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The effect on wood components during soda pulping

Pretreatment and pulping of forest residues in a biorefinery concept

Master's thesis in Innovative and Sustainable Chemical Engineering

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Cover:
Photographs of milled raw materials and pulps after alkaline hydrogen peroxide pretreatment followed by 120 minutes of soda pulping. Pine wood meal (top left), pine wood pulp (top right), bark meal (bottom left), bark pulp (bottom right).

Gothenburg, Sweden 2018

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The effect on wood components during soda pulping

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Abstract

The growth in population and constantly rising material and energy demand have a large impact on the global climate as well as environmental issues. Implementation of biorefineries and the mindset to utilise waste as resource is a necessary development for a decreased environmental impact. One possible biorefinery route is using renewable lignocellulosic biomass as raw material and turn it into a spectrum of products which are currently produced from fossil raw material.

In this study alkaline hydrogen peroxide pretreatment followed by soda pulping of pine wood meal and softwood bark meal have been examined. The raw materials were chosen to be used as a model for forest residue, since they both can be found in it. The pine wood meal and softwood bark meal was investigated to gain further knowledge of the change in the chemical composition in forest residues during soda pulping combined with pretreatment. This was done in order to further examine a possible future implementation of forest residues as raw material in a biorefinery concept.

The best result regarding delignification on pine wood meal after soda pulping was achieved with alkaline hydrogen peroxide pretreatment conducted at 60°C with an alkaline hydrogen peroxide content of 3.3 wt. % for 60 minutes. The delignification rate was high during the main part of the pulping but after 120 minutes of soda pulping the delignification rate of pine wood meal decreased significantly. Furthermore the molecular weight of the lignin in pine wood meal decreased with increased pulping time.

For the bark meal no such trends could be observed for either the delignification rate or the molecular weight.The pine wood meal works as a model for the forest residue mixture, since similar trends in decrease of Klason lignin and molecular weight of lignin could be seen. Forest residues shows great potential to be used as raw material in an alkaline hydrogen peroxide soda pulping biorefinery, providing sulphur free low molecular weight lignin for future application products such as chemicals, carbon fibres and bio-fuels.

Keywords: Soda pulping, biorefinery, forest residues, alkaline hydrogen peroxide, pine wood, bark

Contents

1 Introduction

1.1 Background

In recent years the use of fossil raw material have been increasing due to growth in population and constantly rising energy demand. This have a large impact on the global climate as well as negative environmental consequences. These factors together with the insecurity that the fossil fuel reserves are going to be depleted shows it is necessary to decrease this usage and increase the implementation of carbon neutral raw materials (Chaturvedi & Verma, 2013).

One possible route to decrease the usage of fossil fuels is various biorefinery concepts and the usage of renewable lignocellulosic biomass as raw material. The main idea of biorefineries are to utilise currently unused process streams, often regarded as residue, and turn them into a spectrum of products which are currently produced from fossil raw material. This would generate a greater product value compared to incinerating the unutilised biomass for energy purposes, which is commonly done today. Pulp and paper mills are one type of industry which have great potential in utilisation of currently unused streams of lignocellulosic biomass, two of these streams are bark and forest residue. The bark is separated at the pulp mills and the forest residues are left in the forests, as they are not desired in the paper production.

In current pulp and paper industry only the stem of the trees are used and the bark and forest residues are incinerated for steam and power production even though there is a huge potential in producing products from these raw material streams. Before the logs are chipped into wood chips there is a debarking operation. Bark makes up for 10-20 % of the mass of wood logs and creates a large side stream that is available for further use (Vane et al., 2006). The bark is not interesting for paper production since it has a high content of extractives, lignin and low content of cellulose. Bark and forest residue can provide additional profit to the paper industry by being processed into high-value green chemicals, bio-oils, dissolving pulp, nanocrystalline cellulose and other products (Vazquez Penas et al., 1992).

1.2 Aim

The object of this project is to investigate the utilisation of bark and forest residue as raw material in a biorefinery concept. A previous study with forest residues was recently performed at the department of Chemistry and Chemical Engineering at Chalmers. In that study forest residue was pretreated with alkaline hydrogen peroxide and delignified during soda pulping, resulting in separation of the wood components i.e. cellulose, hemicellulose and lignin.

The forest residue mixture contained different wood parts such as stem wood, branches and bark with origin from both softwood and hardwood. This complex mixture made it hard to evaluate and understand the impact of the pretreatment and delignification processes.

This work is therefore aimed to further study the effects that pretreatment with alkaline hydrogen peroxide combined with soda pulping have on the specific wood parts, pine wood and softwood bark.

2 Theory

2.1 Wood structure and morphology

All species of trees can be divided into softwood or hardwood trees. Softwood trees are also referred to as gymnosperms and hardwood to angiosperms. There are about 30000 angiosperms and 520 gymnosperms known in the world. Gymnosperms are the types of trees which has needles instead of leaves, which are kept for at least a couple of years and they are more abundant in colder regions. Some examples of gymnosperms are spruce and pine. Angiosperms are the types of trees which has leaves, which in cooler climate is lost in the fall and they are the more common type of trees in most parts of the world, some examples of angiosperms are birch, oak, beech and aspen (Henriksson et al., 2009).

The trees consists of different parts of wood, outer layer bark, phloem, cambium, sapwood, heartwood and pitch. The different part varies in chemical composition as well as function. Chemical components which varies in the different parts of the tree are for example cellulose, hemicellulose, lignin and extractives (Henriksson et al., 2009).

The wood cells in trees are made up by several layers and their functions are mainly to provide mechanical strength, act as a storage of nutrients and transport liquid. The cells are mostly longitudinally oriented and are connected to each other through pits, which are openings with a membrane where liquid can be transported through (Henriksson et al., 2009).

2.1.2 Cellulose

Cellulose is the most abundant organic biopolymer on the planet and corresponds to about 40-50 % of the total mass in trees. The amount of cellulose may differ between hardwood and softwood as well as between different parts of the tree, such as the stem and the bark. Cellulose is a linear polymer which consist of D-glucopyranose units that are connected through 1-4-glucosidic linkages which forms a carbohydrate chain with up to 20 000 monomers. Depending on the number of glucose units in the carbohydrate chain it is said to have a degree of polymerisation (DP) and the average DP of wood cellulose is around 8000 units. The hydroxyl groups which the glucose units have enables the possibility of hydrogen bonds between the different cellulose chains, forms sheets of cellulose. The sheets are stacked on each other through the influence of hydrophobic interactions i.e. van der Waals bonds (Lennholm & Blomqvist, 2009). The effect of the increased packing results in a higher crystallinity, and wood cellulose can contain close to 65 % of crystalline areas (Rowell et al., 2012).

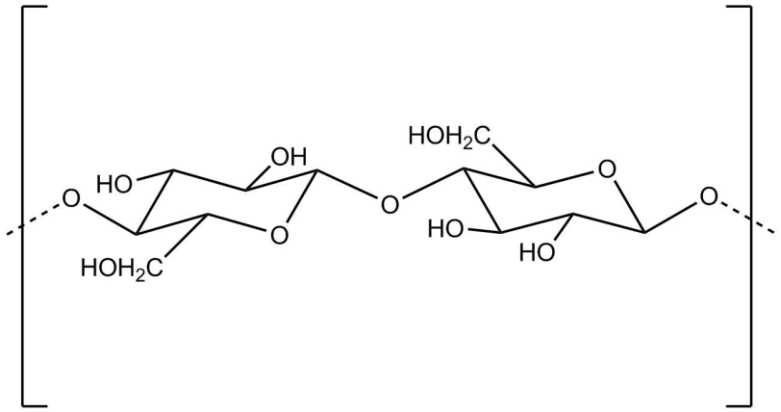

Figure 1: Molecular structure of a cellulose unit.

2.1.3 Hemicellulose

Wood have a number of different hemicelluloses and together they are one of the main type of components in wood and makes up for about 20-35 % of the dry weight depending on the wood type. Hemicelluloses are carbohydrate chains just like celluloses are, though there are some major differences. For instance the degree of polymerisation is considerably lower for the hemicellulose, which is around 100-200, and it has an entirely amorphous structure. Their function is to work as so called structural carbohydrates and support the cell wall structure. Hemicelluloses are mainly composed of a different pentose (D-xylose and L-arabinose) and/or hexose (D-glucose, D-mannose and D-galactose) sugar monomers (Teleman, 2009).

2.1.3.1 Glucomannans

Glucomannans are found in both hardwood and softwood. Glucomannans has a linear backbone which is assembled of 1-4-linked β-D-mannopyranosyl and β-D-glucopyranosyl residues. Hardwood glucomannans are partially acetylated at the mannose units and have an average DP of 60-70. Softwood glucomannans contain partially acetylated mannose units, but they also have side groups which have galactose units. The average DP of softwood glucomannan is around 100 (Rowell et al., 2012).

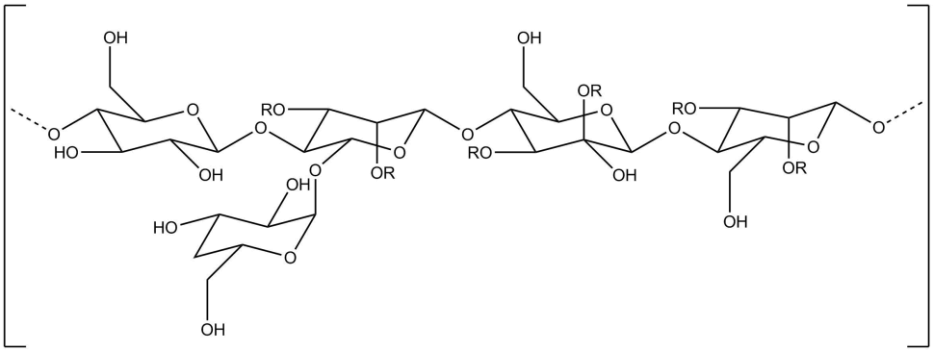

Figure 2: Molecular structure of a softwood glucomannan unit.

2.1.3.2 Xylans

Wood xylans has a β-1-4-D-xylopyranosyl residue backbone and are linear polysaccharides that exist in both softwood and hardwood, though the structure differ. Both hardwood and softwood xylan contain 4-O-methyl-D-glucoronic acid side groups, but the frequency of these side groups are higher in softwood xylans which makes them more acidic than hardwood xylans. Further difference between hardwood and softwood xylans are that hardwood xylans have acetyl side groups and softwood xylans have L-arabinose side groups. O-acetyl-(4-O-methylglucurono)xylan or often called glucuronoxylan, is the most common hemicellulose in hardwood, while the most common xylan in softwood is arabinoglucuronoxylan (Teleman, 2009).

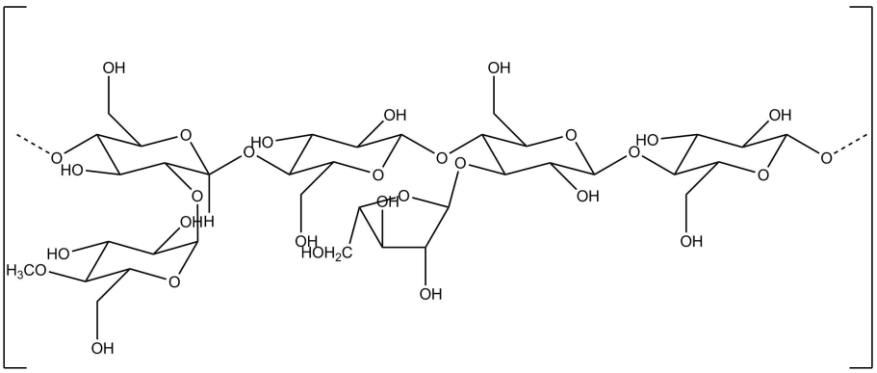

Figure 3: Molecular structure of an arabinoglucuronoxylan unit.

2.1.4 Lignin

Lignin is the second most common biopolymer on earth. It acts as a glue which fills the space around the other wood components fixating them in a matrix which makes the fibres stiff and provides mechanical support. Other functions of lignin is to make the cell walls hydrophobic and protect the cell wall from microbial degradation such as mould, fungi and bacteria. The amount as well as the structure of the lignin may vary between different types and species of wood. For

softwood the amount of lignin vary between 26-32 % and for hardwood the amount vary between 20-26 % (Sjöström, 1993).

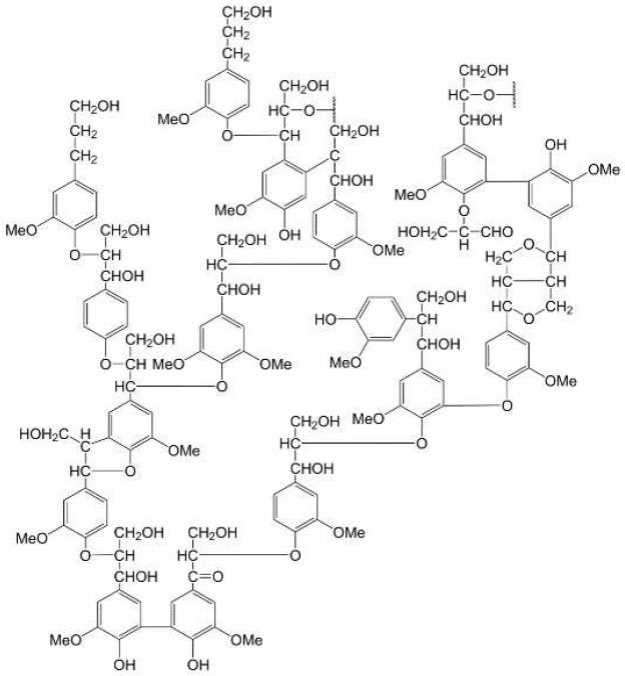

Figure 4: Proposed structure of softwood lignin. Adapted from Adler (1977).

Lignin has a very complex structure of a three-dimensional web of connected monomers. The three most common phenyl propane monomers, which the three-dimensional web consist of, are p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. The amount of each monolignol, the collective name of the monomers, varies in different wood species. Hardwood contain both coniferyl- and sinapyl alcohol of around equal parts, while softwood almost solely contain coniferyl alcohol. Gras lignin contain all three common monomers, but have a larger amount of p-coumaryl alcohol than of the other two monomers (Henriksson, 2009).

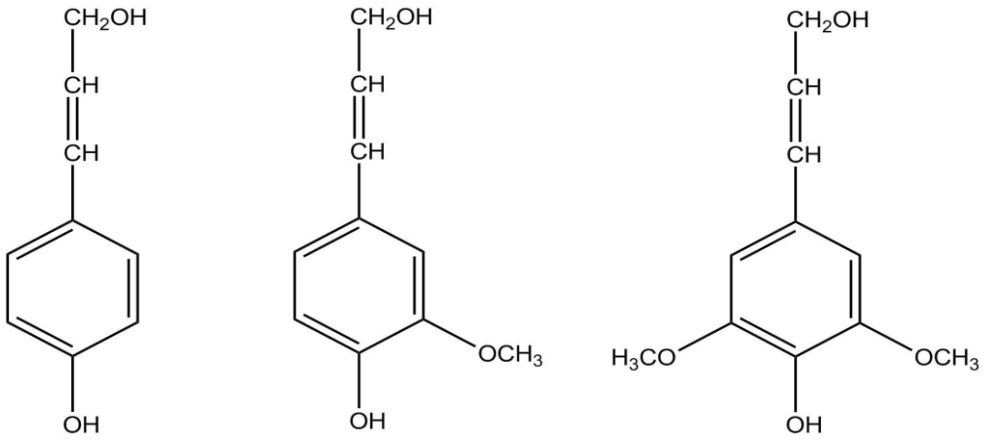

Figure 5: Molecular structure of the three lignin monomers units. From left to right: p-coumaryl alcohol, sinapyl alcohol and coniferyl alcohol.

The structure of lignin is considered to be random. It has however been shown that lignin commonly has one-third carbon-carbon (C-C) linkages and two-thirds ether (C-O-C) linkages with β-O-4 bonds being the most common. The frequency of the different bonds vary for different wood types and the amount of β-O-4 bonds is a bit lower in softwood compared to hardwood (Henriksson, 2010).

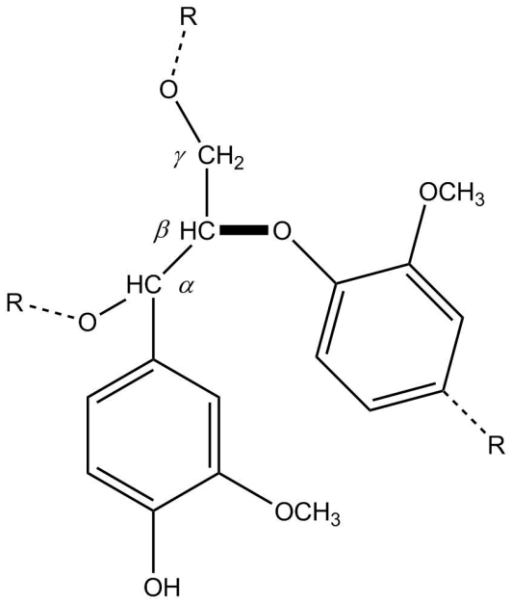

Figure 6: Illustration of the β-O-4 bond (bold) between two lignin monomers.

2.1.4.1 Potential applications for lignin

Due to the complex structure of lignin there are a number of potential applications which can be divided into groups depending on prospects on when the applications may potentially be on the market. The first group are applications which are already on or soon to be on the market and these are lignin used for fuel and syngas. The second group is relatively close future applications and these are macromolecule derived products such as carbon fibres, wood binders and polyurethane foams. The third group is applications which can be on the long-term market and that could be aromatics where the lignin structure is cleaved without the aromatic rings being destroyed. These may replace aromatic groups from fossil raw material in making of benzene, toluene, phenol and xylene (Holladay et al., 2007). In Table 1 the different applications and some potential products can be seen.

Table 1: Potential applications and products of lignin.

Potential applications	Products
Fuel and syngas	**Methanol, Ethanol, Hydrocarbon gases**
Macromolecules	**Carbon fibres, Polymer modifiers, Resins/Adhesives/Binders**
Aromatic chemicals	**Benzene, Toluene, Phenol, Vanilla, DMSO**

2.1.5 Extractives

Extractives are components in wood which can be extracted using a variety of solvents. They are small molecules of low weight, usually divided into four main groups; phenolic compounds, aliphatic compounds, terpenes and terpenoids and waxes. Extractives have multiple functions in trees, for example to protect the trees from insects and fungi and act as energy reserve. There is usually only a few percentages of extractives in wood, although there are parts with higher content of extractives such as bark and branches. The amount and composition of extractives vary a lot between different wood species and may also vary significantly between trees of the same species due to age, climate and genetics. In bark the composition of extractives are usually very different from the stem wood and there are extractives typical for bark only. Some of these typical extractives are suberin, tannins and betulinol. Suberin is a polymeric substance and has a structure built up similar to lignin, as an aromatic matrix that is cross-linked with aliphatic components. Tannins is a phenolic extractive mainly present in bark but can also exist in the heartwood of some wood species

and betulinol is a triperpene found in large quantities in birch bark and it is what gives the birch bark its white colour (Björklund Jansson & Nilvebrant, 2009).

2.1.6 Bark

Bark is a different tissue compared to stem wood and can be divided into two fractions, outer and inner bark. The chemical composition of the bark can vary between different spices of wood as well as for outer and inner bark of the same tree. The outer bark mainly acts as a protecting wall made of dead tissue to protect the tree from dehydration, bacteria and fungus. The inner bark consists of living cells which are responsible for transportation of water and nutrients. The bark contain a larger amount of lignin and extractives compared to stem wood and is not used for paper making and is instead removed and commonly burned at the pulp and paper mills. The bark is removed for a number of reasons such as; containing a very low portion of fibres that can be used for paper making, high content of extractives results in a drastically increased need of cooking chemicals used in the cooking process. Bark residue may cause dark spots on the paper due to bark cells not being decomposed in the cooking or bleaching processes. Since bark is around 10-20 wt. % of the total dry mass of the logs that is a huge resource that could be utilised into products (Brännvall, 2009). Although it is known that bark contain larger amounts of lignin and extractives it is difficult to determine the exact amounts. This since the analysis methods established for wood are not possible to use for bark since it contain additional different compounds. The methods that can be used to examine the amount of extractives in bark shows a large variance which makes the amounts uncertain (Rowell et al., 2012).

2.2 Pretreatment of raw material

Some of the reasons to use a pretreatment process is to extract hemicelluloses and extractives, to open up the wood structure, disintegrate the lignin structure, depolymerise hemicelluloses and solubilise lignin and hemicelluloses. Pretreatment technologies are generally categorised into chemical, physical, physiochemical and biological. Chemical pretreatments often remove and disintegrate the hemicelluloses and lignin, thus disintegrating the lignin structure. Physical pretreatment increase the surface area by reducing the size of and opens up the structure and creates cracks in the raw material, done through e.g. grinding. The physiochemical pretreatment methods occur at high pressure and temperature, therefore good control of the operating conditions are crucial. Biological pretreatment methods are used to break down lignin and hemicellulose in lignocellulosic biomass by using microorganisms (Maurya et al., 2015).

2.2.1 Alkaline peroxide pretreatment

Alkaline hydrogen peroxide (AHP) treatment has been frequently used as a pulping and bleaching method in the pulp and paper industry. In recent years the methods' capability to be used as pretreatment on lignocellulosic biomass has been investigated. The usage of AHP as pretreatment has shown to selectively sustain cellulose while removing lignin, as well as converting hemicelluloses into useful organic acids. Studies of AHP treatment suggest an increase of water absorbance, which would be beneficial for pulping properties (Alvarez-Vasco & Zhang, 2017).

The most effective delignifying properties of AHP pretreatment has been shown to be of alkaline conditions of a pH around 11.6. To keep the pH at 11.6 is of great importance during the reaction: according to Reaction 1 the dissociation of hydrogen peroxide and formation of perhydroxyl occurs below this pKa (Alvarez-Vasco & Zhang, 2017).

$$H_2O_2 + OH^- \rightleftharpoons H_2O + HOO^-$$

Reaction 1: Dissociation reaction of hydrogen peroxide.

The formed perhydroxyl anion can then react with undissociated hydrogen peroxide into very reactive radicals according to Reaction 2. These radicals, $\cdot OH^-$ and $O_2^-\cdot$, are believed to interfere with the wood matrix and break its structure, although the exact mechanisms of the delignifying reactions remain unknown (Gould, 1985).

$$H_2O_2 + HOO^- \rightleftharpoons \bullet OH + \bullet O_2^- + H_2O$$

Reaction 2: Reaction between hydrogen peroxide and perhydroxyl ion.

2.3 Chemical pulping processes

The purpose of the pulping is to remove the lignin from the other components so they can be utilised (Brännvall, 2009). The pulping process is the stage where fiber liberation takes place in the pulping process and is mainly done through delignification. The delignification is achieved through addition of chemicals and at elevated temperature, making the lignin water soluble. The pulping process is often called cooking, even though it is unwanted for the cooking chemicals to actually boil. To get a good delignification during the pulping there are some typical operations done before the chemicals are added and the temperature increased (Gellerstedt, 2009). Common operations prior to cooking, to make the delignification more efficient, are steaming and impregnation of the wood

with the cooking chemicals used. There are various pulping processes using different chemicals depending on the desired pulp properties and level of delignification (Brännvall, 2009).

The three most established chemical pulping processes are kraft-, sulfite- and soda pulping though the latter one only plays a minor role in the present pulping industry. The active ions varies for the different pulping processes and they are hydroxide and hydrosulfide ions for kraft cooking, bisulfite/sulfite ions for sulfite cooking and sodium hydroxide for soda cooking (Gellerstedt, 2009).

2.3.1 Soda pulping

Soda pulping is a chemical pulping method using sodium hydroxide as its delignification chemical and the method was invented in England 1851. When the Kraft process was discovered most soda pulping mills were converted into Kraft pulping mills (Biermann, 1996). The Kraft process yields a stronger pulp and is a more energy efficient process through the burning of black liquor (Gellerstedt, 2009). Today there is an increasing interest in soda pulping due to the biorefinery concept which has increased the demand for sulphur free lignin and nanocrystalline cellulose. The process structure of soda pulping mills have many similarities to the process structure of Kraft pulping mills, which makes for an interesting process alternative. Benefits of having a sulphur free process is a decrease in sulphur aerial emissions and no need for additional desulphurisation process steps (Gomes et al., 2014).

There are multiple delignification reactions that vary in magnitude and importance. The most important and most frequent delignification reactions in soda pulping is the cleavage reaction of the non-phenolic β-O-4 bonds, which can take place at alkaline conditions (Gellerstedt, 2009). The non-phenolic β-O-4 bond cleavage results in the formation of a phenolic lignin end group and an epoxide, which may participate in further reactions through nucleophile activation of NaOH (Heitner et al., 2010).

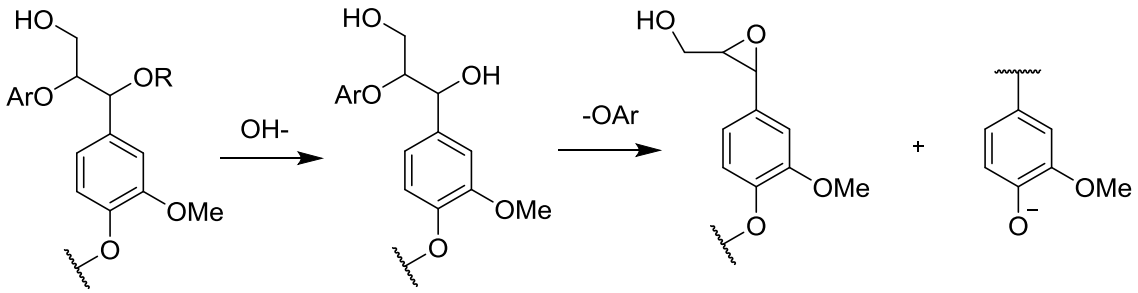

Figure 7: Illustration of cleavage of non-phenolic β-O-4 structures in lignin.

Another important delignification reaction is the cleavage of phenolic β-O-4 bonds. In this reaction there is a quinone methide formed which can react further and release formaldehyde and form an enol ether structure or it may either undergo a condensation- or reduction reaction (Heitner et al., 2010). In Kraft pulping the hydrosulphide ion reacts with the quinone methide to cleave phenolic β-O-4 bonds, decreasing the amount of enol ether formation (Pasco & Suckling, 1994).

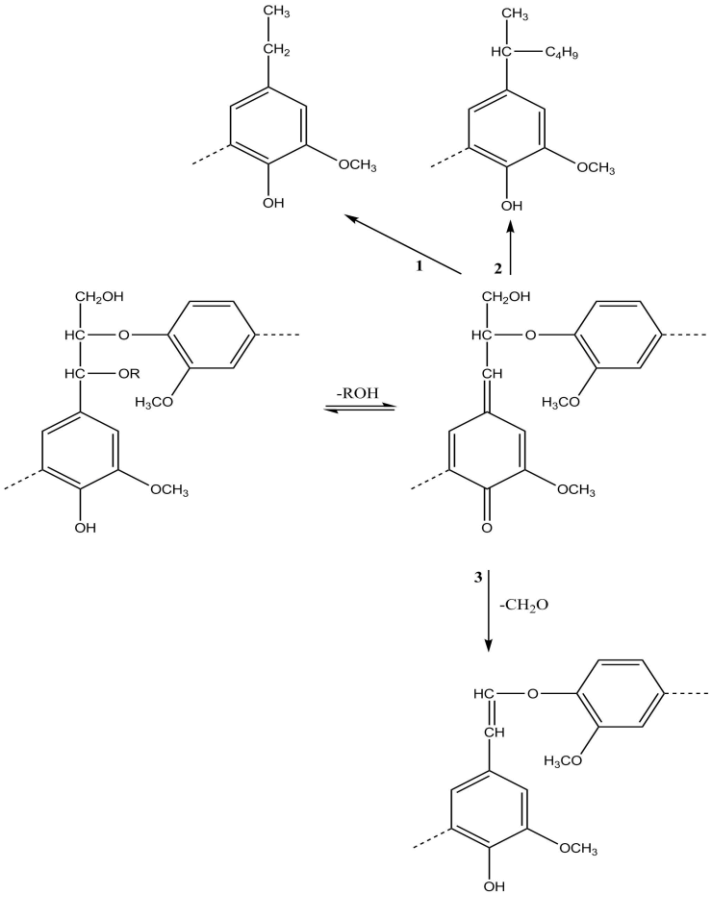

Figure 8: Illustration of the different reaction of phenolic β-O-4 structures in lignin. Reduction reaction (1), condensation reaction (2) and elimination reaction into an enol ether from quinone methide (3).

Another reaction of importance is the formulation of stilbenes from lignin β-5 which has a similar reaction pathway as for the non-phenolic β-O-4 reaction (Heitner et al., 2010).

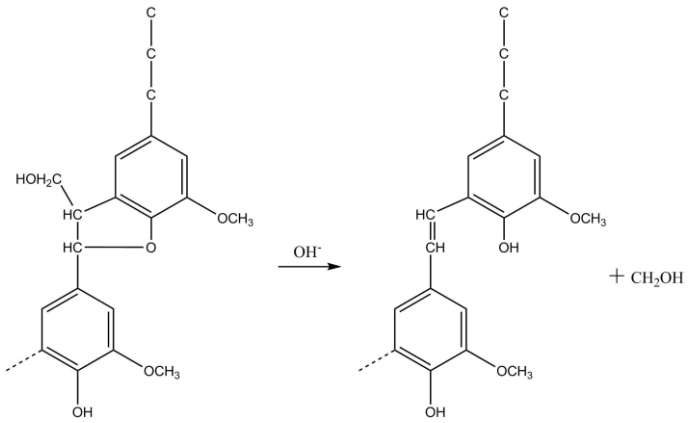

Figure 9: Illustration of β-5 lignin bond reaction under alkaline conditions.

Besides delignification there are other chemical reactions occurring during soda pulping such as various reactions with the carbohydrates. During these reactions the carbohydrate chains, cellulose and hemicellulose, are depolymerised leading to unwanted yield loss of cellulose and hemicelluloses. The two main carbohydrate reactions occurring are peeling and alkaline hydrolysis (Gellerstedt, 2009).

During peeling reactions the carbohydrate chains are depolymerised at the reducing end-groups. The peeling reactions begin immediately after the carbohydrates come in contact with alkaline solution and increases at elevated temperatures. Some of the reducing end-groups will react into an aldehyde and some into a keto form resulting in an equilibrium formed between the two during the alkaline pulping. Both forms may undergo a β-elimination reaction. When the keto form undergo elimination a sugar monomer will be removed and a new reducing end-group is formed. For the aldehyde form the β-elimination reaction will result in a stabilisation of the carbohydrate chain after the sugar monomer is removed (Gellerstedt, 2009). The peeling and stabilisation are reactions competing for the same reaction sites and the level of depolymerisation is therefore decided by how fast each reaction is (Sjöström, 1993).

Alkaline hydrolysis of glucosidic linkages is another factor for depolymerisation. During alkaline hydrolysis carbohydrate chains are cleaved resulting in shorter chains and higher frequency of reducing end-groups which can undergo peeling reactions. Alkaline hydrolysis takes place at higher temperatures around 170 ^{o}C and above (Gellersted, 2009).

2.4 The biorefinery concept

There is an ongoing debate in today's society regarding the dependence of petroleum based energy resources, as the feasibility regarding its climate impact is questioned. To find better alternatives global research programs has during the last two decades been steered towards discovery of new and sustainable energy sources, as the future climate and global economy cannot depend on fossil fuels (De Bhowmick et al., 2017). The solution to the future energy and climate challenge will most likely be based on a usage of a variety of energy platforms such as water, wind, solar, fission and fusion, along with biomass.

One promising alternative to utilise biomass is the biorefinery concept and its possibility to use renewable resources as raw material for the production of materials and chemicals. The most acknowledged definition of a biorefinery has been written by the International Energy Agency (IEA); "Biorefining is the sustainable processing of biomass into a spectrum of marketable products and energy" (Cherubini, 2010).

2.4.1 Lignocellulosic biomass

Lignocellulosic biomass is a versatile raw material with potential to produce a wide range of products including energy, materials and chemicals. To utilise this potential the availability, production cost and value on the market must be assessed thoroughly. The current production rate of lignocellulosic biomass has been estimated to $2x10^{11}$ tons per year, although three percentage is used in non-food based areas. There are various lignocellulosic biomasses that are mostly derived from wheat, rice, corn stover, barley straw, sugarcane bagasse and wood. Comparing cost of the energy content ($/GJ), lignocellulosic feedstock is around 50% lower than other feedstock. Even if cellulosic biomass cannot meet the total demand, the high production rate and low cost of the raw material makes for a good case for further development as many different value added products can be made (De Bhowmick et al., 2017).

2.4.2 The forest biorefinery

The purpose of the forest biorefenery concept is to upgrade the lignocellulosic biomass into a variety of different materials and chemical products. There is currently a lot of material from the trees that are not fully utilised and end up as by-products at pulp and paper mills or left in the forest. From an economical point of view, it is a good idea to utilise the already built infrastructure around existing pulp and paper mills. Bark and forest residue, such as tops and branches, are potential raw material that today is poorly used and often discarded as residue material having a low value. The bark is

removed from the trunk of the tree and most often incinerated to produce steam. Forest residue is mostly left in the forest or used as fuel (Le Normand et al., 2014).

One potential process design to utilise these two lignocellulosic raw materials in a biorefinery is shown in Figure 10 below.

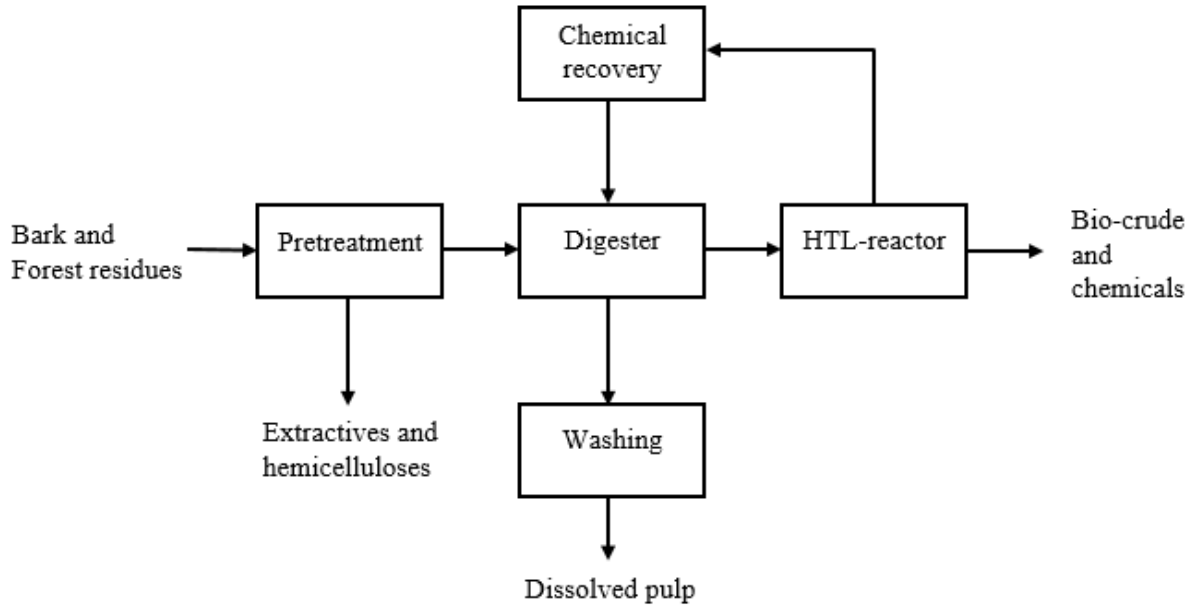

Figure 10: Flowsheet for the proposed forest residue biorefinery.

The first process step is pretreatment and this is done to make the following delignification step more efficient and also to extract some of the wood constituents such as extractives and part of the hemicelluloses. From the digester two fractions will be separated. One fraction containing cellulose that after further purification ends up as dissolving pulp. Dissolving pulp is a high-grade pulp mainly containing cellulose and it is mostly used for manufacturing of cellulose based fibres used in the textile industry (Bajpai, 2012). The other fraction is the spent cooking liquor containing dissolved lignin, sugar monomers and extractives. This lignin containing fraction could then be subjected to hydrothermal liquefaction (HTL), with the purpose to depolymerise lignin into bio-crude and other chemicals. HTL is a thermochemical conversion process that uses water as solvent to turn biomass into liquid fuels by using subcritical water to create an environment that can dissolve un-polar polymers like lignin into mostly liquid components (Elliott et al., 2015).

3 Method

3.1 Raw material

The raw material used in this study were pine wood meal from Scots pine (pinus silvestris) that had been air-dried and prepared using a Wiley mill with a sieve (<1 mm) and bark meal mixture of spruce and pine from Södra Skogsägarna, that had also been air-dried and prepared in the same way as the pine wood meal. Both the pine wood and the bark meal where kept in closed containers in room temperature. The dry content was calculated for both samples by weighing three 1 gram samples of each before and after drying them in an oven at 105 °C.

3.2 Alkaline hydrogen peroxide (AHP) pretreatment

In Table 2 the different process conditions used during alkaline hydrogen peroxide (AHP) of pine wood meal and bark meal is shown.

Table 2: The different pretreatment conditions.

Sample	Time [minutes]	Temperature [°C]	H_2O_2 concentration [wt. %]
Pine wood meal	**60**	**20**	**3.3**
Pine wood meal	**60**	**60**	**3.3**
Pine wood meal	**60**	**60**	**1.1**
Bark meal	**60**	**20**	**3.3**
Soxhlet extracted bark meal	**60**	**45**	**3.3**

The pretreatment was done by mixing 5 grams of dry sample with either 315 mL or 338 mL of distilled water followed by 35 mL or 11.6 mL of 30 wt. % hydrogen peroxide under constant stirring to achieve a 3.3 wt. % or 1.1 wt. % hydrogen peroxide solution. The pH of the solution was then changed from around 6 to 11.5 using 50 wt. % sodium hydroxide solution in order to maximise the reaction rate. Using vacuum filtration the solution was then filtered of and the filtrate was collected for further analysis. The filter cake was washed using 250 mL of deionised water and then dried in a convection oven at 40 °C for 72 hours (Gould, 1985).

3.3 Soda pulping

The soda pulping was performed by placing autoclaves in a temperature controlled vessel filled with polyethylene glycol. To get a concentration that could be approximated as constant bulk concentration a solids to liquor ratio of 1:150 was used. When preparing the cooking liquor 14.5 grams of sodium hydroxide was dissolved into 450 grams of deionised water. A sample of 3 grams of dry, raw or pretreated, pine wood or bark meal was then placed into the autoclave and the cooking liquor was poured in as well.

Four autoclaves were placed in the heating vessel having a temperature of 80 °C. The temperature was increased to 170 °C at a rate of 1 °C/minute and the timing for the autoclaves was started when the temperature reached 170 °C. The pulping times that were examined were 30, 60, 120, 180 minutes.

When the pulping was completed the autoclave was cooled in a water bath. The pulp was then filtered from the cooking liquor by using a Büchner funnel with a polypropene mesh. The cooking liquor was retained for further analysis. The saved pulp was then washed with 2 liters of deionised water and placed in a convection oven at 40 °C for 72 hours.

3.4 Extractives

Using the Tappi T204 cm-07 standard method the amount of non-volatile, solvent-soluble material in the bark meal could be quantified. The solvent used in this method can be either an ethanol/benzene mixture, acetone or dichloromethane. In this study only acetone was used due to its lower toxicity and superior solving properties. 20 grams of bark meal was divided in two and put in extraction thimbles made of cellulose, which were placed in soxhlet extractors. 400 mL of reagent grade acetone was poured into an extraction flask and set to heating that was adjusted to create a boiling rate which resulted in at least 24 extractions throughout the duration of four hours. After the 24th extractions were completed the extraction flasks were removed and the solvent was evaporated partly to a volume around of 25 mL. The remaining solution were then transferred to a smaller flasks of known weight and evaporated in a rotary evaporator to approximate dryness. The flasks were then dried in a convection oven at 105 °C for 24 hours and then allowed to cool in a desiccator for at least half an hour before they were weighed and the final amount extractives could be calculated using Equation 1 below.

$$Extractives\ [wt.\%] = \frac{(weight\ of\ oven\ dried\ extractives\ [g])}{(weight\ of\ oven\ dried\ bark\ meal\ [g])}\ x\ 100$$

Equation 1: Method used for calculation of extractives.

3.4.1 GC-MS/FID spectroscopic analysis

The evaporated extractives from the soxhlet extraction of bark meal was analysed using a gas chromatography of the model Agilent 7890A, Agilent 5975C Stockholm, equipped with parallel flame ionised detection, FID, and mass spectrometer, MS, detection operating in an electron ionisation mode. The extractives were semi-quantified using heptadecanoic acid methyl ester as internal standard and the derivatives were protected by trimethylsiyl (TMS). The solution was derived using 0.1 mL of BSTFA (99:1; *N*, *O*-bis(trimethylsilyl)trifluoroacetamide: chlorotrimethylsilane) as TMS reagent. Through an autosampler a volume of 1 µl of the solution was injected to the gas chromatographic system. The analytes were then separated and divided in two chromatographic columns using helium as carrier gas (HP-5MS, 30 m long, 0.25 mm internal diameter and 0.25 µm stationary phase thickness). The flow rates for the columns were 0.6 mL/min for the FID column and 1 mL/min for the MS column. The different temperatures set for the system were 300 °C for the injector, 250 °C for the FID detector and 50 °C for the GC oven before being set to increase with 2 °C/min after 2.25 minutes up to 300 °C. The temperature of the GC were then set to hold 300 °C for 30 minutes. The quadrupole and the MS source temperatures were adjusted to 150 °C and 250 °C. The spectral interpretations were carried out using the NIST MS search programme (version 2.0) functioning on the NIST/EPA/NIH Mass Spectral Database 2011 (NIST 11).

3.5 Klason analysis

3.5.1 Acid-insoluble lignin

The Klason method is based on subjecting water-insoluble fractions to acid hydrolysis of carbohydrates. The non-soluble residues were categorised as acid insoluble lignin or Klason lignin. The analysis methodology used by Theander and Westerlund (1986) was followed with the exception of some changes in the dilution step. 200 mg of sample was oven dried for 24 hours at 105 °C and then subjected to 3 mL of 72 wt. % sulphuric acid and carefully stirred and placed under vacuum for 15 minutes. Then the samples were placed in a 30 °C water bath for 1 hour, during this time the samples were stirred after 20 minutes and 40 minutes. The samples were then diluted with addition of 84 grams of deionised water and covered in aluminium foil and placed in a 125 °C heated autoclave for 1 hour. After cooling down the samples were filtrated and the soluble and insoluble lignin separated. To determine the amount of Klason lignin, the soluble lignin was dried for 24 hours at 105 °C and then weighted. From the soluble part, the filtrate, two dilutions were made. One by using 1 mL of filtrate with addition of 2 mL of 200mg/l fucose as internal standard and one with 5 mL filtrate and 2 mL internal standard. Both solutions were diluted up to 50 mL by

adding deionised water. The diluted 1 mL samples were used to measure the content of arabinose, rhamnose, galactose, xylose, mannose and acid soluble lignin, while the 5 mL samples were used to measure the glucose content.

3.5.2 Acid-soluble lignin high-performance liquid chromatography

To calculate the amount of acid soluble lignin a UV spectroscopy was used to measure the absorbance value at 205 nm. The UV spectrometer used was Analytik Jena with an absorbance constant of 110dm^3/g cm and Specord 205 (Dence, 1992).

3.5.3 Carbohydrate analysis using

By using high-performance liquid chromatography, HPLC, analysis the total composition of sugar monomers in the filtrate can be acquired by addition of fucose as internal standard. Two dilutions with the same concentration of internal standard were made from the filtrate, one diluted ten times and one diluted fifty times. The more diluted sample was used to detect glucose. Before injection to the HPLC the samples were filtered through a PVDF syringe filter (<45µm). The type of HPLC used was a Dionex ICS-5000 with CarboPac PA1 columns with NaOH/NaAc, 0.2M, and NaOH as eluents. To perform detection measurements an Electrochemical Detector was used and the software used was the Chromatography Data System Chromeleon version 7.1.3.2425.

3.6 Gel permeation chromatography

Using gel permeation chromatography, GPC, the polydispersity, DP, and molecular weights were measured. The molecules are sorted depending on their size using liquid column chromatography technique (Striegel et al., 2009). Lignin samples of 10-15 mg were dissolved into 10 mL DMSO. 100 µL of the dissolved sample was mixed with 4 mL DMSO, resulting in a concentration of 0.25 mg/mL. The GPC used was a Polymer laboratories PL-GPC 50 plus integrated system which was connected to ultraviolet, UV, and refractive index, RI, detectors. The wavelength use for the UV measurements was 280 nm (Polymer Laboratories, Varian Inc.). The chromatography columns, which were one PolarGel-M guard (50x7.5 mm) and two PolarGel-M (300x7.5 mm), were coupled in series with mixed types of pores 8 µm in size. Dimethyl sulfoxide (DMSO/LiBr (10 mM) was used a mobile phase with the flow rate of 0.5 mL/min.

3.7 IR

Infra-red spectroscopy was used to analyse lignin structure differences of both pretreated and untreated soda lignin from bark- and pine wood meal (Mattson et al, 2017). The instrument used was a PerkinElmer Frontier, GladiATR, PIKE Technologies, Madison, WI, USA, which recorded

the spectra with the resolution of 4 cm^{-1} corresponding to 32 scans. Then the spectra were compared to typical absorbance patterns for lignin.

4 Results & Discussion

4.1 Pretreatment

The nomenclature used in this work is found in Table 3. Table 4 show the chemical composition of the main wood constituents, i.e pine wood and bark meal, on the different samples after alkaline hydrogen peroxide, AHP. Besides lignin also small amounts of nonpolar polymers in the wood, such as extractives and suberin, may be included in Klason lignin measure.

Table 3: Numeration of the different samples. Nomenclature is used continuously.

Sample	Number
Pine wood meal (untreated)	**#1**
Pretreated pine wood meal 20 °C, 3.3 wt% H_2O_2, 60 min	**#2**
Pretreated pine wood meal 60 °C, 3.3 wt% H_2O_2, 60 min	**#3**
Pretreated pine wood meal 60 °C, 1.1 wt% H_2O_2, 60 min	**#4**
Bark meal (untreated)	**#5**
Pretreated bark meal 20 °C, 3.3 wt% H_2O_2, 60 min	**#6**
Soxhlet bark (untreated)	**#7**
Pretreated soxhlet bark 45 °C, 3.3 wt% H_2O_2, 60 min	**#8**

Table 4: Weight percentage of wood sugar content and lignin after Klason analysis of the different samples.

	Arabinose	Rhamnose	Galactose	Glucose	Xylose	Mannose	Klason Lignin	ASL	Other
#1	**0.77**	**0.12**	**1.26**	**42.1**	**4.67**	**11.5**	**27.2**	**0.55**	**11.8**
#2	**0.69**	**0.04**	**1.18**	**42.6**	**4.33**	**10.8**	**25.8**	**0.74**	**13.9**
#3	**0.69**	**0.06**	**0.78**	**46.9**	**3.82**	**11.4**	**24.7**	**1.02**	**10.3**
#4	**0.68**	**0.07**	**0.87**	**44.3**	**3.78**	**12.5**	**25.3**	**1**	**11.5**
#5	**3.43**	**0.30**	**2.08**	**25.8**	**2.81**	**2.80**	**39.0**	**2.39**	**21.4**
#6	**4.71**	**0.30**	**2.25**	**39.8**	**4.63**	**3.63**	**15.4**	**1.29**	**28.0**
#7	**3.30**	**0.00**	**2.06**	**23.8**	**2.49**	**2.30**	**37.2**	**1.72**	**27.2**
#8	**4.15**	**0.00**	**2.09**	**32.9**	**4.84**	**3.54**	**17.3**	**1.39**	**33.7**

Generally small effects on the sugars in the pine wood meal was found after the alkaline hydrogen peroxide pretreatment compared to untreated reference pine wood meal. The small change in carbohydrates that can be detected are most likely due to oxidative reactions on the hemicelluloses, since the weight percentages decreases mainly for galactose, 1.26 % to 0.78 %, and xylose, 4.67 % to 3.78 %. These sugars correlate to the hemicelluloses galactoglucomannan and arabinoglucuronoxylan, which are present in softwood. The increase of glucose after pretreatment is most likely an effect of hemicelluloses being degraded, while the glucose which is mostly found in cellulose remain less effected and are enriched in the pretreated solid fraction.

The monomeric sugars detected in the bark meal were mainly arabinose, galactose, glucose, xylose and mannose which are the same as for the pine wood meal, though the weight percentages vary. These monomeric sugars and amounts match well with the quantities in spruce and pine (Le Normand, et al 2014; Burkhardt et al 2013). For the bark meal no clear trends regarding the oxidative pretreatment effects on the carbohydrates could be observed.

Analysing the lignin fraction in the untreated and the pretreated pine wood meal yielded the amount of Klason lignin and acid soluble lignin, ASL, for the samples. Only a minor effect on the lignin by pretretment of the pine wood meal was detected. The harshest pretreatment, #3, resulted in the largest decrease of 2.55 wt. % of the Klason lignin and an increase of 0.47 wt. % of the ASL.

The lignin in softwood bark meal subjected to the pretreatment was effected to a larger extent than the pine wood meal. This trend on the weight percentage can be seen for both the bark meal, 39.0 % to 15.4 %, as well as the bark meal subjected to soxhlet extraction, 37.2 % to 17.3 %. The amount of Klason lignin removed from the bark meal and the soxhlet extracted bark meal was 23.6 wt. % and 19.8 wt. %. The results for the bark meal indicate a large uncertainty due to a significant amount of other substances, not measured with the methods used in this study.

For both the pine wood meal and the bark meal a bleaching effect by the hydrogen peroxide pretreatment was observed. This was most notable on the bark meal since the colour changed from originally rich brown to a more off white colour with a yellow hint.

To control the error margin of the Klason method, duplicates for samples #1, #2, #5 and #6 were made to compare the spread of the results. The spread was insignificantly small and showed that the method used was accurate.

4.2 Soda pulping

Table 5 shows wt. % of the chemical composition of the samples for the different residence times of soda pulping.

Table 5: Weight percentage of carbohydrate content and lignin after Klason analysis of the different soda pulping samples from untreated and AHP pretertment of pine wood and bark meal, see Table 3 for number code.

	Arabinose	**Galactose**	**Glucose**	**Xylose**	**Mannose**	**Klason Lignin**	**ASL**	**Other**
#1								
30	0.22	0.23	58.3	2.22	5.67	12.0	0.56	20.8
60	0.16	0.20	63.7	2.26	6.13	7.66	0.60	19.3
120	0.08	0.08	72.7	1.66	4.81	3.56	0.71	16.4
180	0.08	0.08	69.7	1.62	5.20	2.40	0.63	20.3
#2								
30	0.27	0.31	59.0	2.49	4.80	14.4	0.78	18.0
60	0.15	0.17	59.1	2.02	4.32	7.65	0.61	25.9
120	0.09	0.10	72.2	1.92	5.45	2.80	0.73	16.7
180	0.07	0.07	71.5	1.79	4.61	2.37	0.63	19.0
#3								
30	0.12	0.07	66.7	1.66	5.08	4.90	0.70	20.7
60	0.09	0.06	69.5	1.71	5.05	2.78	0.70	20.0
120	0.07	0.04	73.2	1.63	4.56	1.24	0.65	18.6
180	0.05	0.03	74.6	1.59	4.41	0.99	0.64	17.7
#4								
30	0.16	0.12	71.6	1.29	4.63	7.03	0.85	14.3
60	0.11	0.09	75.5	1.25	5.1	3.72	0.76	13.4
120	0.07	0.06	75.6	1.09	4.06	2.21	0.7	16.2
180	0.05	0	75.7	0.86	4.17	1.24	0.69	17.3
#5								
30	0.69	0.84	26.7	4.19	2.62	14.8	0.64	49.5
60	0.57	0.87	26.4	4.46	2.75	16.8	0.65	47.5
120	0.35	0.72	28.0	3.67	2.58	11.2	0.63	52.8
180	0.25	0.61	26.3	3.34	2.26	10.3	0.53	56.4
#6								
30	0.35	0.32	25.9	3.07	1.63	23.7	0.83	44.3
60	0.22	0.25	24.2	2.44	1.34	27.7	0.69	43.2
120	0.12	0.17	23.9	1.84	1.11	24.3	0.64	47.9
180	0.11	0.18	26.3	1.84	1.20	23.7	0.46	46.2
#8								
30	0.51	0.54	69.0	3.33	1.19	7.46	0.81	17.2
60	0.42	0.53	70.1	3.24	1.25	6.01	0.75	17.7
120	0.26	0.44	71.8	2.57	0.99	4.85	0.83	18.3
180	0.17	0.34	67.7	2.4	1.15	7.92	0.59	19.8

As can be found in Table 5 there is a large influence on the carbohydrates during the soda pulping due to the highly alkaline conditions at elevated temperatures between 80 °C up to 170 °C. The major degradation of the carbohydrates in pine wood meal occurs within the heating period, from 80 to 170 °C which takes around one and a half hour to reach, and the first 30 minutes of pulping. The monomeric sugar that decreases the most during this period is galactose, that is reduced the most in pulping of pine wood meal with AHP at 60 °C (#3 and #4) where the decrease was from 0.07 and 0.12 to 0.03 and 0 wt. % respectively. Xylose and mannose were also reduced substantially to approximately half the value of start content. For the pulping with AHP at 60 °C (#3 and #4) the xylose went from 1.66 and 1.29 to 1.59 and 0.86 wt. % and mannose decreased from 5.08 and 4.63 to 4.41 and 4.17 wt. % respectively. These observations show a more severe degradation of the hemicellulose carbohydrates than the glucose mainly present in cellulose. Between 30 and 180 minutes of pulping no major difference on the monomeric wood sugars was observed, although a trend in a small amount of degradation over time could be detected.

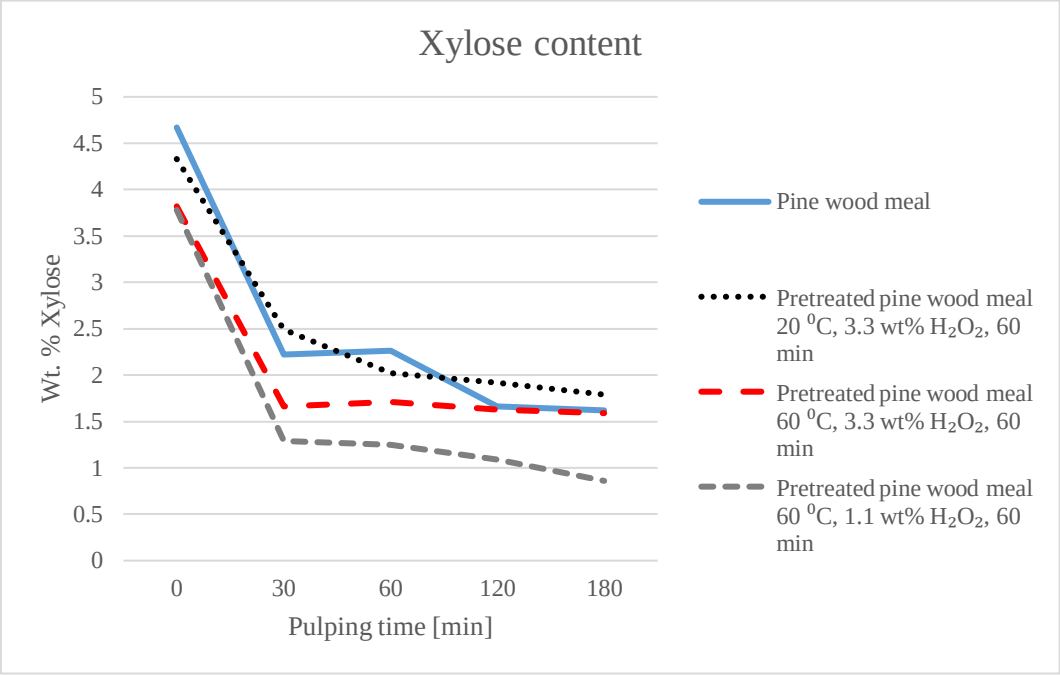

Figure 11: Results of xylose content in weight percentage after alkaline hydrogen peroxide pretreatment followed by soda pulping of pine wood meal. The zero-point on the x-axis shows the values prior to the warm-up period, the other times are set after the warm-up period.

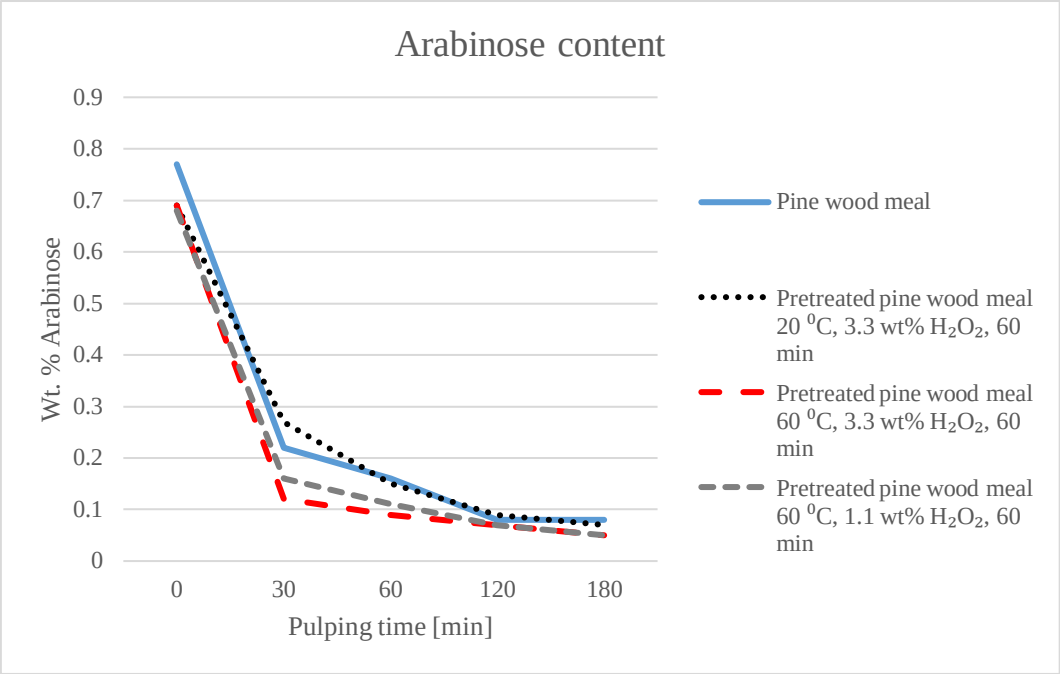

Figure 12: Results of arabinose content in weight percentage after alkaline hydrogen peroxide pretreatment followed by soda pulping of pine wood meal. The zero-point on the x-axis shows the values prior to the warm-up period, the other times are set after the warm-up period.

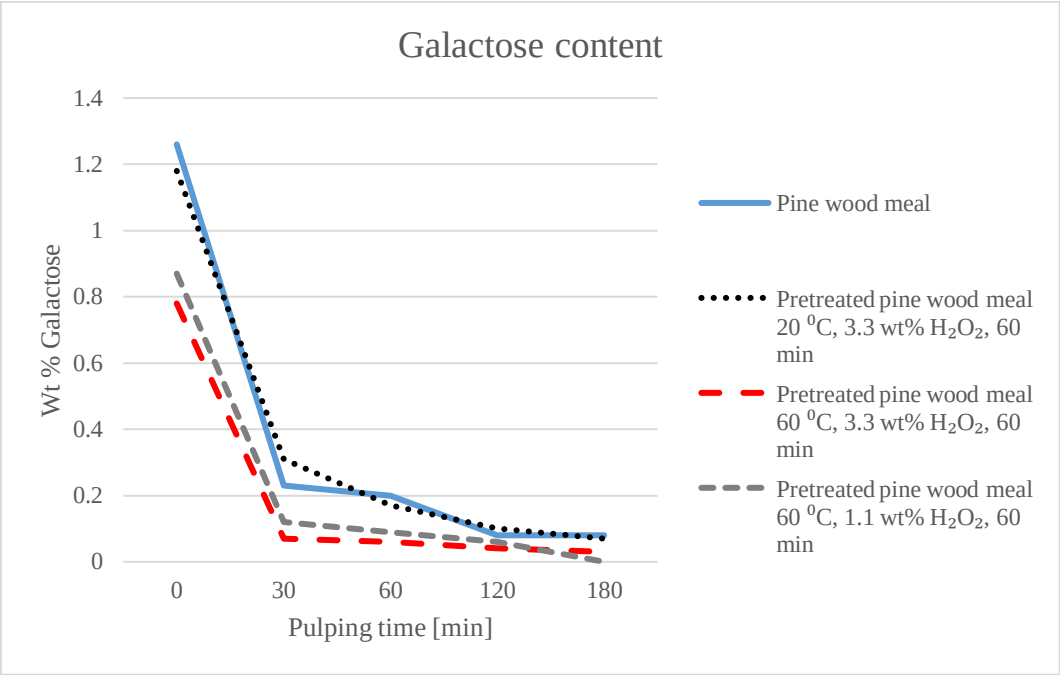

Figure 13: Results of galactose content in weight percentage after alkaline hydrogen peroxide pretreatment followed by soda pulping of pine wood meal. The zero-point on the x-axis shows the values prior to the warm-up period, the other times are set after the warm-up period.

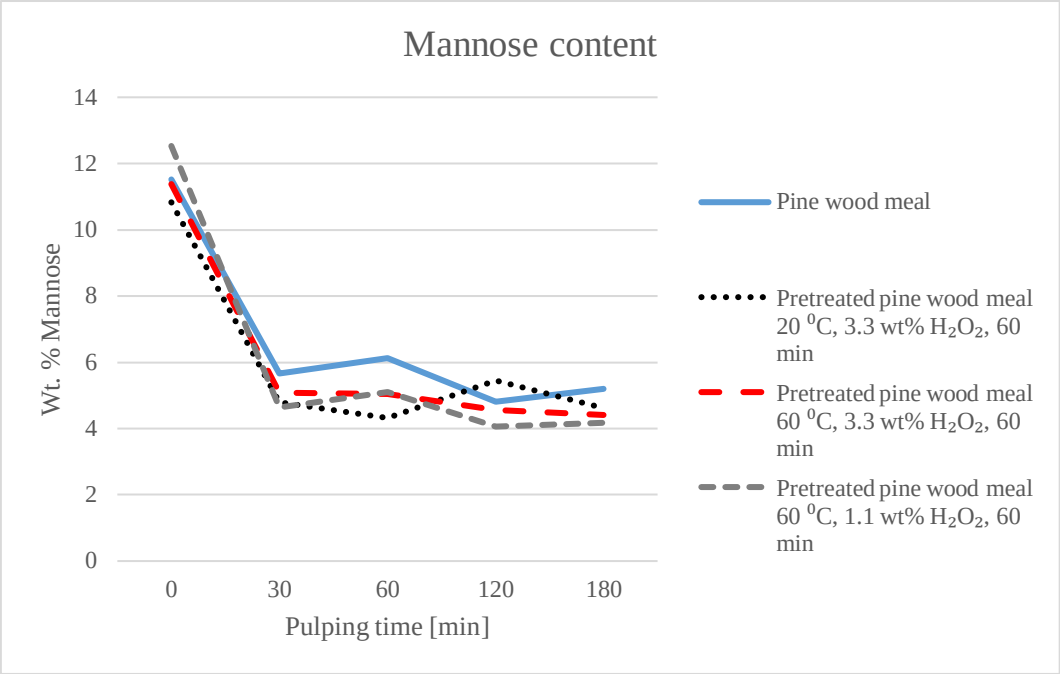

Figure 14: Results of mannose content in weight percentage after alkaline hydrogen peroxide pretreatment followed by soda pulping of pine wood meal. The zero-point on the x-axis shows the values prior to the warm-up period, the other times are set after the warm-up period.

One possible reason for the fast degradation of hemicelluloses in the start of the pulping may be due to the galactose side groups being cleaved from the glucomannan backbone at a very high rate, which can be seen in the Figure 13. The stagnation in degradation rate which occurs later in the pulping for mannose may be due to the strong interactions between cellulose fibres and glucomannans (Eronen et al., 2011; Wang et al., 2017).

A possible reason for the stagnation of degradation of xylose after 30 minutes of pulping may be due to acetyl groups formed during the AHP pretreatment. The acetyl side groups may enable better interaction with the hydrophilic cellulose parts and hydrophobic lignin, making them more resistant to degradation (Busse-Wicher et al., 2014). The stagnation is however more likely because of arabinose and uronic acid side groups.

In a previous study by Wigell et al., it was found that the degradation of xylan correlates with the degree of delignification during soda pulping of softwood meal, which was also found in this study. This correlation may be due to interaction and chemical bonding between xylan and lignin (Wigell et al., 2007). A difference in xylose to lignin yields could be seen for the pretreated samples, see Figure 15. The yield of xylose removed corresponding to the yield of lignin were lower for the samples pretreated at 60 °C compared to the other samples. This may be due to a higher degree of oxidation achieved for the AHP pretreatments at 60 °C. Although similar trends

were found comparing the studies it should be noted that less data points were used to construct the trend lines in this study, which increase the uncertainty of the results.

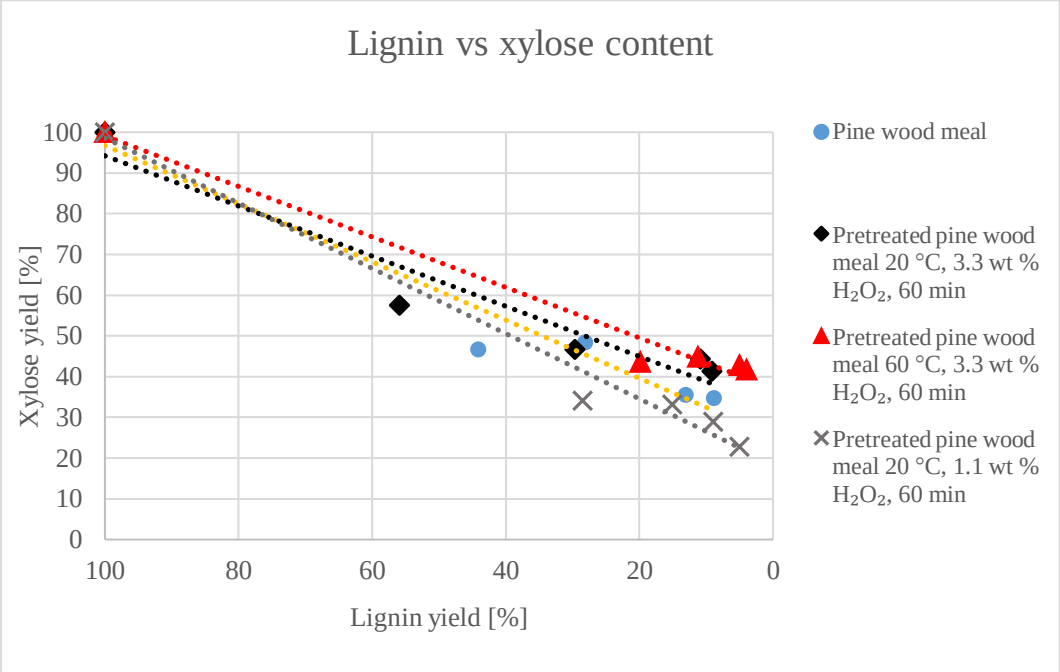

Figure 15: Results of xylose yield as a function of the delignification for the pine wood samples during soda pulping.

The effect of the soda pulping on the bark meal carbohydrates follows a similar trend as the pine wood meal results. The major degradation occurs within the heating period, from 80 to 170 °C which takes around one and a half hour to reach, and the first 30 minutes of pulping. The monomeric sugars that degraded the most was arabinose and galactose. The arabinose was reduced from 0.35 and 0.51 to 0.11 and 0.17 wt. % for the pulps with AHP (#6 and #8) respectively. The galactose went from 0.32 and 0.54 to 0.18 and 0.34 wt. % for the AHP soda pulps. A continued small decrease was observed over longer pulping times. The amounts of glucose remain unchanged throughout the pulping indicating low degradation of the celluloses (Le Normand et al., 2014).

In Figure 16 the difference in Klason lignin content for the different pine wood meal pulps are plotted against time of pulping. The data can also be found in Table 5. All the samples had around 25 wt. % Klason lignin prior to the soda pulping.

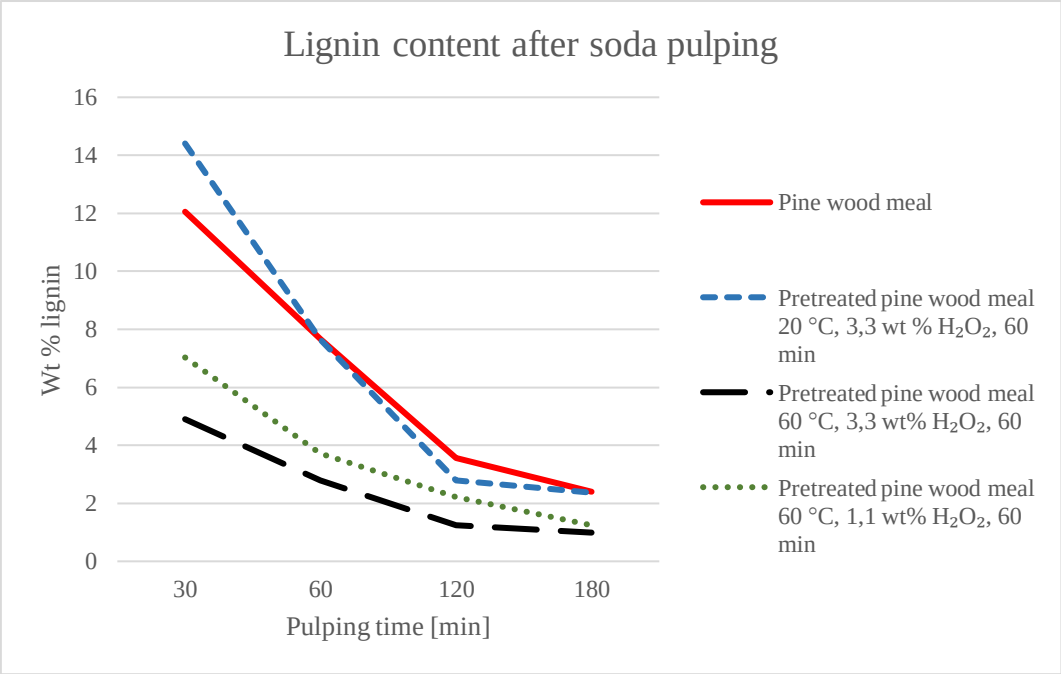

Figure 16: Results of Klason lignin content in weight percentage after alkaline hydrogen peroxide pretreatment followed by soda pulping of pine wood meal.

In Figure 16 it can be seen that after 180 minutes of soda pulping the lignin content is about the same for the pine wood meal and the 20 °C AHP. The Klason lignin amount is slightly lower for the 60 °C AHP pretreated soda pulp, showing that final weight percentage of Klason lignin is most effect by the temperature during the AHP pretreatment. A major part of the delignification occurs during the heating period and the first 30 minutes of pulping. Very good results was found for the 60 °C AHP pretreated pine wood meals, that had a Klason lignin wt. % of 4.90, compared to the untreated pine wood meal that had 12.05 wt. %, after 30 minutes of soda pulping.

In Figure 17 the difference in Klason lignin content for the different bark meal pulps are plotted against time of pulping. The plot data can be found in Table 5.

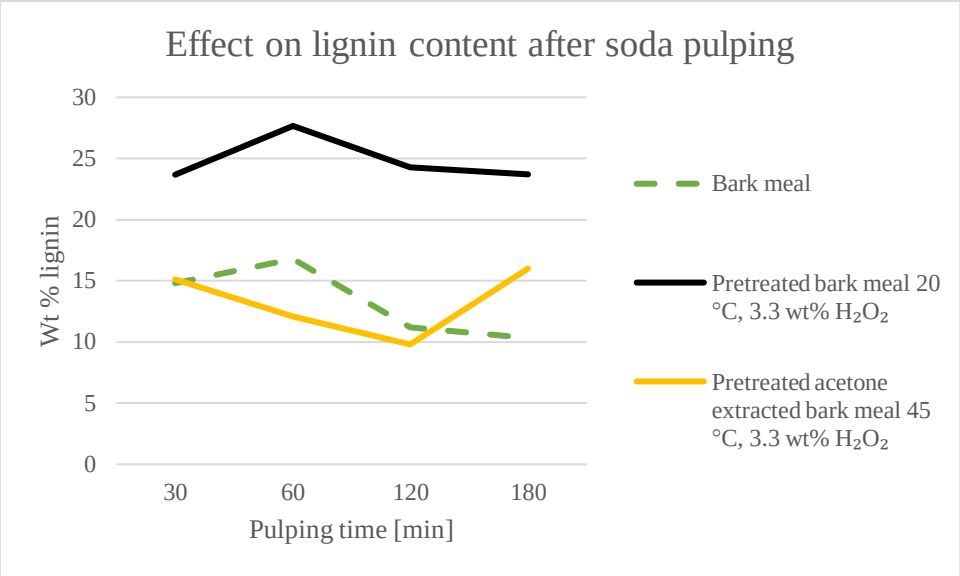

Figure 17: Results of Klason lignin content in weight percentage after alkaline hydrogen peroxide pretreatment followed by soda pulping of bark meal.

Untreated bark decreased from approximately 15 to 10 wt. % in klason lignin during the cooking interval 30-180 minutes. The AHP bark meal gave contradictory higher levels of klason lignin approximately 25 wt. %, compared to untreated bark meal. An attempt to remove the extractives from bark meal was done by extraction with acetone. This sample was then subjected to AHP followed by soda pulping for 30-180 minutes, yielding klason lignin levels in the same range as untreated bark.

No concluding results was observed from the Klason lignin analysis of bark meal from softwood. Previous studies by Burkhardt et al, has shown the difficulty in doing compositional analysis using the Klason lignin method on softwood biomass including bark. Bark contains significantly larger amounts of lignin, extractives, ash and other components that are difficult to extract. It is not only the amount, but also the complexity and type of extractives in bark that differs from softwood making it complicated. The results depends strongly on solvent used in the extraction and examples of solvents are acetone, ethanol, water or ethanol-benzene. To remove all extractives multiple solvents has to be used, as there are extractive components in bark that are both polar and nonpolar. It has been shown that for bark without an extraction step before the Klason analysis method, an overestimation of the lignin content can occur although the carbohydrate content only shows minor variations (Burkhardt et al., 2013). Another source of error for the bark samples were that the bark soda pulp was hard to completely dissolve with sulphuric acid in the Klason method, which may have resulted in a higher measured lignin content.

4.2.1 Concluding discussion regarding chemical composition of pulp after soda pulping

During the soda pulping an effective removal of lignin, xylose and mannose has been shown, without signs of cellulose solubilisation. The effect became more evident when an AHP preatretment at 60 °C were used prior to the soda pulping, which resulted in that lignin and hemicelluloses were almost completely removed after 30 to 60 minutes of soda pulping. The decrease in levels of xylose and mannose correlates to a decrease in the hemicelluloses xylan and glucomannan. This shows that the pulp has a great potential to be used as dissolving pulp, where low lignin and hemicellulose content are desired together with a high cellulose yield. Representative characterisation of dissolving pulps found in literature has a xylan content around 3.5 wt. %, which the AHP soda pulping method in this study achieved (Sixta, 2006).

4.3 GPC

The molecular weight of precipitated lignin were analysed using gel permeation chromatography, GPC, and the molecular weight and polydispersity could then be plotted against pulping time. The results are illustrated in Figure 18 and 19. LignoBoost softwood Kraft lignin from Bäckhammar was used as a reference since this is currently the most feasible lignin separation technique for Kraft pulping.

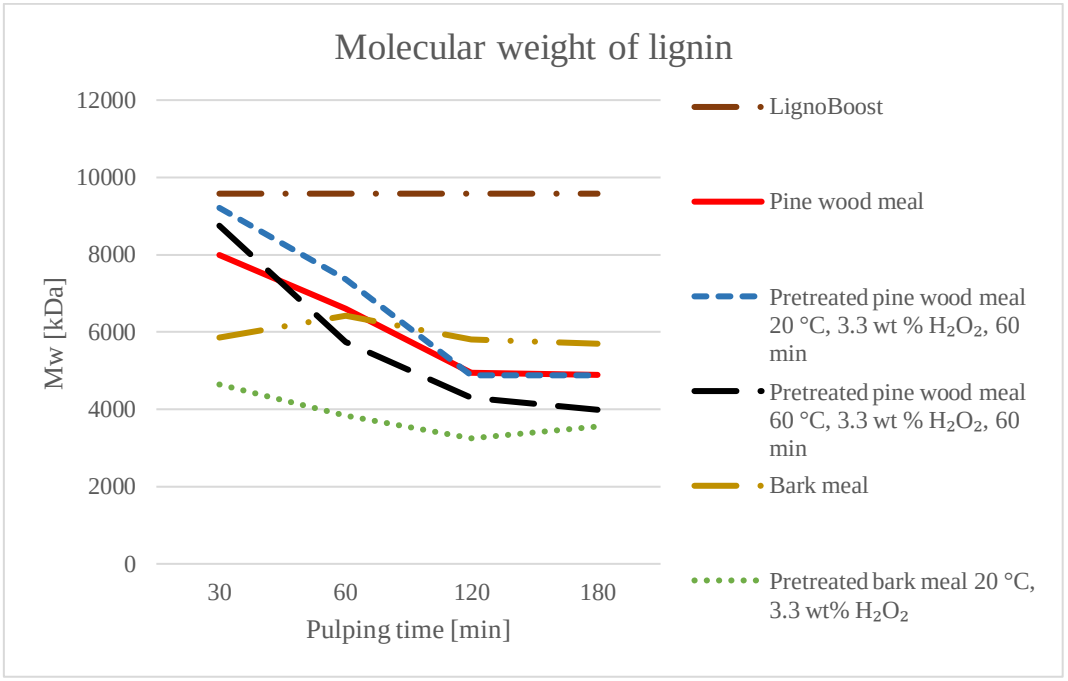

Figure 18: Molecular weight of lignin for the different samples of pine wood meal and bark meal using LignoBoost softwood Kraft lignin from Bäckhammar as reference.

For the pine wood meal a decrease in molecular weight could be observed over increased pulping time. The same trend was found for pine wood meal with AHP, though the molecular weight was

slightly higher after 30 minutes of pulping comparted to untreated. Both the AHP samples decreased at a faster rate than the untreated pine wood meal. It can be observed that for all the pine wood meal samples a stagnation in the decrease of molecular weight occurs after 120 minutes of pulping. The pulp with AHP at 60 °C reached the lowest molecular weight.

For the untreated bark meal there were no significant change of molecular weight observed and the bark meal subjected to AHP show a slight decrease.

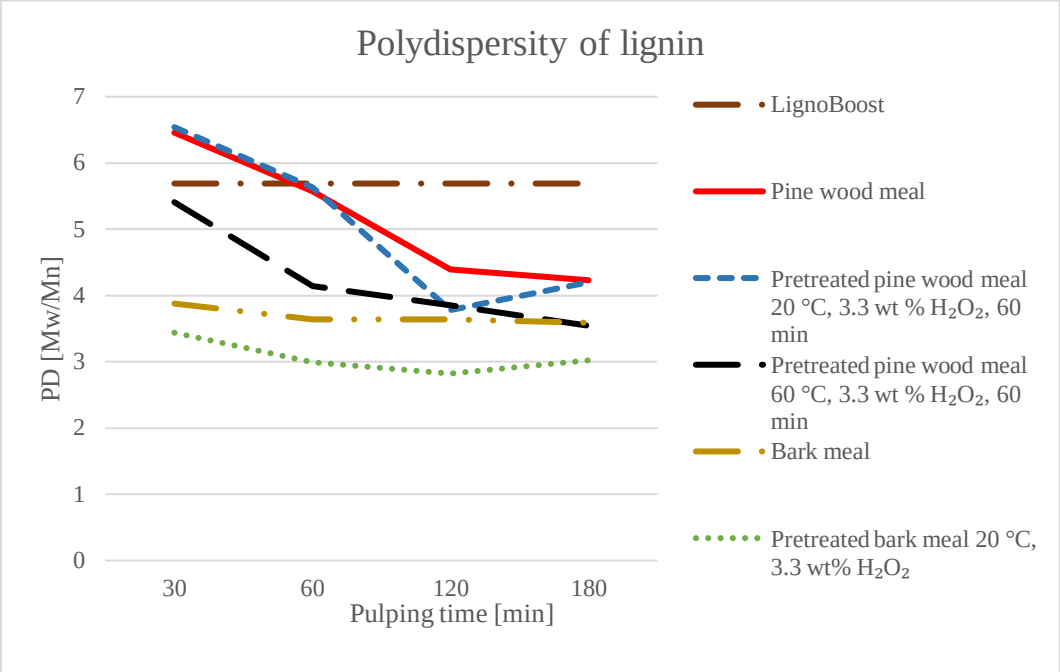

Figure 19: Result for polydispersity of lignin for the different samples of pine wood meal and bark meal using LignoBoost softwood Kraft lignin from Bäckhammar as reference.

The same trends that was detected in molecular weight was seen for polydispersity although the changes were smaller. This indicates a trend of more homogenous molecular weight with increased pulping time. The reason for this is most likely that that dissolved lignin fragments continues to disintegrate in the solution.

In order to minimise source of error all the measured samples were performed in one series along with known reference samples. For all measurements duplicate samples were performed.

4.4 Comparison with forest residues study

In a previous study conducted at Forest Products and Chemical Engineering at Chalmers University of Technology a forest residue mixture where examined in the same way as pine wood meal and bark meal were examined in this study. The results on molecular weight and Klason lignin can be seen in Figure 20 and 21, compared with the pine wood meal and bark meal results.

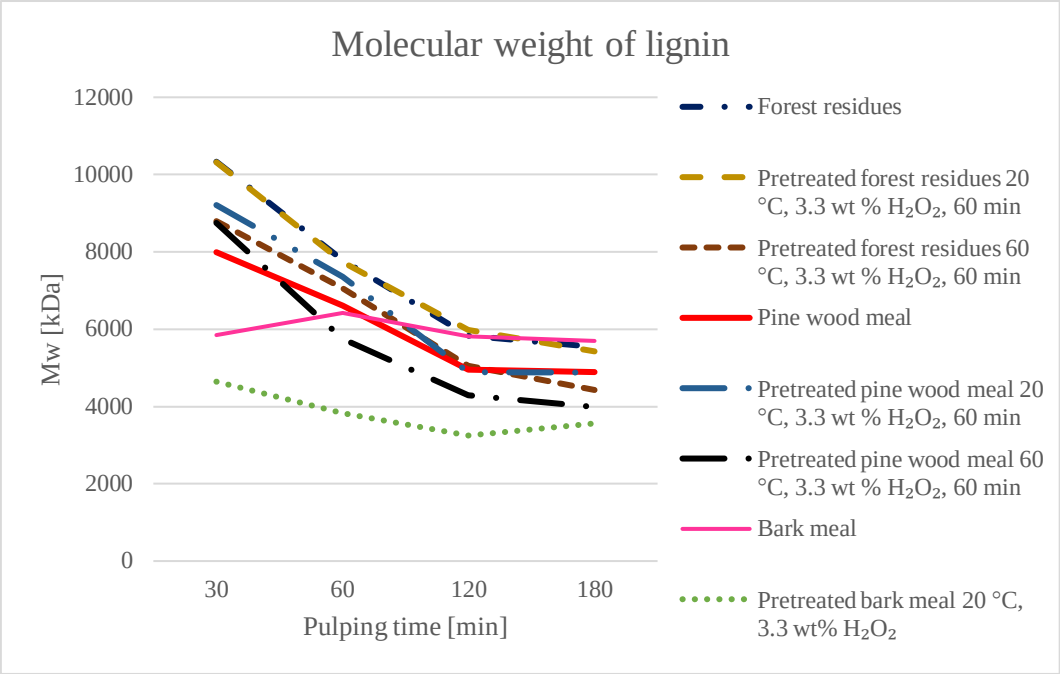

Figure 20: Result for molecular weight of lignin for the different samples of pine wood meal, bark meal and forest residues from the previous study (Martinsson & Sonne, 2017).

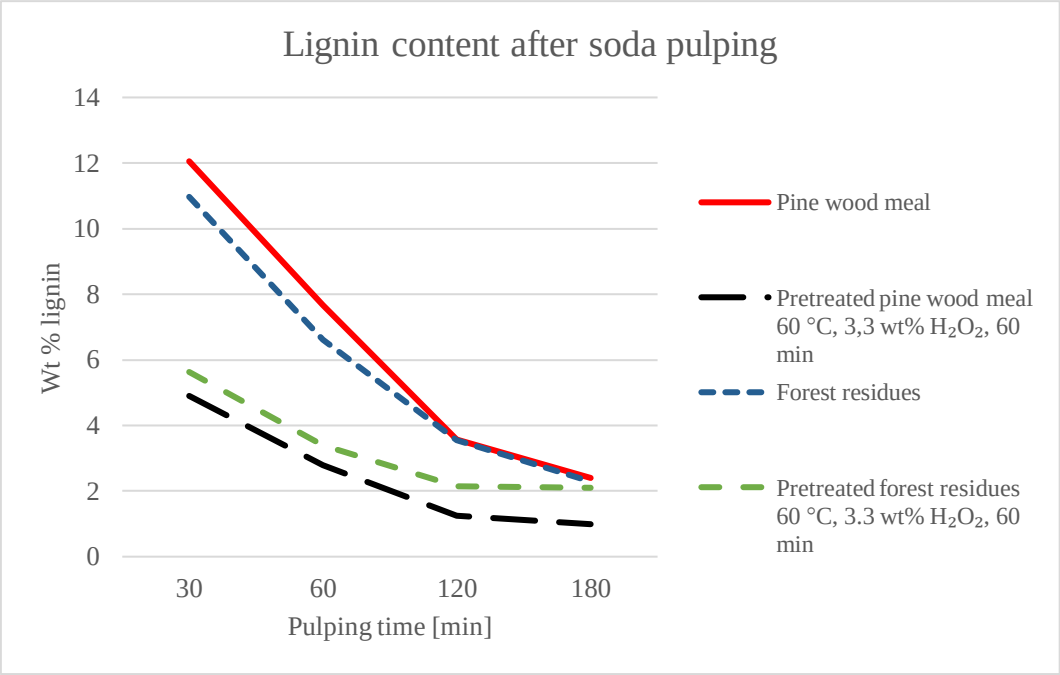

Figure 21: Results of Klason lignin analysis for two samples of pine wood meal and two samples of forest residues from the previous study (Martinsson & Sonne, 2017).

Both the molecular weight as well as the Klason lignin of the forest residues shows a similar result as for the pine wood meal with decreasing numbers over the pulping time. The Klason lignin final value becomes lower for the pretreated pine wood meal than for the pretreated forest residues. There

is also larger differences between the untreated and the pretreated pine wood meal than for the untreated and pretreated forest residues in decreased molecular weight.

The forest residues in the previous study contained a mixture of branches, bark and wood from both softwood and hardwood. The mixture of components might be the reason to why the final weight percentage of lignin is slightly higher for the forest residues. This might be due to the difference in composition of hemicelluloses in hardwood and softwood, difference in structure of the lignin in hardwood and softwood, and it may also be due to the bark present in the forest residues. This may be one reason to why the molecular weight of the forest residues does not decrease as much as for the pine wood meal. It can be seen in Figure 20 that the molecular weight of the bark remains relatively constant over pulping time.

Since the trends are the same for pine wood meal and the forest residues it show a potential to work as a model material for further optimisation of the AHP pretreatment followed by soda pulping of forest residues and receive a better understanding of the pulping mechanisms.

4.5 IR

4.5.1 Pine wood and bark meal ATR-IR

The infrared analysis technique, ATR-FTIR, was chosen for investigation of chemical composition of the AHP pretreated pine wood and bark meal samples, the results can be found in Figure 22. Both untreated and AHP pretreated raw material samples, as well as soxhlet extracted bark was analysed. The FTIR is useful for detection of functional groups in the carbonyl region, this region is between 1820-1540 cm^{-1} where ester, carboxylic acid, ketone and aldehyde, show strong specific stretching absorbance (Faix, 1992).

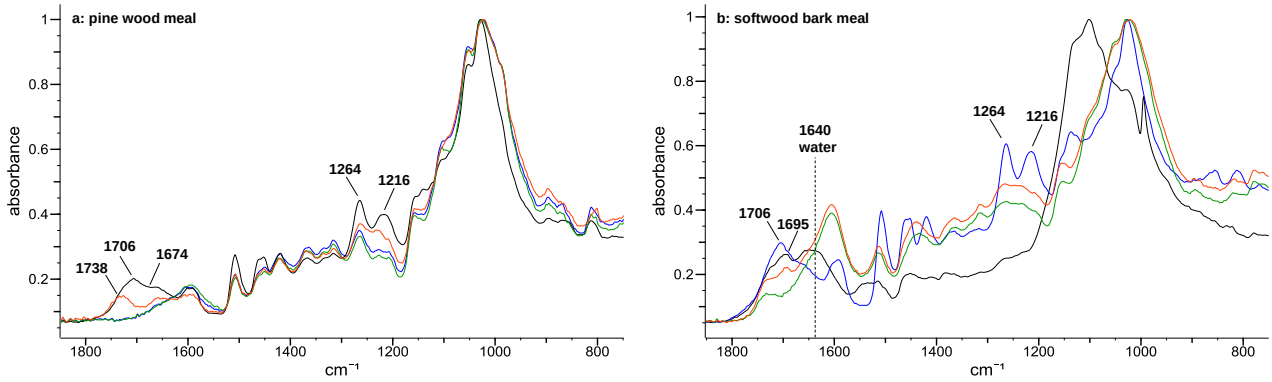

Figure 22: Infrared spectra (ATR-IR) 1800-800 cm^{-1} of untreated and AHP treated pine wood and softwood bark meals. In the left picture pine wood meal is shown: untreated (red); AHP, 1.1 wt. % H_2O_2, 60 °C, 60 min (black); AHP, 3.3 wt. % H_2O_2, 20 °C, 60 min (blue); AHP, 3.3% H_2O_2, 60 °C, 60 min (green). In the right picture softwood bark meal is shown: untreated (red); AHP, 3.3 wt. % H_2O_2, 20°C, 60 min (black); extractive free bark: untreated (green); AHP, 3.3% H_2O_2, 45 °C, 60 min (blue). Spectra normalised to highest band 1029-1026 cm^{-1} except for AHP treated bark, 3.3 wt. % H_2O_2, 20 °C, 60 min, to 1102 cm^{-1}.

Comparing untreated pine wood with oxidative AHP pretreated pine wood samples clearly shows an incorporation of conjugated carbonyl groups at 1690-1705 cm^{-1} and unconjugated at 1705-1720 cm^{-1}, for 1.1 wt. % AHP pretreatment. This is an indication that the oxidation has occured in the pine wood meal lignin. Increasing the AHP pretreatment concentration to 3.3 wt. % for both 20 °C and 60 °C completely removed the carbonyl absorbance, illustrated by the blue and green lines in Figure 22 (a). This finding is hard to explain and needs to be further investigated.

It is likely that a substantial deacetylation of hemicellulose have occurred during the AHP treatment since the hemicellulose specific absorbance of acetyl groups at 1734 cm^{-1} is not found after AHP treatment of pine wood meal (Bui et al., 2015; Singh & Sivanandan, 2014). From carbohydrate analysis in chapter 4.1 we acknowledged that the hemicellulose content only changes slightly after AHP pretreatment.

All bark meal samples, both untreated and soxhlet extracted, were oxidised after the AHP treatment. In the ATR-IR spectra, Figure 22 (b), both untreated and AHP pretreated bark show incorporation

signals of conjugated carbonyl groups at 1690-1705 cm^{-1} and unconjugated carbonyl groups at 1705-1720 cm^{-1}. Although the samples were dried, sign of water disturbances can be found at 1640 cm-1 which might affect the results.

The conclusion is that the AHP treatment affects the carbonyl groups in both pine wood and bark meal. This has also been shown in previous studies that oxidation of both the conjugated and unconjugated carbonyl groups increase the delignification during soda pulping (Hagström-Näsi & Sjöström, 1987; Gierer & Norén, 1982).

4.5.2 Pine wood lignin from soda pulping

Investigation of the different alkaline lignins from untreated and AHP treated pine wood meal and bark meal was made with ATR-IR in order to reveal any structural changes related to delignification time and AHP pretreatment.

Visual inspection of the IR absorbance bands in carbonyl region at 1820-1540 cm^{-1} and fingerprint region at 1700-700 cm^{-1} shows two different types of spectra. In Figure 23 AHP pretreated alkaline lignin time fractions after 30 and 60 minutes were significantly different with respect to the later time fractions after 120 and 180 minutes and all the untreated alkaline time fractions. The change in IR absorbance spectra indicates that AHP affected the lignin fraction in pine wood meal during the pretreatment through oxidation reactions of the carbon-lignin network.

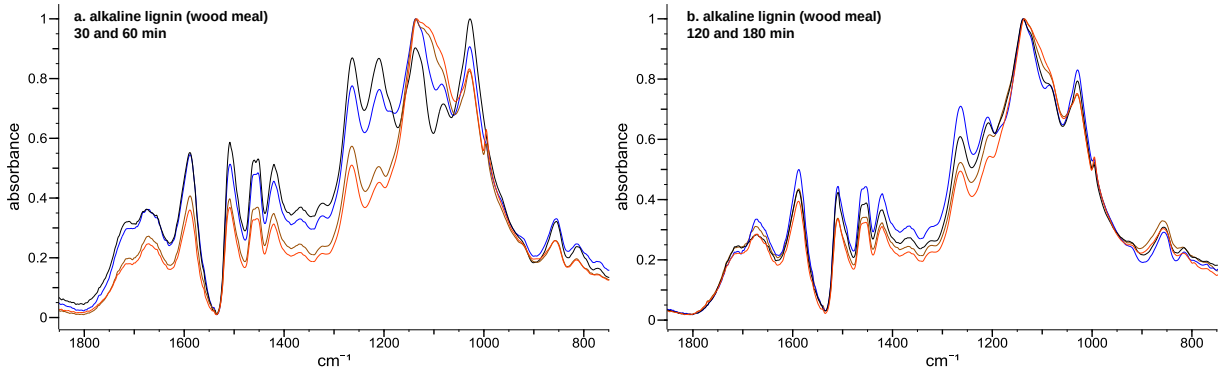

Figure 23: Infrared spectra (ATR-IR) of untreated and AHP pretreated pine wood lignins. In the left picture 30 and 60 minutes of pulping are shown: untreated 30 minutes (red); untreated 60 min (brown); AHP, 3.3 wt. % H_2O_2, 60 °C, 30 min (black); AHP, 3.3% H_2O_2, 60 °C, 60 min (blue). In the right picture 120 and 180 minutes of pulping are shown: untreated 120 min (red); untreated 180 min (brown); AHP, 3.3 wt. % H_2O_2, 60 °C, 120 min (black); AHP, 3.3% H_2O_2, 60 °C, 180 min (blue). Spectra normalised to highest band 1136-1138 cm^{-1} except for the AHP pretreated pine wood (3.3% H_2O_2, 60°C) lignin at 30 min (to 1027 cm^{-1}).

In the carbonyl region both conjugated and unconjugated carbonyl (C=O) absorbance intensity increased after AHP oxidation for the 30 and 60 minute time fractions for the pine wood meal, see Figure 23. This change is accompanied with a large increase in intensity of signals at 1264 cm^{-1} and 1205 cm^{-1} in the fingerprint region. These absorbance bands have contribution of C-O stretching from carbonyls, ethers and alcohol structures (Coates, 2006; Heitner et al., 2010).

In summary one possible interpretation is that oxidative AHP pretreatment changes the lignin structure by formation of carbonyls and other oxygen structural motif. This change may contribute to the enhanced delignification that have been detected with AHP pretreatment, discussed in chapter 4.2. In a similar study with mild oxidative pretreatment of pine wood followed with alkaline delignification an increased delignification rate was also detected. The authors proposed that this effect could be related to demethoxylation and incorporation of carbonyls and quinone structures in the lignin (Hagström-Näsi and Sjöström 1987).

After 120 minutes of soda pulping, the FTIR spectra of the AHP pretreated pine wood meal is very similar to all the time fractions of untreated alkaline pine wood lignins. This indicates that the final AHP alkaline lignin is similar to the untreated alkaline lignin from pine wood meal.

4.5.3 Bark lignin from soda pulping

In Figure 24 the ATR-IR spectra of untreated and AHP pretreated alkaline lignin can be found. Analysing bark is complex due to the large variety of different organic polymers existing in bark, i.e. lignin and extractives. The guaiacyl lignin unit's specific absorbance was detected at the points; 1715, 1588, 1509, 1466, 1452, 1422, 1369, 1318, 1264, 1205, 1137, 1081 and 1030 cm^{-1}, illustrated in Figure 24. The signal intensities differ compared too alkaline lignin from pine wood meal, indicating that this is a mixture of polymers. Although high absorbance in the carbonyl region and the fingerprint region, C-O, related frequencies of 1050-1300 cm^{-1} was found, no clear difference between untreated and AHP pretreated bark lignin could be detected in accordance to previous studies (Coates 2006; Heitner et al. 2010).

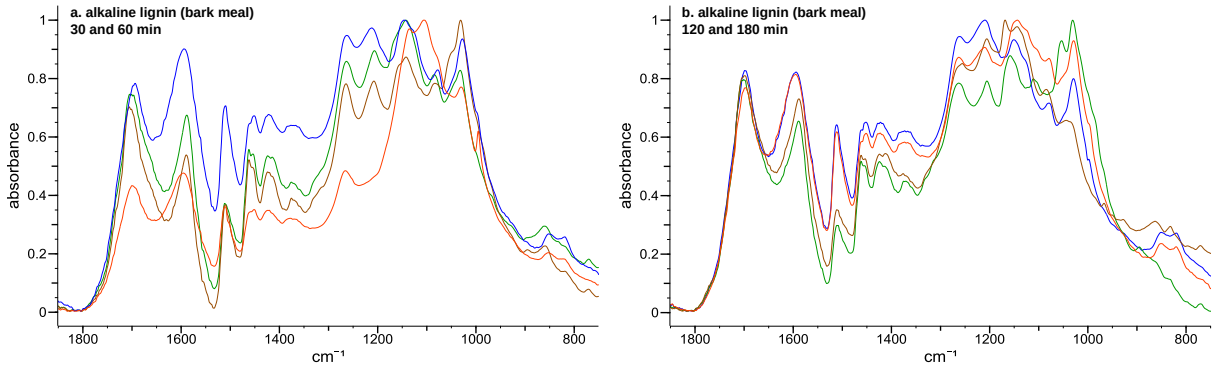

Figure 24: Infrared spectra (ATR-IR) of untreated and AHP pretreated softwood bark lignins. In the left picture 30 and 60 minutes of pulping are shown: untreated 30 minutes (red); untreated 60 min (blue); AHP, 3.3 wt. % H_2O_2, 20 °C, 30 min (brown); AHP, 3.3% H_2O_2, 20 °C, 60 min (green). In the right picture 120 and 180 minutes of pulping are shown: untreated 120 min (red); untreated 180 min (blue); AHP, 3.3 wt. % H_2O_2, 20 °C, 120 min (green); AHP, 3.3% H_2O_2, 20 °C, 180 min (brown). Spectra normalised to highest band 1000-1300 cm^{-1}.

4.6 NMR spectroscopic analysis

The nuclear magnet resonance spectroscopic analysis technique is an excellent tool to determine specific chemical structures in macromolecules such as lignin. The high resolution two-dimensional $^{13}C,^{1}H$-correlated Heteronuclear Single Quantum Coherence NMR technique (2D HSQC NMR, 2D NMR) have been used for investigation of the inter-unit linkages in lignin which are β-O-4, β-β and β-O-5 bonds. The specific chemical shifts for these inter-unit linkages have been reported earlier and were used for interpretation of the 2D NMR spectrums (Balakshin et al. 2003; Mattsson et al. 2016).

A previous study reported that both untreated and AHP pretreated forest residue alkaline lignins were absent of β-O-4 lignin inter-unit linkages after 180 minutes of soda pulping. All specific β-O-4 cross-peaks from α-CH, β-CH and γ-CH were absent from both syringyl (S) and guaiacyl (G) connected aromatic rings (Martinsson & Sonne, 2017).

The pine wood meal confirmed the findings for the alkaline forest residue lignin since no lignin β-O-4 linkages could be detected after 120 minutes of soda pulping, for both untreated and AHP pretreated pine wood meal. Bark meal lignin was more difficult to analyse since it is composed of other types of lignin structures than pine wood meal. No lignin inter-unit linkages, β-O-4, β-β or β-O-5 bonds, was present after the soda pulping for either of the untreated or the AHP pretreated bark, see Figure 25.

The NMR results imply that most of the delignification, for both bark and pine wood meal, was completed after 120 min and that soda chemistry effectively depolymerised both phenolic and non-phenolic fractions of lignin β-O-4 bonds.

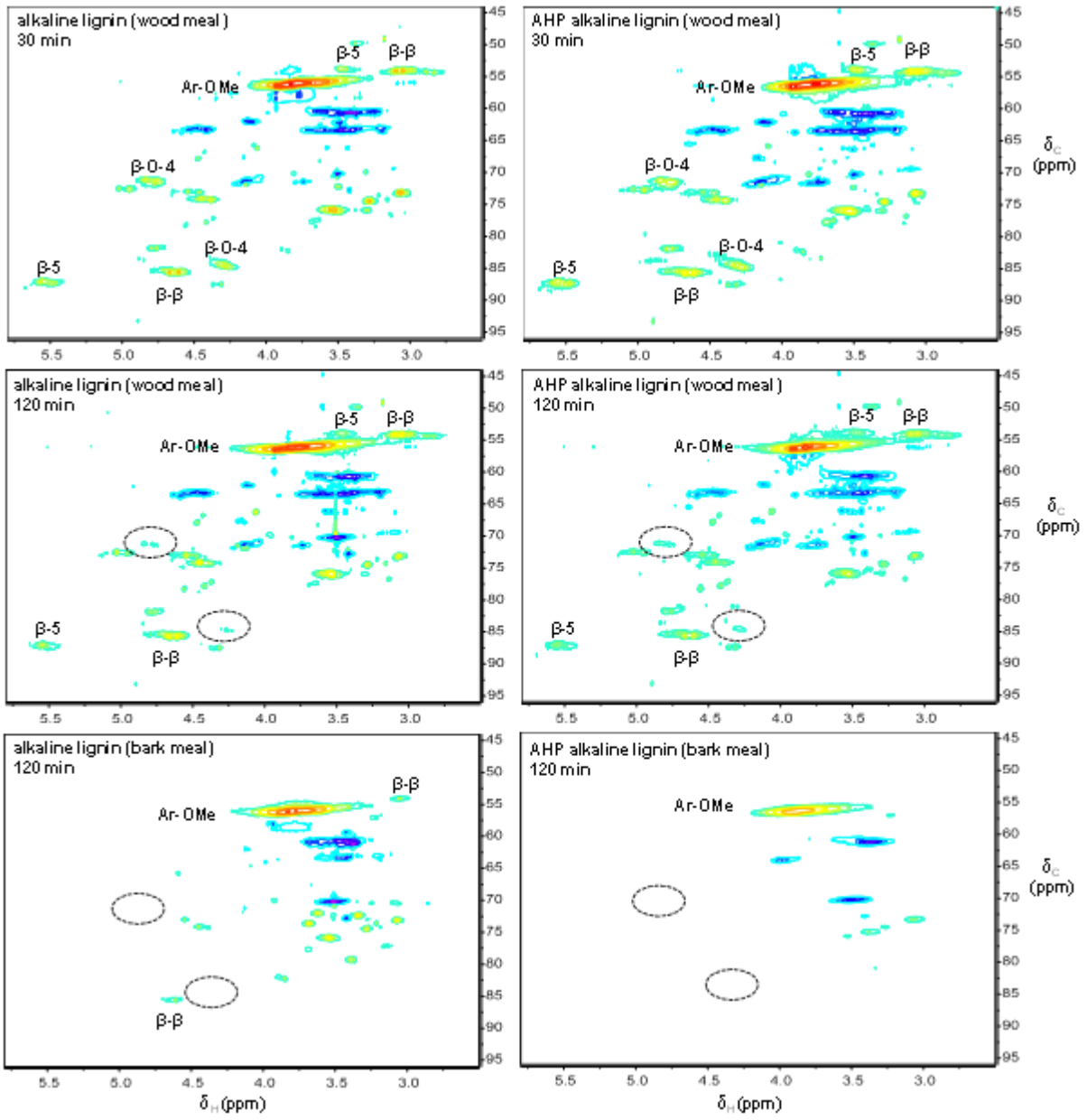

*Figure 25: The Inter-unit aliphatic lignin region/oxygenated aliphatic region δ_C/δ_H 44-96/2.5-5.2 ppm of 2D NMR spectra (800 MHz, DMSO-*d6*) of untreated and AHP pretreated alkaline lignin from pine wood and softwood bark.*

4.7 Extractives in bark

Using a GC-MS/FID the acetone soluble extractives where analysed. The main compounds and compound classes as well as their percentage occurrence can be seen in Table 6.

Table 6: Content of extractive compounds received from soxhlet extraction of the softwood bark meal using acetone.

GC-FID (Area %)	Compound	Compound Class
2	Linolenic acid	fatty acid
5	β-Sitosterol	sterol
7	Pimaric acid	resin acid
7	9,12-Octadecadienoic acid	fatty acid
8	Abietic acid	resin acid
11	Octadecenoic acid	fatty acid
14	Isopimaric acid	resin acid
30	Dehydroabietic acid	resin acid

The weight percentage average of extractives calculated from soxhlet extraction using acetone for two samples of bark was 9.73 wt. %. This is more than double the amount extractives found in spruce and pine wood (Björklund Jansson & Nilvebrant, 2009).

5 Conclusion

- Pine wood is a good model material for forest residue in soda pulping, with an AHP pretreatment
- Bark as sole raw material is not suitable in a soda pulping biorefinery concept
- The negative effects of bark was not as evident in a forest residue mixture
- The delignification was improved using an AHP pretreatment prior to soda pulping
- The most effective delignification of pine wood meal was achieved with AHP 3.3 wt.% H_2O_2, 60^0C for 60 minutes
- The molecular weight of the lignin decreased for the pine wood meal with increasing soda pulping time
- The molecular weight of the lignin remained constant for bark with increasing soda pulping time
- No lignin β-O-4 inter-unit linkage was detected after 120 minutes of soda pulping with NMR analysis for either untreated or AHP pretreated pine wood meal
- Forest residues has a good potential to be used as raw material in an AHP soda pulping biorefinery to create materials and chemical products

5.1 Concluding discussion

In this study forest residues, stem wood, branches and bark as raw material in a biorefinery concept have been examined. The use of an oxidative pretreatment of alkaline hydrogen peroxide, AHP, followed by soda pulping of the low cost material forest residues would be very beneficial for production of future biorefinery products such as bio-fuel, chemicals and dissolved pulp. For a better understanding of the combined effects of AHP pretreatment and soda pulping to separate the lignin, hemicellulose and cellulose from forest residues more studies are needed. This study is therefore focused on investigation on the effects of AHP pretreatment and soda pulping on two of the components found in the forest residues, i.e. pine wood and softwood bark, as model materials.

Pine wood meal pretreated at 60°C with 3.3 wt. % alkaline hydrogen peroxide prior to soda pulping gave the largest effect on both delignification and decrease in molecular weight of the lignin followed by the 60°C with 1.1 wt. % hydrogen peroxide pretreatment, just as for the previous study on forest residues (Martinsson & Sonne, 2017). This indicates that the temperature is the parameter with the highest impact in the AHP pretreatment process. The effect on delignification and decrease in molecular weight of lignin were both more evident after the soda pulping when an AHP pretreatment had been used on the raw material.

The highest rate of delignification, during the soda pulping, was found for all pine wood samples up to 120 minutes of pulping. After 120 minutes of pulping the delignification rate decrease significantly. It can be concluded that the delignification was more of less finished after 120 minutes, an important parameter indicating this are the low Klason lignin content in the pulps, see Figure 16. The NMR spectra of alkaline lignins, which shows complete absence of lignin β-O-4 bonds after 120 minutes of soda pulping. It is likely that beneficial structural changes have taken place at carbonyl functionalities in the lignin structure by oxidative AHP pretreatment of pine wood and bark meal, that opens up for a faster delignification during soda pulping.

For the carbohydrates in the pinewood the largest decrease was found up to 30 minutes of pulping, indicating that most of the carbohydrate degradation have already taken place during the heating up period or within the first 30 minutes of pulping. The influenced carbohydrates indicates that the degradation occurring is mainly of the hemicelluloses. This can be observed by the decreased levels for xylose and arabinose, which correlates to arabinoglucuronoxylan, and for galactose and mannose, which correlates to galactoglucomannan.

In this study it was concluded that sole bark meal is not a suitable raw material in an AHP soda pulping biorefinery. The negative effects of the bark was not as evident when it was present as a

component in the forest residues. The bark meal showed a large decrease in Klason lignin during the preatreatment, however the Klason analysis method is not suitable for bark making the result difficult to evaluate. A minor decrease in the molecular weight of the lignin in the bark meal was found, in contrast to the pine wood meal and forest residues. Although it can be noted that the NMR spectra indicated a complete absence of lignin inter-unit linkages, β-O-4, β-β or β-O-5, after 120 minutes of soda pulping for all bark meal samples.

This study successfully shows that using pine wood meal as raw material mimics the effects of a forest residue mixture containing stem wood, branches and bark, from both hardwood and softwood. In both pine wood and forest residues the delignification showed a decreasing trend of lignin molecular weight, from 30 to 120 minutes, using soda pulping for both untreated and AHP pretreated samples. Therefore forest residues shows great potential to be used as raw material in an AHP soda pulping biorefinery, providing sulphur free low molecular weight lignin for future application products such as chemicals, carbon fibres and bio-fuels.

6 Future work

Before implementation of an AHP pretreatment followed by soda pulping in a biorefinery concept, using forest residues as raw material, there are multiple areas that needs to be further investigated.

Looking at the molecular level, more knowledge of the effect of variation in the forest residue composition, e.g. hardwood, softwood and bark needs to be examined. The structural changes occurring during the AHP pretreatment and in the soda pulping remains unclear and further understanding to why the delignification is improved and the molecular weight of the softwood lignin is decreasing is needed.

The proposed process design needs to be scaled up and more precise mass balances needs to be calculated to examine if the process is viable.

The possible application of the materials received in the proposed process is something that needs to be analysed. The conditions for production of dissolving pulp as well as usage of the lignin fraction for production of bio-crude and other chemicals needs to be met before the process can be deemed technically and economically feasible.

7 References

Adler, E. (1977). Lignin chemistry-past, present and future. *Wood Science and Technology, 11*(3), 169-218. doi:10.1007/BF00365615

Alvarez-Vasco, C., & Zhang, X. (2017). Alkaline hydrogen peroxide (AHP) pretreatment of softwood: Enhanced enzymatic hydrolysability at low peroxide loadings. *Biomass & Bioenergy, 96*, 96-102. doi:10.1016/j.biombioe.2016.11.005

Bajpai, P., & SpringerLink (e-book collection). (2012;2011;). *Biotechnology for pulp and paper processing* (1. Aufl.;1st; ed.). New York: Springer.

Balakshin, M.Y., Capanema, E.A., Chen, Gracz, H.S. (2003) Elucidation of the Structures of Residual and Dissolved Pine Kraft Lignins Using an HMQC NMR Technique. Journal of Agricultural and Food Chemistry. 51(21):6116-6127

Biermann, C. J., ScienceDirect (e-book collection), Ebook Central (e-book collection), & Knovel (e-book collection). (1996). *Handbook of pulping and papermaking* (2nd;2; ed.). San Diego: Academic Press.

Björklund Jansson. M, Nilvebrant. N (2009). Wood Extractives. In: M. Ek, G. Gellerstedt and G. Henriksson (Ed.), *Pulp and paper Chemistry and technology – Wood Chemistry and Wood Biotechnology*. Berlin: Walter de Gruyter.

Brännvall. E (2009). Wood handling, *Pulp and paper Chemistry and technology – Wood Chemistry and Wood Biotechnology*. Berlin: Walter de Gruyter.

Brännvall. E (2009). Pulping technology, *Pulp and paper Chemistry and technology – Wood Chemistry and Wood Biotechnology*. Berlin: Walter de Gruyter.

Bui, N.Q., Fongarland, P., Rataboul, F., Dartiguelongue, C., Charon, N., Vallée, C., Essayem, N. (2015) FTIR as a simple tool to quantify unconverted lignin from chars in biomass liquefaction process: Application to SC ethanol liquefaction of pine wood. Fuel Processing Technology. 134:378-386

Burkhardt, S., Kumar, L., Chandra, R., & Saddler, J. (2013). How effective are traditional methods of compositional analysis in providing an accurate material balance for a range of softwood derived residues? *Biotechnology for Biofuels, 6*(1), 90. doi:10.1186/1754-6834-6-90

Busse-Wicher, M., Gomes, T. C. F., Tryfona, T., Nikolovski, N., Stott, K., Grantham, N. J., Dupree, P. (2014). The pattern of xylan acetylation suggests xylan may interact with cellulose microfibrils as a twofold helical screw in the secondary plant cell wall of arabidopsis thaliana. *The Plant Journal, 79*(3), 492-506. doi:10.1111/tpj.12575

Cherubini, F. (2010). The biorefinery concept: Using biomass instead of oil for producing energy and chemicals. *Energy Conversion and Management, 51*(7), 1412-1421. doi:10.1016/j.enconman.2010.01.015

Christopher H.Vane, Trevor C.Drage & Colin E.Snape (2006) Bark decay by the white-rot fungus Lentinula edodes: Polysaccharide loss, lignin resistance and the unmasking of suberin. *International Biodeterioration & Biodegradation, 57, issue 1,* 14-23. https://doi.org/10.1016/j.ibiod.2005.10.004

Coates, J. (2006) Interpretation of Infrared Spectra, A Practical Approach. In: Encyclopedia of Analytical Chemistry. John Wiley & Sons, Ltd.

De Bhowmick, G., Sarmah, A., & Sen, R. (2017). Lignocellulosic biorefinery as a model for sustainable development of biofuels and value added products. *Bioresource Technology, 247*, 1144-1154. doi:10.1016/j.biortech.2017.09.163

Elliott, D., Biller, P., Ross, A., Schmidt, A., & Jones, S. (2015). Hydrothermal liquefaction of biomass: Developments from batch to continuous process. *Bioresource Technology, 178*, 147-156. doi:10.1016/j.biortech.2014.09.132

Eronen, P., Österberg, M., Heikkinen, S., Tenkanen, M., & Laine, J. (2011). Interactions of structurally different hemicelluloses with nanofibrillar cellulose. *Carbohydrate Polymers, 86*(3), 1281-1290. doi:10.1016/j.carbpol.2011.06.031

Faix, O. (1992) Fourier Transform Infrared Spectroscopy. In: Methods in Lignin Chemistry. Eds. Lin, S.Y., Dence, C.W. Springer Berlin Heidelberg, Berlin, Heidelberg. pp. 83-109

Gellerstedt. G (2009). Chemistry of Pulping. In: M. Ek, G. Gellerstedt and G. Henriksson (Ed.), *Pulp and paper Chemistry and technology – Wood Chemistry and Wood Biotechnology*. Berlin: Walter de Gruyter.

Gierer, J., & Norén, I. (1982). Oxidative pretreatment of pine wood to facilitate delignification during kraft pulping. *Holzforschung, 36*(3), 123-130. doi:10.1515/hfsg.1982.36.3.123

Gomes, F. , Santos, F. , Colodette, J. , Demuner, I. and Batalha, L. (2014) Literature Review on Biorefinery Processes Integrated to the Pulp Industry. *Natural Resources*, **5**, 419-432. doi: 10.4236/nr.2014.59039.

Gould, J. M., & Gould, J. M. (1985). studies on the mechanism of alkaline peroxide delignification of agricultural residues. *Biotechnology and Bioengineering, 27*(3), 225-231. 10.1002/bit.260270303

Hagström-Näsi, C., & Sjöström, E. (1987). Oxidative pretreatment of pine wood prior alkaline pulping. Part II. Characterization of lignin by spectroscopic methods. *Holzforschung, 41*(1), 39-45. doi:10.1515/hfsg.1987.41.1.39

Heitner, C., Dimmel, D., Schmidt, J. A., & CRCnetBASE (e-book collection). (2010;2016;). *Lignin and lignans: Advances in chemistry* (1st ed.). Boca Raton: Taylor & Francis.

Henriksson. G, Brännvall. E and Lennholm. H (2009). The Trees. In: M. Ek, G. Gellerstedt and G. Henriksson (Ed.), *Pulp and paper Chemistry and technology – Wood Chemistry and Wood Biotechnology*. Berlin: Walter de Gruyter.

Henriksson. G (2009). Lignin. In: M. Ek, G. Gellerstedt and G. Henriksson (Ed.), *Pulp and paper Chemistry and technology – Wood Chemistry and Wood Biotechnology*. Berlin: Walter de Gruyter.

Holladay JE, White JF, Bozell JJ, Johnson D (2007). Top Value-Added Chemicals from Biomass Volume II - Results of Screening for Potential Candidates from Biorefinery Lignin

Lennholm. H and Blomqvist. K (2009). Cellulose. In: M. Ek, G. Gellerstedt and G. Henriksson (Ed.), *Pulp and paper Chemistry and technology – Wood Chemistry and Wood Biotechnology*. Berlin: Walter de Gruyter.

Le Normand, M., Moriana, R., Ek, M., Fiber- och polymerteknologi, Skolan för kemivetenskap (CHE), KTH, & Träkemi och massateknologi. (2014). Isolation and characterization of cellulose nanocrystals from spruce bark in a biorefinery perspective. *Carbohydrate Polymers, 111*, 979-987. doi:10.1016/j.carbpol.2014.04.092

Le Normand, M., Moriana, R., Ek, M., Fiber- och polymerteknologi, Skolan för kemivetenskap (CHE), KTH, & Träkemi och massateknologi. (2014). The bark biorefinery: A side-stream of the forest industry converted into nanocomposites with high oxygen-barrier properties. *Cellulose, 21*(6), 4583-4594. doi:10.1007/s10570-014-0423-z

Martinsson, A., Sonne, I. (2017). *From residues to resource - pretreatment and pulping of forest residues in a biorefinery concept*

Mattsson, C., Andersson, S.-I., Belkheiri, T., Åmand, L.-E., Olausson, L., Vamling, L., Theliander, H. (2016) Using 2D NMR to characterize the structure of the low and high molecular weight fractions of bio-oil obtained from LignoBoost™ kraft lignin depolymerized in subcritical water. Biomass and Bioenergy. 95:364-377

Maurya, D. P., Singla, A., & Negi, S. (2015). An overview of key pretreatment processes for biological conversion of lignocellulosic biomass to bioethanol. *3 Biotech, 5*(5), 597-609. doi:10.1007/s13205-015-0279-4

PASCO, M., & SUCKLING, I. (1994). lignin removal during kraft pulping - an investigation by thioacidolysis. *Holzforschung, 48*(6), 504-508. 10.1515/hfsg.1994.48.6.504

Roger M. Rowell, Roger Pettersen, and Mandla A. Tshabalala (2012) *Handbook of Wood Chemistry and Wood Composites*, Second Edition. 33 -72

Sixta, H. (2006). *Handbook of pulp: Vol. 2*. Weinheim: Wiley-VCH.

Striegel, A., Yau, W.W., Kirkland, J.J. & Bly, D.D. (2009). *Modern Size-Exclusion Liquid Chromatography: Practice of Gel Permeation and Gel Filtration Chromatogrphy*. Wiley.

Singh, K., Sivanandan, L. (2014) Changes in wood during mild thermal decay and its detection using ATR-IR: a review. Journal of Agricultural Science and Applications. 3(1):1-7

Sjöström, E., & ScienceDirect Archives (e-book collection). (1993). *Wood chemistry: Fundamentals and applications* (2nd ed.). San Diego, California;London, England;: Academic Press, Inc.

Teleman. A (2009). Hemicelluloses and pectins. In: M. Ek, G. Gellerstedt and G. Henriksson (Ed.), *Pulp and paper Chemistry and technology – Wood Chemistry and Wood Biotechnology*. Berlin: Walter de Gruyter.

Theander, O., & Westerlund, E. A. (1986). Studies on dietary fiber. 3. improved procedures for analysis of dietary fiber. *Journal of Agricultural and Food Chemistry, 34*(2), 330-336. 10.1021/jf00068a045

Vazquez Penas, D., Lage Yusty, M. A., & Parajo Linares, J. C. (1992). Chemical-biotechnological processing of pine bark. *Journal of Chemical Technology and Biotechnology, 54*(1), 63-74. 10.1002/jctb.280540112

Chaturvedi, V., & Verma, P. (2013). An overview of key pretreatment processes employed for bioconversion of lignocellulosic biomass into biofuels and value added products. *3 Biotech, 3*(5), 415-431. 10.1007/s13205-013-0167-8 Wang, X., Li, K., Yang, M., Wang, J., & Zhang, J. (2017). Hydrolyzability of mannan after adsorption on cellulose. *Cellulose, 24*(1), 35-47. doi:10.1007/s10570-016-1098-4

Wigell, A., Brelid, H., & Theliander, H. (2007). Degradation/dissolution of softwood hemicellulose during alkaline cooking at different temperatures and alkali concentrations.