Studies of the Impregnation Stage in Kraft Pulping of Hardwood

JONAS GAREMARK
Studies of the Impregnation Stage in Kraft Pulping of Hardwood

Jonas Garemark

Master’s Thesis in Chemical Engineering for Energy and Environment (30 ECTS credits)
Degree Progr. in Chemical Engineering for Energy and Environment 120 credits
Royal Institute of Technology, 2018
Supervisor: Elisabet Brännvall, Rise Bioeconomy
Examiner: Mikael Lindström, KTH

Keywords: Impregnation, kraft pulping, hardwood, alkali consumption, homogeneous delignification

Royal Institute of Technology
School of Engineering Sciences in Chemistry, Biotechnology and Health

KTH CBH
CBH SE-100 44 Stockholm, Sweden
www.kth.se/cbh
Acknowledgement

This degree project has been performed at RISE Bioeconomy as a final part of the Master's programme in Chemical Engineering for Energy and Environment. Before I initiated the project, my knowledge about digesting of pulpwood was limited. During the course of my work, I have learned everything from handling of raw material to processing pulp and paper chemistry. Furthermore, I have gained an idea of how research and the paper industry interacts. Throughout this intriguing project, I have interacted with several individuals. The project has included many elements, where the staff at RISE Bioeconomy have shown support and dedication towards my learning in every moment. I would like to thank all the staff who helped me during the work.

I want to give special thanks to:

Elisabet Brännvall, my supervisor at RISE Bioeconomy, who has been a great support throughout the work by communicating knowledge about the scientific progress, impregnation and kraft cooking. Elisabet has also supported me during the course of my work by providing guidelines about report writing.

Special thanks to Gonzalo Soler who shared his expertise in impregnation and cooking of wood.

Many thanks to Lars Norberg who through the course of my work has shared his comprehensive knowledge.

Special thanks to my examiner Mikael Lindström for providing necessary guidelines, helping me with communication and for sharing extensive knowledge of the kraft process.

Jonas Garemark

Stockholm, 8 June 2018
Abstract

In kraft pulping, one of the main issues is the extensive wood losses. With increasing prices of woody biomass an incentive towards minimizing the wood losses exists. Amongst the various process steps, the impregnation of wood chips has shown to enhance the cooking by providing a homogeneous distribution of chemicals inside the chips. It is proven that a more proficient impregnation phase can improve the overall yield in kraft pulping. However, there is a lack of scientific research comparing different impregnation techniques for hardwood. Hence, this thesis will attempt to clarify the impregnation of hardwood.

The impregnation efficiency was studied by comparing three different impregnation methods: High Alkali Impregnation (HAI), Extended Impregnation (EI) using a low alkali level and a Reference Impregnation (REF) to enable a comparison to the industrially established conditions. The cases were compared by analysing the yield, selectivity and homogeneity. The comparison was also made under cooking conditions with the objective to understand the impact of impregnation on the subsequent cooking phase. The cooking procedure was assessed by analysing the degree of delignification, yield and reject content.

In impregnation, most chemical consuming reactions occurred within the first 10-30 minutes, mainly contributed by deacetylation. HAI obtained the fastest homogeneous distribution of OH⁻ (~60 min), but the fastest dissolution of wood. The effect was contributed by the high [OH⁻], providing fast diffusion of ions and rapid dissolution of xylan. In the contrary, EI attained the highest impregnation yield after a given impregnation time but required a prolonged duration to obtain a chemical equilibrium between the free and bound liquor (~120 min). REF showed a higher yield than HAI and similar chemical equilibrium as EI. The hydrosulphide sorption in impregnation was highest for EI due to the high initial sulphidity charge and similar for REF and HAI. For impregnations at 115°C, the HS⁻ sorption was significantly increased for all cases, resulting from delignification.

In the subsequent cooking phase, it was prevalent that impregnation of chips under EI conditions were easier delignified, leading to a reduced cooking time to reach the defibration point. Birch was more prone to delignification than eucalyptus. In turn, eucalyptus also obtained a higher defibration point. Highest total cooking yield at similar kappa numbers was achieved with REF conditions, followed by HAI and lastly the EI conditions. The high yield of REF in contrast to HAI could be explained by an improved xylan yield due to an alleviated hydroxide level. The low yield of EI can be assigned to continues peeling due to the prolonged impregnation and loss of xylan when removing black liquor after impregnation. In terms of production rate, yield, energy and chemical consumption the REF is the most efficient impregnation condition for birch kraft cooking in this batchwise laboratory kraft cooking procedure.
Sammanfattning


Under impregneringsförsöken inträffade de flesta kemikaliekonsumerande reaktionerna inom 10–30 minuter, främst bidragen av deacetyleringsreaktioner. HAI erhöll den snabbaste homogena fördelningen av OH⁻ (~ 60 min), dock med konsekvensen att snabbast upplösa trämaterialalet. Effekten bidrogs av den höga [OH⁻], vilket gav snabb diffusion av joner och snabb upplösning av xylan. EI erhöll det högsta impregneringsutbytet efter en given impregneringstid men krävde en förlängd uppehållstid för att erhålla en kemisk jämvikt mellan den fria och bundna vätskan (~ 120 min). REF visade ett högre utbyte än HAI och liknande kemisk jämvikt som EI. Sorption av vätesulfidjoner vid impregnering var högst för EI på grund av den höga initiala svavelhalten följt av REF och till sist HAI. För impregnering vid 115°C ökade HS⁻ upptaget betydligt för alla metoder, orsakad av delignifiering.

I den efterföljande kokningsfasen var det framträdande att impregneringen av flis under EI-förhållanden lättare delignifierades, vilket resulterade i en reducerad kokningstid för att nå defibratoringspunkten. Björk var mer benägen att delignifieras än eukalyptus. I sin tur fick eukalyptus även en högre defibratoringspunktt. Högsta totala kokningsutbytet vid snarlika kappatal uppnåddes med REF-förhållandenet, följt av HAI och slutligen EI. Det höga utbytet av REF jämfört med HAI kunde förklaras av ett förbättrat xylanutbyte på grund av den lägre hydroxidnivån. Det lägre utbytet av EI kan förklaras på grund av den större utsträckning av peelingreaktion på grund av den förlängda impregneringen och förlust av xylan vid avlägsnande av svartlut efter impregneringen. Sammanfattningsvis, i termer av produktionshastighet, utbyte, energi och kemikalieförbruk var REF den mest effektiva impregneringsmetoden vid massatillverkning av björk i denna studie.
**List of Abbreviations**

DP – Degree of polymerization

DS – Dry Solids

ML – Middle Lamella

S1 – Inner Layer of The Secondary Cell Wall

S2 – Secondary Cell Wall

S3 – Outer Layer of The Secondary Cell Wall

P – Primary Cell Wall

ECCSA – Effective Capillary Cross-Sectional Area

EI – Extended Impregnation

L/W – Liquid-to-Wood ratio

EA – Effective Alkali [mol/L]

E.A. – Effective Alkali g NaOH/ g wood

HAI – High Alkali Impregnation

LCC – Lignin Carbohydrate Complexes

MeGlCA – 4-O-Methyl-α-D-2 Glucuronic Acid

o.d.w – Oven dry wood

[X] – Concentration of specified substance

Eu or Eucal – Eucalyptus

TAC – Total Alkali Consumption

[HS-]/[OH-] – The ratio of hydrogen sulphide concentration to hydroxide concentration

Bir – Birch
# Table of content

1 **INTRODUCTION** ........................................................................................................ 1  
  1.1 BACKGROUND ........................................................................................................... 1  
  1.2 PROBLEM STATEMENT .............................................................................................. 2  
  1.3 AIM AND OBJECTIVES ............................................................................................. 3  
  1.4 DELIMITATIONS ......................................................................................................... 3  
  1.5 OUTLINE ................................................................................................................... 3  

2 **THEORETICAL BACKGROUND** ............................................................................. 4  
  2.1 KRAFT PULPING ....................................................................................................... 4  
  2.2 IMPREGNATION TODAY ............................................................................................. 5  
  2.3 WOOD COMPOSITION .............................................................................................. 5  
  2.4 FIBRE MORPHOLOGY ............................................................................................... 7  
  2.5 IMPREGNATION OF WOOD CHIPS ......................................................................... 7  
  2.6 PATH OF PENETRATION ........................................................................................... 9  
  2.7 IMPREGNATION REACTIONS .................................................................................. 11  
  2.8 DISSOLUTION AND DEGRADATION OF XYLAN ..................................................... 17  
  2.9 IMPREGNATION METHODS ....................................................................................... 19  

3 **EXPERIMENTS** ..................................................................................................... 21  
  3.1 MATERIALS .............................................................................................................. 21  
  3.2 IMPREGNATION ....................................................................................................... 21  
  3.3 EVALUATION OF SPENT LIQUOR AND IMPREGNATED CHIPS ............................ 22  
  3.4 KRAFT COOKING ..................................................................................................... 24  
  3.5 ANALYSES ............................................................................................................... 25  
  3.6 IMPREGNATION REPEATABILITY .......................................................................... 26  

4 **RESULTS AND DISCUSSION** ............................................................................. 27  
  4.1 MASS BALANCE ....................................................................................................... 28  
  4.2 IMPREGNATION ....................................................................................................... 29  
  4.3 KRAFT COOKING ..................................................................................................... 39  
  4.4 IMPREGNATIONS IMPACT ON COOKING .............................................................. 45  

5 **CONCLUSION** ....................................................................................................... 46  

6 **FUTURE WORK** ..................................................................................................... 48  

TECHNICAL TERMS ....................................................................................................... 49  

BIBLIOGRAPHY ............................................................................................................. 50  

APPENDIX ...................................................................................................................... 51
1 Introduction

1.1 Background

In chemical kraft pulping, wood chips are subjected to an alkaline solution in which fibres are liberated by means of chemical action that dissolve lignin from the wood matrix. The objective in kraft pulping is to remove lignin while maintaining the carbohydrate portion of the wood. The dissolution of carbohydrates is inevitable in an alkaline environment, however, preventive measures can be taken to increase the pulp yield. One important factor is an adequate impregnation of the wood chips, making the wood more accessible in the cooking procedure. A high degree of impregnation gives the chips a homogeneous distribution of chemicals in the wood, leading to a more selective delignification.

Contemporary research has focused on improving the yield in the kraft pulping process. Likewise, several authors have reported the favourable effects of an adequate impregnation phase [1-3]. A proficient impregnation does not only increase the pulp yield but can contribute with reduced reject content, increased pulp strength and make the pulp more prone to bleaching [1]. The indirect effect of a more efficient pulping is a reduced need of energy intensive operations and treatment chemicals, leading to an abatement of cumbersome environmental impacts. Furthermore, the wood accounts for 30-50% of the total production cost and is foreseen to increase. Renewable energy targets (e.g. The European Energy Directive) will accelerate the demand of woody biomass in the energy sector. Consequently, more competition will result in higher raw material costs [4]. Hence, an increased yield can improve the overall profitability of pulping.

The kraft cooking of wood chips is initiated as chemicals are transported into the wood chips. Upon penetration and diffusion of the cooking liquor different chemical activities transpire. Most prominent is the deacetylation of hemicelluloses, followed by neutralization of acids, deprotonation of functional groups, minor delignification and carbohydrate degradation by peeling. Some reactions decrease the carbohydrate yield, whilst others make the wood more benign to defibrate during the cooking process. Therefore, it is important to understand the chemical occurrences in order to utilize impregnation conditions that can take use of the beneficial reactions while mitigating the undesirable. Upon completion of an impregnation, the wood chips will be surrounded by spent cooking liquor, called free black liquor. Due to penetration and diffusion during the impregnation procedure the wood will contain black liquor inside its structure, called bound liquor. To obtain the impregnation effectiveness, the impregnated chips must be analysed and the black liquors must be investigated.

An incentive towards increasing the pulp yield without mitigating the production rate exist. Several technologies have been hypothesised to accomplish this. One interesting method is to subject the wood chips to an impregnation with high alkali concentration under a short duration. It has been shown that high alkali conditions improve the rate of diffusion and induce rapid removal of acetyl groups, both which improves ion mobility. The High Alkali Impregnation (HAI) is proposed to obtain a homogeneous impregnation of active chemicals whilst mitigating the temporal effects on the carbohydrate constituents [2]. Another interesting method is the extended impregnation, an impregnation that uses low alkali concentrations and a high liquor-to-wood ratio, whilst prolonging the duration of the impregnation [5, 6]. Both techniques will be investigated in this thesis.
This study will involve the digesting phase in kraft cooking, including both impregnation and cooking of wood chips. The hardwood species eucalyptus and birch will be impregnated at various conditions by modifying the temperature, liquor-to-wood ratio, chemical charge and time. The evaluation will illustrate the conditions at which the most efficient impregnation is obtained, assessed by concentration differences in free and bound liquor, homogeneity and yield.

1.2 Problem statement

The kraft process is the most accomplished pulping technique of modern times. The process has been utilized and continuously improved for over 100 years. Nevertheless, it is not without flaws. One of the main issues is the low yield compared to other pulping processes. An objective towards minimizing the wood consumption in the kraft process exist, as substantial losses of valuable carbohydrates proceeds.

Through scientific endeavours, knowledge about the prevailing chemical reactions has been readily documented. Yet, finding techniques to prevent degradation of carbohydrates is an ever-ongoing search without a definite answer. Applying knowledge attained from comprehensive research on wood, the experimental procedures can be modified in an attempt to improve the cooking efficiency. Amongst the various stages of kraft cooking, the impregnation phase has a central role on the cooking performance. However, the impregnation phase is not extensively studied. Therefore, many potential optimisation opportunities could be obtained.

RISE Bioeconomy has acknowledged the gap between industrial and scientific accomplishments. Today, the company has an interest to increase the pulping yield by investigating the impregnation phase of kraft pulping. Many researchers have attempted to understand the impregnation phase. However, contemporary research mainly covers modelling of diffusion and reaction mechanisms. There is a lack of research comparing different analogies and impregnation methods. Thus far, RISE Bioeconomy has investigated different impregnation conditions for softwood. However, more information on how the impregnation impacts hardwood is needed. Subsequently, this thesis will attempt to clarify the impregnation of hardwood.
1.3 Aim and objectives

The overarching aim of this study is to identify the impregnation efficiency under different conditions. The analysis will illustrate the condition at which the most homogeneous impregnation is obtained, measured as alkali concentration achieved in the bound liquor as compared to the concentration in the free liquor. The study will also depict the selectivity of the impregnation in terms of dissolved wood, measured as yield after impregnation at different parameters.

This thesis will involve impregnation and cooking of birch in order to understand the consumption of alkali at different times. Eucalyptus, pine and spruce will also be utilized in an attempt to compare their efficiency to the birch specie. The behaviour of the impregnation liquor and the liquor entrapped in the chip will be analysed with an objective to determine the time at which a chemical equilibrium between the free and bound liquor is reached. The impregnation is followed by a subsequent kraft cook to understand the effects induced by the former impregnation stage. The impact will be evaluated by analysing the yield, reject content and residual lignin of the obtained pulp. The cooking procedure will utilize identical cooking conditions to properly understand the influence of the impregnation phase. This thesis will illustrate the thermal, temporal and chemical effect on the impregnation efficiency. The objectives are:

- Compare the alkali concentration in free and bound liquor to evaluate the homogeneity of the impregnation
- Obtain the condition at which the impregnation is the most efficient, in terms of homogeneity, temperature, chemical charge and duration.
- Obtain an understanding of how the subsequent cooking is affected by the impregnation phase
- Find the condition where the highest cooking yield is obtained

1.4 Delimitations

This study focus on the impregnation stage in kraft pulping. The cooking of wood chips following impregnation will only be performed to supplement the impregnation results. The impregnation and kraft cooking is restricted to a batch procedure using autoclaves.

1.5 Outline

This thesis is divided into several chapters. The first chapter provides necessary background to understand the problem and purpose of the thesis. In Chapter 2, the theoretical background is described with the intention to provide fundamental knowledge about the impregnation in order to grasp why the proposed impregnation methods are used and to fully comprehend the subsequent results. The experimental procedure is described in chapter 3, involving utilized materials, analyses methods and experimental repeatability. In chapter 4, the results and discussion is presented. The results are subsequently concluded in chapter 5, followed by future recommendations in chapter 6.
2 Theoretical background

2.1 Kraft pulping

Chemical cooking of wood is performed with an objective to liberate fibres by dissolving lignin from the wood matrix. The chemical cooking obtains long and flexible fibres due to the non-mechanical actions during the pulping process. As a consequence, almost 50% of the wood is dissolved, since most lignin is solubilized and some carbohydrates constituents are lost during the pulping [7]. Originally, the chemical pulping was performed with the soda process, accordingly, soda (Na_2CO_3) and CaCO_3 was used to dissolve the wood. The process obtained low pulp yields, however, at that time, the strength of the pulp was higher than the available mechanical processes. Thus, the soda process was continued as a cooking process. However, in 1879 the German chemist Carl F. Dahl introduced sodium sulphate (Na_2SO_4) as a cooking chemical in the soda process. Consequently, the pulp yield was increased and the pulp strength was significantly improved. The cooking process was therefore named kraft pulping, since kraft means strength in German [7].

Nowadays, kraft pulping is mostly performed as a continuous process where wood chips are immersed in the active chemicals OH^- and HS-, also called white liquor. The process is often divided into impregnation and cooking, where the impregnation is a pressurized procedure where the white liquor penetrates and diffuse into the wood matrix under moderate temperatures to enhance the subsequent cooking. The cooking process then proceeds at temperatures of 140-170°C for 3-4 hours [7]. Process parameters for impregnation and cooking is vital for the resulting end-product. Hence, there is a need to yield a white liquor with a desired amount of hydrosulphide and hydroxide ions. The hydrosulphide portion of the liquor is obtained by hydrolysis of Na_2S in water, according to equation 1. Sodium hydroxide is then added to this solution to attain the desired concentration of OH^-.

\[ \text{Na}_2\text{S} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \text{NaSH} \]  

When calculating the desired amount of chemicals, one could use the total concentration of HS^- and OH^-, more traditionally the terms effective alkali (E.A.) and sulfidity are used to express the content of HS^- and OH^- in the white liquor. The sulfidity can be calculated by equation 3. The E.A. involves both the OH^- acquired from the NaOH stock solution and the additional OH^- that was obtained from the hydrolysis of Na_2S. The E.A. is further expressed as the amount of alkali per kilogram wood, according to equation 4.

\[ n_{ea} (mol) = n_{\text{NaOH}} + n_{\text{Na}_2\text{S}} \]  

\[ \text{Sulfidity (\%)} = \frac{2 \cdot n_{\text{Na}_2\text{S}}}{2 \cdot n_{\text{Na}_2\text{S}} + n_{\text{NaOH}}} \cdot 100\% = \frac{n_{\text{Na}_2\text{S}}}{n_{\text{Na}_2\text{S}} + n_{\text{EA}}} \cdot 100\% \]  

\[ \text{Effective alkali (\%)} = \frac{n_{\text{EA}} \cdot 40}{m_{\text{wood}}} \cdot 100\% \]

Another parameter besides concentrations of active chemicals is the liquid-to-wood ratio (L:W). The ratio describes the amount of liquor compared to dry weight of wood. This includes the water content in the chips to the total volume of cooking liquor. A normal L:W in industrial operations ranges from 3 to 5 L/kg [7].
2.2 Impregnation today

The modern conventional continuous kraft digester has an impregnation retention time of 40-60 minutes at 100–130°C and a E.A. and sulphidity charge of 16-20% and 20-30%, respectively, for hardwood species. During the duration, liquor penetrates the chips and a homogenous distribution of active chemicals should be obtained. The chips fed to the digester has a dimension of 1-3 cm in length and 0.2-1 cm in thickness. Before introducing the chips to the impregnation vessel, a pre-steaming is performed. Steam is applied to moisturize and heat the chips. Under the pre-steaming the air entrapped in cavities of the chips will expand, causing displacement of air from the chips. Subsequently, the chips are transported to the impregnation vessel, where the chips are saturated with WL and BL. In continuous digesting of chips, about 40-60% of the total alkali charge is consumed during the impregnation phase [7, 8].

In continuous digesting, there are two common techniques; hydraulic or steam/liquor phase. In addition, the hydraulic digesting can utilize a single or two-vessel digesting system. For a single-vessel hydraulic digester, the impregnation occurs in the top of the digester where indirect heating in dual circulations is used to obtain the targeted cooking temperature. In a two-vessel steam/liquor phase digester the impregnation takes place in an independent vessel [9]. This thesis will not attempt to mimic the industrial impregnation. Instead, the impregnation will be a batchwise procedure where steel autoclaves are heated in a glycol bath and only one single initial charge of active chemicals is infused.

2.3 Wood composition

Before describing the chemical reactions occurring in the wood during impregnation it is important to understand the fundamental components of wood. The main constituents are cellulose, hemicellulose and lignin. The proportions of the composition differ depending on wood type. Here, the general composition of hardwood will be described.

2.3.1 Cellulose

Cellulose, the main constituent of wood, comprising about 40% of the total substance in dry wood, primarily found in the secondary cell wall of the fibres [10]. In pulping, cellulose is the most crucial component to preserve due to its strength bearing properties. Cellulose consists of linear unbranched chains of monosaccharides, more specifically, chains of glucose units structured by means of β-1,4-glycosidic bonds [11]. The chains are structured in layers and have a tendency to form hydrogen bonds. Due to Van der Walls forces and hydrophobic interactions the linear polysaccharides form crystalline structures that can have a Degree of Polymerization (DP) of up to 10 000 mono-saccharide units. The structures have crystalline, para-crystalline and non-crystalline areas along the strands [12]. The polysaccharide strands further bundle up as organized micro-fibrils. In turn, the micro-fibrils are the building blocks for fibrils and fibrils forms the final cellulose fibres [13]. Consequently, cellulose is a strong material with a Young’s modulus of 130 GPa [7], similar to cast iron.
2.3.2 Hemicelluloses

Hemicelluloses can be seen to have a gluing role in the cell wall and is the second most abundant constituent of dry wood, comprising about 30%. In pulping, hemicellulose is more easily dissolved than cellulose but sought for in the end-product, since it can provide strength properties [7]. Similar to cellulose, hemicellulose is a carbohydrate consisting of branched polysaccharides. In the contrary to cellulose it has an amorphous structure resulting from its heterogeneous polysaccharides that only can form a DP up to 200 [7]. Of all hemicelluloses, xylan and glucomannans are commercially the most important.

In hardwood species, glucuronoxylan is the most found hemicelluloses [13]. The glucuronoxylan constitutes around 15-30% of the hardwood and is built up by xylose units, with side branches of 4-O-methylglucuronic acid (MeGlcA). Moreover, the xylose units are highly acetylated as around 70% of the xylose is acetylated at either the C-2 or C-3 position. In turn, the glucomannans comprise 2-5% of the hardwood and are built up by linked mannose and glucose groups in a ratio of about 1:2. In contrast to the xylan the mannoses have very low degree of acetylation [14]. In the cell wall the hemicelluloses form covalent bonds to lignin, but does also interact with the cellulose microfibrils. These are called lignin carbohydrate complexes (LCC) [14], seen in Figure 1.

2.3.3 Lignin

Lignin, comprising about 30% of dry wood substance, exhibits a complex structure of interconnected aliphatic and aromatic monolignols. In contrast with the carbohydrates, the lignin is racemic and does not inhibit a determined DP. The basis of the lignin is its three monomers; p-cumaryl alcohol, coniferyl alcohol and synapyl alcohol and the lignin structure is built up by varies cross-linked ethers and carbon-carbon bonds. In hardwood, the most prevalent bond is a β-aryl-ether-bond. In the cell wall, lignin has the ability to interact with polysaccharides, in form of covalent and non-covalent bonds. Subsequently, lignin-carbohydrate networks form in the cell wall. Resultantly, the cell wall becomes stiff, which in turn prevents swelling in water. This property is import since it gives the wood the ability to transport water. In kraft pulping, as much lignin as possible is solubilized and degraded to obtain fibres that are strong and flexible [7].

![Figure 1. Network of interconnected lignin carbohydrate complexes (LCC)](image)
2.4 Fibre morphology

The fibres obtained during kraft pulping are essentially cells. Depending on raw material, the composition varies. In angiosperms (hardwood), the cell composition is more complex than for gymnosperm (softwood), and the variability of cell composition between hardwoods is high. For hardwoods, the most prominent cells are; libriform fibres, vessel elements and parenchyma cells. These cells are short fibres and the heterogeneous mix obtains an average fibre length of 0.4 – 1.8 mm [7]. The cell walls are held together as a layered structure. Starting from the exterior of the cell wall, one can find the lignin rich middle lamella (ML), the primary wall (P), the secondary cell wall (S2) and the warty layer [10].

All layers serve a different purpose in the cell wall. For example, the ML’s purpose is to bind the cells together. The ML together with the primary wall has a high degree of lignification and contains 20-25% of the total lignin content in wood [10]. Thereafter, the secondary wall is compiled by three layers: inner(S1), middle(S2) and outer layer (S3). Together they are built up by lamellae of parallel microfibrils, in which 50% of the woods cellulose can be found together with lignin and hemicelluloses [15]. Layer S1 and S3 can inhibit a few lamellae, while the thicker S2 layer can have more than 150 lamellae. Therefore, S2 can contribute up to 70% of the total lignin content in wood. Following is the primary cell wall, containing 20% of the wood cellulose [13], having networks of xylloglucans bonded to cellulosics. In addition, the xylloglucan can bond to pectins and within the primary wall lignin can be found to covalently bond to pectins and proteins, creating cross-linked networks [16, 17]. Lastly, the amorphous warty layer is a thin membrane that can be found at the inner surface of the cell wall. The warty layer can only be found in some hardwood species, whilst present in all softwood species [13]. The cell wall layers can be seen in Figure 2.

![Layered structure of cell wall](image)

*Figure 2. The layers of the cell wall. Figure made by author, inspiration from [10]*)

2.5 Impregnation of wood chips

For a successful cooking process the degree of impregnation of the wood chips is essential. During the impregnation procedure, the wood chips are immersed in a liquid of active chemicals containing HS⁻ and OH⁻ ions. The main objective with the impregnation is to ensure a complete penetration of the active chemicals into the chips that lead to an even distribution of chemicals from the surface to the centre of the chips. The lesser the concentration gradient, the more homogenous the delignification will be in cooking. If the advection and diffusion of chemicals
is not sufficient the centre of the chips will obtain a critical alkali level, seen in Figure 3. The subsequent cooking will attain a lower degree of delignification in the critical region that lead to a higher kappa number in that area [1]. Accordingly, a high degree of impregnation will lead to a higher carbohydrate yield, increased pulp strength, less reject content and a narrower kappa number distribution [1].

Figure 3. Hydroxide concentration gradient in a wood chip. Illustrating a sufficient and insufficient impregnation

The most important factors to obtain a high degree of impregnation are:

- Chip thickness
- Concentration of active chemicals
- L:W
- Temperature
- Removal of entrapped air

The dimension of the wood chips is the most important factor for penetration, the degree of impregnation can be improved by using thin wood chips, in which the length of diffusion is shorter. Thus, leading to less internal mass transfer resistance [18, 19]. The driving force for diffusion is the concentration difference, if high alkali concentrations in the free liquor is introduced the diffusion in the capillaries of the cell wall will be more rapid, resulting in an increased ion transport. The diffusion can be further enhanced by means of a higher liquor-to-wood ratio. Increasing the L:W gives an increment of active ions (hydroxide and hydrogen sulphide) at the same concentration. Beneficially, a higher concentration of active chemicals can be achieved for the duration of the impregnation [5, 6].

The impregnation can be further improved by exposing the chips to pre-steaming for the purpose to remove entrapped air. Increasing the temperatures will also lead to an improved mass transfer since reaction rates increases with higher temperature [19]. Above 150ºC the reaction rates are higher than mass transfer. Studies have shown that the free liquor successfully can be transferred to the internal area without increasing the concentration of the internal alkali, due to the alkali consuming reactions in the cell wall [19].
2.6 Path of penetration

The impregnation initiates as liquid penetrates the wood matrix through cavities and capillaries in the wood. The penetration of liquor can occur in radial, longitudinal and tangential direction. For hardwood, the capillaries are primarily the vessel elements which are penetrated through the longitudinal direction. The initial penetration occurs through vessels or fibre lumina that are in contact to the chips surface and continues until the cavities and air-filled voids are completely occupied with liquor, seen in Figure 4 and Figure 5. The penetration is influenced by the pore size distribution of the wood, therefore, in hardwood, considerable penetration occurs in the vessel systems, where the rate is driven by the pressure gradient and proceeds in a relatively rapid pace compared to diffusion [20].

Figure 4. Illustration of the initial penetration in the longitudinal direction, including an enlargement of a pit membrane.

Figure 5. Illustration of the subsequent penetration and diffusion.

Figure 6. This illustration demonstrates the diffusion that proceeds after completed penetration.
When the structure is filled with liquor (Figure 5), penetration of chemicals cannot continue, instead diffusion takes place. Diffusion occurs as ions are transported into the fibre walls and is controlled by the concentration of dissolved active chemicals according to Fick’s law of diffusion and the effective capillary cross-sectional area (ECCSA) [21, 22]. Diffusion is independent of the presence of vessel cells, instead the diffusion can occur across the cell wall, being limited to the total cross sectional area [23]. Therefore, diffusion is dependent on the inherent density of the wood and the cell wall swelling that prevails under alkaline conditions. Due to the structure of the wood, the area of paths available for diffusion is significantly higher in the longitudinal direction. However, when submitted to the alkaline solutions of pH>13 the fibres swell and the ECCSA in radial and tangential direction increases greatly. This phenomenon can be seen in Figure 7

![Diagram](image)

*Figure 7. The ECCSA in longitudinal, radial and tangential direction at different pH [21, 23]*

The angiosperms cells are connected by “pits” in the radial direction, uniting the neighbouring cells. Common for hardwood is that slits in vessels also can occur between tangential walls, although more common if several vessels are adjacent to each other. The penetration from the vessel cells usually continue to libriform cells, vertical parenchyma and ray cells through pits, such as scalariform perforation plates of the cell wall or ray cell channels that provides lateral movement of reagents [24, 25]. According to Wardrop and Davies, the penetration through ray cells take place faster than the surrounding fibres [24]. In heartwood, development of tylose in the vessel cells greatly reduce the penetrability. Penetration of parenchyma is more accessible than fibres because the parenchyma has more pits and a thinner cell wall than the fibres [24]. In short, the reagents penetrate vessel cells (Figure 4) in which further penetration take place through pits to the adjacent cells lumen (Figure 5). From the lumen the reagent diffuse through capillaries of the cell wall passing the S3 into the S2 layer further to the more porous and more lignin rich S1, P and ML [24] (Figure 6).

From a plant morphological standpoint, distinctions of the degree of penetration can be seen. Early-wood have fibres with a wider lumen and a cell wall with a higher degree of perforation, it is therefore easier to penetrate the late-wood [26]. The distribution of cooking chemicals will differ depending on the morphological differences in hardwood species. For example, a diffuse porous specie will have a more uniform penetration than a ring porous specie. In softwood, the differences in penetrations of sapwood and heartwood has also been found [27, 28]. The rate of penetration in sapwood can be 4-times faster than in heartwood, but sapwood may have more variations [28, 29]. Furthermore, birch is more easily penetrated than spruce and pine. Even though birch is a dense wood the accessibility is granted by the wide vessel elements [30].
2.7 Impregnation reactions

During the impregnation procedure, several different reactions occur as the active chemicals diffuse and react with the wood components. Many reactions take place during the impregnation, including physical dissolution. However, the main reactions during impregnation are: deacetylation, peeling and stopping reactions, alkaline hydrolysis and delignification reactions.

2.7.1 Deacetylation

Most hardwoods are highly acetylated, representing ~3-4\% of the o.d.w, where the largest portion is found on the hemicelluloses [31]. The acetyl groups are mainly found on the glucuronoxylan part of the hemicelluloses. When alkali is introduced the acetyl groups are removed from the hemicellulose. The deacetylation reaction changes the physical characteristic of the cell wall and makes it more accessible [32]. In kraft cooking the pH is high (>11), these alkaline conditions will make carboxylic groups act like acids, in which they dissociate. The deprotonation will make the fibres swell, increasing the ECCSA. In turn, deacetylation also contributes to more diffusion paths as acetyl groups often are bonded to carboxylic groups. Thus, the deacetylation removes interconnected crosslinks [21, 33]. An example of this is the increased accessibility of birch when submitted to deacetylation. The birch is hypothesized to have strong internal hydrogen bonding between acetyl and hydroxide groups. It is then proposed that the deacetylation remove the crosslinks. Hence, minimizing the constraints towards fibre-swelling [21]. Besides the swelling, an improved capacity of ion transportation is obtained, promoting further pulping. The result of the deacetylation is an accumulation of sodium acetate, which will be found in the spent liquor [21]. An illustration of the xylan’s acetyl and carboxylic groups can be seen in Figure 8.

![Figure 8. Molecular structure of glucuronoxylan. Structure made by author with inspiration from [34].](image)

Deacetylation is the most prominent reaction occurring in the impregnation phase and consumes most of the alkali under impregnation. Studying Figure 9, one can see that the stoichiometric consumption of the deacetylation reaction and the total consumption of alkali is in close proximity. This means that deacetylation is the most significant reaction, but that other reactions also consume alkali in the impregnation phase.
Figure 9. The effect of deacetylation on the total consumption of alkali [35]

Since deacetylation is the main reaction during impregnation it can be seen as an index for the action rendered by the alkali. According to Zanuttini. et al., wood acts as a glassy polymeric solid. This means an evolving boundary region separates an inner unreacted core of the wood that has not been reached by the alkali from an outer swollen shell. These two regions are distinguished by a reaction zone. It is in the reaction region the deacetylation and other alkali consuming reactions occur [22, 33]. This render the opportunity to model the alkali action on wood according to the shrinking core phenomenon [36]. The zones can be seen in Figure 10.

Figure 10. The shrinking core model of wood chips in an alkaline solution. Figure modified with permission by Elisabet Brännvall [37]

The reaction front will progressively move towards the core of the chips. This is an interesting view to analyse the impregnation, since diffusion in the heterogeneous and anisotropic wood structure does not follow Fick’s law of diffusion [38], since upon advancement of the chemical front the diffusion properties varies. The deacetylation analogy may sufficiently provide information of how far gone the impregnation is. A homogeneous impregnation is synonymous with obtaining an efficient cooking. Therefore, having a low degree of acetyl groups throughout the chips after impregnation is a sign of a sufficient impregnation, seen in Figure 11.
Besides deacetylation of xylan, pectins can also be deacetylated. In Figure 12, one can see the homogalacturonan acetylated groups and the deacetylation when introduced to hydroxide ions. The galacturonic acids are esterified with acetyl groups, positioned at the C-2 or C-3 hydroxyl [39].

---

**Figure 11. Homogenous and inhomogeneous impregnation of chips.**

**Figure 12. Acetylated and methylated homogalacturonan when interacting with hydroxide ions. Molecular structure made by author.**
2.7.2 Peeling and stopping reactions

Prevalent in the impregnation phase is the carbohydrate peeling reactions. The reactions transpire as polysaccharides are peeled from the reducing end groups [14], usually called primary peeling [21]. Secondary peeling is when alkaline hydrolysis has taken place on the carbohydrates, creating new end-groups that can be submitted to further peeling [21]. The alkaline peeling requires high temperature. Due to the moderate temperatures in impregnation, the peeling of cellulose is not predominant, although the hemicelluloses are much more prone to degradation as they inherent a low DP and an amorphous structure [14]. In the case of hardwood, being rich in xylan, one would believe that the losses of xylan would be great. Interestingly, most xylan is dissolved during the pulping process and is found as a polysaccharide in the liquor [21].

![Figure 13. Schematic reaction mechanism for the end-wise peeling. Molecular structure drawn by author.](image)

Kraft pulping of hardwood obtains higher carbohydrate yields than kraft pulping of softwood. Due to xylan’s intrinsic resistance towards alkaline pulping [21]. The accumulation of peeled-off groups is formed into acids and are found in the liquor as different hydroxy acids, acetic and formic acid. For each peeled off monosaccharide unit, 1.6 acid equivalents are produced [21]. Since the peeling reactions is prevalent in the initial phase of the cooking, a significant amount of alkali (60% of the charged alkali) is consumed to neutralize the hydroxy acids that were peeled from the polysaccharide chains and the acetic acid from deacetylation. Green et al., found that the peeling reactions exhibits a linear relation with temperature and has a constant reaction rate above alkali concentrations of 0.5 mol/L. The authors also concluded that the peeling reactions is unaffected by the sulphidity and that peeling reactions also are prevalent at higher temperatures [40].

The peeling-reactions are interrupted by the competing reactions called stopping reactions, in which stable carboxylic acid groups are formed at the reducing end [21]. The conversion hinders the peeling process to continue, thus, the carbohydrate losses comes to a halt.
2.7.3 Alkaline hydrolysis

At higher temperatures in alkaline conditions the cellulose chain can be randomly cleaved leading to depolymerization, seen in Figure 14. The hydroxyl group at the second carbon is ionized, resulting in an attack of the first carbon and the bond of the glucose unit is cut from the chain [21]. In addition to the new shorter carbohydrate chains, new reducing end-groups is now available for further peeling reactions to transpire. This is the aforementioned secondary peeling (section 6.3). Since the alkaline hydrolysis generally takes place at higher temperatures the reaction does not contribute to large losses during the impregnation phase. The most prominent effect of the alkaline hydrolysis is a lower viscosity, due to an average loss in DP in the pulp.

![Figure 14. Simplification of the alkaline hydrolysis reaction. Figure created by author, inspiration from [41].](image)

2.7.4 Lignin reactions

The most abundant linkages in the lignin structure are α and β-aryl-ether bonds, the cleavage of these linkages are also the main cause of lignin degradation during kraft pulping [7, 21]. In the lignin matrix, the most easily cleaved linkage is the α-aryl-ether bonds in phenolic arylpropane units, giving an elimination of the α-substituent. The cleavage results in a formation of a quinone methide structure. The prerequisite for this formation is the absence of additional β-aryl-ether bonds and an ionization of the phenolic group by the alkaline action. The phenolic β-aryl-ether bond can further be attacked by hydrogen sulphide ions in a rapid pace, leading to lignin degradation [41]. Delignification reactions on phenolic β-aryl ether structures can be seen in Figure 15. The sulphur bound to the structure will subsequently reoccur in the cooking liquor. Unlike hydroxides the sulphides are not consumed, rather sorption occurs.

![Figure 15. Reactions occurring for phenolic β-aryl ether structures during kraft pulping. Figure made by author, inspiration from [41].](image)
Kraft delignification can be divided into three phases, separated by different kinetics; initial, bulk and residual phase delignification. For the impregnation, the initial delignification is of interest and will be the focus in this segment. In the initial delignification, removal of α and β-aryl-ether bonds to phenolic groups are the main reactions. β-aryl-ether bond cleavage can also occur in non-phenolic groups but at a much slower rate. The rate of the reaction is controlled by the concentration of hydroxide ions. The reaction can be seen in Figure 16. The lignin structure also includes other C-C bonds, cleavage of these bonds can lead to elimination or reduction of side groups. One critical example is the formation of enol ether from the quinone methide intermediate after α-aryl-ether cleavage. The consequence of this formation is a structure that is alkaline resistant [7]. To prevent this formation a high hydrogen sulphide charge can be utilized, this is one of the main characteristics of EI (section 7.1) as a high charge of HS\(^-\) is used. Similar is the cleavage of methyl-aryl-ether bonds. The methoxyl groups are cleaved primarily by hydrogen sulphide ions, but can be attacked by hydroxide ions as well. Finally, different condensation reactions can proceed during pulping [41].

![Figure 16. Cleavage of β-aryl-ether bonds on non-phenolic lignin units. Figure made by author, inspiration from [41]](image1)

Hardwood lignin is rich in sinapyl alcohol which in turn contains many β-aryl-ether-bonds [41]. During pulping, the rate determining delignification reaction is cleavage of the β-O-4 bonds, thus, hardwood is faster delignified than softwood [7].

![Figure 17. Formation of enol ether. Figure made by author, inspiration from [41]](image2)

The delignification in the initial phase is known to remove around 20% of the lignin content [7]. Justifiably, research has shown that the impregnation phase can reach a maximum lignin removal of 23% if an E.A. of over 12% is utilized. After a E.A. of 12% the lignin removal is unaffected by the hydroxide charge, subsequently, the lignin removal levels out and becomes constant at the 23% mark [42]. Furthermore, it was found that an E.A. over 12% does not
promote carbohydrate degradation and a higher [HS]/[OH] ratio does not seem to affect the degradation of carbohydrates during the impregnation phase [42]. There is also a lack of information regarding hydrosulphide reactions with carbohydrates. However, contemporary research claim that hydrosulphides do not primarily react with carbohydrates [30].

2.8 Dissolution and degradation of xylan

Hardwood species are rich in xylan which in turn has 4-O-methyl-α-D-2 glucuronic acid (MeGlcA) groups linked to the xylan backbone, found on 10-20% of the xylose units. During pulping the MeGlcA groups gets attacked by hydroxide ions, the groups are partially removed from the backbone, releasing methanol as a reaction product. Consequently, another substituent can be released from the structure, the so-called Hexenuronic acid (HexA) [41, 43]. This reaction does not directly lead to a loss in yield, but has a significant impact on the kappa number as it is a chemical consuming molecular structure [21]. The amount of HexA will level off as the cooking proceeds, since the dissolution and degradation of the molecular structure becomes much higher than the formation [21]. For hardwood species, the maximum HexA content will be found at the end of cooking, due to the slow rate of HexA formation throughout the cook. In addition, the HexA formation will increase with increased amount of hydroxide ions [44].

The glucuronic acid of the xylan makes it prone to dissolve in alkaline conditions. In contrast to peeling, the dissolution represents 5 times more loss of xylan [46]. Xylan is somewhat resistant towards the endwise-peeling reaction (primary peeling), the galacturonic acid undergo changes during alkaline conditions that makes it less inclined to the peeling [47]. Dissolution is a larger issue, especially at high E.A. The higher the E.A. the more xylan will be dissolved and degraded. However, with E.A. over 15% the removal of xylan becomes relative constant. Maximum removal of xylan during the impregnation phase is 28%, under conventional conditions for Eucalyptus wood [42].
2.8.1 The Donnan effect and ionic strength in kraft cooking

In kraft cooking, the active chemicals have counter ions to balance the charge, in other words, to reach an electric neutrality. In terms of HS⁻ and OH⁻ the counter ion is Na⁺, which can be seen in technical terms. In this study, Na₂CO₃ is utilized in order to control the ionic strength of the white liquor. Having a large portion of cations can be very beneficial in cooking of hardwood, but can also contribute with some drawbacks, one of which is the reduced solubility of lignin. Thus, increasing the ionic strength will lead to a lower delignification [48]. However, it is not the chemical reaction rates that are mitigated, instead the phenomenon is described by the Donnan effect [49].

For impregnation, the Donnan effect can be described as follows: impregnation initiates as hydroxide ions diffuse into the chips. In the chips, ionization of acetyl, carboxyl and other functional groups produce a negative charge in the area of the reactions, giving a swollen wood shell, see Figure 10. The ionization of acid groups on the fibre wall will establish a concentration gradient as the acid groups cannot leave the gel between the bound and free liquor [49]. This produces an osmotic effect, resulting in water diffusing into the fibres. An electric potential is established over the membrane. Development of the negative charge in the bound liquor counterbalances the concentration of hydroxide ions, preventing [OH⁻] to be even on both sides of the membrane. At the same time, the negative charge in the bound liquor attracts sodium ions to migrate from the free liquor (contributed by NaOH, Na₂S and Na₂CO₃) to the bound liquor in the fibre wall. This leads to a higher [Na⁺] in the bound liquor than in the free liquor, which has been seen by several researchers [50, 51]. The high ionic strength will retain the lignin in the fibre wall, thus, lignin fragments cannot leave the bound liquor. This is why delignification decreases with higher ionic strength. In cooking, this will lead to a larger amount of residual lignin [48], but in impregnation where delignification already is constricted a higher ionic strength can be advantageous.

In the laboratory scale, the ionic strength is controlled with either NaCl, Na₂CO₃ or Na₂SO₄. This thesis utilizes a Na₂CO₃ stock solution. Na₂CO₃ has shown to be beneficial when impregnating hardwood species, since it can mitigate the effect calcium ions has on lignin solubility. CO₃²⁻ can precipitate the naturally abundant calcium (CaCO₃), which was shown by Lundqvist et al., giving an almost 50% reduction in kappa number compared to using NaCl at same parameters [52]. This justifies the use of Na₂CO₃ in this thesis, since the main raw material is birch.

2.8.2 Other alkali consuming reactions

A large amount of carboxylic acid, acetic acid, formic and hydroxy acids are formed from the unselective nature of kraft cooking. Likewise, these acids become neutralized by the alkali, consuming a substantial amount of alkali. In kraft pulping of birch, 57-71% of the charged alkali is used to neutralize acids throughout the cook. About 1/3 of the total amount of produced acids are originating from the impregnation phase [53]. Pectins are rapidly dissolved in alkaline solutions [54]. An alkali consuming reaction is the hydrolysis of methylated pectins. In an alkaline pre-treatment performed by Konn et al., it was shown that demethylation of pectins were responsible for 10-15% of the total alkali consumption on a spruce wood. Pectins can therefore be identified as a factor during the impregnation phase [55].
2.9 Impregnation methods

This thesis will investigate three different impregnation methods; Extended Impregnation (EI), high alkali impregnation (HAI) and conventional impregnation (REF).

2.9.1 Extended Impregnation

Different techniques to maintain the carbohydrate yield has been proposed. One is the Extended Impregnation (EI). The idea of EI is to utilize lower temperatures and higher L:W at a prolonged duration of time. Since high temperature and hydroxide concentration inflicts strongly with carbohydrate degradation the method can obtain higher carbohydrate yields, however, decreasing the production rate. The foundation of the EI method relies on the diffusion and reaction rates. At a given temperature the rate of diffusion is lower than the rate of reaction. Therefore, the rate of reaction changes significantly faster with temperature than diffusion, see Figure 19. Prolonging the impregnation and lowering the temperature ensures proficient diffusion whilst limiting the chemical reactions [5, 6].

![Figure 19](image)

Figure 19. Representation of the relative rate change in alkali-consuming reactions and temperature.[5]

An important parameter of the EI is the high L:W, giving an increased number of hydroxide ions without increasing the concentration. In turn, more alkali will be available throughout the cook, never reaching critical levels. A core idea of the EI is to shift the defibration point to a higher kappa number to give less reject content at a given kappa number. Consequently, the cook can be terminated at a higher kappa number [5, 6]. Having a prolonged impregnation will affect the production rate, unless large impregnation vessels are used.
2.9.2 High alkali impregnation

In contrast to EI, the High Alkali Impregnation (HAI) method utilizes an almost opposite approach. The high alkali impregnation incorporates an increased concentration of E.A. during the impregnation stage to obtain a higher pulp yield whilst increasing the production rate [2]. The basis of HAI is the high E.A. charge, giving higher diffusion rates into the chips. Since diffusion is the rate controlling mechanism, possibilities to restrict temperature and time is obtained. As a result, less strain is subjected to the carbohydrates due to the temporal effect that otherwise would cause more peeling reaction.

Deacetylation is the most alkali consuming reaction during impregnation. Consequently, the acetyl groups must be removed from the wood in order for bulk delignification to take place. Increasing the alkali concentration increases the rate of deacetylation, improving the production rate as cooking may proceed faster. Thus far it has been proven that a 2% yield increase can be obtained with spruce [2].

In justification of the HAI method is the proposed increase of the stopping reaction at high alkali concentrations [56], preventing peeling to further progress. According to Lai et al. the peeling and stopping reaction rates are highly dependent on the alkali concentration. This was found by studying the behaviour of the reactions when submitting a polysaccharide amylose to different levels of alkali [57]. The peeling reaction rates increases with increased alkali concentration up to 0.1 mol/l, then remains unchanged. Similar results was found by Green et al. for wood polysaccharides, seeing a constant behaviour after 0.5 mol/L [40]. Meanwhile, the stopping reaction rate increases up to a hydroxide concentration of 1.5 mol/l. Consequently, the stopping reactions are favoured over the peeling reactions at high alkali concentrations. When the alkali concentration is increased the stopping reactions are enhanced and an increment in glucomannan yield is obtained. This phenomenon has been seen in several studies [2, 56, 58].

In Table 1, a comparison of the methods can be seen.

<table>
<thead>
<tr>
<th>High Effective Alkali</th>
<th>Extended Impregnation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.7 [OH⁻]</td>
<td>0.7 [OH⁻]</td>
</tr>
<tr>
<td>+ Fast deacetylation</td>
<td>+ Preserve carbohydrates</td>
</tr>
<tr>
<td>+ Fast diffusion</td>
<td>+ Increased xylan yield (due to reprecipitation of dissolved xylan and decreased degradation due to less hydroxide concentration) [42]</td>
</tr>
<tr>
<td>+ Promotes stopping reactions over peeling [57]</td>
<td></td>
</tr>
<tr>
<td>+ Increased rate of delignification</td>
<td>+ High L:W = higher total amount active ions at the same concentration, which leads to a higher concentration of active chemicals throughout the impregnation phase</td>
</tr>
<tr>
<td>+ Higher yield of glucomannans [58]</td>
<td></td>
</tr>
<tr>
<td>+ Possibly less peeling due to a temporal reduction</td>
<td></td>
</tr>
<tr>
<td>- Faster dissolution and degradation of xylan [42]</td>
<td>- Proceeds for a longer duration = reduced production rate</td>
</tr>
</tbody>
</table>

Table 1. Foreseen occurrences in comparison to a conventional impregnation procedure
3 Experiments

The main objective of the experimental part was to study the consumption of chemicals during the impregnation phase and its subsequent consequences. The study thoroughly monitored the consumption of hydroxide ions, whilst also investigated the sorption of hydrogen sulphide ions. The chemical profiles were assessed in both the free liquor surrounding the chips after impregnation and the liquor entrapped inside the chips. The pH and dry solid content of the liquors were also analysed. In addition, the wood yield after impregnation was assessed.

The impregnation study was followed by kraft cooking to evaluate how impregnation at different conditions affects the subsequent cooking phase. The pulps attained after cooking were assessed by analysing the screen yield, reject content and residual lignin (kappa number determination).

3.1 Materials

Birch (Skärblacka, 2012), Eucalyptus Urograndis (Uruguay, 2008) and a mix of Swedish spruce/pine was used in the experiments. The chips were screened to obtain a chip thickness of 4-8 mm, no bark or knots were included in the samples. A stock solution of NaOH and Na₂S were prepared for the white liquor. The sodium hydroxide stock solution was obtained by dissolving pastilles of puriss grade in deionized water. The hydrogen sulphide stock solution was obtained by dissolving technical grade flakes of sodium sulphide in deionized water.

3.2 Impregnation

The impregnation procedure was performed with steel autoclaves, each with a volume of 2.5 dm³. All impregnations performed had samples of 150 g oven dry (o.d.w) chips. The impregnation procedure was initiated as the chips were deaerated in the steel autoclaves for 30 minutes. The white liquor was prepared from stock solutions of NaOH and Na₂S. All experiments were performed with the same initial charge of [HS⁻], 0.35 M for all samples. The [OH⁻] of the white liquor was prepared to yield 0.7, 1.3 and 1.7 M [OH⁻]. In turn, the white liquor was prepared to have an intended liquor-to-wood ratio of 3.5:1 for the samples with 1.3 M and 1.7 M and 8:1 for the samples with [OH⁻] of 0.7 M. The parameters for the 3 different impregnation methods can be seen in Table 2. Accordingly, the three hydroxide concentration levels were performed at the temperatures 115°C, 105°C and 95°C. From the vacuum obtained in the autoclaves, the white liquor was suctioned into the vessels.

<table>
<thead>
<tr>
<th></th>
<th>[OH⁻] [mol/L]</th>
<th>Initial NaOH charge [g]</th>
<th>[HS⁻] [mol/L]</th>
<th>Initial Na₂S charge [g]</th>
<th>[Na₂CO₃] [mol/L]</th>
<th>L:W</th>
</tr>
</thead>
<tbody>
<tr>
<td>EI</td>
<td>0.7</td>
<td>33.6</td>
<td>0.35</td>
<td>32.8</td>
<td>0.045</td>
<td>8:1</td>
</tr>
<tr>
<td>REF</td>
<td>1.3</td>
<td>27.3</td>
<td>0.35</td>
<td>14.3</td>
<td>0.1</td>
<td>3.5:1</td>
</tr>
<tr>
<td>HAI</td>
<td>1.7</td>
<td>35.7</td>
<td>0.35</td>
<td>14.3</td>
<td>0.1</td>
<td>3.5:1</td>
</tr>
</tbody>
</table>

The autoclaves were positioned in a glycol bath where the impregnation took place. The autoclaves were placed with an inclination to ensure homogenous mixing when the autoclaves
The first impregnation series of birch chips were performed in an electrically-heated glycol bath, whilst all other impregnations were performed in a steam-heated glycol bath. The autoclaves were placed in the glycol bath for 10 minutes to acquire a sufficient temperature profile in the autoclaves before initiating the actual impregnation.

### 3.3 Evaluation of spent liquor and impregnated chips

When the impregnation was completed the autoclaves were placed in a water bath for cooling. The spent liquor from the impregnation was drained from the chips and collected. The volume and mass of the drained liquor ($V_{\text{drained}}$, $m_{\text{drained}}$) was analysed and the chips were collected in bags, which were weighted and recorded. In addition, the bags containing the chips were placed in a centrifuge followed by a centrifugation for 1 min to further remove liquor from the chips surface, the weight prior and after the centrifugation was recorded ($\Delta m$). The density of the drained free liquor ($D_{\text{free}}$) was assessed by knowing the volume and weight of the liquor, see equation 5. In turn, the drained liquor lost during centrifugation could be added to the free liquor portion, according to equation 6.

The chips were further emerged in deionized water (1.3 M = 2 L, 1.7 M = 3 L, 0.7 M = 1 L), where they were contained for 48h under moderate shaking to reach an equilibrium with the motive to remove the bound liquor inside the chips. The volume of bound black liquor was assessed by subtracting the volume of free black liquor from the total volume, seen in equation 7. The [HS⁻] and [OH⁻] of the drained free black liquor was determined with two titration methods (section 3.4). Since the bound liquor is diluted during leaching, equation 8 must be used to obtain the true [OH⁻] of the bound liquor. The concentrations were further used to calculate the total alkali consumption during impregnation, according to equation 9. The leached liquor was too depleted of hydrosulphide ions, thus, only the residual alkali was tested on the bound liquor. An overview of the evaluation procedure can be seen in Figure 20.

After leaching, the chips are washed for 10 hours, followed by over-night drying at 105°C. Afterwards, the chips are weighted to obtain the yield. pH was determined for all liquors; white liquor, black liquor and bound black liquor. The Dry Solids (DS) of the drained free liquor and bound liquor were assessed by weighting 10 ml and 25 ml, respectively. The liquids were placed in heating cabinets for at least 24 hours, thereafter the dried samples were weighted. An overview of how to obtain the free and black liquors can be seen in Figure 45.
Figure 20. Evaluation of spent liquor and chips.

\[ D_{\text{free}} = \frac{V_{\text{drained}}}{m_{\text{drained}}} \]  \[ V_{\text{Free}} = V_{\text{drained}} + \Delta m \cdot D_{\text{free}} \]  \[ V_{\text{Bound}} = V_{\text{tot}} - V_{\text{free}} \]  \[ C_{\text{Bound}} = \frac{C_{\text{b,diluted}} \cdot (V_{\text{deionized}} + V_{\text{bound}})}{V_{\text{bound}}} \]  \[ TAC = C_{\text{initial}} \cdot M_{w, NaOH} \cdot \frac{V_{\text{tot}}}{m_{w}} - \frac{C_{\text{free}} \cdot V_{\text{free}}}{m_{w}} - (C_{\text{bound}} \cdot V_{\text{bound}}) \cdot M_{w, NaOH} \]
3.4 Kraft cooking

Kraft cooking was performed in order to evaluate the influence of the impregnation phase on the subsequent cooking procedure. All cooks were initiated with an impregnation stage, according to aforementioned principles (section 3.2). The cooking of chips was performed with the same steel autoclaves as utilized in the previous impregnation stage. The autoclaves were positioned in a steam-heated glycol bath where impregnation and cooking took place. All cooks were performed under uniform conditions. Likewise, after impregnation the autoclaves were placed in a cooling bath, followed by addition of WL or removal of BL in order to obtain an initial hydroxide concentration of 0.6 M and L:W = 5, in each autoclave, according to Table 3. The autoclaves where then positioned back into the glycol bath for cooking at 155°C. The impregnations prior to kraft cooking were treated at 105°C and involved samples of 1.7 [OH⁻], 1.3 [OH⁻] and 0.7 [OH⁻], in which were further cooked to a specified H-factor. The heating profile of the impregnation and kraft cooking procedure can be seen in Figure 21. The conditions for all impregnations with subsequent cooking can be seen in Table 3.

After cooking, the chips were collected by removing the black liquor followed by washing with deionized water for 10 hours. Thereafter, the chips were defibrated in a NAF water jet defibrator. The apparatus had a Wennberg screen with a slit width of 2 µm. From defibration, screened fibres and reject content was obtained. The screened fibres or pulp was centrifuged to reach a dry content of approximately 25%. The centrifuged pulps were placed at room temperature for at least 4 hours, in order to acclimatize to yield a homogenous moisture content. This was followed by disintegrating the pulps. Afterwards, the pulp was weighted and samples were taken out to measure the dry content. The samples were placed in a drying cabinet overnight at 105°C. Finally, the kappa number of the resulting pulps were measured.
Table 3. Conditions for the cooking process

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>HAI</td>
<td>30</td>
<td>105</td>
<td>0.6</td>
<td>0.4</td>
<td>400</td>
<td>155</td>
<td>Birch</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>105</td>
<td>0.6</td>
<td>0.4</td>
<td>400</td>
<td>155</td>
<td>Birch</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>105</td>
<td>0.6</td>
<td>0.4</td>
<td>600</td>
<td>155</td>
<td>Birch</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>105</td>
<td>0.6</td>
<td>0.4</td>
<td>700</td>
<td>155</td>
<td>Birch</td>
</tr>
<tr>
<td>REF</td>
<td>30</td>
<td>105</td>
<td>0.6</td>
<td>0.4</td>
<td>400</td>
<td>155</td>
<td>Birch</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>105</td>
<td>0.6</td>
<td>0.7</td>
<td>600</td>
<td>155</td>
<td>Birch</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>105</td>
<td>0.6</td>
<td>0.7</td>
<td>700</td>
<td>155</td>
<td>Birch</td>
</tr>
<tr>
<td>EI</td>
<td>120</td>
<td>105</td>
<td>0.6</td>
<td>0.4</td>
<td>400</td>
<td>155</td>
<td>Eucal</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>105</td>
<td>0.6</td>
<td>0.4</td>
<td>400</td>
<td>155</td>
<td>Birch</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>105</td>
<td>0.6</td>
<td>0.4</td>
<td>600</td>
<td>155</td>
<td>Birch</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>105</td>
<td>0.6</td>
<td>0.4</td>
<td>700</td>
<td>155</td>
<td>Birch</td>
</tr>
</tbody>
</table>

### 3.5 Analyses

#### 3.5.1 Hydroxide titrations

The hydroxide concentration in the white liquor was determined according to SCAN-N 2:88. Determination of the residual alkali concentration was performed according to SCAN 33:94. The method is a potentiometric titration with hydrochloric acid. The titration calculation accounts for the acid consumption due to organic components in the black liquor, compensating by utilization of a correction factor. This method is used for the free and bound black liquor obtained from the impregnation procedure. The method has an error of ± 0.03 mol/L [OH⁻].

#### 3.5.2 Hydrogen sulphide titration

The hydrogen sulphide content is measured with a potentiometric titration with a silver nitrate solution according to SCAN-N 31:94. Much caution must be taken when storing and handling the liquor samples as hydrogen sulphide is easily oxidized. The method has an error of 0.03 mol/L [HS⁻].

#### 3.5.3 Dry solids determination

To understand how much solid content that was extracted during impregnation or cooking a drying procedure was utilized. 10 ml of free BL or 25 ml of entrapped BL was weighted in glass containers and dried for at least 24 hours. Thereafter, the glass containers were weighted once more in order to obtain the amount of dry solids in the samples. Keep in mind, lignin is solubilized and will be present to some degree in the samples. Lignin has the propensity to create a gel layer, which retain water as the layer protects the substance beneath to be exposed. Therefore, some samples may obtain an insufficient evaporation of water.
3.5.4 Kappa number determination

Kappa number, a method to analytically assess the lignin content in a pulp. The kappa number is correlated to a change in lignin content, but can give faulty values due to HexA content or other permanganate consuming substances. Therefore, the kappa number may not be fully reliable on evaluating the lignin content in pulped hardwood species. The kappa number is defined as the volume of KMnO$_4$ (0.1 N) consumed per 1 gram of oven-dried pulp [8]. The kappa number determination was performed according to ISO 302.

3.6 Impregnation repeatability

Repeatability of the experimental phase is an important aspect for future scientific endeavours. Likewise, the experimental phase is designed to have a high repeatability. However, deviations in experimental procedures are inevitable. The impregnations performed in a laboratory scale can yield different results. For example, variabilities due to inhomogeneous stock solutions, raw materials, changes in humidity or use of different equipment give rise to deviations. To illustrate the repeatability of the impregnations in this thesis, all impregnations were performed twice under the same conditions. The repeatability in impregnation (0.7 M, 115 ºC) can be seen in Table 4. In the table, yield, dry solids and [OH$^-$]$_{free}$ is illustrated.

<table>
<thead>
<tr>
<th>0.7 M 115 ºC</th>
<th>Yield [%]</th>
<th>[OH$^-$]$_{free}$ [mol/L]</th>
<th>Dry solids [g/kg wood]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Impregnation 1</td>
<td>74.21</td>
<td>0.22</td>
<td>534</td>
</tr>
<tr>
<td>Impregnation 2</td>
<td>74.27</td>
<td>0.26</td>
<td>587</td>
</tr>
<tr>
<td>Average</td>
<td>74.24</td>
<td>0.24</td>
<td>560</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>0.03</td>
<td>0.02</td>
<td>26</td>
</tr>
</tbody>
</table>

Table 4. Repeatability in impregnation
4 Results and discussion

The results and discussion chapter is divided into several parts. The first part will involve impregnation of birch and eucalyptus chips. The second part will encompass the cooking results. The final chapter will involve a conclusion by comparing the three impregnation procedures and their effect on cooking, in order to find the most efficient impregnation conditions.

The main objectives in the impregnation procedure was to analyse the consumption of alkali, hydrosulphide uptake, accumulation of dry solids and yield. A red line throughout the results is the comparison between High Alkali Impregnation (HAI) and Extended Impregnation (EI), in contrast to impregnations performed with industrially utilized conditions, called reference (REF) in this chapter. The results are divided into segments beginning with mass balances in order to thoroughly illustrate the occurrences in the system and to easier obtain an overview of the impregnation procedure. Thereafter, the alkali behaviour during impregnation will be explained, with focus on the consumption of alkali in free and bound liquors at various conditions. This is followed by subsections describing the impregnation yields, accumulation of dry solids and hydrosulphides behaviour during impregnation.

The latter part of the results will involve cooking of wood chips, where the impact of impregnation on the subsequent cooking will be explained. Lastly, the results will end with an attempt to compare the HAI and EI, with an objective to obtain the most efficient impregnation condition.

Before introducing the results, it must be acknowledged that experimental errors may exist in any quantitative experimental process. Rigorous scientific methods have been used, although deviations may occur due to use of different pipets in titration, humidity variations in the lab, using different bags to remove the surface BL or leaching samples for a prolonged duration.
4.1 Mass balance

Birch chips were impregnated at three different conditions: 18.2% E.A., 42.4% Sulphidity (Reference Impregnation), 23.8% E.A., 34.1% Sulphidity (High Alkali Impregnation) and 22.4% E.A., 66.7% sulphidity (Extended Impregnation) at 95°C, 105°C and 115°C. In Figure 22, a mass balance using the three different impregnation conditions at 105°C is illustrated. The figure demonstrates the impregnation performance after 120 minutes of impregnation.

EI obtains the highest yield and largest total consumption of chemicals. One would believe that a large consumption of NaOH would result in more peeling reactions, leading to lower yields. This is not the case for EI. It could be proposed that the high L:W makes the liquor more dilute but still has a large amount of active ions to mobilize into the wood and react more effectively, namely contributing to more deacetylation and neutralization. Interestingly, EI also bring about more Na$_2$S uptake. In chapter 2.8.2, it was mentioned that hydrosulphides do not primarily react with carbohydrate constituents. Accordingly, the higher uptake of Na$_2$S for EI is most likely due to reactions with lignin. Examining the behaviour of HAI, it is seen that it obtains the lowest yield, almost as high NaOH consumption as EI and lowest uptake of Na$_2$S. In contrast to EI, the chemical consumption in HAI seems less optimal, procuring more peeling reactions. Expectedly, the REF impregnation has yield and consumption in-between the high and low concentration impregnations.

In the following subsections, yield, dry solids, HS$^-$ uptake and OH$^-$ consumption will be discussed in detail.
4.2 Impregnation

Impregnations are initiated as autoclaves filled with chips and impregnation liquor are immersed into a heated glycol bath. At completion, the chips will be surrounded by spent impregnation liquor, which is called free liquor in this thesis. In addition, the chips have absorbed impregnation liquor, this is called bound liquor. These liquors are titrated in order to understand how much alkali that was consumed during the impregnation procedure.

4.2.1 Free and bound liquor

In Figure 23 it is seen that the bound curves have higher hydroxide concentration than the free curves, this may not seem theoretically intuitive as the bound liquor should not be able to hold higher concentrations than the free liquor. However, this has been seen in previous research and is a result from the complicated laboratory procedures [30]. Fortunately, these are systematic errors, which does not affect the interpretation of the results. Therefore, the relation between curves and points are valid.

![Figure 23. OH⁻ concentrations after impregnation, for both free and bound liquor.](image)

In the initial stage of impregnation, the free liquor penetrates and diffuses into the chips. Consequently, chemical reactions transpire in which deacetylation reactions occur rapidly. The chemical activity will open up the structure, providing a higher ion mobility into the chips. Subsequently, the concentration of the bound liquor increases significantly. The first 10 minutes of the impregnation consumes significant amounts of alkali, mainly due to the deacetylation of xylan. During this initial impregnation the dissolution of extractives [41], hydrolysis of...
methylated pectins [55], continuous peeling and neutralization of acids also consume alkali [59]. The decrease in [OH⁻] in free liquor and increase of [OH⁻] in the bound liquor continues until about 20-30 minutes. Thereafter, the free liquor curves levels out but some curves decrease, caused by the ongoing peeling reactions. Although, one would expect that deacetylation continue past the 30 min point, since some chips are not fully penetrated (Figure 31, Figure 32 and Figure 33), even though concentrations of both free and bound liquor seems fairly constant after 30 min. Beyond 30 minutes the alkali concentrations are steady. This does not correlate to a completion of deacetylation. Since the diffusion occurs in a stepwise manner, most chips are not fully penetrated at 30 min. This is especially true for REF and EI conditions where the concentration gradient is smaller. Comparing birch to spruce/pine it is prominent that the birch specie has a much faster penetration and diffusion, showing almost no profile or unreached cores, seen in Figure 32 and Figure 34, both impregnated under HAI conditions.

The total consumption of alkali can be seen in Figure 24 where similar tendencies for EI and HAI can be seen, due to the high total charge of alkali (0.7 M = 224 g/kg wood, 1.7 M = 238 g/kg wood, 1.3 = 182 g/kg wood). Thus, higher charge per kilogram wood give more active molecules that can mobilize from the bulk liquor to diffuse and react with the wood, leading to more consumption. HAI has a high alkali concentration throughout, whilst EI has a concentration profile that does not decrease to much towards the end of impregnation, due to the high total charge. Hence, the availability of alkali is larger and more reactions can occur throughout the process. Hultholm investigated the L:W behaviour by using various L:W ratios, [OH⁻] and temperature. It was found that a higher L:W ratio will provide more ions to mobilize from the bulk and diffuse into the chips. The phenomenon was prominent at all concentration and temperatures. For example, using a [OH⁻] = 0.7 M and L:W = 3:1 and another impregnation of [OH⁻] = 0.7 M and L:W = 9:1, the latter will give a significantly higher concentration inside the chips due to the high L:W [30].

Having high alkali concentration will be cumbersome on the carbohydrate portion. This is in fact the case, as HAI obtains the lowest yield at a specified time of all cases (Figure 28). The alkali consumption at 115ºC is significantly higher than for 95ºC or 105ºC. This could be a consequence of delignification taking place at 115 ºC.
Taking a closer look at the concentration curves of free liquor and bound liquors, seen in Figure 25. Less alkali should be consumed for the eucalyptus since it has less xylan than birch [60]. Otherwise, the birch curves are in a fundamentally correct order. For the free and bound liquor, HAI obtained the highest concentration, followed by REF and EI. Looking at the free curves, highest concentration remained after impregnation at 95°C, since diffusion and chemical reaction rates are suppressed at lower temperatures, less alkali will be consumed. In contrast, diffusion and kinetics are enhanced by higher temperatures, leading to improved consumption. It is therefore reasonable that the curves orders were 95 °C, 105 °C and 115°C. The bound curves have the same behaviour, since the free and bound liquor wants to attain a chemical equilibrium between each other. In large, the initial concentrations have a much larger impact on the remaining concentration than the temperatures. Although, clear differences can be seen at different temperatures. For example, for HAI approximately a 0.1 mol/L difference can be seen between 95°C and 115°C at any point.

![Figure 25. [OH⁻] for the free and bound liquor at different temperatures.](image)

### 4.2.2 Birch vs Eucalyptus

Two impregnation conditions were performed with a lower dilution factor during leaching. The previous impregnation series utilized: HAI (1.7 [OH⁻]) = 3 L, REF (1.3 [OH⁻]) = 2 L and EI (0.7 [OH⁻]) = 1 L. However, in this impregnation series where birch and eucalyptus was analysed the leach was performed with 1 L deionized water for all cases. Resultantly, the curves
in Figure 26 showed a more intuitive behaviour. The figure shows a comparison between birch and eucalyptus with the different impregnation methods at 105ºC.

![Figure 26](image)

*Figure 26. Hydroxide concentration of free and bound liquor for birch and eucalyptus.*

In Figure 26, the birch reaches an equilibrium with HAI at ~60 min but is not seen for the REF nor EI. This could be due to the Donnan effect (Described in segment: 2.8.1). The Donnan effect will give repulsion to OH⁻ ions, however, can be mitigated by a high ionic strength. The concentration of Na⁺ is highest in HAI and lowest for REF. The reason why HAI reaches an equilibrium could be explained by the larger concentration gradient between free and bound liquor, see the mass balance in Figure 22 where HAI clearly has more alkali in the bound liquor. At high concentrations, swelling, chemical reactions and an increase of ECCSA occurs faster, which results in a more porous structure with less resistance to ion transportation.

In wood, the charged groups are primarily carboxyl groups, more specifically from the MeGlcA [21]. In chapter 2.3.2, it was mentioned that xylan is rich in MeGlcA. Therefore, the intrinsic charge of fibres in hardwood is particularly significant. In turn, birch possess more xylan than eucalypt [61, 62], which means birch is more prone to the Donnan effect. The results seen in Figure 26 is in line with previous research on birch impregnation [63], and contrary to others [30]. Egas et al., reached an equilibrium after 200 minutes with 165ºC and a significantly lower alkali charge compared to this thesis. Mättänen and Tikka also studied the hydroxide concentrations after impregnation of eucalyptus, including a pre-steaming procedure that resulted in curves that did not reach an equilibrium within 30 minutes [20]. The authors utilized up to 120 ºC without reaching an equilibrium, although, only using half the initial charge of NaOH compared to a REF impregnation in this thesis. Reaching an equilibrium at 60 min with much higher alkali content is therefore reasonable. Hultholm found a similar tendency,
however, the free and bound curves under similar conditions as in this thesis reached an equilibrium at 30–60 minutes of impregnation [30].

Summarizing Figure 26, HAI reaches equilibrium fastest (~30 min for eucalypt, ~60 min for birch) while REF and EI showed similar tendencies, reaching at equilibrium at ~60 min for eucalypt and ~120 min for birch.

Birch consumed much more alkali than eucalyptus at any duration, seen in Figure 27. The higher alkali consumption for birch could be due to the greater xylan content. Birch (Betula verrucosa) approximately has 27.5% glucuronoxylan, while eucalyptus (globulus) has 19.9 % [60]. More xylan contributes with more acetyl groups and additional uronic acid groups (MeGlcA). The prominent deacetylation reaction and cleavage of MeGlcA or production of HexA will consume alkali. Accordingly, birch should obtain more consumption than eucalyptus, which it does. Another interesting aspect of the eucalyptus impregnation is that HAI attained the highest consumption of alkali, where EI looks similar to REF. This is not seen for the birch. Perhaps the diffusion is harder or for eucalyptus or a retardation of the diffusion is seen. A large concentration gradient perhaps can induce the mobilization of ions which give rise to more chemical activity, while EI and REF does not have the same capabilities due to the alleviated concentration levels.

![Figure 27. Total alkali consumption for birch and eucalyptus at 105°C](image-url)
4.2.3 Yield

The obtained yields from the impregnation experiments can be seen in Figure 28. Yield decreased with higher temperatures, time and alkali concentration. The extent of peeling reactions will increase with higher [OH\textsuperscript{−}], this is clearly seen in Figure 28 as HAI and REF obtains the lowest yields at any impregnation duration. EI with its low [OH\textsuperscript{−}] gave the highest yields at any given temperature and time. When examining the curves, the behaviours seems to be fairly the same in all impregnation cases. Eucalyptus obtained the highest yield, even higher than birch at 95ºC. With an exception for EI, where the curves are similar.

![Figure 28. Yield after impregnation for HAI, REF and EI at various temperatures.](image)

4.2.4 Hydrosulphide

When investigating Figure 29, one must keep in mind that the HS\textsuperscript{−} remaining in the bound liquor cannot be accounted for, as it is readily oxidized after the leaching sequence.

![Figure 29. Uptake of HS at different initial conditions and temperature](image)

For the hydrosulphide sorption, one can see that the temperatures 105ºC and 95ºC have curves that are hard to distinguish at all [OH\textsuperscript{−}] conditions. Surprisingly, the 115ºC curve is easily differentiated from the lower temperatures in all cases. The higher HS\textsuperscript{−} sorption at 115ºC may indicate that delignification reactions have begun. The initiation of delignification seems to appear already at 30 min for all cases at 115 °C. This is a likely phenomenon as sorption in
Lignin is strongly dependent on temperature, but also the hydroxide ion concentration [64, 65]. In turn, the alkali consumption at 115 °C is analogous to the HS⁻ uptake at 115 °C. Figure 24 demonstrates the total alkali consumption, where the increased consumption is especially conspicuous at 115 °C, for all impregnation methods. Although, EI shows a less prominent trend. The increased alkali consumption and hydrosulphide uptake should justify that delignification did occur.

For delignification to begin, the alkali consuming deacetylation reactions must be readily completed. The behaviour at 115°C indicate and support stronger evidence that a complete hydrolysis of acetyl groups has been achieved in the areas at which diffusion has prevailed after 30 minutes. Keep in mind that deacetylation will continue with the evolution of the reaction zone (segment 2.7.1), until the centre of the chip is reached. This does only describe that the reached areas have obtained a complete hydrolysis of acetyl groups. Since no reactions occur between hydrosulphides and carbohydrates [30], it can be determined that the increased uptake of HS⁻ is due to degradation of lignin.

Unlike hydroxide, hydrosulphide is a significantly weaker base. However, it is a strong nucleophile with a distinct reaction pattern, cleavage of β-aryl-ether bonds described in Figure 15. This reaction is competing with hydroxide ions, accordingly, research has found that the uptake of HS⁻ decreases with higher alkali charge [30, 65]. This occurrence is seen in Figure 29, in which uptake is slightly lower in the HAI impregnation compared to reference. In Figure 29, it is clearly seen that the uptake of HS⁻ is significantly higher in EI. The sulphidity charge in EI is 66.7%, in contrast to 18.2% in HAI and 42.4% in REF. Expectedly, having more active ions available will provide more chemical reactions to transpire. In line with previous research, the uptake trends are similar [30]. Figure 29 shows that uptake is rapid until 30-60 minutes, thereafter, the rate of HS⁻ uptake stagnates.

According to Olm et al., the uptake of HS⁻ will increase with higher [HS⁻]:[OH⁻] ratio, until 6:1. Thereafter, the uptake of HS⁻ remains constant [65]. This is not true in this thesis, however, Olm et al. used softwood. In this thesis ratios were: HAI = 4.9, REF = 3.7, EI = 2. The result can be explained as EI had a very high initial charge of HS⁻ compared to the other cases. Higher charges of HS⁻ will increase the HS⁻ uptake, according to Olm et al. In this thesis, HAI had the highest [HS⁻]:[OH⁻] of 4.9, but lowest uptake of HS⁻. EI had the lowest ratio, but resulted in the highest uptake.

### 4.2.5 Dry solids

After impregnation, the resulting free and bound BL contain a substantial amount of organic and inorganic material, in which the composition varies depending on the impregnation conditions. To the organic compounds; polysaccharides, carboxylic acid, extractives, xylan polymers, some solubilized lignin and a minor portion of resin and fatty acids can be found [66-68]. Impregnation of hardwood will rapidly dissolve acetyl groups, galactans and mannans, which will be a significant portion of the organic compounds in the spent liquor [69]. More specifically, BL from birch impregnation will be rich in sodium acetate salt, accumulated by the neutralisation of acetic acid [21]. The main inorganic compounds in the spent liquor are: residual alkali, sodium salts and thiosulphate from oxidation of hydrosulphides [66-68]. In impregnation of eucalyptus, one would also find CaCO₃, obtained from precipitation between the abundant Mg²⁺ in eucalyptus and Na₂CO₃ [52].
In Figure 30 the DS content for HAI, REF and EI is illustrated. The DS content largely increases with impregnation time and temperature, where a fast increase occurs within the first 30 minutes. Analogous to consumption of alkali, within 30 minutes the rapid deacetylation is a significant factor to the increased DS. It is known that higher hydroxide concentrations will provide faster diffusion due to a concentration difference between the free and bound liquor. Therefore, a large concentration gradient will take place resulting in faster diffusion and consequently a faster deacetylation. This is clearly seen for HAI and REF where the concentrations are higher, in contrast to the lower concentration of EI which obtains a smaller slope for birch within the first 30 minutes. However, EI attains more DS than HAI and REF due to a larger initial charge of alkali. The high DS in EI cannot only be explained by dissolution of lignin and carbohydrates. One must remember that EI has a significantly larger charge of Na₂S, which also will result as sodium salt in the spent liquor (see mass balance Figure 22). Lastly, higher alkali charges will provide more active hydroxide ions, that potentially can react with the carbohydrate constituents. Nevertheless, EI obtains the highest yield (Figure 28) which means the alkali consumption was more optimally utilized.

The DS curves in Figure 30 at 105ºC depicts another behaviour. The curves reach a maximum at 30 minutes, followed by a slight decrease to 60 min where it remains relative constant. This is particularly prominent for eucalyptus. Besides the behaviour 105ºC portrays, the curves do not stagnate. This should mean that deacetylation and peeling reactions still prevails, in which peeling increases with temperature and [OH⁻].

From investigating the HS⁻ uptake curves in Figure 29 and DS curves in Figure 30 it can be understood that some DS content at 115ºC is provided by delignification. The HS⁻ uptake was predominantly high for the EI case. Consequently, solubilized lignin could be a significant factor for the DS increase. The continuous increase of DS seen in EI is contributed by the large amount of OH⁻ and its L:W. This keeps the concentration more stable throughout the impregnation, compared to HAI and EI. Even at a latter part of impregnation the [OH⁻] is not diminished, whilst a larger reduction is seen for HAI and REF. This is a probable reason why EI obtains curves that are more linear than HAI and REF.
4.2.6 Chip profiles

One way to obtain a comprehension if the impregnation has been insufficient is by ocular examination of the chips. A sufficient impregnation can be distinguished from an insufficient by visually seeing a profile towards the centre of the chips. An adequate impregnation should obtain chips with no visual profiles. Before observing the chips, keep in mind that it is sometimes hard to distinguish fully impregnated chips from inadequately impregnated chips. The chips sometimes attain brighter spots on the surface, obtained during the photo session as the surface tend to become dry. This should not be confused with the liquid profiles of the chips.

Starting with the reference impregnation, Figure 31, clear profiles can be seen up to 60 minutes of impregnation. For HAI, Figure 32, profiles can be seen until 30 min. Unlike REF and HAI the extended impregnation only have profiles at 10 minutes. In comparison to softwood (Figure 34) the birch impregnations has much less prominent profiles.

![Figure 31. REF chips in profile after impregnation](image1.png)

![Figure 32. HAI chips in profile after impregnation](image2.png)

![Figure 33. EI chips in profile after impregnation](image3.png)

![Figure 34. Chips of spruce/pine in profile after impregnation](image4.png)
4.2.7 HAI vs EI

One of the objectives in this thesis is to compare the different cases in an attempt to evaluate their efficiencies. The two impregnation methods HAI and EI will be compared in order to get a more comprehensive understanding of their impregnation performances. The two concepts have different core principles. EI utilizes a high L:W ratio and low alkali concentration for a prolonged duration, while HAI uses a low L:W ratio and high alkali concentration. The basis of both methods is to obtain a higher yield while gaining other benefits as energy-and chemical savings. The idea of this comparison is to highlight these features.

From the mass balance in Figure 35, HAI obtains a higher yield, whilst EI consumes more chemicals. However, a clear distinction was seen when investigating the profiles of the chips. HAI obtained chips that exhibited cores that had not been reached by liquor (Figure 36). Meanwhile, EI show no prevailing tendency towards this behaviour (Figure 37). Therefore, using HAI for 30 min will possibly result in an inhomogeneous distribution of chemicals. Keep in mind, in industrial impregnations the chips have a moisture content of about 50% which enhances penetration and diffusion significantly. The chips that are subjected to impregnation in this thesis are dry. If advection and diffusion of chemicals is insufficient the subsequent cooking will obtain a broad kappa number distribution, giving less selective delignification, subsequently leading to lower yield, decreased pulp strength and more reject content [1].

<table>
<thead>
<tr>
<th>IN</th>
<th>Volume</th>
<th>NaOH</th>
<th>Na2S</th>
<th>Na2CO3</th>
<th>Wood</th>
<th>Moisture in wood</th>
<th>OUT</th>
<th>Wood</th>
<th>Dry solids</th>
<th>Free St</th>
<th>NaOH</th>
<th>Na2S</th>
<th>Na2CO3</th>
<th>Bound St</th>
<th>NaOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAI</td>
<td>814 ml</td>
<td>36.4 g</td>
<td>14.1 g</td>
<td>5.5 g</td>
<td>150 g</td>
<td>10.5 g</td>
<td></td>
<td>118.2 g</td>
<td>48.2 g</td>
<td>316.6 ml</td>
<td>9.7 g</td>
<td>7.8 g</td>
<td>5.7 g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EI</td>
<td>1189 ml</td>
<td>33.3 g</td>
<td>32.5 g</td>
<td>5.7 g</td>
<td>150 g</td>
<td>10.5 g</td>
<td></td>
<td>116.1 g</td>
<td>78.9 g</td>
<td>990.9 ml</td>
<td>9.7 g</td>
<td>33.9 g</td>
<td>14.4 g</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 35. Mass balance comparing HAI and EI for on birch at 105ºC. HAI impregnated for 30 min, whilst EI impregnated for 120 min.**

**Figure 36. Chips after impregnation using the HAI method at 105ºC and 30 min.**

**Figure 37. Chips after impregnation using the EI method at 105ºC and 120 min.**
From a visual inspection of Figure 33, EI attains chips with almost no visual chemical profiles at any duration of impregnation. Instead, the liquor appears to fully penetrate the chips. Keep in mind, the images only represent a few chips, therefore no conclusions should be drawn from these solely. Overall, impregnation with EI for 120 min seem to obtain a higher degree of penetration than HAI for 30 min. Hence, with the objective to acquire chips with a homogenous distribution of chemicals the EI method is for this comparison preferable.

4.3 Kraft cooking

Kraft cooking was performed to understand the effects induced by different impregnation methods. This section will evaluate the cooking process by analysing the yield, reject content and kappa number. All cooks were performed at uniform conditions, the only changing variable is the impregnation. The results can be seen in Table 5.

Table 5. Results from kraft cooking with different impregnation methods.

<table>
<thead>
<tr>
<th>Cooking</th>
<th>Impregnation method:</th>
<th>Impregnation Time [min]</th>
<th>H-factor</th>
<th>Residual alkali [mol/L]</th>
<th>Reject content [%]</th>
<th>Total Yield [%]</th>
<th>Kappa number</th>
<th>Wood type</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAI</td>
<td>30</td>
<td>400</td>
<td>0.27</td>
<td>1.9</td>
<td>51.2</td>
<td>22.0</td>
<td>Eucal</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>400</td>
<td>0.34</td>
<td>1.4</td>
<td>49.6</td>
<td>17.6</td>
<td>Birch</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>600</td>
<td>0.31</td>
<td>0.4</td>
<td>49.3</td>
<td>14.0</td>
<td>Birch</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>700</td>
<td>0.31</td>
<td>0.4</td>
<td>49.4</td>
<td>13.1</td>
<td>Birch</td>
<td></td>
</tr>
<tr>
<td>REF</td>
<td>30</td>
<td>400</td>
<td>0.29</td>
<td>1.0</td>
<td>49.8</td>
<td>16.3</td>
<td>Birch</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>600</td>
<td>0.27</td>
<td>0.2</td>
<td>55.5</td>
<td>15.2</td>
<td>Birch</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>700</td>
<td>0.26</td>
<td>0.3</td>
<td>49.9</td>
<td>13.8</td>
<td>Birch</td>
<td></td>
</tr>
<tr>
<td>EI</td>
<td>120</td>
<td>400</td>
<td>0.26</td>
<td>0.5</td>
<td>49.8</td>
<td>17.7</td>
<td>Eucal</td>
<td></td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>400</td>
<td>0.31</td>
<td>3.3</td>
<td>51.0</td>
<td>19.5</td>
<td>Birch</td>
<td></td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>400</td>
<td>0.33</td>
<td>0.9</td>
<td>49.4</td>
<td>15.8</td>
<td>Birch</td>
<td></td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>600</td>
<td>0.30</td>
<td>0.4</td>
<td>47.9</td>
<td>13.3</td>
<td>Birch</td>
<td></td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>700</td>
<td>0.29</td>
<td>0.3</td>
<td>48.7</td>
<td>13.2</td>
<td>Birch</td>
<td></td>
</tr>
</tbody>
</table>

Before discussing the results, experimental errors and potential deviations must acknowledged. Firstly, the REF cooks at H-factor 600 and 700 had a large initial charge of HS⁻. The high initial charge came about from a calculation error, however, sorption of HS⁻ did not seem to change drastically. Another error was found in the Wennberg screen as residual fibres were deposited and stuck under the screen. This resulted in a high yield of the H-factor 600 point for REF since fibres from an earlier screening procedure was gained in this sample. This was the first sample in the machine. Hence, the succeeding samples are probably not affected since the first sample seemed to have “rinsed” the screen. Consequently, the yield point for REF at H-factor 600 is not used in the plots.

In Figure 38 the residual alkali concentration be seen, presented for both the impregnation and cooking. As a reminder, the kraft cooks always begin with an initial EA of 0.6 M. For the cooks, the highest consumption of EA is seen for the eucalyptus. Looking at the impregnations,
eucalyptus had a significantly lower alkali consumption than birch. Thus, low need of EA in the impregnation may lead to a higher consumption in cooking. This analogy can be further justified since at any given H-factor the consumption is lowest for HAI and highest for REF. In the impregnation, the total consumption was in the opposite order, seen in Figure 24.

In terms of cooking yield (Table 5), highest was obtained by the REF followed by HAI and lastly EI. This is interesting, since it was hypothesized that EI would obtain higher yields from putting less strain on the carbohydrates. However, the temporal effect seems to be more significant than expected. One factor that might contribute to the lower yield of EI is the removal of BL after impregnation. In segment 2.9.2, Table 1, the dissolution and reprecipitation of xylan was shown [42]. A portion of the xylan will be dissolved in the impregnation phase of cooking. This portion is prone to reprecipitation at a later stage of the cook. Since half of the volume for EI was removed after impregnation the potential yield increase due to reprecipitation is lost.

Dissolution and reprecipitation of xylan might have had a significant impact on the results. After impregnation, no BL was removed from HAI and REF (birch). These obtained higher yield than EI, which had half of its BL volume removed after impregnation. Furthermore, Wigell et al., found that a higher alkali concentration will decrease the xylan yield significantly [70]. Since REF has 1.3 [OH⁻] and HAI 1.7 [OH⁻] the degradation of xylan will be more predominant for HAI. Increased yield in xylan for REF might justify why REF obtained a higher total yield than HAI.

Before drawing any conclusions, the kappa numbers have to be analysed (Figure 39). It was found that the REF impregnation had highest yield at lowest kappa numbers, followed by HAI. EI had higher yield than HAI at around kappa 16 but declines rapidly towards kappa number 13. Cooks for EI at H-factor 600 and 700 are in close proximity when analysing the kappa number. This is probably due to the low lignin content at those kappa numbers. Due to MeGlcA, the formation of Hexenuronic acid will occur and will represent a portion of the kappa number. In addition, the yield is lower at 600 than 700, which may be an experimental error. Wood is an anisotropic material, thus variance will exist. Nevertheless, both points for EI is lower than REF and HAI. Therefore, it might be true that EI obtains more wood losses.

Figure 38. Hydroxide concentration against time and yield against time during impregnation and cooking. Impregnations were performed at 105°C at various conditions and cooking at 155°C.
Figure 39. Yield against kappa number after cooking.

In Figure 40, a comparison of EI at 60 and 120 min was performed to understand if the EI could be used at shorter durations. In terms of hydroxide, 60 min consumes more alkali for the same H-factor (H: 400). However, the 60 min EI obtains 3.3% reject content which is detrimental for a cooking procedure. The definition of the defibration point is said to be the kappa number at which 1% reject content is obtain. Hence, an EI with 60 min impregnation does not reach the defibration point. Consequently, 60 min does not provide with a sufficient impregnation even though 60 min visually seemed to have a homogenous impregnation (Figure 33), this was not the case.

Figure 40. Comparison of EI at 60 and 120 min for birch.

Looking at the kappa number from another perspective (Figure 41), it becomes clear that a given kappa number is reached faster with EI than HAI or REF. This might have an industrial significance since the production rate will be affected. Reaching a much lower kappa number than ~16 (defibration point for hardwood) is not always sought for. If a low amount of reject content is obtained the pulp can be further processed in the oxygen delignification stage that
follows the digester in a kraft pulping plant. Oxygen delignification is less cumbersome on the carbohydrates. Hence, achieving a low kappa in cooking is not necessary. REF and EI reaches ~16 fairly quickly (H-factor 400) but at longer durations the HAI obtains lower kappa than REF whilst also approaching the EI at H-factor 700. It might seem unintuitive that HAI attains higher kappa number than REF at H-factor 400, it might be caused by hexenuronic acid. Formation of hexenuronic acid increases with more hydroxide ions [44], accordingly, HAI has much more hydroxide ions than REF. Therefore, the higher kappa at H:400 for HAI could be caused by formation of HexA.

In cooking, not all chips are completely defibrated. The inadequately defibrated wood material is collected as shives after cooking, also called reject content since it cannot be used for further processing. Figure 42 demonstrates the reject content at different kappa numbers. The methods are in proximity of each other at any kappa number but in a more detailed assessment the REF has lowest reject content followed by HAI and lastly EI. REF has a smaller span, making it harder to know if it stays true for all kappa numbers. At the lowest kappa numbers for HAI and EI the reject is almost the same. The 60 min EI obtains too much reject content, which also is true for the 30 min HAI with eucalyptus. In Figure 42, it is clear that eucalyptus is harder to delignify than birch. With an H-factor of 400 the eucalyptus HAI sample obtains significantly higher reject content and kappa number than HAI for birch. It could be understood that eucalyptus has a higher defibration point than birch. Furthermore, the EI sample for eucalyptus does reach within the defibration point but at a greater kappa number than for the birch sample. In section 2.9.1, the fundamental principles of EI was explained. One of the core principles is to attain low reject content at a higher kappa numbers. In accordance, the phenomenon is seen for both eucalyptus and birch in Figure 42. Although, much more prominent for the eucalyptus sample.
Figure 42. Reject content after the subsequent cooking at 155°C. The defibration point is portrayed a with dotted line.
4.3.1 Total alkali consumption in cooking

As previously mentioned, a lower alkali consumption in impregnation will give an increment in cooking. Looking at the total consumption of impregnation and cooking (Figure 43) it is seen that EI consumes more alkali in both impregnation and cooking, leading to an overall higher consumption.

The statement of increased consumption in cooking if impregnation consumed less alkali can be further justified in Figure 44. From Table 5, the 60 min EI method consumed more alkali in cooking than 120 min EI. However, the overall consumption at the same H-factor (H:400) is smaller for 60 min EI. The chips were not sufficiently impregnation at 60 min EI. The additional consumption due to the temporal difference in 120 min EI seem to be necessary to obtain a sufficient impregnation.

Figure 43. The total consumption of alkali for HAI, REF and EI with birch and eucalyptus. Dotted line distinguishes the impregnation and cooking.

Figure 44. The total alkali consumption for 60 min EI with birch
4.4 Impregnations impact on cooking

A final comparison was made between HAI and EI. The performance at the defibration point for each method can be seen in Table 6. HAI needs a longer cooking time than EI to reach the defibration point, however, the total duration is shorter. EI obtains an increment in yield, while also reaching the defibration at a slightly higher kappa number. EI consumes more chemicals than HAI, while also obtaining a significant abatement in production rate. Overall, HAI and EI obtains almost the same yield and kappa while EI consumes more chemicals with a greatly reduced production rate. The pronounced benefits of utilizing EI was not seen in this thesis. These results are somewhat in line with previous obtained results [3]. Tavast and Brännvall compared a EI with a REF cook for softwood. The EI obtained a reduction in production rate, a shorter cooking time, higher yield and an increment in total time. Although, the difference in production rate is significantly greater in this thesis. It is clear from the table that neither HAI nor EI was the most efficient. The REF obtained higher productions rate, highest yield with the least consumption of alkali. REF is concluded to be the most impregnation conditions in this thesis.

Table 6. A comparison between HAI and EI at the defibration point. Kappa number at the defibration point was calculated with extrapolation of Figure 42. Yield was calculated using the trend line equation in Figure 39. Alkali consumption was obtained with interpolation in Figure 43 and the production rate had a calculation basis of 1000 kg wood

<table>
<thead>
<tr>
<th></th>
<th>Imp [min]</th>
<th>Cooking [min]</th>
<th>Total time [min]</th>
<th>Yield at defibration point [%]</th>
<th>Kappa at defibration point</th>
<th>Alkali consumption [g/kg wood]</th>
<th>*Production rate [kg/h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAI</td>
<td>30</td>
<td>119</td>
<td>149</td>
<td>49.4</td>
<td>16.1</td>
<td>192</td>
<td>199</td>
</tr>
<tr>
<td>REF</td>
<td>30</td>
<td>88</td>
<td>118</td>
<td>49.8</td>
<td>16.5</td>
<td>188</td>
<td>252</td>
</tr>
<tr>
<td>EI</td>
<td>120</td>
<td>85</td>
<td>205</td>
<td>49.7</td>
<td>16.4</td>
<td>202</td>
<td>146</td>
</tr>
</tbody>
</table>

* Production rate is based on 1 ton of wood
5 Conclusion

This study involved impregnation and cooking of hardwood with the main objective to understand the consumption of alkali at different impregnation conditions and to evaluate the homogeneity, measured as alkali concentration achieved in the bound liquor as compared to the concentration in the free liquor. The thermal, temporal and chemical effect on the impregnation were analysed with the goal to clarify the impregnation of hardwood. A High Alkali Impregnation (HAI), a Reference Impregnation (REF) and an Extended Impregnation (EI) was compared and assessed by analysing the impregnation efficiencies in terms of selectivity, homogeneity and yield. The comparison was also made under cooking conditions with the objective to understand the impact of impregnation on the subsequent cooking phase. The main findings in this study were:

Impregnation

- In impregnation, most chemical consuming reactions were found to occur within the first 10-30 minutes, mostly contributed by deacetylation. The chemical activities were the most rapid for HAI. The high diffusion rate provided a fast transportation of \(\text{OH}^-\), obtaining significantly higher \([\text{OH}^-]\) in the bound liquor at an early stage of impregnation compared to REF and EI. At 105°C, a chemical equilibrium between the free and bound liquors was seen at ~60 min for HAI, ~120 min for REF and EI using birch. In turn, eucalyptus reached an equilibrium at ~30 min with HAI and ~60 min with REF and EI. Resultantly, a sufficient distribution of hydroxide ions in the chips is obtained fastest with HAI.

- In impregnation, the yield at any duration of time was highest for EI, followed REF and HAI. The mild chemical conditions for EI lead to a more selective impregnation due to less strain on the carbohydrate constituents while \([\text{OH}^-]\) in HAI contributed with more wood losses. EI also obtained the highest total consumption of alkali in impregnation, followed by HAI and lastly the REF impregnation. The total alkali consumption also increased with higher temperature and time.

- The \([\text{HS}^-]\) sorption in impregnation was highest for EI due to the high initial sulphidity charge. REF and HAI obtained similar sorption during impregnation. The sorption of \([\text{HS}^-]\) increased with temperature and time. Moreover, the delignification transpired already at 115°C as the sorption increases significantly for all impregnation methods. The \([\text{HS}^-]\) sorption appear independent of hardwood type as eucalyptus and birch obtains similar sorption at same conditions.

Kraft cooking

- EI obtains a cooking where the chips are easier delignified. EI provides a homogenous distribution of chemicals in impregnation, in turn, extensive diffusion is not necessary in cooking, leading to a faster and homogenous delignification in the cooking stage. Resultantly, the EI method obtains a reduced cooking time.

- A faster delignification was shown for birch in contrast to eucalyptus. In addition, the defibration point for birch was found to be around kappa number ~16 for all methods.
Furthermore, the defibration point for eucalyptus seem to be at a higher kappa number than birch.

- The obtained chips after 60 min impregnation with EI conditions did not portray visual liquid profiles to the centre of the chips. However, decreasing the impregnation time from 120 min to 60 min for EI showed a detrimental effect on reject content. An inadequate impregnation was obtained.

Highest total cooking yield at similar kappa numbers was achieved by utilizing REF conditions, followed by HAI and lastly the EI conditions. The high yield of REF in contrast to HAI could be explained by an improved xylan yield due to an alleviated hydroxide level. The low yield of EI can be assigned to continued peeling due to the prolonged impregnation and loss of xylan when removing black liquor after impregnation.

In terms of production rate, yield, energy and chemical consumption the REF is the most efficient impregnation condition for birch kraft cooking in this batchwise laboratory kraft cooking procedure. REF acquired a sufficiently homogenous impregnation while using a moderate [OH⁻] and short impregnation time. A total digesting time of 118 minutes or cooking to an H-factor of 400 was enough to reach below the defibration point in the case of REF.
6 Future work

This thesis has primarily focused on the impregnation phase of kraft digesting. Resultantly, much emphasize was set towards characterizing the individual impregnation conditions at different parameters with an objective to compare their impregnation efficiencies. Due to time restrictions in this thesis, the cooking phase was not extensively studied. In kraft digesting the resulting pulp obtained after cooking has the most significance. Therefore, future work should analyse the cooking efficiencies using different impregnation conditions with an emphasize on the latter stage of kraft digesting, the cooking phase. The cooking investigation should also be more quantitative, where a large span of kappa numbers should be examined to obtain comprehensive trends that could support different impregnation methods.

The analyses of the resulting pulp should also be accentuated by measuring the viscosity to understand the degree of cellulose degradation. A carbohydrate analysis on the impregnated chips could be performed with the objective to acquire the degree of different chemical reactions. Likewise, the conditions could be modified to take advantage of the more beneficial reactions, such as deacetylation and delignification. Another useful application would be to analyse the impregnated wood chips according to Inalbon et al. [71]. The analysis methodology is to impregnate cubes of wood, when complete the cube is immersed in liquid nitrogen. The area of the wood that is of interest to analyse is then cut into thin slices, in which the slices are further analysed. This enables the opportunity to thoroughly examine the actual chemical occurrences that has transpired during the impregnation procedure.

In the cooking phase of this thesis some black liquor was removed after impregnation to reach a wanted hydroxide concentration. This removes valuable xylan. For future work, the chemical concentration levels should not be modified through removal of black liquor, since it can affect the results.
**Technical terms**

**White liquor** is the primary liquor that is utilized to pulp wood. The white liquor contains the main active ions: HS\(^-\) and OH\(^-\). Basic chemical reactions to obtain the white liquor can be seen below:

\[
NaOH + H_2O \rightarrow Na^+ + OH^- + H_2O \quad [10]
\]

_Hydrolysis of NaOH_

\[
Na_2S + H_2O \rightarrow 2Na^+ + S^{2-} + H_2O \quad [11]
\]

\[
S^{2-} + H_2O \rightarrow HS^- + OH^- \quad [12]
\]

_Hydrolysis of Na\(_2\)S_

**H-factor**, a fundamental unit used to express the temperature and time as a single variable during cooking. The H-factor is derived from Arrenhius equation and is based on the reaction rate of bulk delignification at 100\(^\circ\)C and can therefore be used to assessed the degree of cooking at any other temperature. The activation energy of bulk delignification (100\(^\circ\)C) in kraft pulping has empirically been set to 134 kJ/mol \[21\]. Therefore, the relative delignification rate can be expressed as equation 13. The extent of delignification is further expressed with a kappa number, which can be adjusted by means of changing the H-factor, given that chemical profiles are correct.\[72\]

\[
\ln(k) = 43.2 - \frac{16113}{T} \quad [13]
\]

The H-factor is then obtained by addition of a time integral, seen in equation 14.

\[
H = \int_{0}^{t} e^{(43.2 - \frac{16113}{T})} dt \quad [14]
\]

**Free black liquor**, the spent black liquor that is surrounding the chips after impregnation or cooking. This liquor is drained by separating chips from the liquor. Centrifugation is also used to remove the free black liquor on the surface of the chips.

**Bound black liquor**, the liquor that has been absorbed into the chips during impregnation. This liquor can be collected by a leaching with deionized water for at least 48 hours.
Bibliography


Appendix

Figure 45. How to obtain the free and bound liquors in impregnation.