CHALMERS
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From Residues to Resource

Pretreatment and pulping of forest residues in a biorefinery concept

Master's thesis in Innovative and Sustainable Chemical Engineering

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Department of Chemistry and Chemical Engineering
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Cover:

Photograph of refined forest residues (left), pretreated forest residues (middle) and the two products after pulping, pulp and lignin (right).

Gothenburg, Sweden 2017

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From Residues to Resources

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Abstract

The implementation of biorefineries in the near future is one of the most important challenges if we are to keep up with an expanding population and reduce our carbon footprint. When moving from fossil based raw materials towards biomass based feedstock, it is important to utilize all fractions of the biomass efficiently to be able to produce as much as possible in a sustainable manner. This means that we must evaluate all possible feedstocks even the ones that today may be considered waste. One such feedstock is forest residues which, today, is mainly burnt or never recovered from the forest.

In this report a suggested forest residue biorefinery is evaluated. In the forest residue biorefinery an alkaline peroxide pretreatment process is used to increase the efficiency of the delignifying step, soda pulping. Soda pulping is chosen because of the sulfur free cooking liquor, which could greatly simplify the recovery process of the cooking chemicals. The resulting carbohydrate fraction could be used to produce a variety of products such as dissolving pulp, nanocellulose or bio-ethanol and the lignin fraction could be used for the production of for example bio-oil.

The alkaline peroxide pretreatment was evaluated by varying the residence time, peroxide concentration and the pretreatment temperature. The pretreatment was followed by a soda pulping and the resulting pulp and lignin fraction was analyzed. A pretreatment with 1.1 % hydrogen peroxide at 60 °C for 1 hour was found to increase the delignifying efficiency of the 1 hour soda pulping with 49% compared to soda pulping without pretreatment. The resulting pulp also showed potential to be used as dissolving pulp for the production of textiles.

Keywords: Forest residues, GROT, biorefinery, alkaline peroxide, soda pulping

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Appendix I I

1 Introduction

1.1 Background

During the last century fossil-based material and products have dominated the market and been a key to the development of today's society. Fossil-based products from non-renewable resources (coal, natural gas and crude oil) contributes to the greenhouse effect as well as global warming. With an increased consumption and material demand from a growing population, the importance of a transition to renewable and sustainable feedstock increases (Zhu et al., 2015). The use of renewable resources and feedstocks, such as lignocellulosic biomass, will lower the carbon footprint compared to the use of fossil-based raw materials.

Today many producers of chemicals and products that utilize a fossil feedstock are looking into the use of a bio-based feedstock. One example for production of bio-based chemicals is the concept of a biorefinery. In a biorefinery, wood can be used as a feedstock to produce a variety of cellulose products, for example pulp and nanocellulose, but also lignin derived chemicals and bio-oils.

When using wood as a feedstock for a biorefinery it is commonly used as whole logs. An alternative to this would be to use forest residues. When producing for example nanocellulose or dissolving pulp, forest residues may be a good option instead of breaking down the long fibres that can be found in logs. Since the longer fibres are not necessary, this also means that methods of delignification that previously been considered as too harsh on the cellulose fibres can be utilized to achieve a more effective delignification.

Forest residues mainly consists of branches, twigs and bark that are left behind when harvesting the trees or thinning the forests (Biswas, Teller, & Ahring, 2015). Today the forest residues are simply burned for energy recovery or left behind in the forest. If this waste could be used as a feedstock instead, it could be used to produce higher value, renewable products.

1.1.1 Aim

The aim of this project is to investigate a possible process route for a biorefinery that would utilize forest residues as a feedstock. Can a sulfur free process approach be applied and thus greatly simplifying the process? If successful, this would mean that a wide spectrum of chemicals and cellulose products could be produced from an abundant resource that would otherwise be burnt or discarded.

To find a potential process route for forest residues, the different process steps in the proposed process, Figure 1, will be optimized and investigated so that two product streams, lignin and carbohydrates, can be recovered. An alkaline treatment will be used as the main delignifying step in combination with an alkaline peroxide pretreatment to increase its performance.

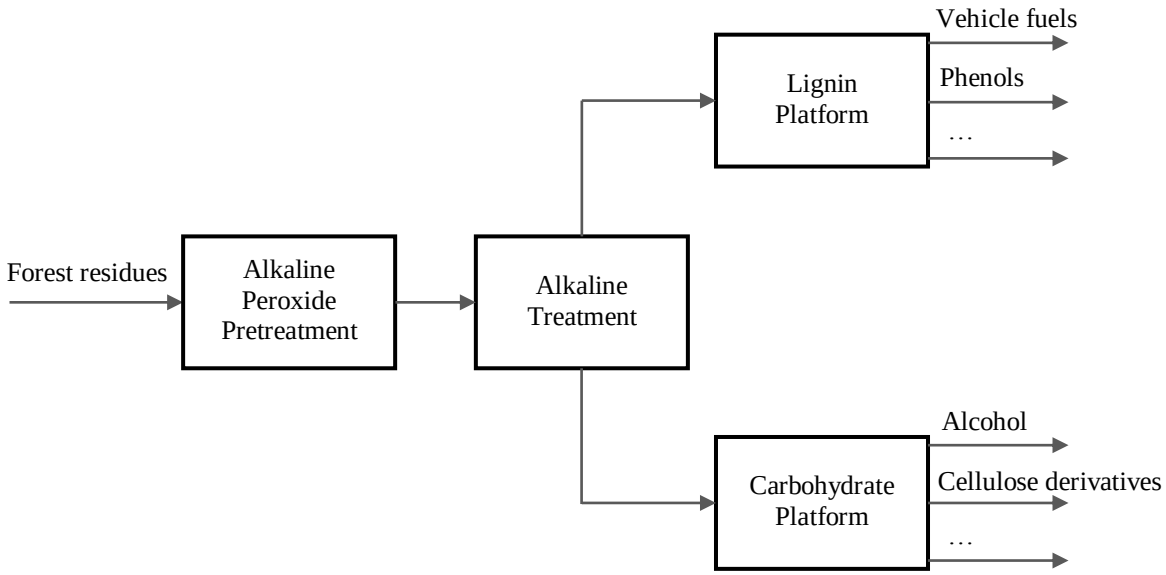

Figure 1. Schematic diagram over proposed process for treating forest residues

2 Theory

2.1 Structure of lignocellulosic biomass

Trees can be classified as hardwood or softwood. Hardwood trees are angiosperms such as birch, beech and oak, which are trees that lose their leaves during the fall. Softwood trees are gymnosperms such as pine, spruce and fir. The main chemical components in both hardwood and softwood are cellulose, hemicellulose, lignin and extractives. Extractives are a low-molecular weight component that together with minerals are of minor share in the tree whereas the cellulose, hemicellulose and lignin are polymers/macromolecules (Fengel, D. & Wegener, G., 1989).

The different classes of trees, softwood and hardwood, are suitable for different products due to their difference in chemical composition and fibre length. The tree itself can also be divided in different parts with different chemical composition. Bark, roots, trunk, needles and branches are such categories where the amount of extractives, carbohydrates and lignin varies in amount (Henriksson, Brännvall & Lennholm, 2009).

2.1.1 Cellulose

Roughly 40-50 percent by weight of the wood consists of cellulose. This amount varies depending on type of wood (softwood or hardwood) but it is also differs in various parts of the tree.

Cellulose consists of 1,4-linked *β-D*-glucopyranose units that together creates a linear polysaccharide as seen in Figure 2. These linear chains are ordered in sheets that are bonded together with hydrogen bonds. These sheets are layered and held together through hydrophobic interactions such as van der Waals forces (Lennholm & Blomqvist, 2009).

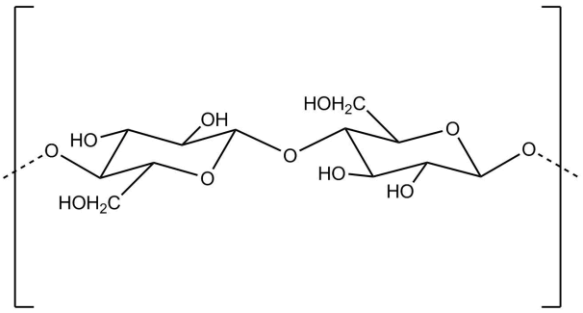

Figure 2. Molecular structure of a cellulose unit

2.1.2 Hemicellulose

Just like cellulose, most hemicelluloses are structural carbohydrates and function as the supporting structure of the cell wall. In the wood matrix, hemicellulose can be found between the cellulose fibrils, surrounded by lignin. Roughly 20-35 percent by dry weight of the wood consists of hemicellulose, this amount varies depending on wood type, and the main building units are hexoses (*D*-glucose, *D*-mannose and *D*-galactose) and/or pentoses (*D*-xylose and *L*-arabinose). The variant of hemicellulose depends on the combination of the different building units and the most common ones in softwood are glucomannan, Figure 3, and arabinoglucuronoxylan, Figure 4. In hardwood the most common hemicelluloses are glucomannan and glucuronoxylan.

Glucomannan in softwood and hardwood has a linear structure which is formed by linking *β*-*D*-mannopyranosyl and *β*-*D*-glucopyranosyl residues into a chain. Branches to this chain are for softwood the *O*-acetyl groups and *α*-*D*-galactopyranosyl units, Figure 3, and for hardwood it is the *O*-acetyl groups (Teleman, 2009).

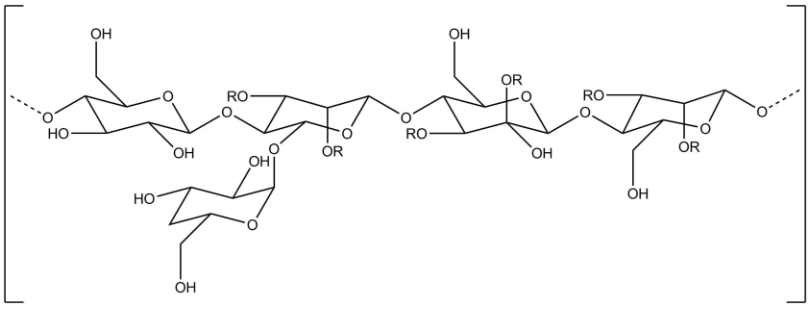

Figure 3. Molecule structure of a softwood glucomannan unit.

Xylan is a mostly linear polysaccharide of *β*-(1→4)-*D*-xylopyranosyl residues and depending on wood type, softwood and hardwood, the side-group and regularity of *4*-*O*-methyl-*D*-glucuroinic acid (MeGlcA) unit distribution differs. Softwood xylan has a regular distribution of MeGlcA units and the side-group *L*-arabinose, Figure 4. The presence of the side-group *L*-arabinose gives the name arabinoglucuronoxylan for softwood. Hardwood has an irregular distribution of MeGlcA units and the presence of an acetyl group gives hardwood xylan the name glucuronoxylan (Teleman, 2009).

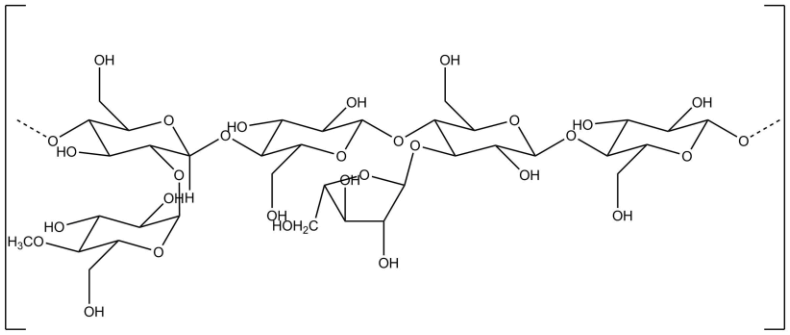

Figure 4. Molecule structure of a arabinoglucuronoxylan unit.

2.1.3 Lignin

Lignin fills the gap between cellulose and hemicellulose and improves the stabilization and fixation of the cell wall as well as protecting the wood against microbial degradation. The complex polymer structure of lignin has a three-dimensional web of monomers that are randomly ordered. These monomers, called monolignols, are *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol, Figure 5. Depending on wood type, the combination of these monolignols differs e.g. softwood lignin consists of almost solely coniferyl alcohol while hardwood lignin is a combination of coniferyl and sinapyl alcohol. *p*-Coumaryl units are mainly found in grass but are also found in small amounts in softwood and can sometimes be found in hardwood (Henriksson, 2009).

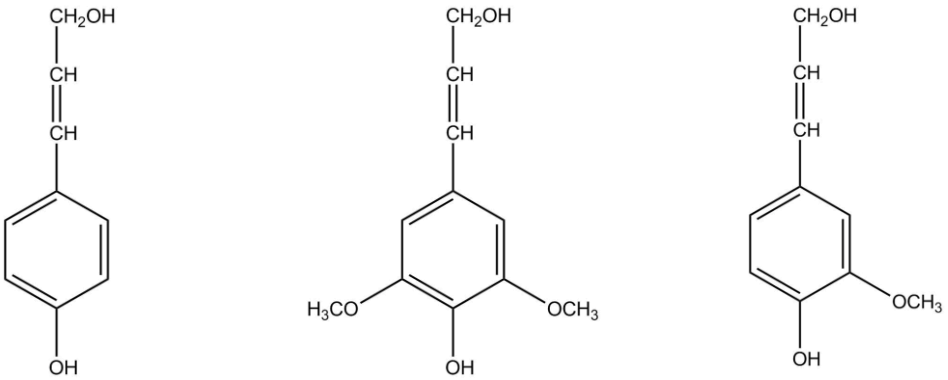

Figure 5. The three monolignols forming the lignin polymer. From left to right: p-coumaryl alcohol, sinapyl alcohol and coniferyl alcohol.

The monolignols creates randomly ordered webs compared to the linear polysaccharides in cellulose, and the monolignols can be connected to each other with a numerous of different carbon-carbon (C-C) and ether (C-O-C) bonds. The most common bond in both softwood and hardwood lignin is the *β-O-4* linkage see Figure 6, other linkages are e.g. *5-5*, *β-5*, *α-O-4* and *β- β* (Henriksson, 2009).

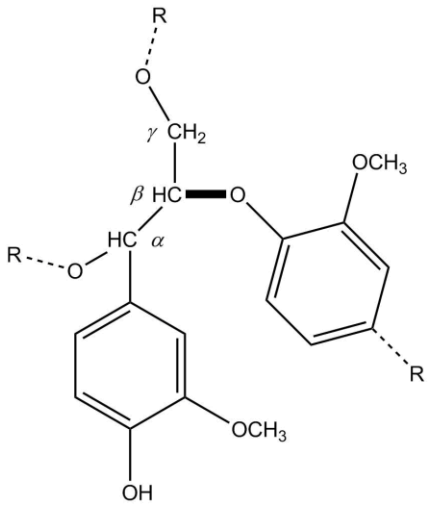

Figure 6. The β-O-4 linkage in lignin (bold).

2.1.4 Extractives

Extractives are smaller molecules that usually consist of 30 or less carbons. These molecules can be extracted from the wood using neutral solvents such as water, acetone or diethyl ether. The amount of extractives and their composition vary considerably between different species of wood (Björklund Jansson & Nilvebrant, 2009).

The extractives can be divided into three main groups: terpenes, phenolic compounds and aliphatic compounds. The main function of these compounds is to preserve and protect the wood, act as a nutrient reserve or as hormones for the plant (Granström, 2005).

2.2 The biorefinery concept

A biorefinery is defined as the sustainable processing of biomass into a spectrum of marketable products and energy (IEA Biomass 2009). Most of the existing biorefineries today focus solely on the production of bioethanol and therefore uses a feedstock that can easily be processed into fermentable sugars.

In a sustainable future, the biorefinery concept is key if we are to meet the society's demand for chemicals, energy carriers and materials. This means that the future biorefineries must be highly integrated, able to utilize a variety of raw materials while being as energy efficient as possible and producing a wide range of products (Aresta, Dibenedetto and Dumeignil 2012).

For a successful biorefinery concept it is of great importance that the process is integrated with the regional infrastructure and market. This means that the biorefinery can utilize byproducts and feedstocks (waste, crops etc.) that are available in the region (Aresta, Dibenedetto and Dumeignil 2012).

2.2.1 The forest residue biorefinery

The proposed biorefinery concept for a forest residue biorefinery is designed to utilize all of the different wood constituents to get the most efficient use of the lignocellulosic material. Many of the biorefinery initiatives of today have been based on producing a single product, such as ethanol or SNG (substitute natural gas), from a lignocellulosic material. Because of the complex nature of lignocellulosic material, this approach can easily result in sub-optimization of the process.

Today, in Sweden, forest residues corresponding to roughly 10 TWh of heating are recovered from harvesting of trees. However, there is a potential to increase this amount threefold during the coming ten years. There is also a great potential in increasing the amount of forest residues recovered from thinning of forests and waste, in the form of sawdust and bark, from saw mills and pulp mills (Skogsstyrelsen, 2017).

By pretreating the forest residues and thereby optimizing the delignification, the forest residue biorefinery could produce a variety of different products. The cellulose fraction that is obtained from the delignification could be used as dissolving pulp for the production of fabrics or to produce other cellulose derivate such as nanocellulose. Nanocellulose has for

example shown potential to be used as a reinforcement agent in composites (Moriana, R., Vilaplana, F., & Ek, M., 2016). The resulting liquid fraction from the delignification contains the spent cooking liquor, dissolved lignin, extractives and sugar monomers. This fraction could potentially be thermally cracked in a hydrothermal liquefaction (HTL) reactor to produce bio-crude that later can be upgraded in a refinery. A schematic process layout of the forest residue biorefinery can be seen in Figure 7.

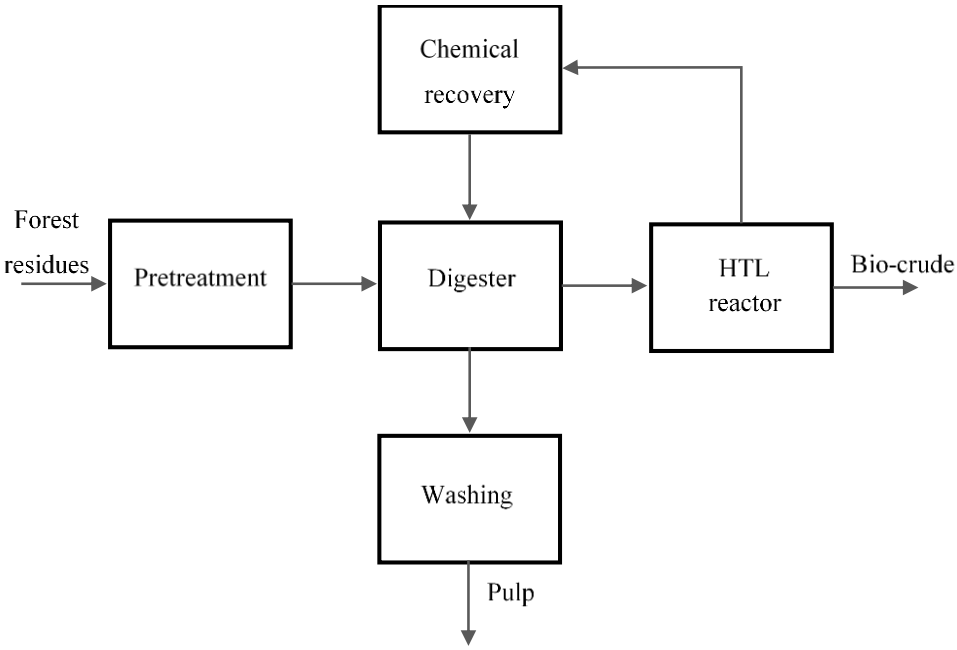

Figure 7. Flowsheet for the purposed forest residue biorefinery.

2.3 Pretreatment processes

2.3.1 Physical pretreatments

2.3.1.1 Steam pretreatment

A common physical pretreatment is steaming of the raw material. Steaming removes air trapped inside the fibre structure by increasing the vapour pressure inside the material as well as by heating the trapped air and thereby displacing it. Air within the fibre structure prevents cooking liquors from penetrating the material and can lead to uneven pulping. Condensed steam within the structure also facilitates liquor penetration through diffusion between liquors of different concentration (Brännwall, 2009).

Steaming, with or without rapid discharge (explosion) into a collecting tank has also proven to hydrolyze hemicelluloses as well as modifying the plant cell wall structure. The hydrolyzed hemicelluloses can be recovered and used for production of biochemicals using fermentation. The modified cell wall structure leads to an increased penetration of cooking chemicals (Ramos, 2003).

When using steaming, the raw material is typically treated with steam at temperatures ranging from 160 to 240 °C and pressures between 0.7 and 4.8 MPa (Ramos, 2003).

2.3.2 Chemical pretreatments

2.3.2.1 Acidic pretreatment

Dilute acid pretreatments have been found to enhance the hydrolysis of hemicelluloses. The acid hydrolysis solubilizes the hemicelluloses and converts them into fermentable sugars, thus eliminating the need for an enzymatic saccharification step that usually follows physical pretreatments when a fermentation is wanted. Acidic pretreatments can be performed at 120-180 °C for 15 to 90 minutes, resulting in yields of xylose as high as 75-90 % (Singh, Shukla, Tiwari, & Srivastava, 2014).

2.3.2.2 Alkaline peroxide treatment.

Hydrogen peroxide is commonly used in the pulp industry as a bleaching agent but it can, under the right conditions, also be used as a delignifying step. Gould (1985) has shown that alkaline hydrogen peroxide solutions can be used to successfully remove roughly half of the lignin present in various types of lignocellulosic material (e.g. wheat straw and corn husks). The alkaline peroxide treatment has also shown to increase the water absorbance of the lignocellulosic material with up to 300 %. This would mean that the material would be more susceptible to a subsequent pulping step (Gould, 1985).

It has been shown that the delignifying properties of alkaline peroxide treatment has its optimum at around pH 11.5-11.6, which is the pKa for the dissociation of hydrogen peroxide according to Reaction 1 (Gould, 1985).

$$H_2O_2 \rightleftharpoons H^+ + HOO^-$$

Reaction 1. Dissociation of hydrogen peroxide

The exact mechanisms behind the delignifying reactions are not know. However, it is believed that the hydroperoxy ions (HOO^-) produced from the dissociation of hydrogen peroxide reacts with undissociated hydrogen peroxide as shown in Reaction 2. The resulting hydroxyl and superoxide radicals are highly reactive and can be incorporated in the wood matrix and thus breaking its structure (Gould, 1985).

$$H_2O_2 + HOO^- \longrightarrow \bullet OH + O_2^{-}\bullet + H_2O$$

Reaction 2. Reaction between undissociated hydrogen peroxide and hydroperoxy anion.

The formed radicals can however also react with each other, in absence of other reactants, to form oxygen and water, Reaction 3 (Gould, 1985).

$$\bullet OH + O_2^{-}\bullet + H^+ \longrightarrow O_2 + H_2O$$

Reaction 3. Formation of oxygen and water from hydroxyl and superoxide radicals.

Gould (1985) also showed that the formation rate of oxygen is dependent on the amount of lignocellulosic material present. The formation of oxygen gas would increase with an increased amount of lignocellulosic material. This suggest that something present in the lignocellulosic material might decompose the hydrogen peroxide. One example of such a reaction would be a Fenton-type reaction with metal ions, Reaction 4(Gould, 1985).

$$2H_2O_2 + OH^- \xrightarrow[M/M^+]{} \bullet OH + O_2^{-}\bullet + 2H_2O$$

Reaction 4. Reaction between hydrogen peroxide and hydroxide, catalyzed by metal ions.

2.4 Pulping processes

2.4.1 Soda pulping

The chemical pulping method using sodium hydroxide as cooking chemical is known as soda pulping. During pulping the cooking chemicals delignifies and liberate cellulose fibers from the wood matrix. The main delignification reactions occurring in soda pulping are the non-phenolic *β-O-4* breakage, Figure 8, and phenolic *β-O-4* breakage, Figure 9 (Lundquist, K., Simonson, R., & Tingsvik, K., 1981). The breakage of the non-phenolic *β-O-4* linkage can be carried out in the presence of an *α*-hydroxyl group from sodium hydroxide. This breakage will generate an epoxide structure and a new phenolic lignin end group.

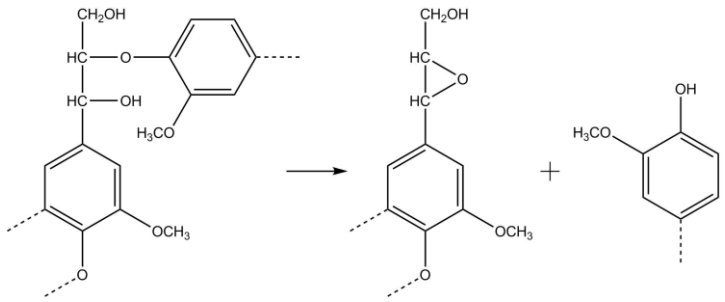

Figure 8. Cleavage of non-phenolic β-O-4 structure in lignin.

During the cleavage of phenolic *β-O-4* bonds, a quinone methide is formed. The quinone methide is then further reacted into an enol ether through an elimination reaction. The enol ether is then slowly degraded through radical reactions. Side reactions to the formation of the enol ether are a reduction and a condensation of the quinone methide (Lundquist, K., Simonson, R., & Tingsvik, K., 1981).

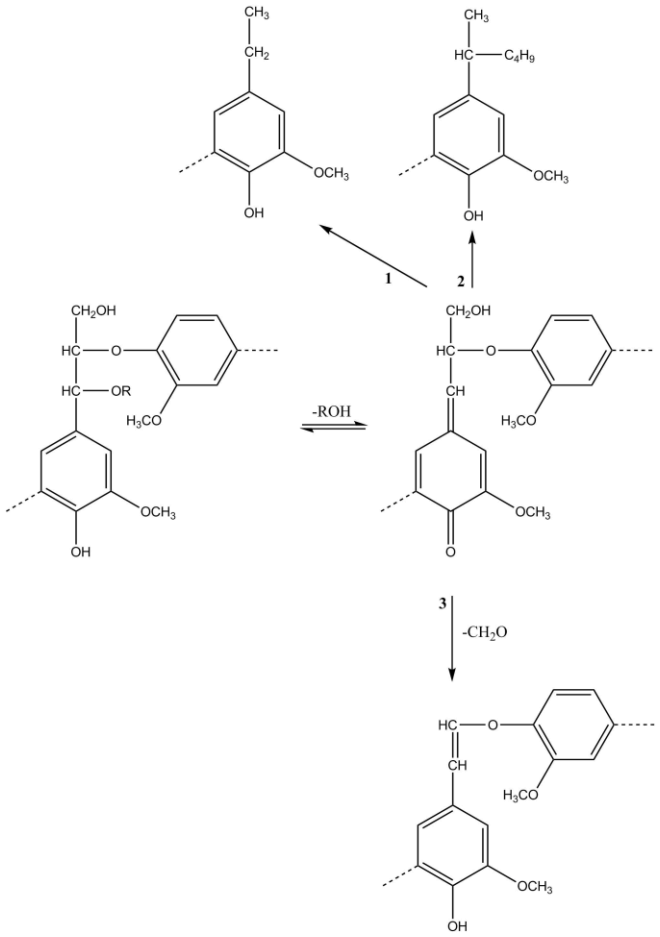

Figure 9. Reactions of phenolic β-O-4 structures in lignin; Elimination reaction of the quinone methide into an enol ether (3) and the competing reactions, reduction (1) and condensation (2).

The reaction of the *β-5* structure under alkaline condition, Figure 10, is after the *β-O-4* breakage the third most important reaction. It is similar to the elimination reaction of a non-phenolic lignin structure where a formation of an epoxide structure and a new hydroxyl end group forms (Lundquist, K., Simonson, R., & Tingsvik, K., 1981).

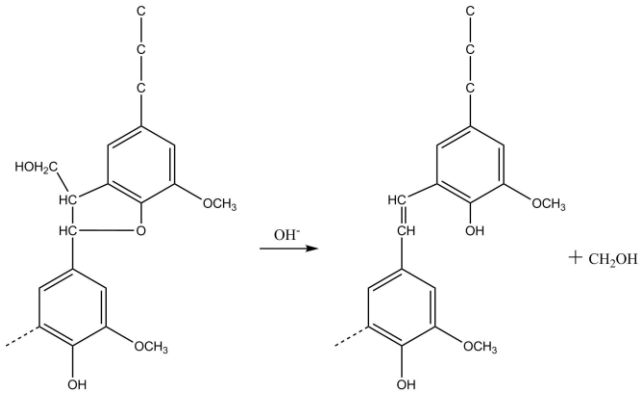

Figure 10. Reaction of β-5 lignin linkage under alkaline conditions.

The effects on the carbohydrates during the pulping procedures are mainly the peeling reaction and alkaline hydrolysis. Peeling reaction occurs under alkaline conditions where the reducing end groups in polysaccharides rearrange and eliminates. The depolymerization of the polysaccharides will after the first sugar unit elimination form a new end groups which after rearrangement is eliminated as well, this sequence will proceed until a stopping reaction occur. The stopping reaction starts with the formation of an acidic, alkali stable, end group that is formed from the cleavage of the glycosidic bond. The stopping reaction and the peeling reaction are competing reactions and decides the extent of the degradation (Gupta , 2008). The stopping reaction normally occurs when 50-100 monomers have been eliminated (Gellerstedt, 2009).

Alkaline hydrolysis creates a cleavage of the cellulose chain, by attacking the carbohydrate chain and break the bond between two sugar units, and form a new reducing end groups, on which secondary peeling occur. The alkaline hydrolysis starts when the soda pulping approaches an elevated temperature and will increase with increased temperature (Gellerstedt, 2009).

2.4.2 Kraft pulping

In kraft pulping the cooking liquor, called white liquor, consists of sodium hydroxide and sodium sulphide. In the white liquor the sodium sulphide is hydrolyzed and hydrogen sulphide ions and hydroxide ions are formed as shown in Reaction 5.

$$Na_2S + H_2O \longrightarrow OH^- + HS^- + 2Na^+$$

Reaction 5. Dissolution of sodium sulphide into hydroxide and hydrogen sulphide ions

Just as in the case of soda pulping, the main delignifying reaction in kraft pulping is the breakage of *β-O-4* bonds that links the monolignol units together. The breakage of these bonds and the introduction of hydrophilic groups in the structure are key to dissolve and remove the lignin from the wood matrix.

The *β-O-4* bonds can be broken in two main ways. Either by cleavage of the bond in the non-phenolic *β-O-4* structure, in the same way as in soda pulping, Figure 8, or in a reaction between hydrosulfide and the quinone methide intermediate formed in the reaction with a phenolic *β-O-4* structure, Figure 9. The reaction between the quinone methide and hydrosulfide is shown in Figure 11.

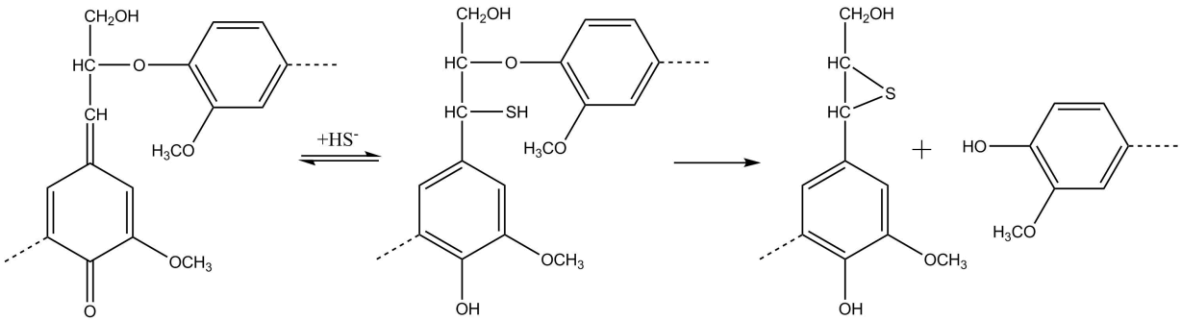

Figure 11. Delignifying reaction between quinone methide intermediate and hydrosulfide

Industrially, the kraft process is designed in a similar way as shown in Figure 12. A kraft pulp mill consists of one or more fibre lines (solid lines) and a chemical recovery cycle (dashed lines). The fibre line represents the production of pulp from the raw material and the chemical recovery cycle is responsible for the regeneration of white liquor.

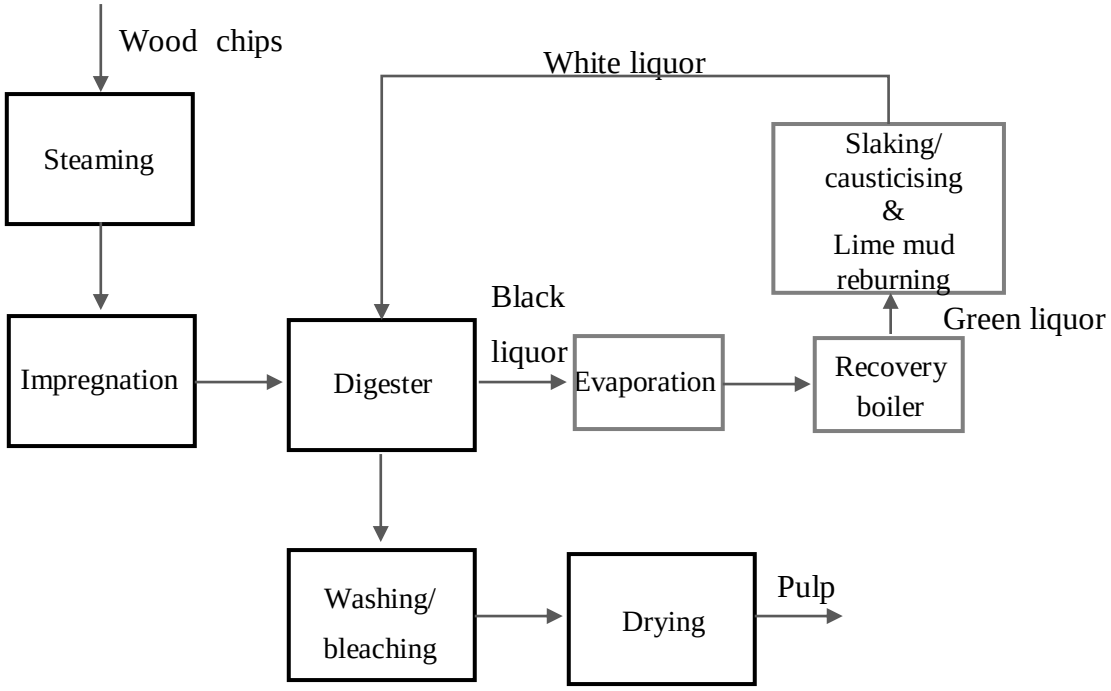

Figure 12. Simplified process layout for a kraft pulp mill

2.4.3 Sulfite pulping

Unlike soda and kraft pulping, sulfite pulping is most commonly used at acidic or neutral conditions, however, alkaline sulfite pulping is also possible. The cooking liquor used in sulfite pulping can be described by Reaction 6. The counter ion for the bisulfite ion is either sodium, calcium or magnesium.

$$HSO_3^- + H_2O \Longleftrightarrow SO_3^{2-} + H_3O^+$$

Reaction 6. Equilibrium reaction for the sulfite system

The dissolution of lignin in the cooking liquor is caused by the hydrophilization of the lignin due to sulfonation reactions between the bisulfite ions and the lignin structure shown in Figure 13.

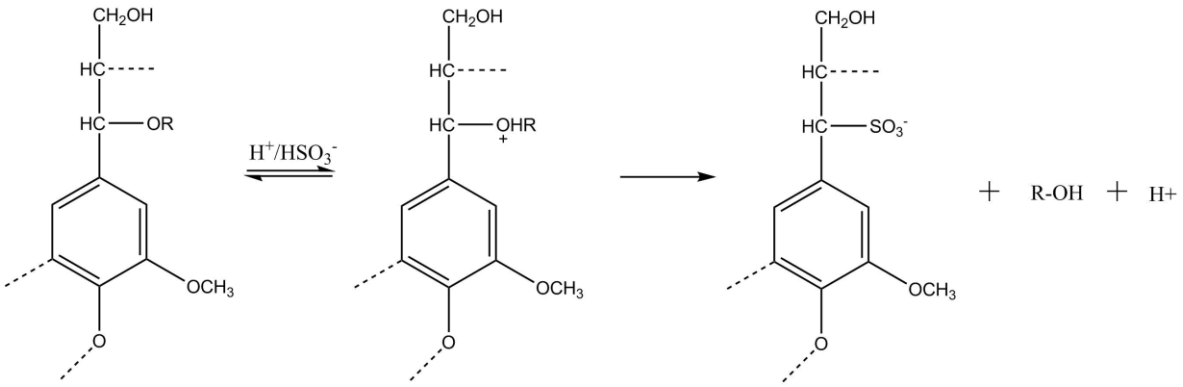

Figure 13. Sulfonation of lignin during acidic sulfite pulping

3 Method

The forest residues were treated as shown in Figure 14 and the cellulose fraction was analyzed after each step to monitor the amount of cellulose, hemicelluloses and lignin that was removed in each step. The precipitated lignin fraction was also analyzed to show the size distribution and structure of the removed lignin.

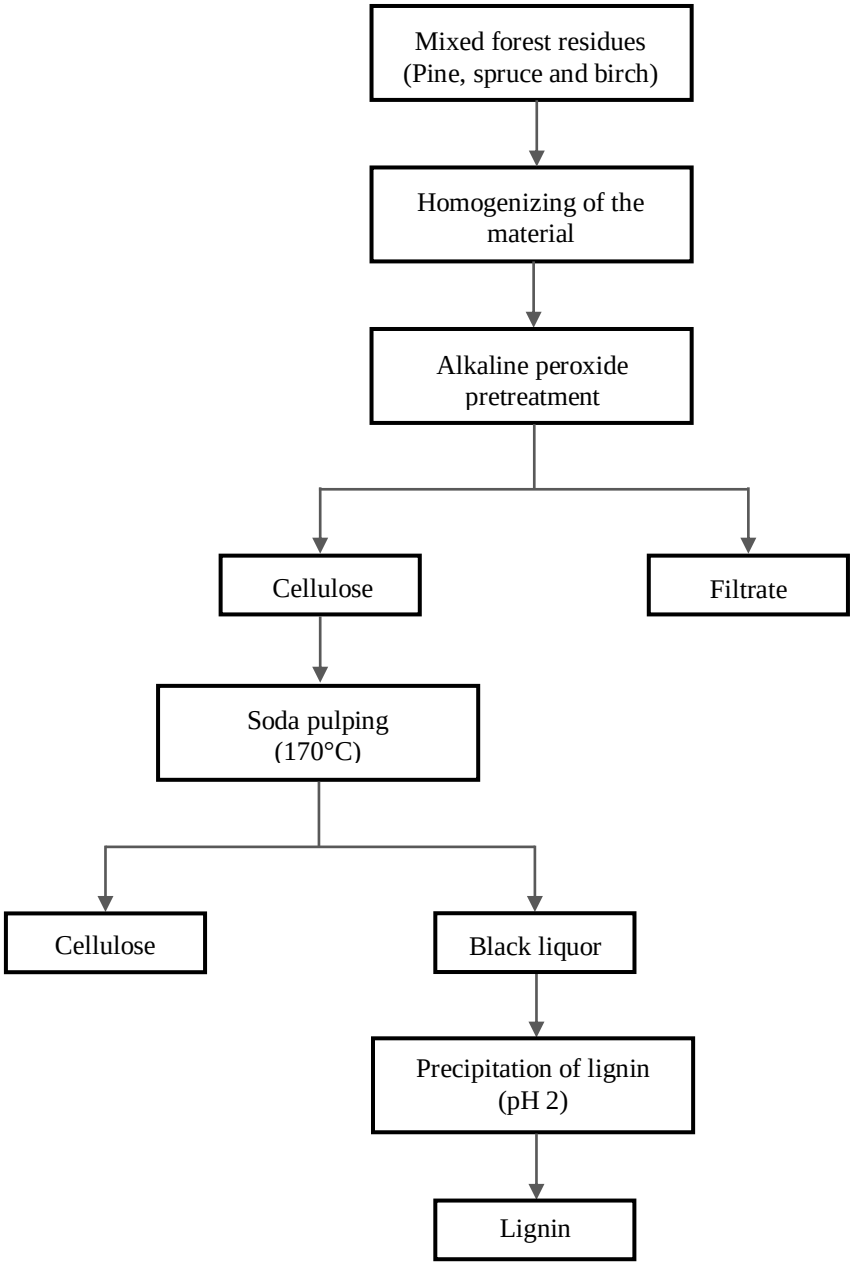

Figure 14. Flowsheet of the different treatments

3.1 Raw material

Forest residues (branches, twigs and bark) from a mixture of softwood and hardwood trees, mainly pine, spruce and birch, were used as the raw material (Domsjö, Örnsköldsvik). Before shipping, the forest residues had been chipped into a more uniform mixture. To further homogenize the material the forest residues were refined. Firstly the forest residues were steamed atmospherically to warm up the equipment. The forest residues were then steamed at 125 °C for 15 minutes followed by processing in a Sprout-Waldron 12-1CP 12 inch disc refiner. The refined forest residues were then packaged in plastic bags and stored at -20 °C in a freezer. Prior to being used in the pretreatments, the refined forest residues were thawed slowly at 8 °C.

3.2 Alkaline peroxide pretreatment

Three parameters were adjusted during pretreatment and these were the residence time, temperature and hydrogen peroxide concentration. The investigated parameter intervals were 1-3 hours, 20-60 °C and 1.1-3.3 % hydrogen peroxide which resulted in eight different runs, Table 1. The procedure of the pretreatment with the parameters 3 hours, 20 °C and 3.3 % is described below. For each pretreatment, 70 grams of reaction solution was used per gram of dry forest residues.

Table 1. Combinations of the three investigated parameters generated the following eight pretreatment conditions.

	Time (h)	**Temperature (°C)**	**H_2O_2 concentration (%)**
1	1	20	1.1
2	1	60	1.1
3	1	20	3.3
4	1	60	3.3
5	3	20	1.1
6	3	60	1.1
7	3	20	3.3
8	3	60	3.3

Refined forest residues were treated with an alkaline hydrogen peroxide solution by mixing 5 grams (dry weight) of the substrate in 315 ml of distilled water. While stirred 35 ml of 30 wt.% hydrogen peroxide was added to the mixture to create a 3.3 % solution of hydrogen peroxide. The pH of the solution was then adjusted to 11.5 with 50 wt.% sodium hydroxide

solution. The suspension was then stirred continuously at room temperature (20 °C) for 3 hours. The insoluble fraction was separated from the mixture by vacuum filtration. The filtrate was collected for further analysis and the insoluble fraction was washed with 250 ml of deionized water (Gould, 1985).

3.3 Soda pulping

The soda pulping was carried out using autoclaves where these were heated using hot polyethylene glycol.

To achieve a near constant bulk concentration, a solids to liquor ratio of 1:150 was used. The cooking liquor was prepared by adding 450 grams of deionized water to 14.5 grams of sodium hydroxide. Once dissolved, the liquor was poured into the autoclave and 3 grams of dry, pretreated forest residues were added.

The autoclaves were then lowered into the cooker and preheated to 80 °C for 20 minutes. After this, the temperature was set to 170 °C. Once 170 °C was reached (after 90 minutes) the timing for the different batches was started. Four different cooking times were investigated; 30, 60, 120 and 180 minutes.

After the pulping, the autoclave was allowed to cool in a water bath. After 5 minutes the autoclave was cool enough to open. The suspension was then filtered through a woven polypropylene mesh using a Büchner funnel. The cooking liquor was saved for analysis and the pulp was washed with 1 liter of deionized water. After washing, the pulp was processed in a pulp disintegrator for 10 minutes, filtered once again and then dried at 40 °C in a convection oven for 72 hours.

3.4 Extractives

The amount of solvent-soluble, non-volatile material in the raw material can be quantified using the Tappi T204 cm-07 standard method. In this method, the extractives can either be extracted using an ethanol/benzene mixture, acetone or dichloromethane. Due to the toxicity of benzene and the lower yields from dichloromethane, acetone was chosen as the preferred solvent.

The sample to be analyzed was dried and ground to pass a 40 mesh screen. 10 grams of the wood meal was placed in an extraction thimble that was positioned in a Soxhlet extraction

apparatus. The extraction flask was then filled with 400 ml of reagent grade acetone and the heating was adjusted so that the boiling rate resulted in no less than 24 extraction during 6 hours. After 6 hours had passed, the flask was removed from the apparatus and the solvent was evaporated partially to reach a final volume of 20-25 ml. The extract was then transferred to a pear-shaped flask of known weight and evaporated to near dryness using a rotary evaporator. The flask and its contents were then dried in an oven at 105 °C for 1 hour, cooled in a desiccator for 30 minutes and finally weighed. The final extractive content was then calculated according to Equation 1.

$$Extractives, \% = \frac{(oven\ dry\ weight\ of\ extracts, g)}{(oven\ dry\ weight\ of\ wood, g)} \times 100$$

Equation 1. Calculation of extractive content

3.5 Ash content

Inorganic compounds present in the raw material can be quantified as ash. The amount of ash was measured by igniting a sample in a muffle furnace at 525 °C according to the Tappi T211 om-02 standard method.

A clean crucible was placed in a muffle furnace at 105 °C for 24 hours and allowed to cool to room temperature in a desiccator. Once cool, the crucible was weighed. Thereafter, a minimum of 1 gram dry weight of the sample was placed in the crucible. The crucible was then placed in a furnace at 100 °C, after which the temperature was raised slowly to 525 °C over a period of 2 hours. Once the sample was completely free of any black particles, the sample was considered completely combusted. The crucible was then removed from the furnace and allowed to cool before being transferred to a desiccator. The crucible and ash were then weighed together and the ash content was calculated as seen in Equation 2.

$$Ash, \% = \frac{(weight\ of\ ash, g)}{(dry\ weight\ of\ sample, g)} \times 100$$

Equation 2. Calculation of ash content

3.6 Klason analysis

3.6.1 Acid-insoluble lignin

The Klason method can be applied to analyze the lignin content of a sample using a strong acid to hydrolyze the carbohydrates. The insoluble residue was classified as the acid insoluble lignin or Klason lignin. The method used was according to the one described by Theander and Westerlund (1986), with some changes regarding the dilution. A sample of 200 mg that had been oven dried at 105 °C for 24 hours was used (Theander. & Westerlund, 1986). The sample was subjected to 3 ml of 72 % sulfuric acid and stirred thoroughly before placed under vacuum for 15 minutes. The sample was then put in a water bath at 30 °C for 1 hour and stirred two times, after 10 minutes and after 30 minutes. To dilute the sample 84 grams of deionized water was added and the suspension was covered with aluminum foil before placed in an autoclave at 125 °C for 1 hour. After the autoclave the sample was filtrated and the soluble and insoluble lignin were separated. The insoluble lignin, Klason lignin, was dried (105 °C) for 24 hours and the amount was determined gravimetrically. From the filtrate two dilutions were prepared, one using 1 ml of filtrate and 2 ml of internal standard (200 mg/l fucose standard) and one using 5 ml of filtrate and 2 ml internal standard. These solutions were then diluted to 50 ml using deionized water (Theander & Westerlund, 1986).

3.6.2 Acid-soluble lignin

The amount of acid-soluble lignin was calculated from the absorbance value using UV spectroscopy at 205 nm in an Analytik Jena, Specord 205 and an absorbance constant of 110 dm^3/g cm (Dence, 1992).

3.6.3 Carbohydrate analysis using High-performance liquid chromatography

The total composition of sugar monomers in the sample can be acquired from the filtrate by addition of an internal standard, fucose, and high-performance liquid chromatography, HPLC, analysis. The filtrate was diluted into two different dilutions, one diluted ten times and one diluted fifty times, both with the same concentration of the internal standard, where the one diluted fifty times was used for the detection of glucose. The solutions were then filtered through a PVDF syringe filter in the size of 0.45 µm before injected in the HPLC. The HPLC instrument used was the Dionex ICS-5000 equipped with CarboPac PA1 columns and the eluents were NaOH and NaOH/NaAc (0.2 M). The detection measurement was an

Electrochemical Detector and the software used was the Chromatography Data System Chromeleon 7 version 7.1.3.2425.

3.6.4 Gel permeation chromatography

Measurements of molecular weights (Mw) and polydispersity (PD) were performed using a gel permeation chromatography (GPC) which sorts molecules depending on size using a liquid column chromatography technique (Striegel, Yau, Kirkland & Bly, 2009). The GPC used was run with a PL-GPX 50 plus integrated system that was connected with Refractive index (RI) and Ultraviolet (UV) detectors. The wavelength of 280 nm was used for UV measurements (Polymer Laboratories, Varian Inc.).

The columns, two PolarGel-M and one PolarGel-M Guard (300×7.5mm and 50×7.5mm), were used and coupled in series with the pore size 8 µm of mixed type of pores. The mobile phase, dimethyl sulfoxide (DMSO)/LiBr (10 mM), was used with a flow rate of 0.5 ml/min. To determine the molecular weight and the PD a 10-point calibration curve with Pullulan standards was used (708000, 375000, 200000, 107000, 47100, 21100, 11100, 5900, 667 and 180 Da, Polysaccharide Calibrations Kit, PL2090-0100, Varian). Cirrus GPC software Version 3.2 was used for data analysis. Samples (2 mg/ml for hemicellulose/cellulose or 0.25 mg/ml for lignin) were dissolved in the mobile phase DMSO/LiBr (10mM). The solution was then filtered using a syringe filter (GHP Acrodisc, d=13 mm, 0.2 µm GHP membrane).

3.7 Scanning electron microscopy (SEM)

Images of untreated forest residue and treated residue, sample 7 (3 h, 20 °C, 3 %), were obtained using a Quanta 200 FEG environmental scanning electron microcopy (ESEM) operating at 0.3 Torr and 3 kV.

3.8 GC-MS/FID spectroscopic analysis of extractives components

A gas chromatographic system of the model Agilent 7890A, Agilent 5975C Stockholm, equipped with parallel flame ionized detection (FID) and mass spectrometer (MS) detection operating in an electron ionization mode was used to analyze the volatile compounds in the evaporated crude extractive residues. The derivatives protected by trimethylsilyl (TMS) were semi-quantified using the internal standard of heptadecanoic acid methyl ester. A sample of 10 mg residue was dissolved using 0.6 ml ethyl acetate and 15-25 mg of the internal standard,

heptadecanoic acid methyl ester (15-20 mg/0.9-1.1 g ethyl acetate), was added to the sample. The solution was then derivatized with 0.1 ml BSTFA (99:1; *N*, *O*-bis(trimethylsilyl)trifluoroacetamide: chlorotrimethylsilane) and TMS reagent. After 30 minutes 1 µl of the solution was injected via an autosampler to the gas chromatographic system. Once injected the analytes were split and separated in two chromatographic columns (HP-5MS, 30 m long, 0.25 mm internal diameter and 0.25 µm stationary phase thickness) using helium as carrier gas. 1 ml/min for the MS column and 0.6 ml/min for the FID column. The temperatures for the system were set to 300 °C for the injector, 250 °C for the FID detector and 50 °C for the GC oven for 2.25 minutes before being raised to 300 °C with 2 °C/minutes, thereafter the temperature of the GC oven is set at 300 °C for 30 minutes. The MS source and the quadrupole temperature were set to 250 °C respectively 150 °C. To carry out the spectral interpretations the NIST MS search programme (version 2.0) operating on the NIST/EPA/NIH Mass Spectral Database 2011 (NIST 11) was used.

4 Results & Discussion

4.1 Characterizing the raw material

The chemical composition of the refined forest residue mixture is presented in Figure 15. The refined forest residues contained roughly 35 % lignin, 60 % carbohydrates, 4 % extractives and 1 % ash.

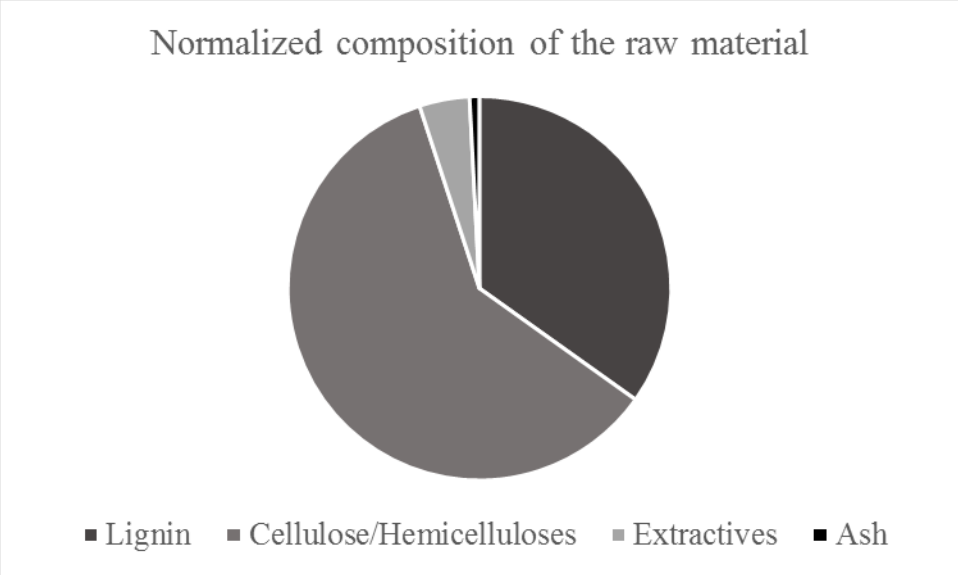

Figure 15. Representation of the normalized composition of the raw material (refined forest residues). 34.84 % lignin, 60.09 % Cellulose/hemicelluloses, 4.24 % Extractives and 0.82 % Ash.

When comparing the non-normalized chemical composition of the refined forest residues with that of untreated forest residues (unpublished data, Joanna Wojtasz-Mucha, Table 2) the refined forest residues seem to be a mixture of branches and wood judging by the amount of arabinose, glucose, xylose and Klason lignin. The low amount of bark present in the refined forest residues is most likely due to the refining of the chipped forest residues. Both the high temperature steam and the possibility that the smaller bark particles may be accidentally separated from the other, larger fibres after the refining may cause the low amount of ash and extractives present in the refined forest residues.

Table 2. Chemical composition of untreated bark, branches, wood and the refined forest residues (mixture of bark, branches and wood).[2]

Sample	**Ara**	**Rha**	**Gal**	**Glu**	**Xyl**	**Man**	**Klason**	**ASL**	**Others**
Bark[1]	3.87	-	1.90	18.09	5.72	1.72	47.01	-	21.70
Branches[1]	2.25	-	3.78	26.29	10.07	4.37	36.43	-	16.81
Wood[1]	0.51	-	0.90	37.75	22.40	3.46	22.39	-	12.60
Refined forest residues	1.25	0.19	1.87	33.00	13.42	5.39	30.06	1.90	12.92

The majority of the contribution to the value for "others" in the chemical composition, Table 2, is likely because of errors in the mass balance. When the same sample was analyzed multiple times it showed good consistency for the Klason lignin. However, the values for the carbohydrates varied. This indicates that the "others" is likely due to errors during the sample preparation. Because of this, when comparing Klason lignin content for different samples, the mass balance will not be normalized since this would likely cause inconsistencies in the results.

4.2 Pretreatment

The chemical composition of the forest residues after alkaline peroxide pretreatment is presented in Table 3, where the results are presented as wt. % of initial sample for all the eight pretreated forest residue samples and the reference sample, G (untreated forest residue). The Klason lignin percentage for the pretreated forest residue samples is roughly 5 percentage points lower than that of the reference, except for sample 1 which was subjected to the weakest pretreatment (1 h, 20 °C, 1.1 %). Sample 1 shows no significant difference in Klason lignin with a percentage of 29.65 wt.% compared to the 30.06 wt.% of the reference sample, G.

[1] Analyzed by Joanna Wojtasz-Mucha
[2] Arabinose (Ara), rhamnose (Rha), galactose (Gal), glucose (Glu), xylose (Xyl), mannose (Man), Klason lignin (Klason), acid soluble lignin (ASL)

Table 3. Chemical composition of refined forest residues after alkaline peroxide pretreatment.[2]

	Ara	Rha	Gal	Glu	Xyl	Man	Klason	ASL	Others
#1 (1 h, 20 °C, 1.1 %)	1.26	0.17	1.67	37.03	14.09	5.26	29.65	2.21	8.65
#2 (1 h, 60 °C, 1.1 %)	0.89	0.17	1.07	41.65	14.92	6.15	24.66	2.13	8.37
#3 (1 h, 20 °C, 3.3 %)	0.98	0.17	1.44	34.76	13.79	5.62	24.78	2.07	16.40
#4 (1 h, 60 °C, 3.3 %)	0.9	0.15	1.15	39.62	13.19	6.27	25.46	1.96	11.30
#5 (3 h, 20 °C, 1.1 %)	0.80	0.16	1.22	37.90	11.22	4.83	24.91	1.68	17.27
#6 (3 h, 60 °C, 1.1 %)	0.66	0.13	0.33	42.83	10.65	4.62	25.32	1.52	13.93
#7 (3 h, 20 °C, 3.3 %)	0.92	0.16	1.35	38.31	12.55	5.15	24.55	1.89	15.12
#8 (3 h, 60 °C, 3.3 %)	0.62	0.11	0.56	44.31	9.99	4.44	24.68	1.59	13.71
G (untreated)	1.25	0.19	1.87	33.00	13.42	5.39	30.06	1.90	12.92

The raw material was also compared to the pretreated forest residues using an environmental scanning microscope (ESEM) to analyze any visual change of the fibres. The fibres before and after pretreatment can be seen in Figure 16. Comparing the surface of the untreated and pretreated forest residues shows that the surface of the pretreated residues have a more porous structure and rougher surface while the untreated residues have a smoother surface. The main effect of the roughness is the increased absorption of liquids.

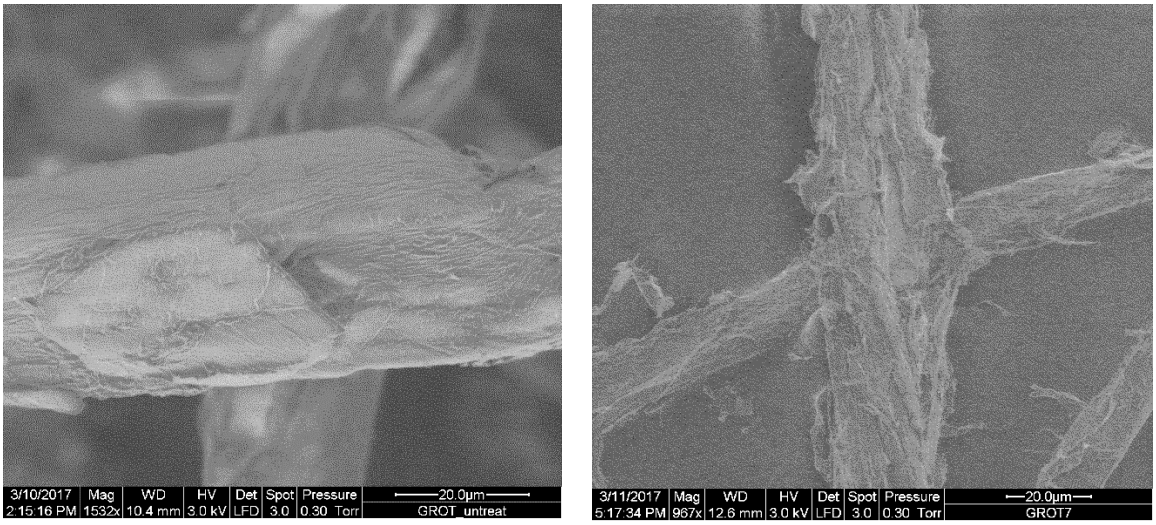

Figure 16. Refined forest residues (left) and forest residues after alkaline peroxide pretreatment (right)

[2] Arabinose (Ara), rhamnose (Rha), galactose (Gal), glucose (Glu), xylose (Xyl), mannose (Man), Klason lignin (Klason), acid soluble lignin (ASL)

4.3 Soda pulping

The chemical composition for the different residence times from the soda pulping is presented in Table 4, which shows the results as wt. % of initial sample for all the eight alkaline peroxide pretreated samples and the reference sample, G, consisting of refined forest residues.

Table 4. Chemical composition of the solid fraction after soda pulping. Of the alkaline peroxide pretreated forest residues (1-8) and an untreated referece, G.[34]

	Arabinose	Galactose	Glucose	Xylose	Manose	Klason	ASL	Others
#1								
30	0.28	0.39	70.89	5.78	3.94	8.97	0.89	8.85
60	0.16	0.34	72.19	5.31	2.65	6.29	0.87	12.07
120	0.07	0.12	73.91	4.24	3.41	5.49	0.69	12.07
180	0.07	0.16	75.40	4.28	3.79	3.95	0.98	11.37
#2								
30	0.15	0.15	71.33	4.63	3.31	5.72	0.87	13.84
60	0.16	0.18	71.56	4.72	4.15	4.85	0.85	13.53
120	0.06	0.08	75.64	4.43	2.34	2.00	0.73	14.72
180	0.05	0.07	72.37	3.55	3.43	2.35	0.75	17.42
#3								
30	0.22	0.25	68.19	4.74	3.67	8.30	0.85	13.78
60	0.15	0.24	71.19	4.79	3.99	6.22	0.84	12.58
120	0.08	0.13	75.85	4.64	3.38	3.18	0.73	12.00
180	0.06	0.08	76.33	3.41	3.56	2.75	0.79	13.03
#4								
30	0.15	0.18	72.69	5.37	3.49	5.63	0.82	11.66
60	0.09	0.13	72.20	4.71	3.39	3.39	0.78	13.78
120	0.06	0.09	76.27	3.94	3.31	2.14	0.72	14.14
180	0.00	0.06	76.02	3.83	2.88	2.10	0.68	13.52
#5								
30	0.30	0.37	73.42	5.27	3.55	9.37	0.92	9.30
60	0.16	0.30	73.89	4.59	3.41	6.11	0.78	12.32
120	0.07	0.13	78.80	4.64	3.35	3.29	0.72	12.23
180	0.00	0.10	79.13	3.64	3.06	3.40	0.70	12.89
#6								
30	0.17	0.19	73.42	5.27	3.65	6.06	0.89	10.36
60	0.12	0.16	73.89	4.59	3.22	3.94	0.82	13.27
120	0.07	0.09	78.80	4.64	3.33	2.89	0.78	9.42
180	0.05	0.06	79.13	3.64	3.22	2.25	0.71	10.94
#7								
30	0.18	0.27	71.27	5.88	3.93	6.64	0.66	11.16
60	0.09	0.18	74.35	5.08	3.68	4.26	0.62	11.74
120	0.05	0.10	77.17	4.20	3.76	1.99	0.54	12.19
180	0.05	0.10	77.95	5.04	3.43	1.20	0.59	11.67
#8								
30	0.16	0.21	73.03	5.15	3.63	5.49	0.86	11.46
60	0.11	0.16	72.73	4.53	3.71	3.58	0.82	14.37
120	0.08	0.07	69.35	3.26	2.56	1.99	0.65	22.05
180	0.04	0.07	77.72	3.43	2.97	1.90	0.67	13.21
G								
30	0.29	0.43	67.27	5.71	4.51	10.97	0.89	9.93
60	0.18	0.30	71.26	5.66	4.36	6.62	0.82	10.80
120	0.08	0.17	76.08	4.84	4.13	3.55	0.77	10.39
180	0.05	0.11	75.32	4.42	3.66	2.29	0.69	13.45

[3] For experimental conditions, see table 1.
[4] Rhamnose was not detected in any of the samples.

In Figure 17 it can be seen that after 180 minutes of soda pulping of the alkaline peroxide pretreated and untreated forest residues, the lignin percentage is roughly the same for all nine samples. Considering the inhomogenity of the starting material some variation is to be expected. However, the majority of the samples follows a clear trend which should suggest that the divergent results for sample number 1 and number 2 are likely caused by errors in the analyzis.

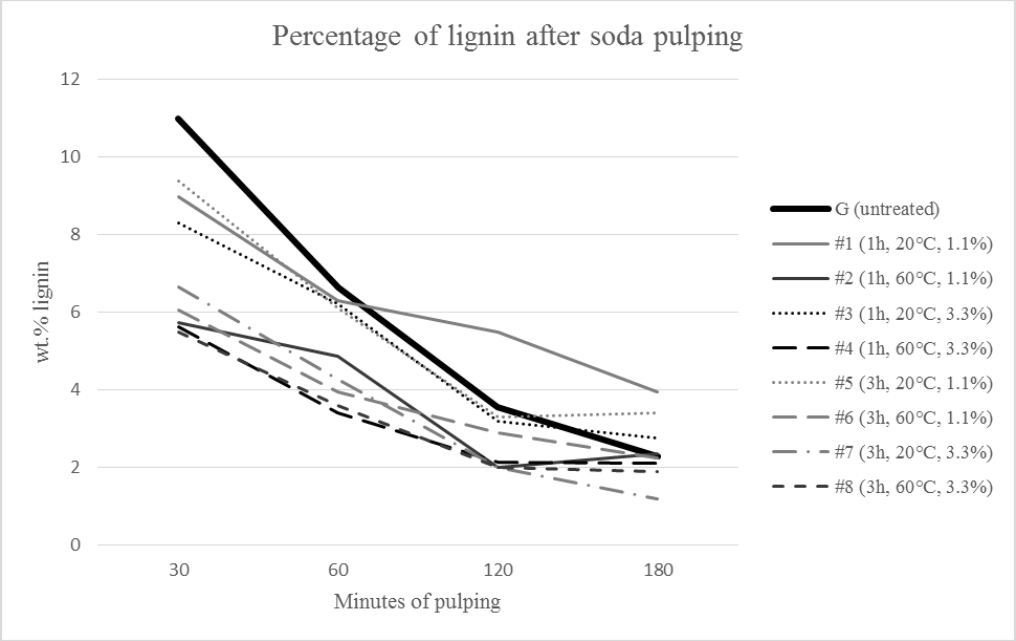

Figure 17. Compiled results for Klason lignin percentage after soda pulping of alkaline peroxide pretreated and untreated forest residues.

Trends for the three different parameters (i.e residence time, temperature and H_2O_2-concentration) that were changed in the pretreatments were analyzed to compare the significance of the parameters during soda pulping. No large differences was found when comparing the final results for the pretreatments conducted with 1.1 % or 3.3 %, or when comparing the pretreatments performed at 1 hour or 3 hours. However, comparing the Klason lignin over the pulping time for the two pretreatment temperature parameters (20 °C and 60 °C) shows that the samples subjected to higher pretreatment temperatures decreases the percentage of lignin faster than the ones subjected to lower pretreatment temperatures. The higher pretreatment temperatures also show a clearer separation from the reference, G, during soda pulping which can be seen in Figure 18 and Figure 19.

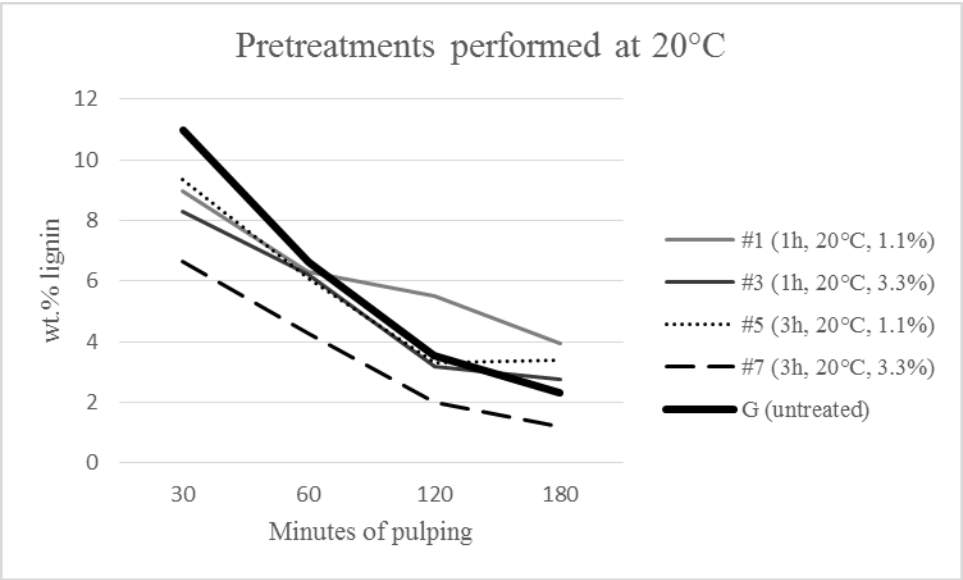

Figure 18. Compiled results for Klason lignin percentage after soda pulping of the alkaline peroxide pretreated forest residues pretreated at 20 °C.

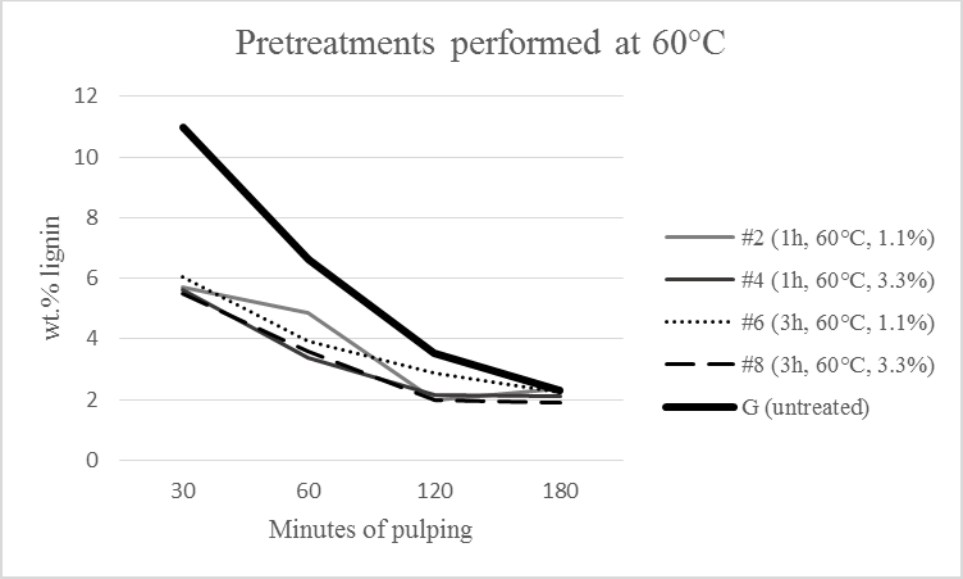

Figure 19. Compiled results for Klason lignin percentage after soda pulping of the alkaline peroxide pretreated forest residues pretreated at 60 °C.

Due to the fact that no clear difference could be seen after soda pulping for pretreatments conducted with 1.1 % or 3.3 % hydrogen peroxide, one more pretreatment was performed. This new pretreatment used 0.56 % hydrogen peroxide and was processed at 60 °C for 1 hour. The results from the soda pulping of this sample (number 0.5) is found in Table 5.

Table 5. Chemical composition after soda pulping of the forest residue sample with the pretreatment parameters 1 hour, 60 °C and the hydrogen peroxide concentration of 0.56 %.

	Arabinose	Galactose	Glucose	Xylose	Manose	Klason	ASL	Others
#0.5								
30	0.13	0.16	64.14	4.35	2.59	9.95	0.68	18.01
60	0.13	0.18	71.55	5.35	3.59	4.94	0.77	13.49
120	0.07	0.10	77.23	3.80	3.18	3.15	0.66	11.81
180	0.05	0.07	75.51	3.17	2.62	2.20	0.68	15.69

When comparing this alkaline peroxide pretreatment (sample number 0.5) to the rest of the forest residues pretreated at 60 °C it separates from the trend, Figure 20. This suggests that the optimum hydrogen peroxide concentration to achieve a faster delignification of the forest residues is somewhere around 1.1 %.

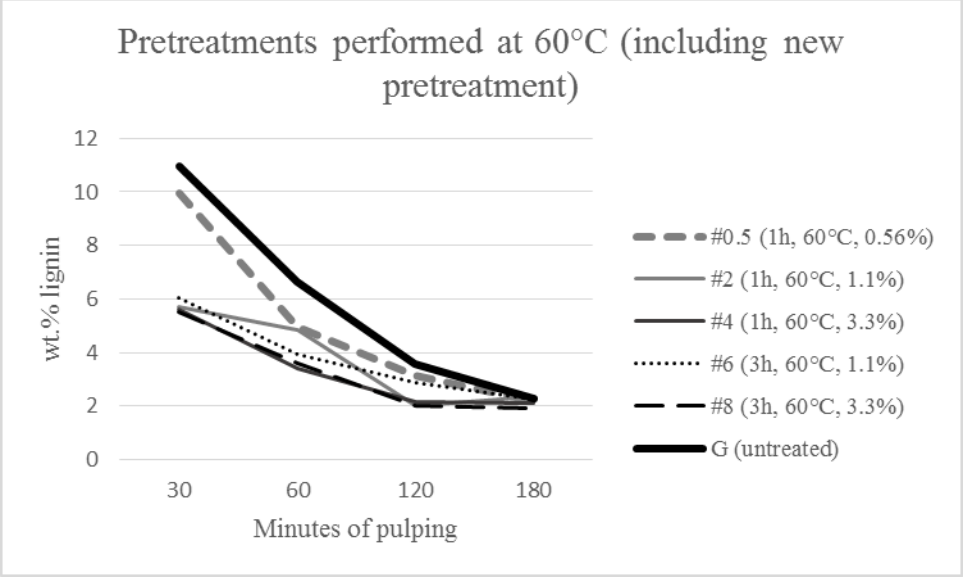

Figure 20. Percentage of Klason lignin for the different alkaline peroxide pretreated forest residues pretreated at 60 °C (including new pretreatment) at different soda pulping times.

The trend graphs for residence time and hydrogen peroxide concentration is found in Appendix I.

4.4 Analysis of pulp

Dissolving pulp used in production of textiles needs, according to Södra Skogsägarna, a molecular weight around 160 kDa. Table 6 shows the molecular weight and polydispersity of the cellulose from sample 7 (3 h, 20 °C, 3 % H_2O_2). This analysis was kindly performed by Södra Skogsägarna. The molecular weight decreases with pulping time except for a deviation of the sample with the pulping time of 180 minutes. Why the result from 180 minutes differs is not known. However, the molecular weight of the samples analyzed at the pulping times of 60 and 120 minutes have a value that is in the suitable range for use as dissolving pulp. Because of this, the deviation of the sample with a pulping time of 180 minutes has a minor significance as a result, since lower pulping times generated acceptable results.

The high polydispersity indicates a wide range of molecular weights, which likely is due to the inhomogeneity of the starting material or because of degrading of the cellulose during the pretreatment. However, in the absence of a reference, it is hard to draw any conclusions from these values.

Table 6. Molecular weight determination of cellulose from soda pulping of alkaline peroxide pretreated forest residues.[5]

	Mn[6] (kDa)	**Mw[6] (kDa)**	**PD[6] (Mw/Mn)**
# 7			
30	26.3	204.6	7.77
60	20.0	163.4	8.17
120	15.4	124.0	8.06
180	20.2	166.3	8.22

[5] Analyzed by Södra Skogsägarna: *N*,*N*-dimethylacetamid/lithium chloride DMAc/LiCl (0.9 % v/w), PLgel Mixed-A columns with RI and MALS detection (Palme et al, 2014).
[6] Number average (Mn), weight average molecular weight (Mw) and polydispersity (PD)

4.5 Analysis of lignin

The number average (Mn) and weight average molecular weight (Mw) of precipitated lignin after soda pulping from three alkaline peroxide pretreated samples (3, 4 and 7), the untreated reference sample (G) and a LignoBoost softwood kraft lignin reference from Bäckhammar are presented in Table 7. The weight average molecular weight and polydispersity for all samples are decreasing during the pulping time interval. The collated results can be seen in Figure 21 and Figure 22.

Table 7. Molecular weight determination of precipitated lignin from alkaline peroxide pretreated forest residues subjected to soda pulping.

	Mn[7] (kDa)	**Mw[7] (kDa)**	**PD[7] (Mw/Mn)**
#3			
30	3.80	16.37	4.31
60	3.51	12.63	3.60
120	3.28	9.85	3.00
180	3.11	8.51	2.74
#4			
30	3.42	13.50	3.95
60	3.38	10.85	3.21
120	3.04	8.17	2.69
180	2.90	7.13	2.46
#7			
30	3.74	19.18	5.12
60	3.66	12.84	3.51
120	3.14	9.26	2.95
180	3.05	7.73	2.54
#G			
30	3.72	17.61	4.73
60	3.30	11.95	3.62
120	3.10	9.23	2.98
180	3.13	8,70	2,79
Reference			
LignoBoost	5.43	17.58	3.24

[7] Number average (Mn), weight average molecular weight (Mw) and polydispersity (PD)

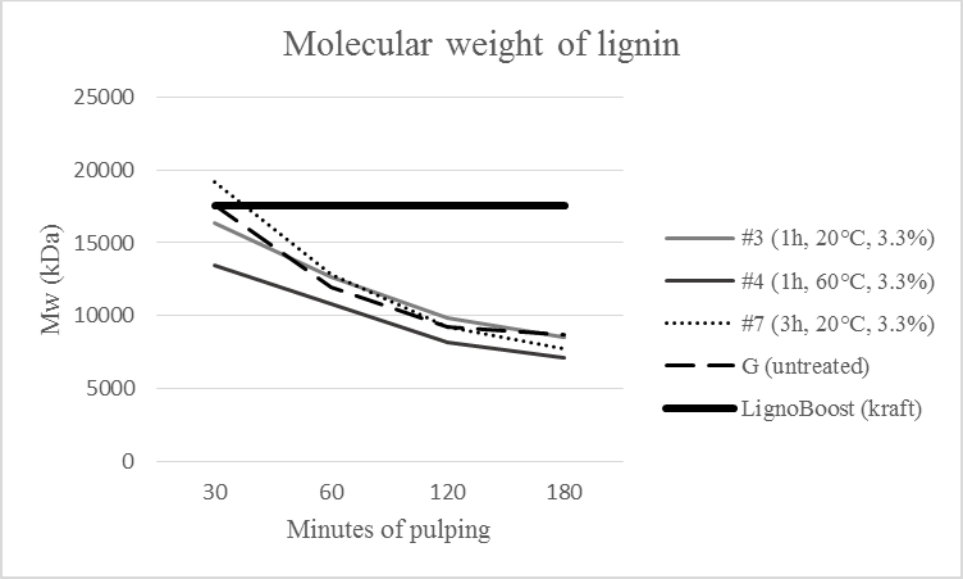

Figure 21. Molecular weight of lignin for the different pulping times for three different alkaline peroxide pretreatments (3,4 and 7), an untreated reference (G) and a LignoBoost kraft lignin as reference.

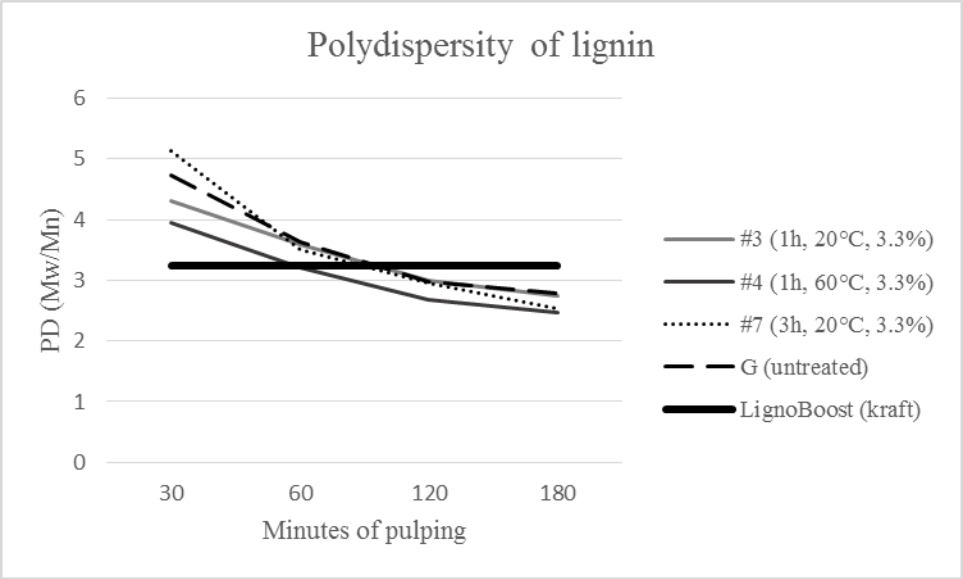

Figure 22. Polydispersity of lignin for the different pulping times for three different alkaline peroxide pretreatments (3,4 and 7), an untreated forest residue reference (G) and LignoBoost kraft lignin as reference.

The results for the forest residue soda lignins shows that the process can produce a lignin having a lower molecular weight than that of the softwood lignoboost kraft lignin and with a lower polydispersity after roughly 60 minutes of pulping for the best case. The three different alkaline peroxide pretreated forest residues shows marginally better result than the untreated sample, G, both in the case of molecular weight and polydispersity. The lower molecular weight could be beneficent for use in the biorefinery concept as it would potentially ease the thermal cracking in the HTL reactor (Nguyen et al., 2014).

The precipitated lignin from 180 minutes soda pulping, both untreated and alkaline peroxide pretreated forest residues was also analyzed using 2D NMR (DMSO-*d*6, 700 MHz, Swedish NMR centre, Gothenburg) (Mattsson et al, 2017). In Figure 23 the inter-unit linkages found in the lignin of untreated and pretreated samples can be seen. The two spectra show minor differences. In both cases the β-β linkage is the dominant inter-unit linkage and the β-O-4 linkage is not present in either of the samples.

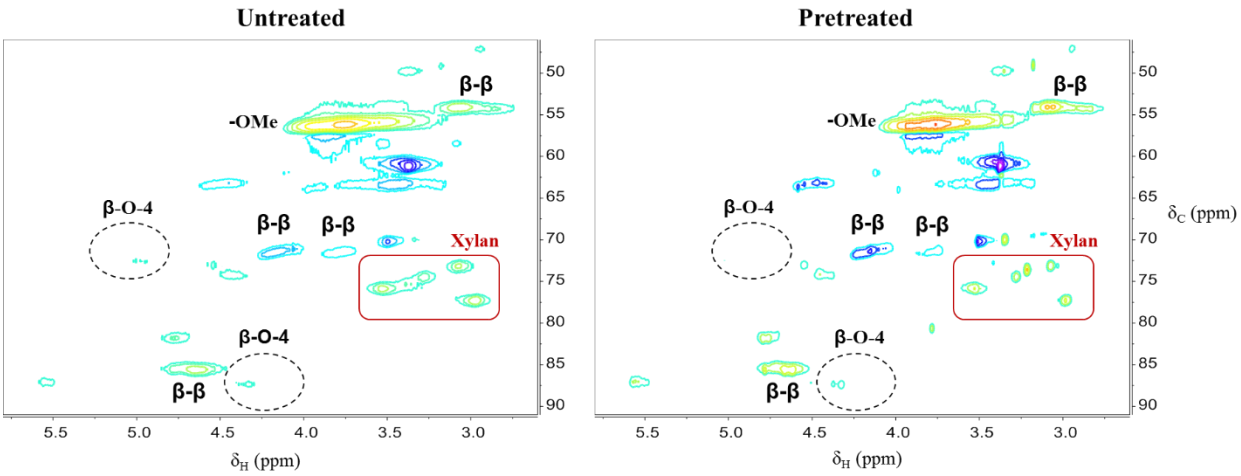

Figure 23. 2D NMR for inter-unit linkages in soda lignin from forest residues after 180 minutes of soda pulping. Untreated reference (left) and pretreated sample 4 (right).

An infra-red spectroscopy was carried out to highlight differences in the lignin structure of soda lignin from pretreated and untreated forest residues (Mattsson et al, 2017). In Figure 24 the absorbance pattern for the reference (blue) and the pretreated sample 4 (red) are presented.

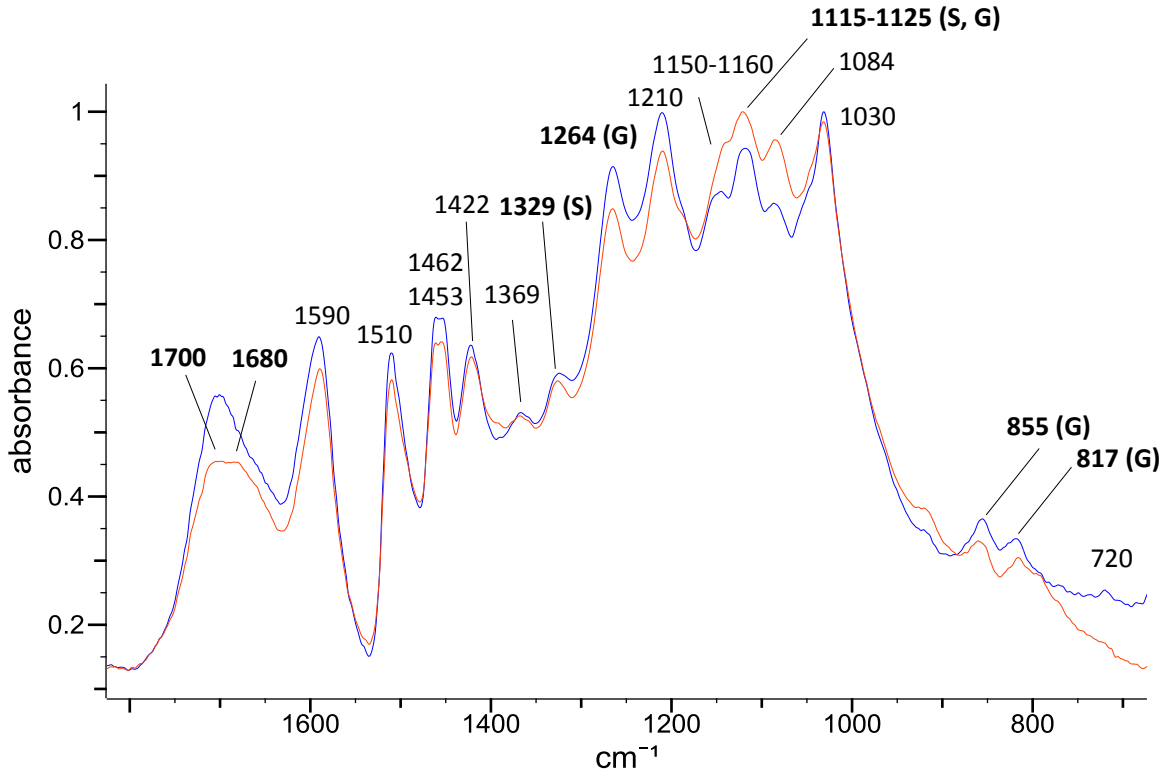

Figure 24. ATR-IR spectrum 1800-700cm^{-1} of precipitated lignin from forest residues after 180 minutes of soda pulping. Red line is the alkaline peroxide pretreated sample, 4, and blue line is the reference (G).

Overall the two spectra shows only minor differences and a typical absorbance pattern for both softwood (1270, 1125, 855 and 810 cm^{-1}) and hardwood (1326 and 1115 cm^{-1}) lignin can be seen. However, in the carbonyl region around 1750-1650 cm^{-1} the pretreated sample shows a broader peak which indicates that the hydrogen peroxide pretreatment have altered the lignin structure by the introduction of conjugated carbonyl groups (1680 cm^{-1}).

4.6 Extractives

The solvent extractives in the refined forest residues were analyzed using GC-MS/FID. The major compounds of the extractives can be found in Table 8.

Table 8. Percentage of extractive compounds found in the refined forest residues by soxhlet extraction with acetone.[8]

Type of Extractives	**Mass fraction %**
Linoleic acid, TMS ester	2.83
"Octadecanoic acid, TMS ester"	2.91
Isopimaric acid, TMS	1.28
Dehydroabietic acid, TMS	3.69
Abietic acid, TMS	1.99
β-Sitosterol, TMS ether	1.56
Betulin	2.64

Extractives solely found in softwood are the resin acids isopimaric acid, dehydroabietic acid and abeitc acid, while extractives such as β-sitosterol and betulin are more commonly found in hardwood. Linoleic acid and octadecanoic acid are fatty acids that are present in both hardwood and softwood, but to a greater extent in hardwood. The results in Table 8 indicates that the average mass fraction percentage of the major extractives compounds for the two extractive samples are roughly equally divided between hardwood and softwood.

[8] Average mass fraction of two extractive samples.

5 Conclusion

This study shows that the combination of an alkaline peroxide pretreatment and soda pulping improves the delignification of forest residues compared to solely using soda pulping. Soda pulping is not used today because of its slow and inefficient delignification compared to kraft pulping. However, if the performance of the soda pulping could be increased, for example with the use of a pretreatment step, the technique shows great potential because of its sulfur free cooking liquor and potentially simpler process layout. Addition of an alkaline peroxide pretreatment before pulping increases the roughness of the fibres and thereby the fibres susceptibility to cooking liquors. The optimum pretreatment parameters were achieved at a temperature of 60 °C, a residence time of 1 hour and a hydrogen peroxide concentration of 3.3 %. The parameter that impacted the result the most was the temperature. The biggest performance differences for the alkaline peroxide pretreated samples and the untreated forest residue sample were found in the shorter pulping times, 30 and 60 minutes, where the alkaline peroxide pretreated samples showed results with up to 50 % lower contents of Klason lignin than the untreated forest residue reference sample.

With an alkaline peroxide pretreatment step, the optimum soda pulping time for the refined forest residues was around 60 to 120 minutes. After 60 and 120 minutes of pulping the amount of Klason lignin had decreased to roughly 4 respectively 2 wt.%. Whereas soda pulping with the same residence time, without the alkaline peroxide pretreatment step, resulted in a Klason lignin contents of 6 wt.% after 60 minutes of pulping and 4 wt.% of Klason lignin after 120 minutes.

After only 60 minutes of pulping, the pretreated forest residue material had an average molecular weight of roughly 160 kDa. Because of the pulps molecular weight and its low lignin content, the produced forest residue pulp shows good potential as a dissolving pulp and for the production of nanocellulose.

The produced lignin fraction from alkaline peroxide pretreated forest residues showed good potential to be used as raw material for the production of bio-fuel in the proposed process layout since the lower molecular weights of the lignin structures, compared to LignoBoost kraft lignin, could potentially facilitate the thermal depolymerization in a HTL reactor.

Overall, the results from a combination of an alkaline peroxide pretreatment and soda pulping has shown that a sulfur free delignification could potentially be used in the purposed forest residue biorefinery. However, this study simply proves the concept of using forest residues as raw material in a biorefinery concept. Extensive research on optimizing the pretreatment and scale up of the process are necessary to move forward.

6 Future work

The next step to continue the research about forest residues as a possible feedstock in a biorefinery would be the upscaling of the process. Would the positive effect on the delignification give similar results if the ratio between forest residues and cooking liquor was changed? The potential of extracting hemicelluloses from the alkaline peroxide pretreatment process would also need to be investigated.

The forest residues analyzed in this report had a high amount of hardwood, in the form of birch, present. This was shown both in the mass balance of the refined forest residues and in the analysis of the extractives content. How would a change in the mixture of softwood and hardwood present in the raw material affect the final product and the process conditions?

The produced cellulose fraction showed potential as a dissolving pulp. However, the impact of oxidation, during the alkaline peroxide pretreatment, on the cellulose structure is not known. Also, further work on optimizing the cellulose fraction for use as dissolving pulp would include an investigation of further removal of hemicelluloses and possibly a posttreatment increased delignification.

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Appendix

Appendix I

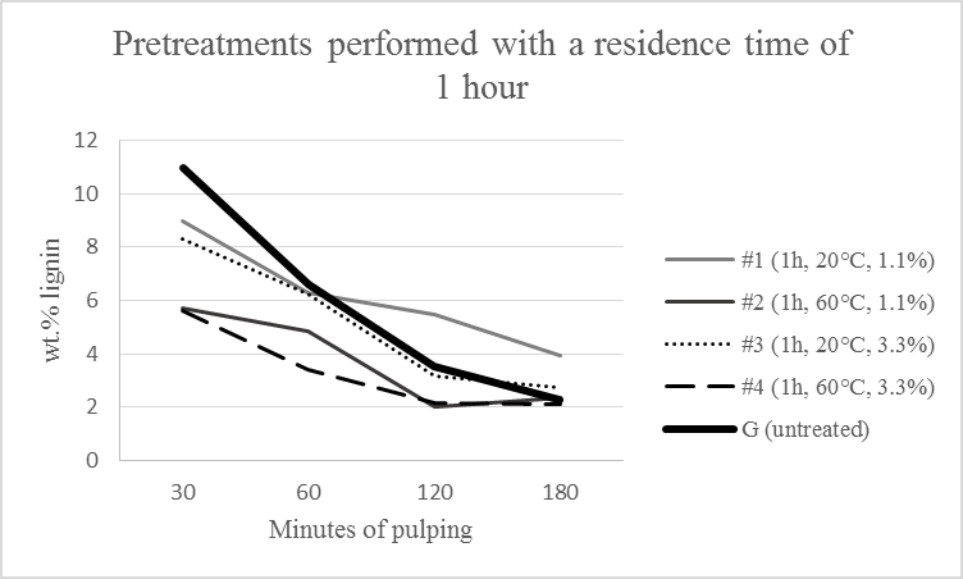

Figure 25. Compiled results for Klason lignin percentage after soda pulping for the pretreatments with a residence time of 1 hour.

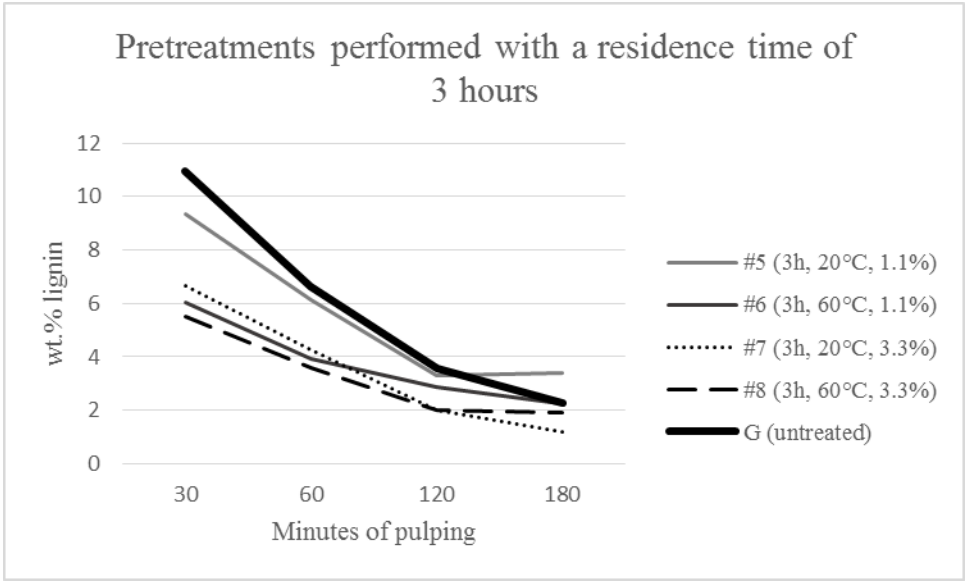

Figure 26. Compiled results for Klason lignin percentage after soda pulping for the pretreatments with a residence time of 3 hour.

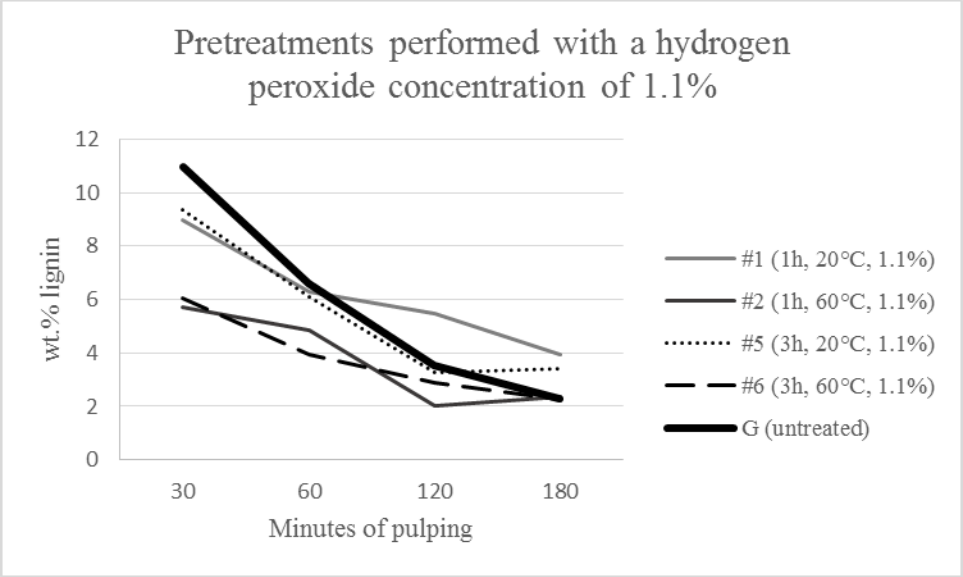

Figure 27. Compiled results for Klason lignin percentage after soda pulping for the pretreatments performed using a 1.1 % hydrogen peroxide concentration.

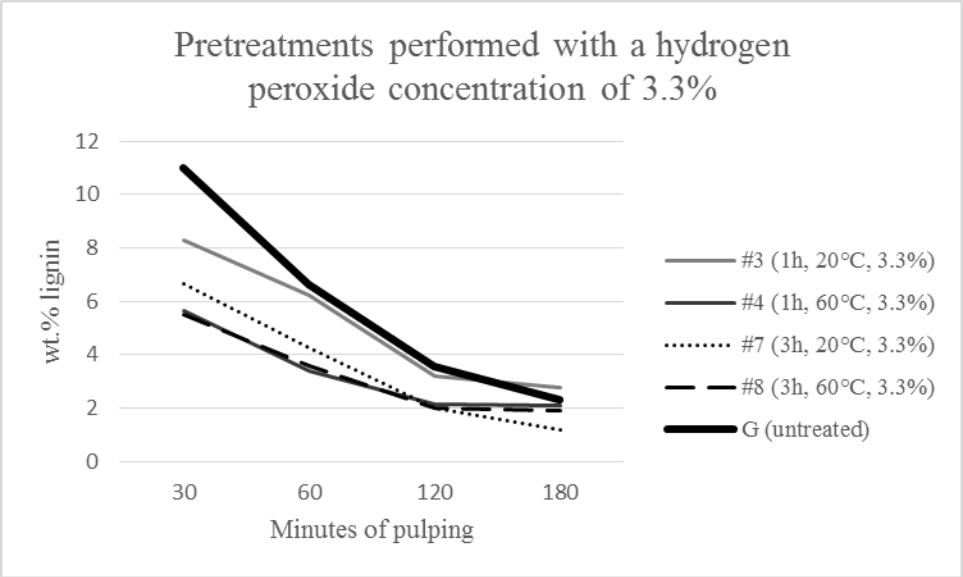

Figure 28. Compiled results for Klason lignin percentage after soda pulping for the pretreatments performed using a 3.3 % hydrogen peroxide concentration.