rejected.

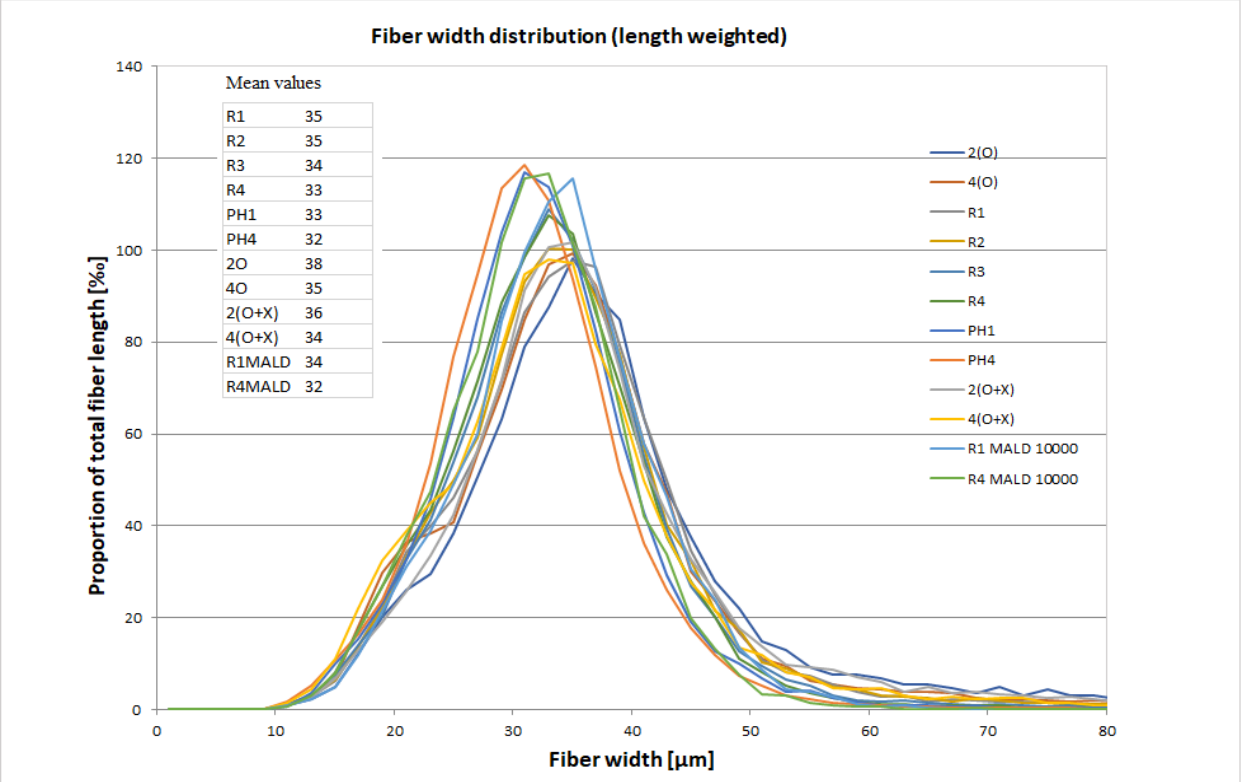

Figure 13: *Fiber width distribution in (µm) of the fibers in each sample mixture, with the mean values in the upper left corner.*

The fiber widths are more evenly distributed around 30-40 µm for all the samples, and there are no peaks at the beginning where thin fibers are present. Therefore, the mean fiber width of the sample mixtures will be well-represented for the fibers in the sheets. The presence of thin fibers in the sheets may not have a significant impact on the mean value, which can make it difficult to reject them. The degree of delignification influences fiber width based on the mean values. More delignified samples in all series have thinner fibers compared to less delignified samples. This is reasonable due to the removal of lignin and the breaking of LCC. Upon analyzing the mean values of the (O) samples in comparison to the (O+X) samples, it can be observed that the removal of xylan molecules breaks down the LCC, leading to thinner fibers. Refining samples 1 and 4 with 10,000 pfi resulted in a width reduction of one unit in both samples.

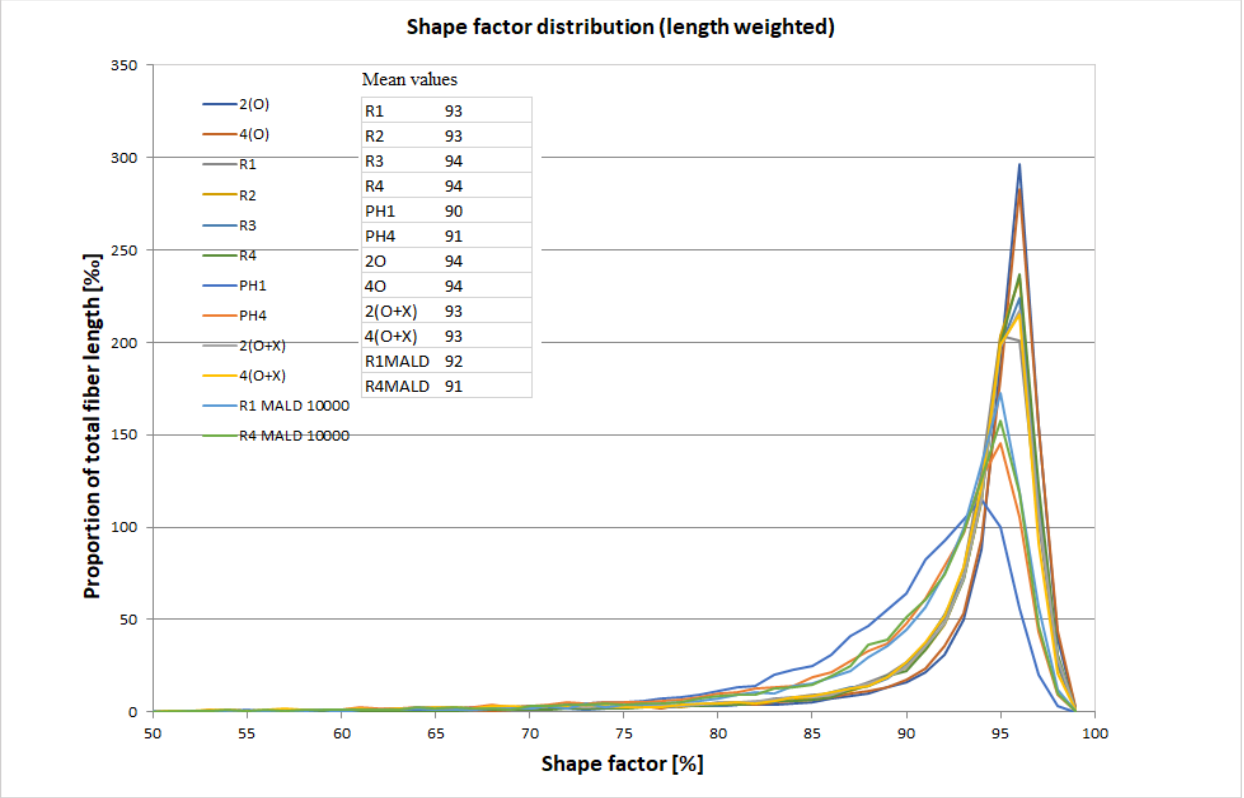

Figure 14: *Fiber shape factor (%) of the fibers in each sample mixture..*

The shape factor, expressed as a percentage, indicates that the majority of fibers in all sample mixtures are quite straight, with mean shape factors exceeding 90%. A higher degree of delignification in both the R and the PH samples moderately increases the shape factor. In contrast, hemicellulose removal does the opposite, i.e., it decreases the shape factor. This is observed in the PH and the (O+X) samples, where the shape factor decreases with three units in the PH samples and only with one unit in the (O+X) samples. Removal of hemicellulose reduces the complexity and overall fiber size, which explains the decreased shape factor. Expectedly, the shape factor should increase with a higher degree of delignification, as lower lignin content makes the fibers less flexible. However, the pfi-refined samples exhibit a lower shape factor, which can be attributed to the refining process that defibrillates the fibers, making them smaller and less rigid.

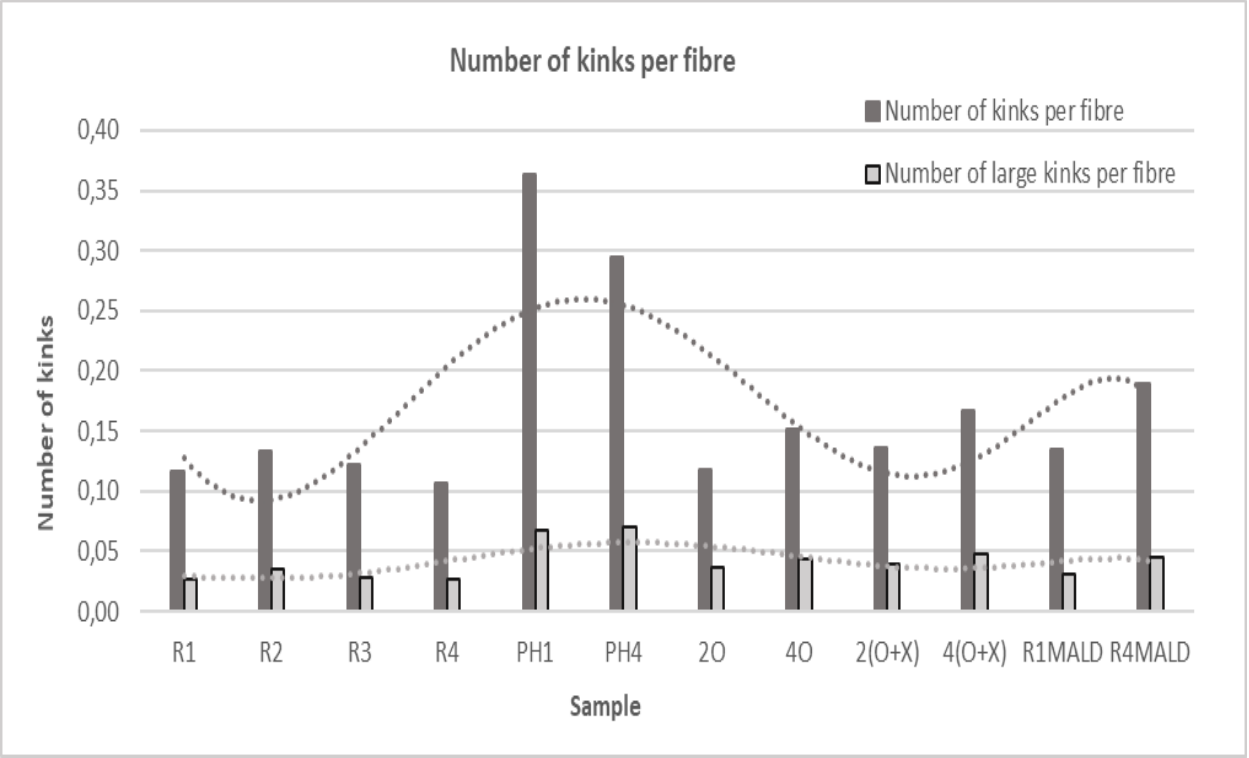

Figure 15: *Number of kinks per fiber present in each sample mixture.*

As depicted in figure 15, there is a minor difference in the number of kinks per fiber between reference samples, with slightly more kinks per fiber in R2 and slightly fewer in R4. All reference samples have a similar number of large kinks. Conversely, the PH samples exhibit the highest number of kinks per fiber, roughly three times that of the corresponding reference samples, with the same number of large kinks. Notably, refining R1 and R4 samples resulted in the most significant increase in the number of kinks for the R4 PFI sample, as evidenced by figure 15.

By comparing the oxygen-delignified samples, sample 4(O) has slightly more kinks per fiber than sample 2(O) but with approximately the same amount of large kinks. After treating the samples with xylanase enzymes, the number of kinks per fiber is increased to the same extent for both samples.

4.3 Tensile Strength

The Ts of the samples in parts II & III is plotted in figure 17, while part I is plotted individually in figure 18. The lignin content in (%) of all samples has been plotted against the Ts, measured in the unit kN/m. In addition, the density of each sheet is also plotted against the Ts, as shown in figure 16.

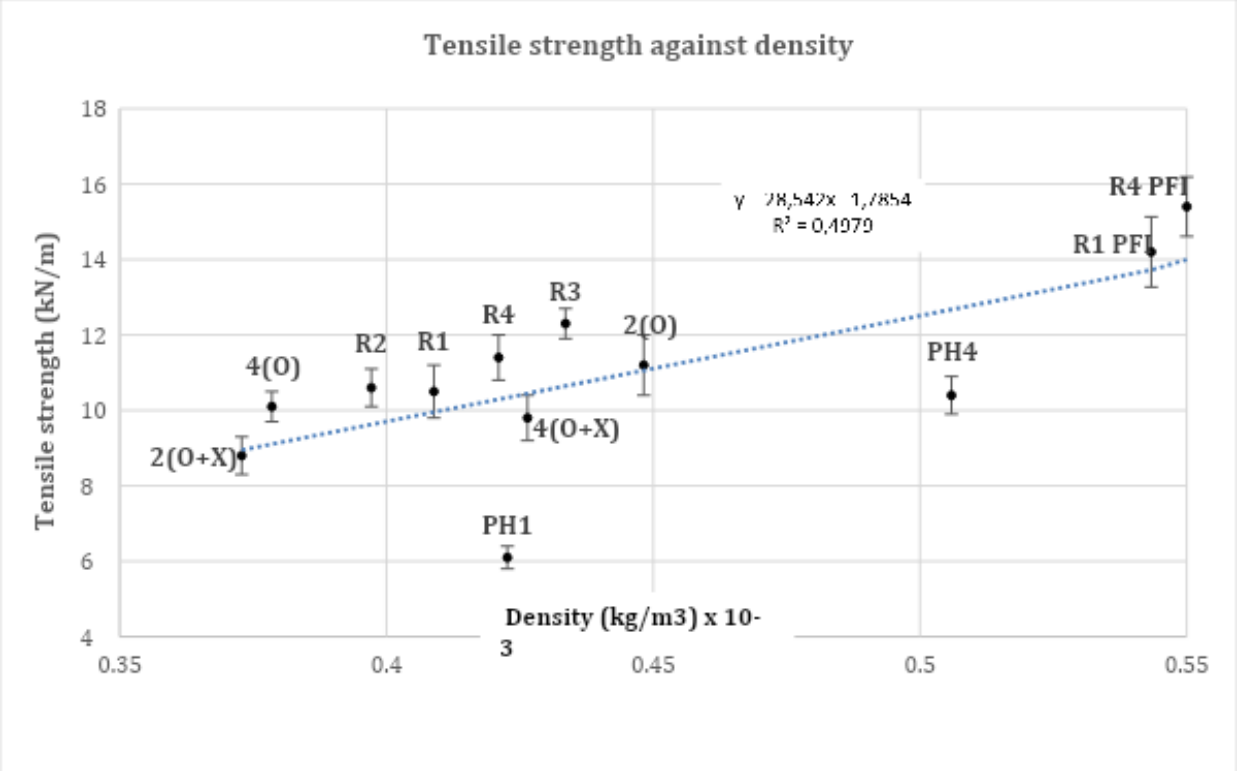

Figure 16: *Tensile strength (kN/m) of all the samples in part I, II & III is plotted against the sheet density measured in kg/m³. The dashed line corresponds to the trend line.*

Figure 16 illustrates the impact of sheet density on Ts, which exhibits a positive trend slope, but with a weak coefficient of determination for the regression R^2. However, the density impact is reasonable because pulling the sheets apart becomes more challenging when more fibers are present per volume unit. This is particularly noticeable in pfi refined samples that exhibit very high sheet densities. Minor deviations, such as those observed between R1 and R2 are not persuasive due to the high stdev overlap. In addition, it is worth noting that the PH samples exhibit a higher sheet density compared to their corresponding R samples, yet they display significantly lower Ts. This suggests that other relevant parameters are also crucial in determining the strength of the samples.

The Ts for the (O) and (O+X) samples do not show consistent behavior. Sample 2(O) has the highest sheet density and hence also the highest Ts compared to the other samples. The same is not observed for sample 4(O+X), which has a significantly higher sheet density but slightly lower Ts than sample 4(O). Nonetheless, comparing the Ts of the samples solely based on their sheet densities can be slightly challenging due to the overlap in stdev, such as between samples 4(O), 4(O+X), and 2(O).

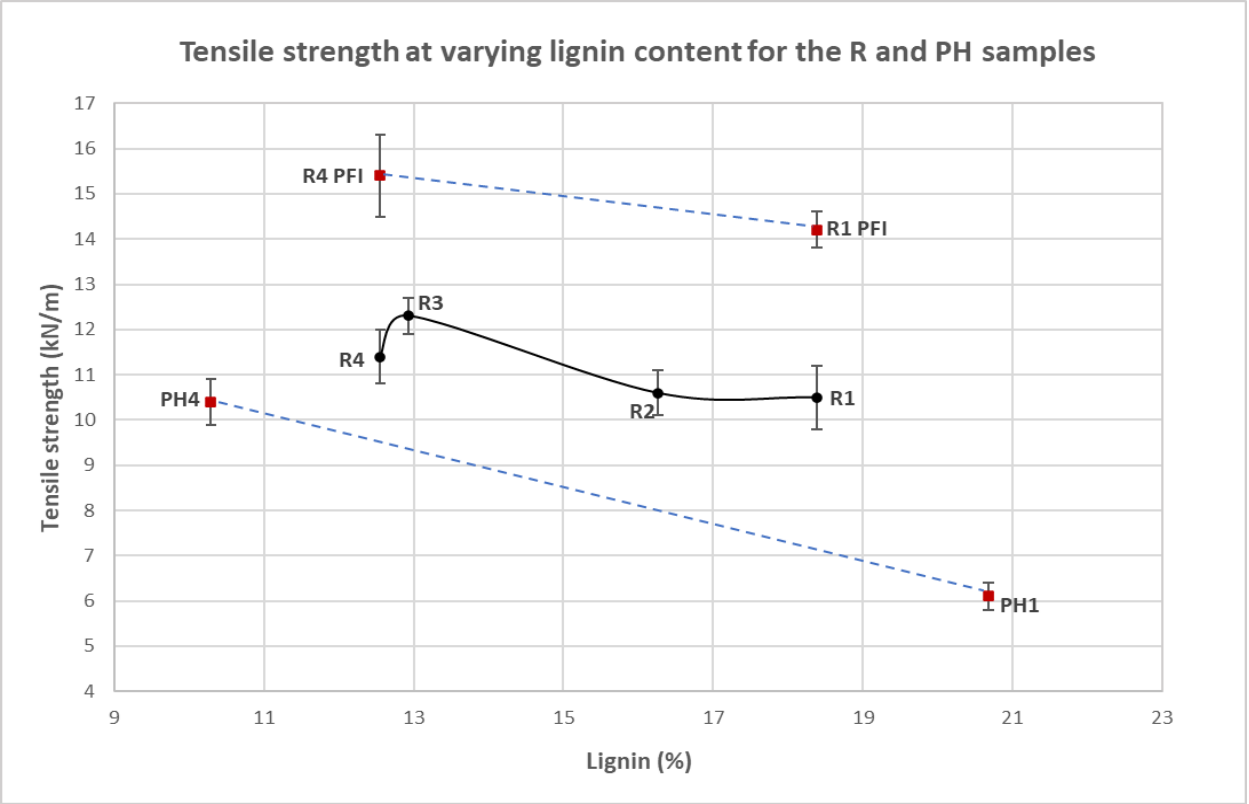

Figure 17: *Tensile strength (kN/m) of the pre-hydrolyzed samples PH1, PH4, reference samples R1-R4, and the refined R1 and R4 plotted against the lignin content (%). The dashed lines correspond to the trend lines.*

Regardless of whether the lignin content is slightly higher or lower in the pre-hydrolyzed samples PH1 and PH4, they have lower Ts than the reference samples R1 and R4. In comparison to their corresponding pre-hydrolyzed samples, sample R1 exhibits a Ts that is around 72% higher, whereas sample R4 displays a Ts that is roughly 9.6% higher than samples PH1 and PH4. The stdev of Ts exhibits a high degree of overlap between samples R1 and R2 when the delignification process leads to a reduction in lignin content, resulting in nearly identical average values. The Ts increases significantly approaching R3, as shown in figure 17, followed by a sudden decrease at sample R4. The overall slope of the trendlines for both the R and PH samples is negative, even though the slope may be weaker due to the overlap in the stdevs. Pfi refining of the samples R1 and R4 increases the Ts by approximately 35% in both cases.

In addition to the density impact, a theoretical suggestion about why the overall Ts trend may increase when the lignin content decreases is that more LCC bounds are present per unit of density when the lignin is removed from the fiber structure. This means that more cellulose molecules exist per unit of density. The abrupt decline observed in sample R4 is difficult to explain since the standard deviations slightly overlap, thereby reducing its credibility. The most plausible explanation is the lower density obtained for sample R4, according to figure 16. When a comparison is made between the PH and the R samples, the suggested theory about the amount of LCC becomes even more reasonable. The removal of hemicellulose from the wood structure causes a breakdown in LCC. Despite the significantly higher sheet densities and SR values of the PH samples in Figures 11 and 16, their Ts remain significantly lower than that of the R samples.

Upon examining Figure 12, it becomes apparent that the fiber lengths are uniformly distributed with only minor variations. Therefore, fiber length does not appear to be a critical parameter to consider. The fiber width could potentially magnify the observed trends in Figure 17, where an increase in delignification results in thinner fibers, as depicted in Figure 13. Wider fibers may have a negative impact on the Ts and tear resistance because of less fiber to fiber interactions per unit of density. However, the PH samples have thinner fibers than the R samples, which means that the fiber width may only have a moderate impact. Another critical parameter is the shape factor shown in figure 14, which should be considered as well. Straight fibers, such as those in the reference samples, could potentially enhance the obtained results due to their greater rigidity and the resulting stronger fiber network. According to figure 15, a high amount of kinks per fiber exists in the PH samples, which may also be a potential cause for the reduced Ts for these samples due to the fact that more weak points are thus present. The pfi refining of samples leads to a significant increase in Ts, which is not surprising given that the fibers become more defibrillated and can be arranged more densely, as demonstrated in Figure 16. The refined samples also have higher SR and thinner fibers than their corresponding reference samples.

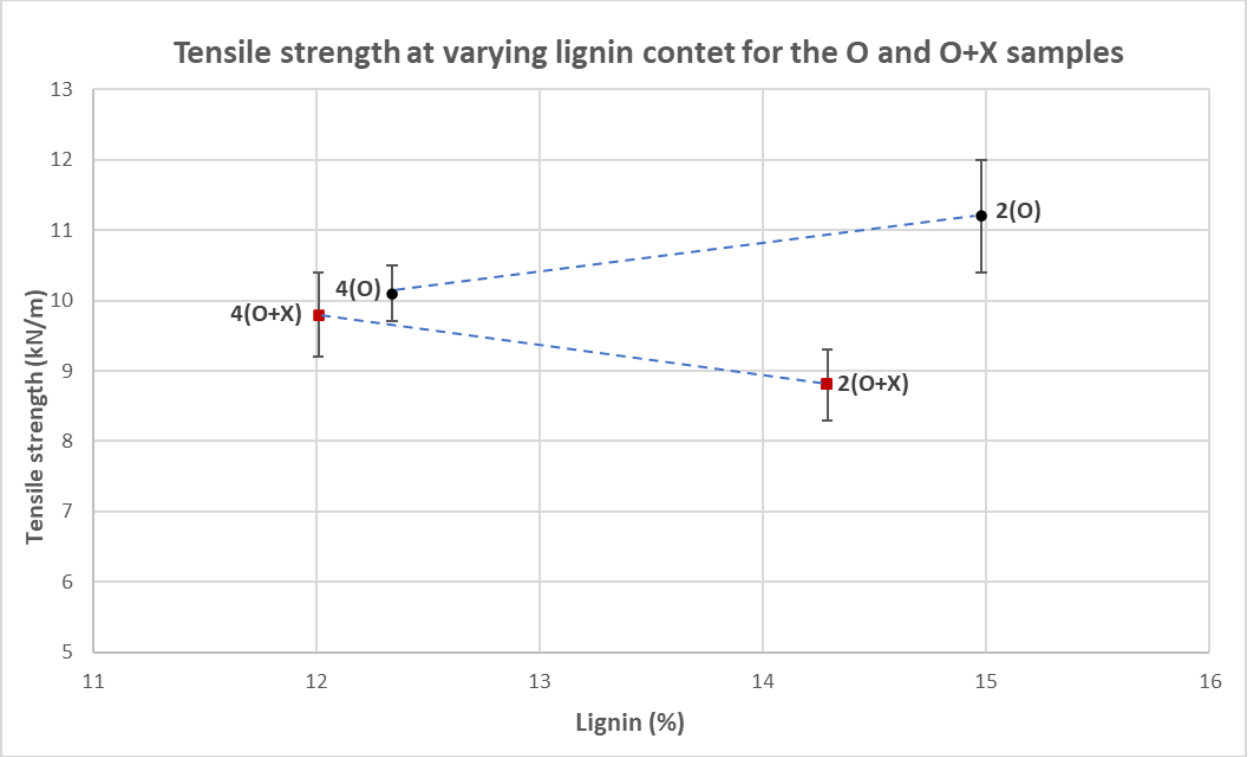

Figure 18: *Tensile strength in kN/m of the oxygen delignified samples (O) and the oxygen delignified + enzyme treated samples (O+X) plotted against the lignin content (%). The dashed lines correspond to the trend lines.*

The Ts for part I are shown in figure 18 above. Sample 2(O) has a higher lignin content than sample 4(O) and approximately one unit higher Ts, which is inconsistent with the previous explanation about the lignin impact. The enzyme-treated samples have lower Ts in both cases when the xylans are removed, which complies with the LCC theory made. The difference in Ts between 2(O) and 2(O+X) is more pronounced than the difference between 4(O) and 4(O+X), as

their stdevs significantly overlap. Sample 2(O) demonstrates approximately 30% higher Ts than sample 2(O+X).

Reducing LCC through enzymatic treatment reasonably leads to a decrease in shape factor in the samples, which could further strengthen the observed trends. The SR numbers are highly even between the samples, except for sample 2(O), which has approximately two SR units lower than the other samples, according to figure 11. This could possibly reduce the Ts, but no such impact is shown. The fiber width may not impact the results since sample 2(O) has the thickest fibers, which contradicts the results obtained in figure 18.

4.4 Compressive strength

The density of each sheet is also plotted against the Cs in the unit kN/m, as shown in figure 19. A relatively linear trend is observed between the Cs values, with a coefficient of determination R^2 of about 0.783. When PH1 is excluded, the R^2 equals 0.96. As there is a strong correlation between density and Cs, to eliminate the density effect, **Cs** is divided by the density to derive the compressive strength index (Csi). In this work, this new measurement is called compressive strength index (Csi). The Csi of the reference samples R1-R4, pre-hydrolyzed samples PH1 & PH4, and refined R1 and R4 are plotted in figure 20 against the lignin content in (%). The oxygen and enzyme-treated samples are compared in figure 21.

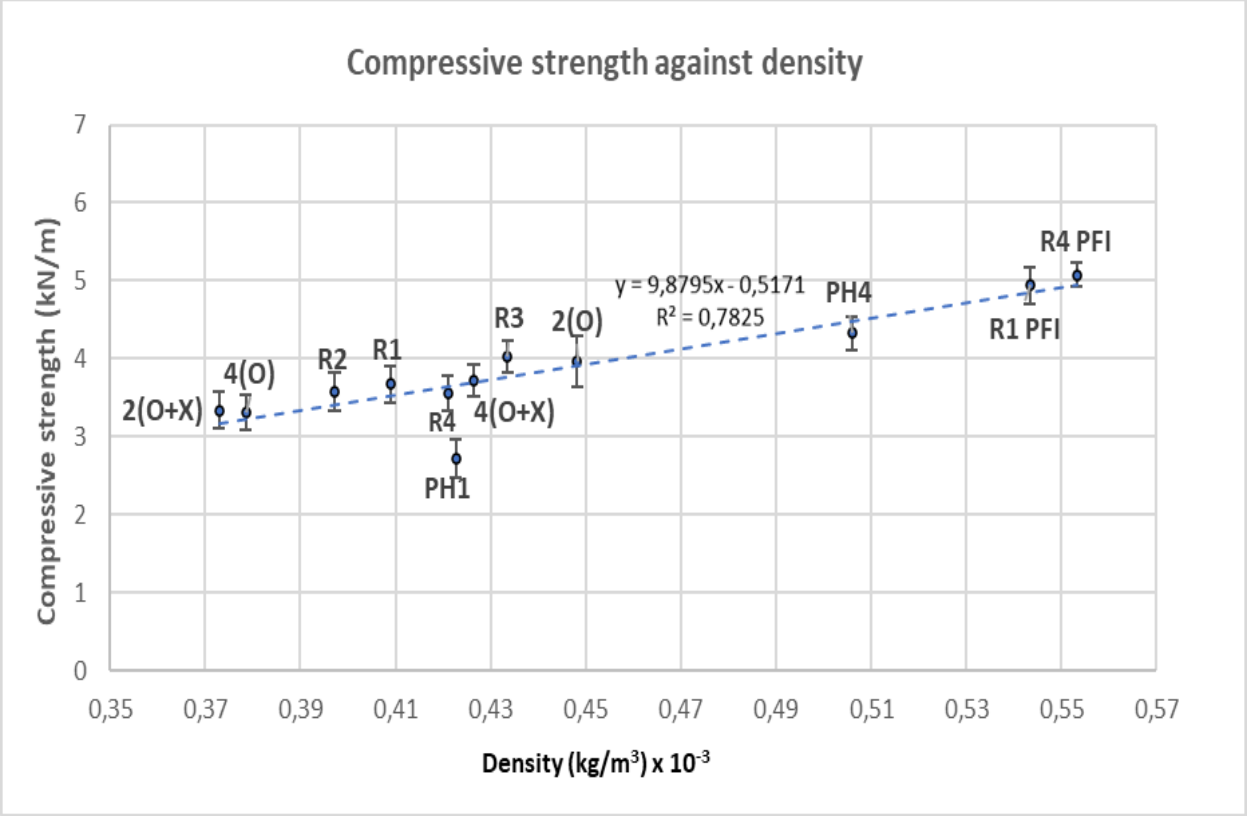

Figure 19: *Compressive strength in (kN/m) of all the samples in parts I, II & III plotted against the sheet density in kg/m³. The dashed line corresponds to the trendline.*

As sheet density increases, Cs also tend to increase. Figure 19 demonstrates that Cs is distributed closely around the trend line, which is a logical outcome as denser packing of fibers requires more resistance to compress the fibers. Sample PH4 conforms to the trend by exhibiting higher Cs than sample PH1. However, even with comparable sheet densities, a notably lower Cs is observed for PH1 compared to the reference sample R1 and the other samples. The refined samples R1 PFI and R4 PFI have higher sheet densities and Cs values than the corresponding reference samples, where both samples have increased their Cs approximately to the same extent.

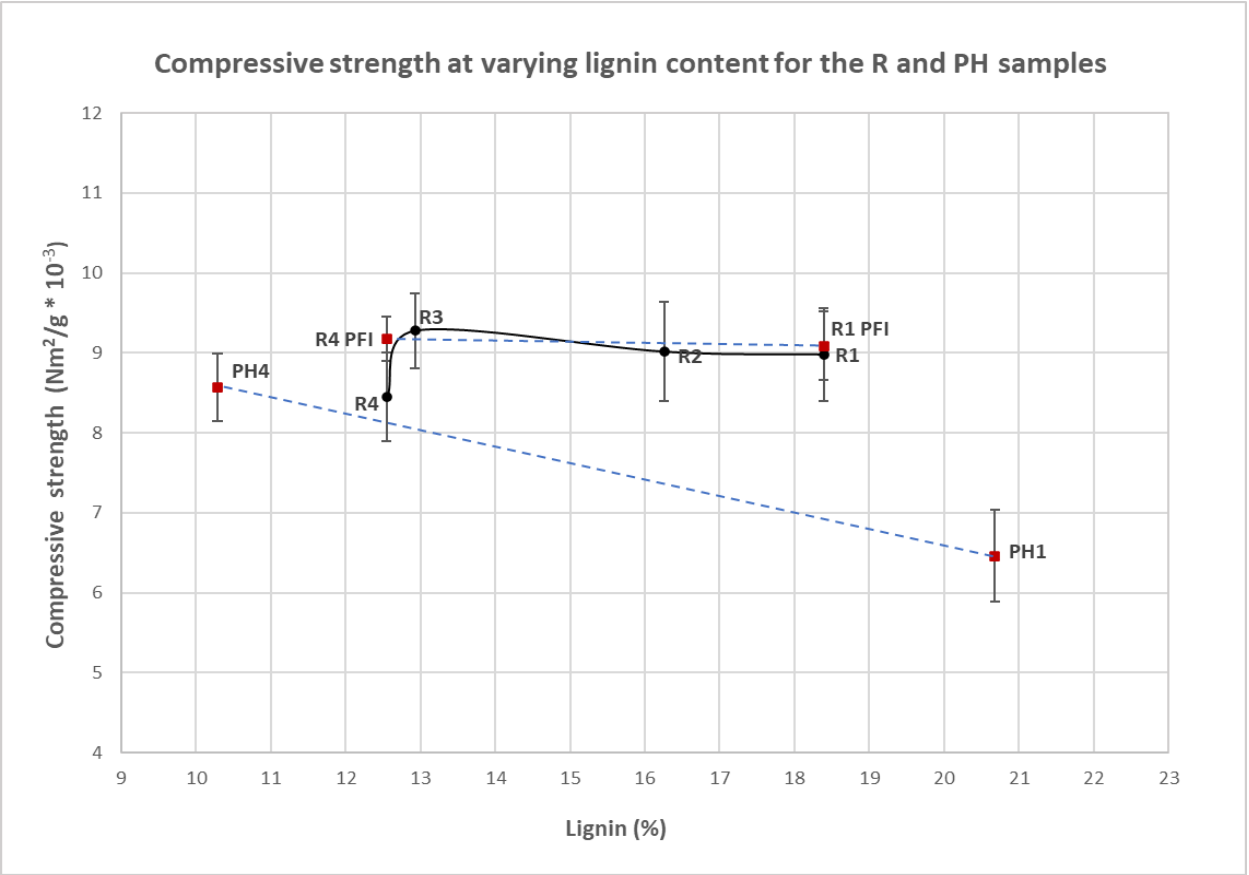

Figure 20: *Compressive strength index in (Nm2/g * 10^{-3}) of the pre-hydrolyzed samples PH1, PH4, reference samples R1-R4, and the refined samples of R1 and R4 plotted against the lignin content in (%). The dashed line corresponds to the trend line.*

As previously mentioned, the Cs is strongly density-dependent, which means that the Csi trend will be relatively horizontal when plotted against the density, as shown in figure 20. The obtained trends are challenging to explain based on other studied parameters due to the significant overlap in stdevs between the samples, rendering the average values somewhat unreliable.

Despite having relatively thin fibers compared to the other samples, as shown in Figure 13, the PH samples and R4 do not account for the decreased Csi. This is because slender fibers are expected to pack more tightly and densely, providing better resistance against deformations. Other important parameters to consider are the shape factor in figure 14 and the number of kinks

per fiber in figure 15. Increased shape factor should reasonably increase the contact area between the fibers and thus enhance the load transfer. The PH samples have the lowest shape factors and highest amounts of kinks per fiber, especially sample PH1, which could be a good potential explanation for the obtained trend in figure 20.

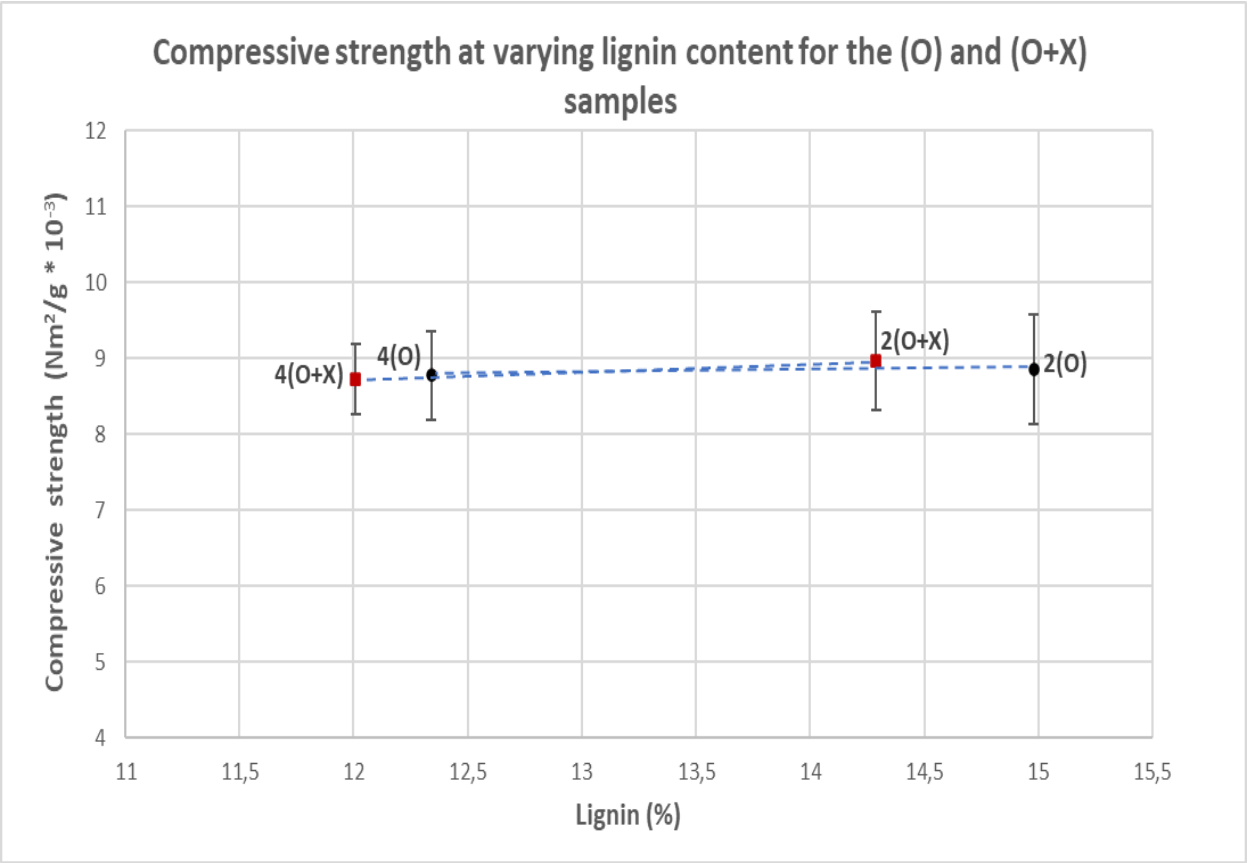

Figure 21: *Compressive strength index in (Nm^2 * 10^{-3}) of the pre-hydrolyzed samples PH1 & PH4, reference samples R1-R4, and the refined samples of R1 and R4 plotted against the lignin content in (%). The dashed lines correspond to the trend lines.*

The outcomes depicted in Figure 21 are in agreement with the preceding explanations, highlighting sheet density as the most significant parameter. The stdev of the Csi values are overlapping highly, which makes it difficult to take other parameters into account. However, even though other parameters such as the fiber width and number of kinks per fiber differ, according to figures 13 and 15, the impact seems to be insignificant in this case.

4.5 Hygroexpansion

The lignin content of the samples is plotted against the HEX, measured as the elongation (%) during humidity fluctuations. The HEX values of the sheets were plotted against the sheet densities (kg/m^3) in figure 22. HEX of the reference samples R1-R4, PH1 & PH4, and the pfi refined samples of R1 and R4 are compared in figure 23. The oxygen and enzyme-treated samples are plotted in figure 24.

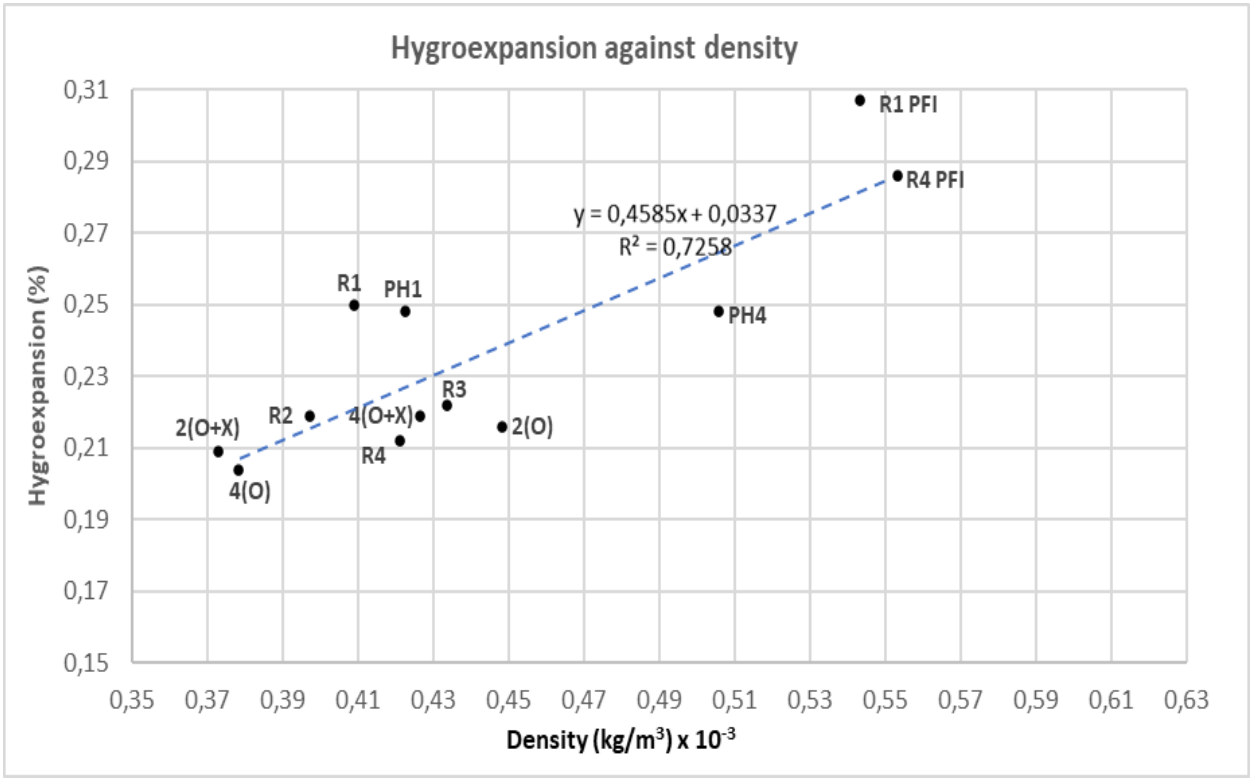

Figure 22: *HEX of all the samples in parts I, II & III plotted against the sheet density. The dashed line corresponds to the trendline.*

Figure 22 displays the distribution of HEX values plotted against sheet densities, closely following a positive trendline, with a coefficient of determination R2 of approximately 0.73. The positive slope and the relatively high R^2 of the trendline indicate that the higher the sheet density, the higher the HEX tends to be. An explanation for why sheets with high density exhibit more expansion during humidity variations is that they contain fewer voids, causing the fibers to separate more extensively. A density increase from sample R2 to R1 increases the HEX by 14%, while a further increase of the sheet density at sample R4 depreciates the HEX by 15%, as shown in figure 22. A slight increase of the HEX is maintained again at sample R3, and the overall trendline between the reference samples is slightly unclear. Comparing the pre-hydrolyzed samples PH4 and PH1 reveals that they exhibit the same HEX behavior, despite PH4 having a significantly higher sheet density. The refined samples have higher sheet densities than their corresponding reference samples and, in turn, higher HEX, almost in the same order of magnitude. The oxygen and enzyme-treated samples also follow the trendline to a certain degree, but there is no clear relationship between the densities and HEX values. However, the HEX values are somewhat irregularly distributed around the general trendline, possibly due to the influence of other parameters.

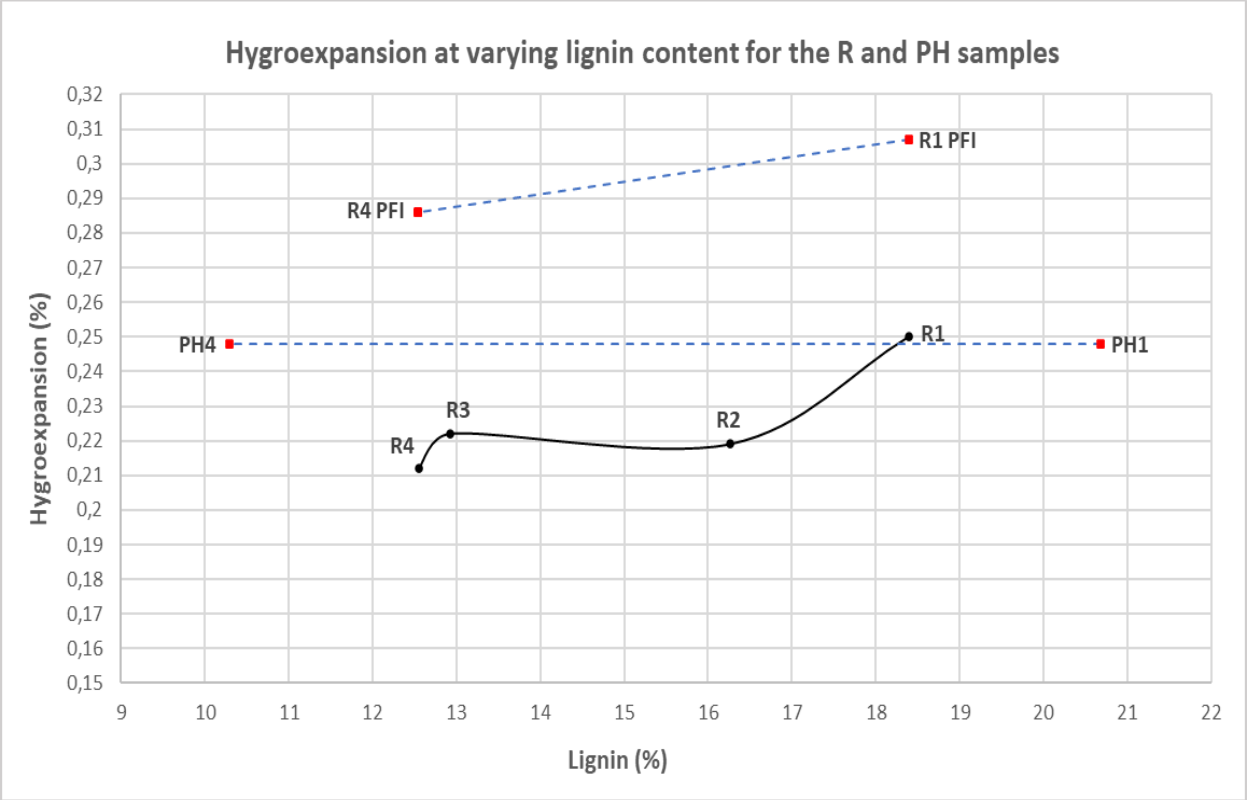

Figure 23: *HEX of the pre-hydrolyzed samples PH1 & PH4, reference samples R1-R4 and the refined R1 and R4 plotted against the lignin content in (%).*

According to figure 23, as the degree of delignification increases, the expansion tendency of the samples decreases, although the difference in HEX between R2 and R3 is insignificant. For example, sample PH4 expands about 17% more than the corresponding reference sample R4, while R1 and PH1 have approximately the same HEX value. When considering the refined samples, R4 PFI demonstrates an expansion tendency about 35% greater, while R1 PFI exhibits an expansion tendency about 23% greater than their respective reference samples.

One possible explanation for the increase in HEX with increased lignin content is that during the cooking process of wood chips, the lignin resolves, creating small cavities within the wood structure. The creation of small cavities may occur primarily in the middle lamella and the spaces between the cell walls during the cooking process, and these spaces are often filled with lignin and hydrophilic compounds such as hemicelluloses, pectins, proteins, acids, and so on. When the humidity level increases and water molecules start to enter the cavities, attractive forces are created between the polar water molecules and the hydrophilic compounds in the wood. This may promote the fiber separation and thus the HEX. However, when the lignin content is reduced during the delignification process, at the same time, more LCC becomes present per unit of density, i.e., more interactions between the fibers. This will, instead in the opposite way, result in a decreased HEX.

Consequently, even if the lignin decreases and the HEX should increase according to the first statement, the dominant factor seems to be the increased LCC per unit of density. Accordingly, the increased HEX for the PH4 sample is probably due to the high sheet density but could also

be amplified by the decreased amount of hemicelluloses and LCC. The reduced amount of hemicelluloses is expected to significantly decrease the amount of LCC and thus increase the HEX compared to the reference samples.

The fiber width, shape factor, SR value, and number of kinks per fiber are investigated by looking for other possible explanations and parameters. The fiber width is lower while the shape factor is higher the more the samples have been delignified, as shown in Figures 13 and 14. Thinner fibers can be packed more tightly, creating more space for swelling and potentially increasing the expansion capability. Conversely, an increase in the shape factor of fibers should lead to a stronger fiber network, which should lead to a decreased HEX. The impact of fiber width on the obtained results is somewhat contradictory, but the shape factor may have contributed to the results depicted in figure 23. Especially when comparing the PH samples with the R samples, the differences in these parameters become more noticeable. The higher amount of kinks per fiber in the PH samples compared to the R samples, as shown in Figure 15, may also be a contributing factor to the observed higher HEX in the PH samples..

Finally, both the refined samples R1 PFI and R4 PFI have a HEX increase approximately to the same degree compared to the corresponding reference samples. The significantly higher sheet densities for the refined samples could be the main reason for this behavior. Other potential reasons include the lower shape factors, according to figure 14, and the decreased fiber width demonstrated in figure 13. Finally, in figure 15, both the refined samples have much more kinks per fiber, which may also be a potential contributing factor to the increased HEX.

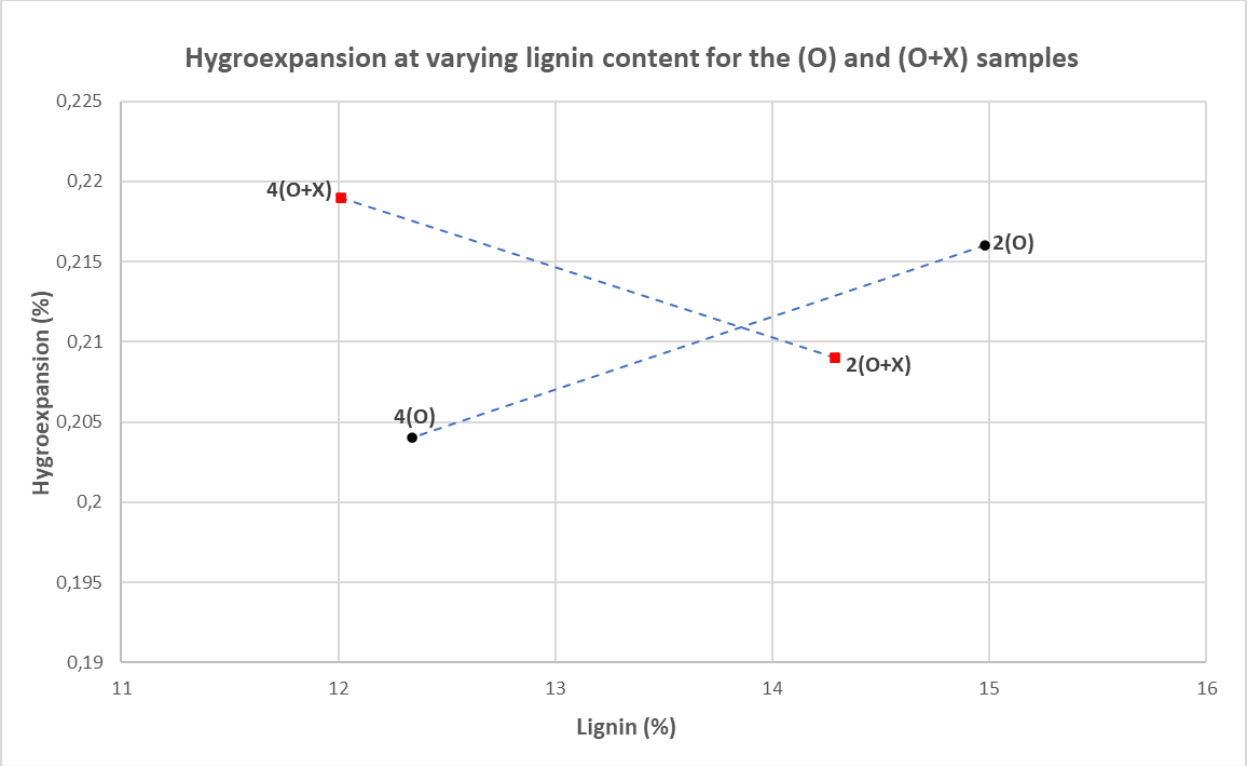

Figure 24: *HEX of the oxygen-delignified (O) samples and the oxygen and enzyme-treated samples (O+X).*

The explanations previously made about the influence of lignin are not consistent with the obtained HEX results for the oxygen and enzyme-treated samples. Sample 2(O), which has a higher lignin content than sample 4(O), also has a higher HEX value, i.e., the same trend as obtained in figure 23. However, the behavior of the enzyme-treated samples is slightly different. Sample 2(O+X) is expanding less than sample 2(O), while sample 4(O+X) is expanding more than 4(O). The observed behavior may be closely associated with density variations and other contributing factors. For instance, figure 15 indicates that 4(O+X) has the highest number of kinks per fiber.

4.6 Iso-brightness

The brightness of the sheets can be observed in Appendix E, with the more delignified samples exhibiting a brighter color. Regardless of whether the lignin content is higher or lower, both the PH samples have a darker color than the R samples. The reason is most likely due to the fact that the removal of hemicellulose increases the concentration of lignin and cellulose. Appendix E shows that all samples from part I are significantly brighter than those in parts II and III. However, this is not surprising since these samples were not refined in the SW, and, consequently, contain more shives. Therefore, to prevent any misinterpretation, the samples from part I should be evaluated separately in figure 25.

Chromophores can influence the brightness of the pulp to a certain extent. The brightness of the sheets before and after removing chromophores is shown in Figure 25.

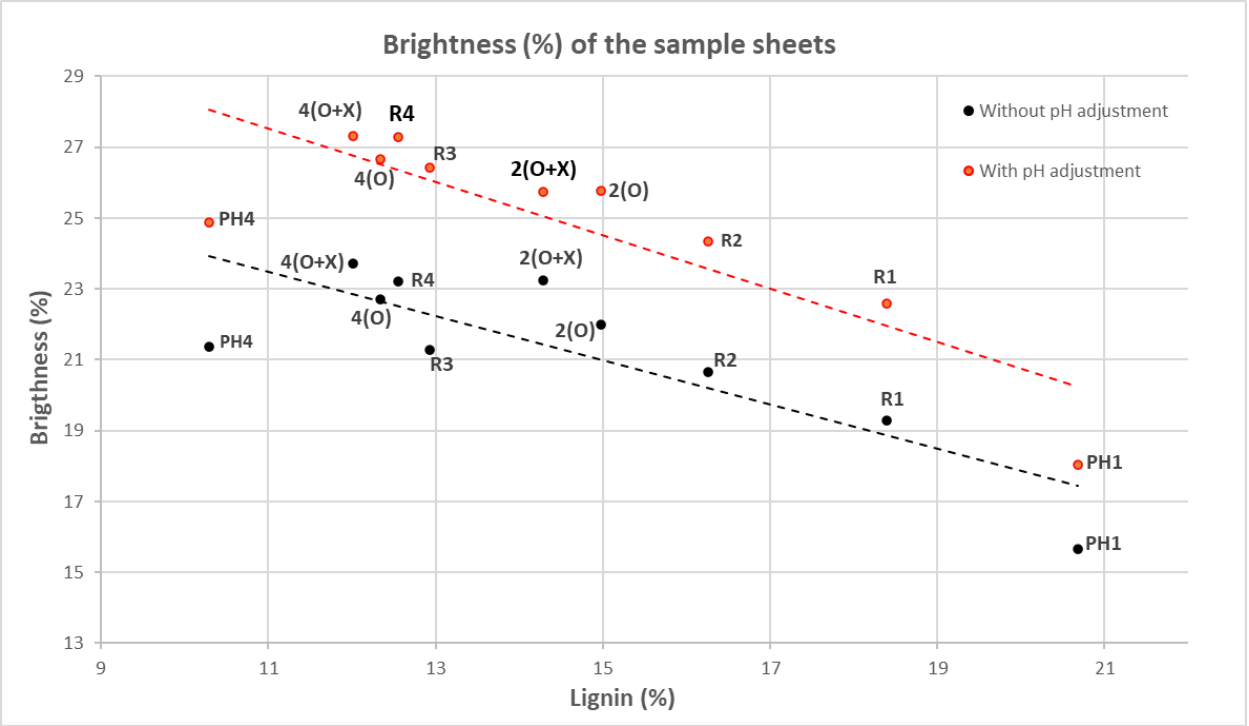

Figure 25: *The brightness (%) of all samples at pH ~ 9-11 and pH 5 for all samples.*

The impact of the lignin chromophores on the brightness is clearly shown in figure 25 above. The trendline represented by the red dashed line corresponds to the sheets where chromophores

have been removed by adjusting the pH from around 10 to 5 using sulfuric acid (H_2SO_4), while the black dashed line represents the trendline of sheets with a pH around 10 and abundant chromophores. A distinct difference in brightness between the unadjusted and adjusted sheets is thus confirmed when the chromophores are eliminated, i.e., the difference between the two trend lines. The brightness of all samples, except for R3 and 2(O+X), improved by around 15-18%. Sample R3 and 2(O+X) showed an improvement of about 24% and 11%, respectively.

5 Multiple regression analysis of the sheet properties

The use of multiple regression analysis (MRA) proves useful when several distinct parameters influence a given dependent variable. The multiple regression program integrated into Microsoft Excel is utilized in this thesis. The significance level is chosen to be 95%, and the key variables are the coefficient, adjusted R^2, P-value for F, and P-value for each independent parameter. It can also be emphasized that the coefficient in the following tables is the relationship between the independent and dependent variable, i.e., the slope of the trendline.

5.1 Multiple regression analysis of tensile strength

By considering all the analyzed parameters and conducting a multiple regression analysis with a confidence level of 95%, it is easier to establish whether the selected independent variables (our parameters) yield a model that fits the Ts. Table 18 reveals that the p-value for fiber length, fiber width, lignin content, and fiber shape factor is not less than the 5% significance level, indicating that these data are statistically insignificant for the regression model at this level of significance. The adjusted R^2, 92%, means that if all the parameters are considered, the regression model will explain the Ts variations with a 92% accuracy. The p-value for F (significant F) is also significantly lower than 5%, according to table 18.

Table 18: *Multiple regression model of the investigated six key parameters as independent variables and how well they describe the tensile strength.*

Regression statistics	
Multiple-R	0,982
R-squared	0,964
Adjusted R-squared	0,919
Standard deviation	0,679
Observations	12

ANOVA	fg	KvS	Mkv	F	p-value for F
Regression	6	60,94	10,16	22,03	0,0019
Residual	5	2,30	0,46		
Total	11	63,24			

	Coefficients	Standard error	t-stat	p-value	Lower 95%	Upper 95%	Lower 95%	Upper 95%
Constant	21,80	48,169	0,45	0,669	-102,02	145,62	-102,02	145,62
Density	0,03	0,006	5,47	0,003	0,02	0,05	0,02	0,05
Lignin (%)	-0,01	0,104	-0,12	0,910	-0,28	0,25	-0,28	0,25
Shape factor	-0,16	0,499	-0,33	0,756	-1,45	1,12	-1,45	1,12
Fiber width	-0,45	0,257	-1,73	0,144	-1,11	0,22	-1,11	0,22
Fiber length	4,42	3,624	1,22	0,277	-4,90	13,73	-4,90	13,73
Number of kinks per fiber	-24,35	6,540	-3,72	0,014	-41,16	-7,54	-41,16	-7,54

Eliminating parameters with a p-value greater than 0.05, such as the shape factor and lignin content, can enhance the adjusted R^2 and significant F. The adjusted R^2 and significant F value can be elevated to 94% and $4.4 * 10^{-5}$, respectively. If the fiber length and width also is rejected, the adjusted R^2 decreases, which indicates that it is not reasonable to reject these parameters even if they do not fulfill the significance criterion. The coefficients are also important and should be considered. The only coefficient showing the wrong relationship trend is the shape factor with a minus sign. Based on the multiple regression analysis, the density, the number of kinks per fiber, fiber length, and width are the most crucial parameters.

5.2 Multiple regression analysis of compressive strength

Similarly, a MRA was conducted for Cs with a significance level of 95%. Therefore, it can easily be determined whether the chosen independent data also provides a better-fit model for the Cs. According to table 19, the p-value for the length, width, and shape factor is not lower than the significance level of 5%, which highlights that these data are not statistically significant for the regression model. With an adjusted R^2 of approximately 96%, the regression model can explain the variation in Cs with 96% accuracy if all parameters are taken into account. This means that all the independent data can more accurately predict the Cs compared to the Ts due to the higher value of the adjusted R^2. The significant F value is also significantly lower than 5%, which indicates that the explanatory parameters together have a statically significant association with the obtained results of Cs as well.

Table 19: *Multiple regression model of the investigated six key parameters as independent variables and how well they describe the compressive strength model.*

Regression statistics	
Multiple-R	0,991
R-squared	0,982
Adjusted R-squared	0,959
Standard deviation	0,135
Observations	12

ANOVA	fg	KvS	Mkv	F	p-value for F
Regression	6	4,87	0,81	44,54	0,00035
Residual	5	0,09	0,02		
Total	11	4,96			

	Coefficients	Standard error	t-stat	p-value	Lower 95%	Upper 95%	Lower 95%	Upper 95%
Constant	18,42	9,576	1,92	0,112	-6,20	43,03	-6,20	43,03
Density	0,01	0,001	7,34	0,001	0,01	0,01	0,01	0,01
Lignin (%)	-0,06	0,021	-3,14	0,026	-0,12	-0,01	-0,12	-0,01
Shape factor	-0,19	0,099	-1,92	0,113	-0,45	0,06	-0,45	0,06
Fiber width	0,09	0,051	1,72	0,147	-0,04	0,22	-0,04	0,22
Fiber length	-0,95	0,720	-1,32	0,243	-2,81	0,90	-2,81	0,90
Number of kinks per fiber	-5,33	1,300	-4,10	0,009	-8,67	-1,99	-8,67	-1,99

By rejecting the parameters having a p-value much higher than 0.05, such as shape factor, fiber length, and fiber width, the adjusted R^2 could not be further improved. This suggests that even though the p-values are not less than the significance level, they should not be rejected. Nevertheless, this claim can be disputed as these parameters exhibit a trend of inverse relationships based on the sign of the coefficients. Nevertheless, as mentioned before, only

having the density as an independent variable, the R^2 value reaches about 78.3% indicating the high-density dependency.

5.3 Multiple regression analysis of hygroexpansion

Finally, an MRA can be performed on the investigated parameters for HEX to determine whether the selected data yields a better fit for the HEX model. In table 20, the p-value for the length, width, and lignin content is not below the significance level of 5%. The adjusted R^2 value is approximately 95%, which indicates that the regression model with the six parameters can explain the variation of the dependent variable very well. The significant F value is also lower than 5%, which indicates that the explanatory parameters together have a statically significant association with the obtained results of HEX.

Table 20: *Multiple regression model of the investigated six key parameters as independent variables and how well they describe the hygroexpansion model.*

Regression statistics	
Multiple-R	0,988
R-squared	0,975
Adjusted R-squared	0,946
Standard deviation	0,008
Observations	12

ANOVA	fg	KvS	Mkv	F	p-value for F
Regression	6	0,0113	0,0019	32,95	0,00073
Residual	5	0,0002	4,84E-05		
Total	11	0,0115			

	Coefficients	Standard error	t-stat	p-value	Lower 95%	Upper 95%	Lower 95%	Upper 95%
Constant	1,498	0,493	2,62	0,029	0,03	2,56	0,03	2,56
Density	0,288	6,20E-05	4,61	0,009	0,00	0,00	0,00	0,00
Lignin (%)	0,002	0,001	2,43	0,093	0,00	0,01	0,00	0,01
Shape factor	-0,014	0,005	-2,22	0,045	-0,02	0,00	-0,02	0,00
Fiber width	0,001	0,003	0,49	0,728	-0,01	0,01	-0,01	0,01
Fiber length	-0,079	0,037	-2,35	0,124	-0,18	0,01	-0,18	0,01
Number of kinks per fiber	-0,210	0,067	-2,74	0,029	-0,36	-0,01	-0,36	-0,01

Eliminating parameters with a p-value greater than 0.05 resulted in an improvement in adjusted R^2 only for fiber width. This indicates that while the p-values of the other parameters exceed the 5% significance level, it is unreasonable to reject them. By rejecting the fiber width as an independent parameter for the MRA, the adjusted R^2 was increased to 95.4%. Regarding the coefficients, the amount of kinks per fiber and the fiber width shows a wrong relationship.

6 Conclusion

The findings suggest that there is a probable rise in Ts (tensile strength) with an increase in sheet density, while lignin content may not have the same effect. Removal of hemicellulose significantly reduces the Ts, as shown in Figures 17 and 18, because when LCC is reduced, the interactions between carbohydrates are broken. The number of kinks per fiber also seems to affect the Ts significantly, where more kinks per fiber weaken the fibers. This is particularly evident in the PH samples. The MRA analysis demonstrates the influence of the parameters, supporting the above conclusions quite well. Finally, while fiber shape factor, width, and length may have some impact on the outcomes obtained, it is likely to be minimal.

As indicated by Figure 19 and the MRA, the Cs (compressive strength) is predominantly reliant on sheet density, which varies almost linearly. Other potential factors that can influence Cs include the number of kinks per fiber and the shape factor, particularly evident in the PH samples.
The HEX (hygroexpansion) is significantly affected by sheet density, with a higher sheet density resulting in a greater HEX value, although the relationship is not linear. Additionally, the lignin content is a crucial parameter to take into account, as a lower lignin content leads to a higher LCC per unit of density, which, in turn, decreases the HEX value. This was more pronounced in the PH samples, where the removal of hemicelluloses led to an increase in HEX. Furthermore, the shape factor was also observed to have an impact on the HEX, as demonstrated by the MRA analysis.

Finally, an investigation was conducted to determine whether the chromophore groups in the lignin molecules affect the brightness of the sheets. The results showed a significant impact of the chromophores, as demonstrated in Figure 25. When the chromophore groups were removed using sulfuric acid, the brightness increased by an average of approximately 15-18%. The samples with more delignification were generally brighter, which is expected as more lignin is removed. Additionally, it is worth noting that the PH samples had a lower brightness than the R samples, as shown in Appendix E. This suggests that the hydrolysis of wood leads to a decrease in brightness.

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8. Appendix

8.1 Appendix A

Calculations of the dryness (wood chips)

1. Weight plate (9,6g), weight plate + wood before (57,9g), weight plate + wood after (44g) = 13,9g moisture
2. Weight plate (16,8g), weight plate + wood before (46,4g), weight plate + wood after (34,9g) = 11,5g moisture
3. Weight plate (11,9g), weight plate + wood before (39,1g), weight plate + wood after (29,5g) = 9,6g moisture
4. Weight plate (11,8g), weight plate + wood before (54,4g), weight plate + wood after (41,2g) = 13,2g moisture

→ dryness calculated by taking moisture content divided by 1 - weight plate + wood before i.e.

→ 1. 1- 13,9 / 57,9 = 0,721
2. 1- 11,5 / 46,4 = 0,6115
3. 1- 9,6 / 39,1 = 0,647
4. 1- 13,2 / 54,4 = 0,69

AVERAGE DRYNESS = 0,665 g/g (0,33 g/g moisture)= 66.5%
Wood needed = 250/0,665 = 375,8g

Calculations of the dryness (BL)

1. wet weight (4,2474g), dry weight (3,635g), sample weight (1,851g)
2. wet weight (4,1371g), dry weight (3,578g), sample weight (1,688g)

→ dryness calculated by taking difference between wet and dry weights (including the plate) and divide it with sample weight i.e.

→ 1. (4,2474-3,635)/ 1,851 = 0,3308
2. (4,1371-3,578)/1,688 = 0,33122

AVERAGE DRYNESS = 33,1 g/g

8.2 Appendix B

(Part I)

Titration BL

HS^- determination

1 ml BL together with 5 ml (28%) NH_3 and 40-50 ml 1M NaOH was titrated with 10 ml $AgNO_3$. Average was taken on four equivalence points.

1. 0,4082 mol/l
2. 0,4191 mol/l
3. 0,4368 mol/l
4. 0,4509 mol/l

→ AVERAGE [HS] = 0,41875 mol/l

OH^- determination

10 ml BL together with ~80 ml deionized water and 10 ml Na_2CO_3 was titrated with HCL. Average was taken on only two equivalence points due to the more stable OH ions.

1. 0,5849 mol/l
2. 0,5870 mol/l

→ Average [OH] = 0,586 mol/l

Weights of the wood chips prepared for Part I

1. 615,3g (wet) - 250g (dry weight) = 365,5g (water inside)
2. 632,7g (wet) - 250g (dry weight) = 382,7g (water inside)
3. 617g (wet) - 250g (dry weight) = 367g (water inside)
4. 623,7g (wet) - 250g (dry weight) = 373,7g (water inside)

BL withdrawn after impregnation (Part I, weighted and titrated HS^-/OH^- of the BL withdrawn).:

1. weight = (1476 ml), [HS] = 0,226 mol/l, [OH] = 0,3060 mol/l
2. weight = (1475 ml), [HS] = 0,220 mol/l, [OH] = 0,2988 mol/l
3. weight = (1483 ml), [HS] = 0,2047 mol/l, [OH] = 0,3052 mol/l
4. weight = (1480 ml), [HS] = 0,2019 mol/l, [OH] = 0,3018 mol/l

BL withdrawn after delignification part I (measured HS/OH of the BL withdrawn, equivalence point 2 times HS).:

1. [HS] = 0,0,2760 + 0,2693 mol/l, [OH] = 0,5566 mol/l
2. [HS] = 0,2688 + 0,2616 mol/l, [OH] = 0,5515 mol/l
3. [HS] = 0,2574 + 0,2640 mol/l, [OH] = 0,5412 mol/l
4. [HS] = 0,2706 + 0,2720 mol/l, [OH] = 0,5410 mol/l

		KOKPROTOKOLL		Autoklavkok						
Datum	2022-10-12	Projekt		Kokserie		Kokare:	G2	Utfört av:		
Ved			torr ved, g	250,0	th		Invägd ved, g	655,5		
								648,70		
								648,2		
								639,1		
							vitlut	SL 1	avd SL 2	
Temp.schema sulfatkok, efter avdrag av lakningsvätska					**Tid, min**	NaOH, M	9,2030	0,5808	0,2386	mol/l
Start temp. 90°C rampning 90-120°C 3°C/min					10	Na2S (HS)	1,6885	0,38175	0,21	mol/l
Impregnering: 120°C i 120 min.					120	Na2S (OH)	1,4165			mol/l
Rampning till kok: 3°/min från 120 till 160°C					13.3	Na2CO3	20			mol/l
Koktemp: **160**										
Koktid: till önskad H-faktor					130	Na2CO3	106,0000	g/mol		

Prov märkning	Vätske Ved	vedvätska ml	tillsatt vatten, ml	tillsatt SL 1 ml	avdrag sl	EA %	NaOH ml	Sulf. %	Na2S ml
1	7,0	405,5	**406,3**	**875,0**	1340,0	17,5	**64**	50,0	**0**
2	7,0	398,7	**413,1**	**875,0**	1340,0	17,5	**64**	50,0	**0**
3	7,0	398,2	**413,6**	**875,0**	1340,0	17,5	**64**	50,0	**0**
4	7,0	389,1	**422,7**	**875,0**	1330,0	17,5	**64**	50,0	**0**
Anm.									
Koksteg	tot vätska	1000,0							
Prov märkning	Vätske Ved	vedvätska ml	tillsatt vatten, ml		Na2CO3 g	EA %	NaOH ml	Sulf. %	Na2S ml
1	4,0	410,0	**346,3**			17,5	**83,6**	50,0	**160**
2	4,0	410,0	**346,3**			17,5	**83,6**	50,0	**160**
3	4,0	410,0	**346,3**			17,5	**83,6**	50,0	**160**
4	4,0	420,0	**337,7**			17,5	**83,5**	50,0	**159**

(Equations 3-6 were used in excel to easily calculate the amounts of the stock solutions needed to achieve the desired sulfidity (%) and EA. The amount of water and BL was also inserted and taken into account to obtain the desired L:W ratio)

Pulp weights and dryness after defibration 1000 x 10:and centrifugation

Dryness (each sample was divided into two portions, spit and pulp, which was afterwards mixed again due to too much reject%):

1.1 plate weight = 86,03 g, pulp wet = 11,505 g, wood dry + plate = 89,15 g → (89,15 - 86,03)/11,505 = 27,11%

2.1 plate weight = 66,75 g, pulp wet = 8,574 g, wood dry + plate = 69,05 g → (69,05 - 66,75)/8,574 = 26,84%

3.1 plate weight = 64,09 g, pulp wet = 8,283 g, wood dry + plate = 66,29 g → (66,29 - 64,09)/8,283 = 26,56%

4.1 plate weight = 65 g, pulp wet = 10,32 g, wood dry + plate = 67,83 g → (67,83 - 65)/10,32 = 26,84%

1.2 plate weight = 64,477 g, pulp wet = 8,926 g, wood dry + plate = 66,947 g → (66,947 - 64,477)/8,926 = 27,63%

2.2 plate weight = 90,4 g, pulp wet = 8,3155 g, wood dry + plate = 92,73 g → (92,73 - 90,4)/8,3155 = 28%

3.2 plate weight = 106,27 g, pulp wet = 5,984 g, wood dry + plate = 107,94 g → (107,94 - 106,27)/5,984 = 27,9%

4.2 plate weight = 91,33 g, pulp wet = 8,815 g, wood dry + plate = 93,744 g → (93,744 - 93,744)/8,815 = 27,38%

Pulp weights:

1.1 + 1.2 = (389,3*0.2711 + 213,3*0,2763)g = 164,474 g

2.1 + 2.2 = (355,9*0,2684 + 260,9*0,28)g = 168,5755 g

3.1 + 3.2 = (314,3*0,2656 + 284,6*0,279)g = 162,88 g

4.1 + 4.2 = (229,7*0,2684 + 380,1*0,2738)g = 165,715 g

Yield after impregnation and delignification:

1. 164,474/250 = 65,8%
2. 168,575/250= 67,43%

3. 162,88/250 = 65,152%
4. 165,715/250 = 66,286%

Oxygen delignification sample 4
m (wood wet) = 532 g
Dryness calculated:
plate weight = 64,09 g, plate + pulp wet = 69,3122 g, plate + pulp dry = 65,6 g
→ (65,8 - 64,09)/(69,3122 - 64,09) = 0,289 i.e 28,9%
Dry weight = 153,748 g
Due to the fact that these teflonized autoclaves hold a maximum weight of 80 g (dry) weight, two portions with each weight of 153,748/2 = 76,874 g (dry) were introduced (266 g of wet pulp).

Weight (after oxygen delignification + washing + centrifugation)
m = 512,3 g
Determination of dryness after the oxygen delignification:
plate weight = 81,040 g, plate + pulp wet = 87,057 g, plate + pulp dry = 82,6382 g
→ (82,6382 - 81,04)/(87,057 - 81,04) = 0,2597 i.e. 25,97%.

Enzymatic treatment sample 4
50 g enzymes /tonne dry pulp is needed (between 25-75 g / tonne suggested)
The amount of pulp is:
m (wet pulp) = 243,9 g (taken from 512,3 g i.e. left 268,4 g)
m (dry pulp) = 0,2597 * 243,9 = 63,17 g → 63,17 * 10^{-6} tonne.
m (enzyme added) = 50*(63,17 * 10^{-6}) = 3,16 g = 3,16 ml

Weight (after enzymatic treatment + washing + centrifugation)
m = 222,8 g
Determination of dryness after the enzymatic treatment:
plate weight = 86,040 g, plate + pulp wet = 88,057 g, plate + pulp dry = 86,568 g
→ (86,568-86,040)/(88,057-86,040) = 0,261675 i.e. 26,17%
m (dry pulp) = 58,3 g

Oxygen delignification sample 2
m (wood wet) = 538 g
Dryness calculated:
plate weight = 61,22 g, plate + pulp wet = 70,02 g, plate + pulp dry = 63,7154 g
→ (63,7154 - 61,22)/(70,02 - 61,22) = 0,2836 i.e 28,36%
Dry weight = 152,56 g
Due to the fact that these teflonized autoclaves hold a maximum weight of 80 g (dry) weight, two portions with each weight of 152,56/2 = 76,28 g (dry) were introduced (269 g of wet pulp).

Weight (after oxygen delignification + washing + centrifugation)
m = 518,1 g
Determination of dryness after the oxygen delignification:
plate weight = 63,82 g, plate + pulp wet = 73,17 g, plate + pulp dry = 66,226 g
→ (66,226 - 63,82)/(73,17 - 63,82) = 0,2573% i.e. 25,73%
Kappa was measured to = 59,235

Enzymatic treatment sample 2 (between 25-75 g / tonne suggested)
50 g enzymes /tonne dry pulp is needed
The amount of pulp is:
m (wet pulp) = 249,7 g (taken from 518,1 g i.e. 268,4 g left)
m (dry pulp) = 0,2573 * 249,7 = 64,2478 g → 64,2478 * 10^{-6} tonne.
m (enzyme added) = 50*(64,2478* 10^{-6}) = 3,2 g = 3,2 ml

Weight (after enzymatic treatment + washing + centrifugation)
m = 229,8 g

Determination of dryness after the enzymatic treatment:
plate weight = 83,215 g, plate + pulp wet = 92,356 g, plate + pulp dry = 85,491 g g
→ (85,491-83,215)/(92,356-83,215) = 0,249 i.e. 24,9%
m (dry pulp) = 57,22 g

(Part III)
Titration BL
HS^- determination
1 ml BL together with 5 ml (28%) NH_3 and 40-50 ml 1M NaOH was titrated with 10 ml $AgNO_3$. Average was taken on two equivalence points.

1. 0,3941 mol/l
2. 0,3694 mol/l

→ AVERAGE [HS] = 0,38175 mol/l

OH^- determination
10 ml BL together with ~80 ml deionized water and 10 ml Na_2CO_3 was titrated with HCL. Average was taken on only two equivalence points due to the more stable OH^- ions.

1. 0,580 mol/l
2. 0,5816 mol/l

→ Average [OH] = 0,5808 mol/l

Weights of the wood chips prepared for Part II

1. 655,5 g (wet) - 250g (dry weight) = 405,5 g (water inside)
2. 648,7 g (wet) - 250g (dry weight) = 398,7 g (water inside)
3. 648,2 g (wet) - 250g (dry weight) = 398,2 g (water inside)
4. 639,1 g (wet) - 250g (dry weight) = 389,1 g (water inside)

BL withdrawn after impregnation (Part III, weighted and titrated HS^-/OH^- of the BL withdrawn), only two samples were titrated and an average was taken (should be enough):

1. weight (1340 ml), [HS] = 0,2010 + 0,2112 mol/l, [OH] = 0,240 mol/l
2. weight (1340 ml), [HS] = — mol/l, [OH] = — mol/l
3. weight (1340 ml), [HS] = 0,2196 + 0,2080 mol/l, [OH] = 0,2371 mol/l
4. weight (1330 ml), [HS] = — mol/l, [OH] = — mol/l

BL withdrawn after delignification part III (measured as HS^-/OH^- of the BL withdrawn, averaged equivalence point 2 times for HS):

1. [HS] = 0,2492 + 0,2564 mol/l, [OH] = 0,5566 mol/l
2. [HS] = mistakenly sabotaged, [OH] = mistakenly sabotaged
3. [HS] = 0,2515 + 0,2418 mol/l, [OH] = 0,6337 mol/l
4. [HS] = 0,2536 +, 0,2448 mol/l, [OH] = 0,6158 mol/l

Datum	2022-10-12	Projekt		Kokserie		Kokare:	G2	Utfört av:		
Ved			torr ved, g	250,0	th		Invägd ved, g	655,5		
								648,70		
								648,2		
								639,1		
							vitlut	SL 1	avd SL 2	
Temp.schema sulfatkok, efter avdrag av lakningsvätska					**Tid, min**	NaOH, M	9,2030	0,5808	0,2386	mol/l
Start temp. 90°C rampning 90-120°C 3°C/min					10	Na2S (HS)	1,6885	0,38175	0,21	mol/l
Impregnering: 120°C i 120 min.					120	Na2S (OH)	1,4165			mol/l
Rampning till kok: 3°/min från 120 till 160°C					13.3	Na2CO3	20			mol/l
Koktemp: **160**										
Koktid: till önskad H-faktor					130	Na2CO3	106,0000	g/mol		

Prov märkning	Vätske Ved	vedvätska ml	tillsatt vatten, ml	tillsatt SL 1 ml	avdrag sl	EA %	NaOH ml	Sulf. %	Na2S ml
1	7,0	405,5	**406,3**	**875,0**	1340,0	17,5	**64**	50,0	**0**
2	7,0	398,7	**413,1**	**875,0**	1340,0	17,5	**64**	50,0	**0**
3	7,0	398,2	**413,6**	**875,0**	1340,0	17,5	**64**	50,0	**0**
4	7,0	389,1	**422,7**	**875,0**	1330,0	17,5	**64**	50,0	**0**

Anm.

Koksteg	tot vätska	1000,0							
Prov märkning	Vätske Ved	vedvätska ml	tillsatt vatten, ml		Na2CO3 g	EA %	NaOH ml	Sulf. %	Na2S ml
1	4,0	410,0	**346,3**			17,5	**83,6**	50,0	**160**
2	4,0	410,0	**346,3**			17,5	**83,6**	50,0	**160**
3	4,0	410,0	**346,3**			17,5	**83,6**	50,0	**160**
4	4,0	420,0	**337,7**			17,5	**83,5**	50,0	**159**

(Equations 3-6 were used in excel to easily calculate the amounts of the stock solutions needed to achieve the desired sulfidity (%) and EA. The amount of water and BL was also inserted and taken into account to obtain the desired L:W ratio)

Wood chips washed with deionized water overnight
Weights of the washed chip samples:

1. 834,5 g
2. 844,6 g
3. 847,4 g
4. 831,9 g

Wood chip samples were further defibrated and refined in the sprout waldron with water, and finally centrifuged
Dryness calculations (oven dried) =

1. plate weight = 65,1045 g, pulp wet = 5,425 g, pulp dry + plate = 66,193 g
2. plate weight = 64,648 g, pulp wet = 4,7245 g, pulp dry + plate = 65,77 g
3. plate weight = 102,33 g, pulp wet = 5,882 g, pulp dry + plate = 103,615 g
4. plate weight = 64,09 g, pulp wet = 5,567 g, pulp dry + plate = 65,420 g

→ 1. (66,193 - 65,1045)/5,425 = 0,20377
→ 2. (65,77 - 64,648)/4,7245 = 0,239
→ 3. (103,615 - 102,33)/5,882 = 0,2218
→4. (65,420 - 64,09)/5,567 = 0,221

1. m = 854 g, dryness = 20,37%, Kappa = 108,665 (109,69 + 107,64)/22
2. m = 653,7 g, dryness = 23,9%, Kappa = 91,86 (92,16 + 91,56)/2
3. m = 681 g, dryness = 22,18%, Kappa = 74,93 (only once due to lack of chemicals)
4. m = 614,1 g, dryness = 22%, Kappa = 68,36 (only once due to lack of chemicals)

(Part II PH)
Weighed wood chips before pre-hydrolysis:

1. 375,2 g i.e. (375,2 - 250 = 125,2 g water)
2. 375,2 g i.e. (375,2 - 250 = 125,2 g water)
3. 375,1 g i.e. (375,1 - 250 = 125,1 g water)
4. 375,4 g i.e. (375,4 - 250 = 125,4 g water)

To get L:W ratio of 7:1, totally 1750 g of water is needed due to 1750/250 = 7

→ 1. 1750 - 125,2 = 1624,8 g water add
→ 2. 1750 - 125,2 = 1624,8 g water added
→ 3. 1750 - 125,1 = 1624,9 g water added
→ 4. 1750 - 125,4 = 1624,6 g water added

The pre-hydrolyzate is poured off and weighed to approximately 1387 g/sample with pH=3,55 (stored in the refrigerator ~4-5 °C and measured the day after).

The same BL was used and no concentration determinations were necessary due to the short timeframe.

Weights of the wood chips prepared for Part II

1. 606,7 g (wet) - 250g (dry weight) = 356,7 g (water inside)
2. 608,2 g (wet) - 250g (dry weight) = 358,2 g (water inside)
3. 608,8 g (wet) - 250g (dry weight) = 358,8 g (water inside)
4. 603,3 g (wet) - 250g (dry weight) = 353,3 g (water inside)

BL withdrawn after impregnation (Part II, weighted and titrated HS^-/OH^- of the BL withdrawn), only two samples were titrated and average was taken (due to lack of time, each sample was titrated only once):

1. weight (1290 ml), [HS] = 0,2121 mol/l, [OH] = 0,2170 mol/l
2. weight (1290 ml), [HS] = – mol/l, [OH] = – mol/l
3. weight (1280 ml), [HS] = 0,1819 mol/l, [OH] = 0,2188 mol/l
4. weight (1280 ml), [HS] = – mol/l, [OH] = – mol/l

BL withdrawn after delignification part II (measured HS/OH of the BL withdrawn):

1. [HS] = 0,2617 mol/l, [OH] = 0,7638 mol/l
2. [HS] = 0,2476 mol/l, [OH] = 0,7320 mol/l
3. [HS] = 0,2597 mol/l, [OH] = 0,7064 mol/l
4. [HS] = 0,2680 mol/l, [OH] = 0,6989 mol/l

Temp.schema sulfatkok, efter avdrag av lakningsvätska				Tid, min	NaOH, M	9,2030	0,5808	0,2179	mol/l
Start temp. 90°C rampning 90-120°C 3°C/min				10	Na2S (HS)	1,6885	0,38175	0,20	mol/l
Impregnering: 120°C i 120 min.				120	Na2S (OH)	1,4165			mol/l
Rampning till kok: 3°/min från 120 till 160°C				13.3	Na2CO3	20			mol/l
Koktemp: 160									
Koktid: till önskad H-faktor				130	Na2CO3	106,0000	g/mol		

Prov märkning	Vätske Ved	vedvätska ml	tillsatt vatten, ml	tillsatt SL 1 ml	avdrag sl	EA %	NaOH ml	Sulf. %	Na2S ml
1	7,0	356,7	**455,1**	**875,0**	1290,0	17,5	**64**	50,0	**0**
2	7,0	358,2	**453,6**	**875,0**	1290,0	17,5	**64**	50,0	**0**
3	7,0	358,8	**453,0**	**875,0**	1280,0	17,5	**64**	50,0	**0**
4	7,0	353,3	**458,5**	**875,0**	1280,0	17,5	**64**	50,0	**0**
Anm.									
Koksteg	tot vätska	1000,0							
Prov märkning	Vätske Ved	vedvätska ml	tillsatt vatten, ml		Na2CO3 g	EA %	NaOH ml	Sulf. %	Na2S ml
1	4,0	460,0	**299,0**			17,5	**83,8**	50,0	**157**
2	4,0	460,0	**299,0**			17,5	**83,8**	50,0	**157**
3	4,0	470,0	**290,3**			17,5	**83,7**	50,0	**156**
4	4,0	470,0	**290,3**			17,5	**83,7**	50,0	**156**

(Equations 3-6 were used in excel to easily calculate the amounts of the stock solutions needed to achieve the desired sulfidity (%) and EA. The amount of water and BL was also inserted and taken into account to obtain the desired L:W ratio)

Wood chips washed with deionized water overnight

Weights of the washed chip samples:

1. 776,2 g
2. 776,6 g
3. 770,7 g

4. 767,2 g

Wood chip samples were further defibrated and refined in the sprout waldron with water, and finally centrifuged
Dryness calculations (oven dried) =

1. plate weight = 65,1018 g, pulp wet = 7,4350 g, pulp dry + plate = 66,9749 g
2. plate weight = 64,6449 g, pulp wet = 12,4538 g, pulp dry + plate = 66,8113 g
3. plate weight = 102,3317 g, pulp wet = 13,5014 g, pulp dry + plate = 104,9216 g
4. plate weight = 64,087 g, pulp wet = 7,099 g, pulp dry + plate = 65,7151 g

→ 1. (66,9749 - 65,1018)/7,4350 = 0,25193
→ 2. (66,8113 - 64,6449)/12,4538 = 0,17395
→ 3. (104,9216 - 102,3318)/13,5 = 0,1918
→ 4. (65,7151 - 64,087)/7,099 = 0,2293

1. m = 548,2 g, dryness = 25,193%, Kappa = 118,085 (118,7 + 117,47)/2
2. m = 732,2 g, dryness = 17,395%, Kappa = 91,375 (91,86 + 90,89)/2
3. m = 625,1 g, dryness = 19,18%, Kappa = 68,45 (68,07 + 68,83)/2
4. m = 512,4 g, dryness = 22,93%, Kappa = 62,085 (61,75 + 62,42)/2

8.3 Appendix C

Sheet making

PH 1

Dryness: 25,193%
Dry mass needed : 50 g
m (wet) = 50/0,25193 = 198,467 g + 3L water mixed
→ diluted with 13-15 L deionized water to get approximately. 3 g/l.
Concentration determination:
Weight (solution) = 239 ml (1)
Weight (filter) = 1,0171 g (1)
weight (fibers + filter) = 1,822 g (1)
weight (fibers) = 1,822 - 1,0171 = 0,8049 g (1)
conc 1 = 0,8049 / 239 = 3,37 g/l
…….
Weight (solution) = 245 ml (2)
Weight (filter) = 1,0298 g (2)
weight (fibers + filter) = 1,8897 g (2)
weight (fibers) = 1,8897 - 1,0298 = 0,856 g (2)
conc 2 = 0,856/245 = 3,51 g/l

Average = (3,37 + 3,51)/2 = 3,44 g/l

Desired sheet weight: 3,81 g
SR measurement fiber weight needed: 2g
→ sheet so.l = 3,81 / 3,44 = 1107,6 g
→ SR sol. = 2 / 3,44 = 581,4 g

PH 4

Dryness: 22,93%
Dry mass needed : 50 g
m (wet) = 50/0,2293 = 218,055 g + 3L water mixed
→ diluted with 13-15 L deionized water to get approximately. 3 g/l.

Concentration determination:
Weight (solution) = 255 ml (1)
Weight (filter) = 1,015 g (1)
weight (fibers + filter) = 1,7862 g (1)
weight (fibers) = 1,7862 - 1,015 = 0,7712 g (1)
conc 1 = 0,7712 / 255 = 3,024 g/l
…….
Weight (solution) = 256 ml (2)
Weight (filter) = 1,012 g (2)
weight (fibers + filter) = 1,9430 g (2)
weight (fibers) = 1,844- 1,012 = 0,832 g (2)
conc 2 = 0,8320/256 = 3,25 g/l

Average = (3,024 + 3,25)/2 = 3,173 g/l

→ sheet so.l = 3,81 / 3,173 = 1200,7 g
→ SR sol. = 2 /3,173 = 630,32 g

R1

Dryness: 20,37%
Dry mass needed : 50 g
m (wet) = 50/0,2037 = 245,46 g + 3L water mixed
→ diluted with 13-15 L deionized water to get approximately. 3 g/l.

Concentration determination:

Weight (solution) = 249 ml (1)
Weight (filter) = 1,0145 g (1)
weight (fibers + filter) = 1,8251 g (1)
weight (fibers) = 1,8251 - 1,0145 = 0,8106 g (1)
conc 1 = 0,8106 / 249 = 3,255 g/l
…….
Weight (solution) = 350 ml (2)
Weight (filter) = 1,0224 g (2)
weight (fibers + filter) = 2,1723 g (2)
weight (fibers) = 2,1723- 1,0224 = 1,1499 g (2)
conc 2 = 1,1499/350 = 3,2854 g/l

Average = (3,255 + 3,2854)/2 = 3,27 g/l

→ sheet sol. = 3,81 / 27 = 1165,513 g
→ SR sol. = 2 / 3,27 = 611,62 g

R2

Dryness: 23,9%
Dry mass needed : 50 g
m (wet) = 50/0,239 = 209,2 g + 3L water mixed
→ diluted with 13-15 L deionized water to get approximately. 3 g/l.

Concentration determination:
Weight (solution) = 283 ml (1)
Weight (filter) = 1,0118 g (1)
weight (fibers + filter) = 2,0141 g (1)
weight (fibers) = 2,0141 - 1,0118 = 1,0023 g (1)
conc 1 = 1,0023 / 283 = 3,54 g/l
…….
Weight (solution) = 312 ml (2)
Weight (filter) = 1,0214 g (2)
weight (fibers + filter) = 2,1209 g (2)
weight (fibers) = 2,1209- 1,0214 = 1,0995 g (2)
conc 2 = 1,0995/312 = 3,524 g/l

Average = (3,54 + 3,524)/2 = 3,533 g/l

→ sheet so.l = 3,81 / 3,533 = 1078,4 g
→ SR sol. = 2 / 3,533 = 566,09 g

R3

Dryness: 22,18%
Dry mass needed : 50 g
m (wet) = 50/0,2218 = 253 g + 3L water mixed
→ diluted with 13-15 L deionized water to get approximately. 3 g/l.

Concentration determination:
Weight (solution) = 253 ml (1)
Weight (filter) = 1,0160 g (1)
weight (fibers + filter) = 1,8729 g (1)
weight (fibers) = 1,8729 - 1,0160 = 0,8569 g (1)
conc 1 = 0,8569 / 253 = 3,386 g/l
…….
Weight (solution) = 218 ml (2)
Weight (filter) = 1,0235 g (2)
weight (fibers + filter) = 1,7477 g (2)
weight (fibers) = 1,7477- 1,0235 = 0,7242 g (2)
conc 2 = 0,7242/218 = 3,32 g/l

Average = (3,386 + 3,32)/2 = 3,353 g/l

→ sheet so.l = 3,81 / 3,353 = 1136,9
→ SR sol. = 2 / 3,353 = 596,48 g

R4

Dryness: 22%
Dry mass needed : 50 g
m (wet) = 50/0,22 = 227,27 g + 3L water mixed
→ diluted with 13-15 L deionized water to get approximately. 3 g/l.

Concentration determination:
Weight (solution) = 252 ml (1)
Weight (filter) = 1,019 g (1)
weight (fibers + filter) = 1,9421 g (1)
weight (fibers) = 1,9421 - 1,018 = 0,9231 g (1)
conc 1 = 0,9231 / 252 = 3,667 g/l
…….
Weight (solution) = 237 ml (2)
Weight (filter) = 1,0273 g (2)
weight (fibers + filter) = 1,8683 g (2)
weight (fibers) = 1,8683- 1,02734 = 0,84096 g (2)
conc 2 = 0,84096/237= 3,548 g/l

Average = (3,667 + 3,548)/2 = 3,60 g/l

→ sheet sol. = 3,81 / 3,6 = 1058,3 g
→ SR sol. = 2 / 3,6 = 555,5 g

---

2 (O_2)

Dryness: 28,9%
Dry mass needed : 50 g
m (wet) = 50/0,289 = 173,01 g + 3L water mixed
→ diluted with 13-15 L deionized water to get approximately. 3 g/l.

Concentration determination:
Weight (solution) = 302 ml (1)
Weight (filter) = 0,928 g (1)
weight (fibers + filter) = 1,867 g (1)
weight (fibers) = 1,867 - 0,928 = 0,939 g (1)
conc 1 = 0,939/302 = 3,109 g/l
…….
Weight (solution) = 283 ml (2)
Weight (filter) = 0,911 g (2)
weight (fibers + filter) = 1,793 g (2)
weight (fibers) = 1,793- 0,911 = 0,882 g (2)
conc 2 = 0,882/283= 3,117 g/l

Average = (3,109 + 3,117)/2 = 3,11 g/l

→ sheet so.l = 3,81 / 3,11 = 1225 g
→ SR sol. = 2 / 3,11 = 643,09 g

---

4 (O_2)

Dryness: 25,97%
Dry mass needed : 50 g
m (wet) = 50/0,2597 = 192,53 g + 3L water mixed
→ diluted with 13-15 L deionized water to get approximately. 3 g/l.

Concentration determination:
Weight (solution) = 300 ml (1)
Weight (filter) = 1,0125 g (1)
weight (fibers + filter) = 2,0150 g (1)
weight (fibers) = 2,0150 - 1,0125 = 1,0025 g (1)
conc 1 = 1,0025/300 = 3,34 g/l
…….
Weight (solution) = 297,07 ml (2)
Weight (filter) = 1,0150 g (2)
weight (fibers + filter) = 2,0280 g (2)
weight (fibers) = 2,0280- 1,0150 = 1,013 g (2)
conc 2 = 1,013/297,07= 3,41 g/l

Average = (3,34 + 3,41)/2 = 3,375 g/l

→ sheet sol. = 3,81 / 3,375 = 1128,9 g
→ SR sol. = 2 / 3,375 = 592,6 g

---

2 (O_2 + X)
Dryness: 25%
Dry mass needed : 50 g
m (wet) = 50/0,25 = 200 g + 3L water mixed
→ diluted with 13-15 L deionized water to get approximately. 3 g/l.

Concentration determination:
Weight (solution) = 204 ml (1)
Weight (filter) = 1,0279 g (1)
weight (fibers + filter) = 1,707 g (1)
weight (fibers) = 1,707 - 1,0279 = 0,6791 g (1)
conc 1 = 0,6791/204 = 3,329 g/l
…….
Weight (solution) = 159 ml (2)
Weight (filter) = 1,0190 g (2)
weight (fibers + filter) = 1,5335 g (2)
weight (fibers) = 1,5335 - 1,0190 = 0,5145g (2)
conc 2 = 0,5145/159= 3,236 g/l

Average = (3,329 + 3,236)/2 = 3,281 g/l

→ sheet so.l = 3,81 / 3,281 = 1161,23 g
→ SR sol. = 2 / 3,281 = 609,57 g

---

4 (O_2 + X)
Dryness: 26%
Dry mass needed : 50 g
m (wet) = 50/0,26 = 200 g + 3L water mixed
→ diluted with 13-15 L deionized water to get approximately. 3 g/l.

Concentration determination:
Weight (solution) = 208 ml (1)
Weight (filter) = 1,0298 g (1)
weight (fibers + filter) = 1,7017 g (1)
weight (fibers) = 1,7017 - 1,0298 = 0,6719 g (1)
conc 1 = 0,6729/208 = 3,23 g/l
…….
Weight (solution) = 222 ml (2)

Weight (filter) = 1,0112 g (2)
weight (fibers + filter) = 1,7726 g (2)
weight (fibers) = 1,7726 - 1,0112 = 0,7614 g (2)
conc 2 = 0,7614/222= 3,43 g/l

Average = (3,23 + 3,43)/2 = 3,34 g/l

→ sheet sol. = 3,81 / 3,34 = 1140,7 g
→ SR sol. = 2 / 3,34 = 598,8 g

R1 refined (10000 pfi)
Dryness: 20,37%
Dry mass needed : 30 g
m (wet) = 30/0,2037 =147,275 g + 3L water mixed
→ diluted with 10 L deionized water to get approximately. 3 g/l.

Concentration determination:
Weight (solution) = 200 ml (1)
Weight (filter) = 0,9964 g (1)
weight (fibers + filter) = 1,454 g (1)
weight (fibers) = 1,454 - 0,9964 = 0,4576 g (1)
conc 1 = 0,4576/200 = 2,29 g/l
…….
Weight (solution) = 217 ml (2)
Weight (filter) = 0,8732 g (2)
weight (fibers + filter) = 1,4827 g (2)
weight (fibers) = 1,4827 - 0,8732 = 0,6095 g (2)
conc 2 = 0,6095/217= 2,32 g/l

Average = (2,29 + 2,32)/2 = 2,3 g/l

→ sheet sol. = 3,81 / 2,3 = 1656,5 g
→ SR sol. = 2 / 2,3 = 869,56 g

R4 refined (10000 pfi)
Dryness: 22%
Dry mass needed : 30 g
m (wet) = 30/0,22 =136,36 g + 3L water mixed
→ diluted with 10 L deionized water to get approximately. 3 g/l.

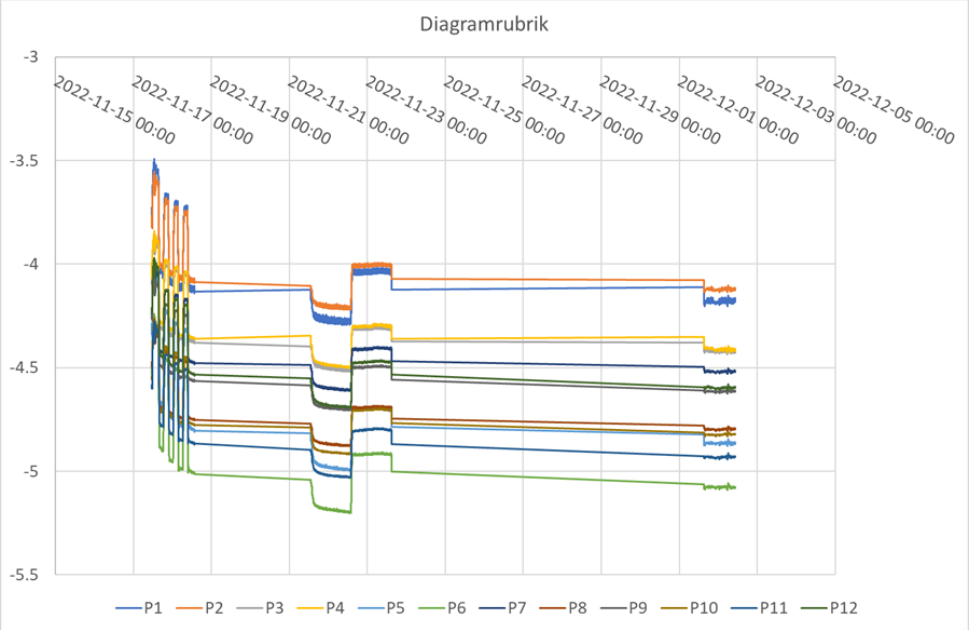
Concentration determination:
Weight (solution) = 213 ml (1)
Weight (filter) = 0,9817 g (1)
weight (fibers + filter) = 1,6121 g (1)
weight (fibers) = 1,6121 - 0,9817 = 0,6304 g (1)
conc 1 = 0,6304/213 = 2,96 g/l
…….
Weight (solution) = 195 ml (2)
Weight (filter) = 0,9664 g (2)
weight (fibers + filter) = 1,5277 g (2)
weight (fibers) = 1,5277 - 0,9664 =0,5613 g (2)
conc 2 = 0,5613/195= 2,88 g/l

Average = (2,96 + 2,88)/2 = 2,92 g/l

→ sheet sol. = 3,81 / 2,92 = 1304,8
→ SR sol. = 2 / 2,92 = 684,9 g

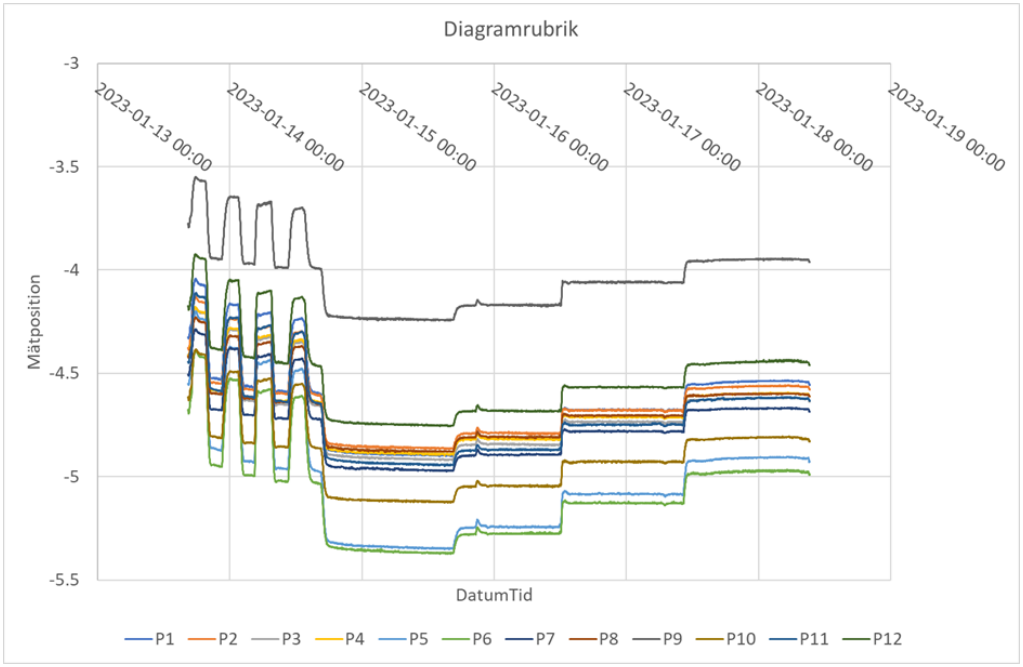
8.4 Appendix D

The two trials were conducted in different ways:
Attempt 1:
· Conditioning/relaxation with cycling climate, 87-50-87-50-87-50-87-50 over a 24-hour period
· Measurement of weight and HEX after relaxation
· Weekend stay with humidity control closed and open chamber 221118-221121
· Level 33% RH in one day, measurement of moisture and weight
· Level 66% RH in one day, measurement of moisture and weight
· Longer pause, after which the measurement was supplemented with an extra one Level 50% RH for one day, measurement of moisture and weight
(The addition was made because I judged that the 50% level after relaxation had not reached equilibrium.)
Drying of samples in an oven and measurement of dry weight



Attempt 2:

· Conditioning/relaxation with cycling climate, 87-50-87-50-87-50-87-50 over a 24-hour period
· Preconditioning at 20%RH for one day
· Level 33% RH in one day, measurement of moisture and weight
· Level 50% RH in one day, measurement of moisture and weight
· Level 66% RH in one day, measurement of moisture and weight
· Drying of samples in an oven and measurement of dry weight
Conditioning/relaxation, preconditioning at 20% RH and leveling at 33% RH took place over the weekend.
Note that the initial preconditioning at 20% RH decreases the length, it has not reached equilibrium. Thanks to this preconditioning, samples reach equilibrium at the 33% level.
In test round 1, you can see that the 33% level has not reached equilibrium, it would probably be needed
1-2 extra days of level maintenance.
Since the 33% level has dropped less, an underestimation of HEXen is obtained.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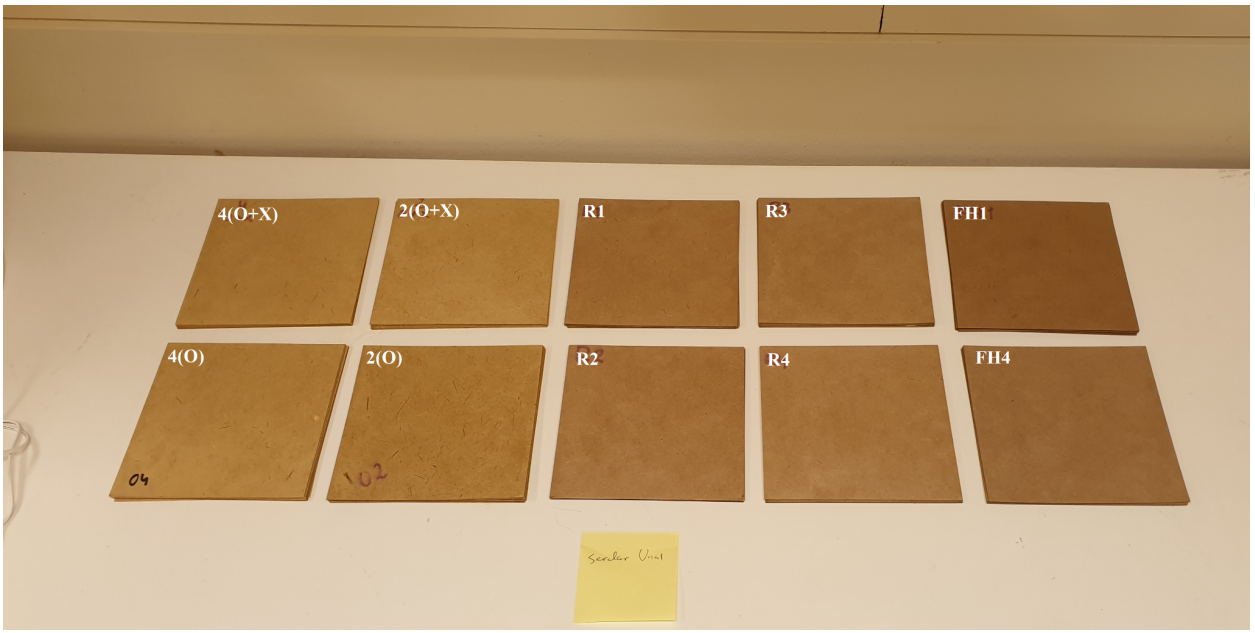
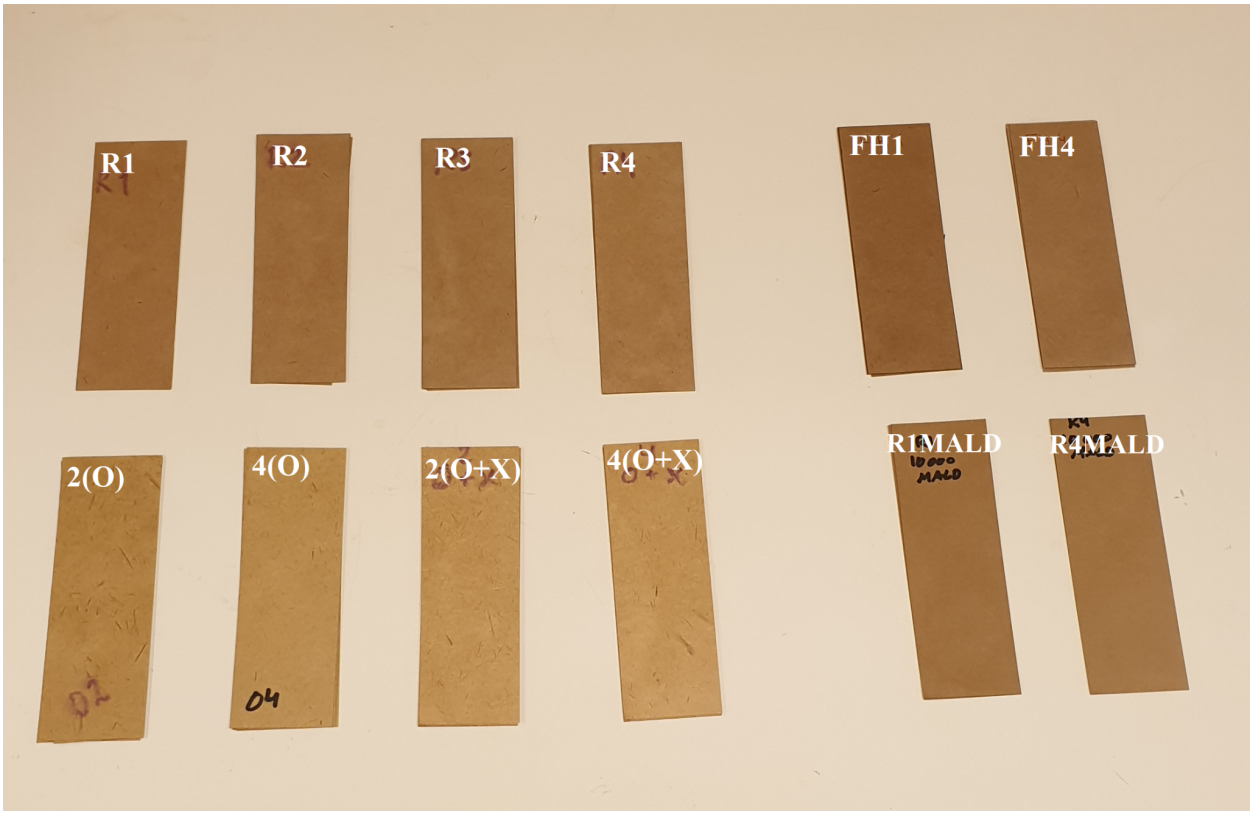
8.5 Appendix E





8.6 Appendix F

AVERAGE FINAL % (2 MEASUREMENTS)

Sample	Arabinose	Galactose	Glucose	Xylose	Mannose
FH 1	0,1	0,1	94,3	3,6	2,0
FH 4	0,0	0,1	94,4	3,6	1,9
R1	1,3	1,2	82,6	7,7	7,2
R3	1,0	0,9	83,5	7,6	7,0
2(O+X)	0,9	0,9	85,1	5,3	7,8
R2	1,1	1,0	82,8	7,6	7,5
R4	1,0	0,8	83,5	7,5	7,2
2(O)	1,6	1,0	80,6	9,1	7,7
4(O)	1,4	0,9	81,1	8,9	7,6
4(O+X)	0,8	0,9	85,3	5,3	7,8

AVERAGE VALUE OF FINAL MG/G (2 MEASUREMENTS)

Acid insoluble residue	Acid soluble residue	Total lignin	carbo-hydrates	Total amount	ligning %
186,9	4,5	191,4	734,0	925,4	=(K53/M53)*100
92,0	4,3	96,3	839,4	935,7	10,29
162,6	5,3	167,9	745,1	913,0	18,39
112,3	5,6	117,9	793,7	911,6	12,93
126,1	9,4	135,5	812,5	948,0	14,29
143,0	4,9	147,9	761,2	909,1	16,26
104,0	5,1	109,1	760,0	869,2	12,55
95,2	5,8	131,6	777,6	878,5	14,98
108,7	6,0	114,6	814,6	929,2	12,34
101,4	4,7	106,1	777,4	883,5	12,01