Resin Profile in a Bleached Kraft Pulp Process

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Abstract

The aim with this project was to investigate how the amount and composition of resins varied during the process producing bleached birch pulp at the mill *SCA Packaging Munksund*. A literature study about how the resin removal can be improved has also been included.

Problems with resins in the process are common at pulp and paper mills, especially when birch is used as a raw material. The resin can cause deposits on the equipment leading to process stops, but also lowered mechanical properties and spots on the paper products.

The addition of tall oil to the digester is one way of improving the removal of resins, seasoning of wood, and a good debarking are other ones. Also the different washing and bleaching steps can affect the amount of resin remaining in the pulp.

In this study pulp samples from eight different positions in the process were analyzed. To extract the samples a Soxtec device was used. Results showed that the most effective resin removal happened during the washing in their first washing step after the digester, a DD-washer. Here 77 % of the resin was removed, of totally 88 % during the whole process. Another step which was effective was the final washing step, the PO-press. About 36 % of the remaining resins in the pulp which entered the PO-press were washed out here.

The extracts were analyzed with GC-FID and GC-MS to identify and quantify the substances, and determine how the composition varied over the manufacturing process. Twelve different compounds were identified, and the birch bark resin, betulinol, turned out to be the hardest component to remove. Over all, the sterols and triterpenols were hard to deresinate, while the removal of resin acids, fatty acids, and fatty alcohols was more effective. The PO-reactors showed a positive effect on the fragmentation of components consisting of long carbon chains and double bonds, like squalene and betulaprenols.

Sammanfattning

Målet med projektet var att utreda hur mängden och sammansättningen av hartser varierade i den blekta björkmassan under tillverkningsprocessen på pappersbruket *SCA Packaging Munksund*. Att göra en litteraturstudie för att ta reda på vilka metoder som kan användas för att förbättra avhartsningen var en annan del av målet.

Att pappers- och massatillverkare har problem med hartser är vanligt, speciellt när björkved används som råmaterial. Hartserna kan orsaka beläggningar på utrustningen som i sin tur kan leda till processtop, men även prickar och försämrade mekaniska egenskaper hos pappersprodukten.

Att tillsätta tallolja till kokaren är en vanlig metod som används för att förbättra hartsreningen, att lagra träet innan koket, och lägga fokus på att förbättra barkningen är andra metoder. Även de olika blek- och tvättstegen som används under tillverkningen av massan kan påverka hartshalten.

I denna studie analyserades massaprover från åtta olika positioner i processen. En Soxtec-utrustning användes för att extrahera massaproverna. Resultatet visade att den mest effektiva avhartsningen sker under tvätten i det första tvättsteget efter kokaren, DD-filtret. Här tvättades 77 % av hartserna ut, och totalt minskade mängden hartser med 88 % under hela processen. PO-pressen var ett annat tvättsteg som var effektivt ur avhartsningssynpunkt. Här togs 36 % av den kvarvarande mängden hartser bort från massan.

Extrakten som erhållits från extraktionen analyserades vidare med GC-MS och GC-FID. Dessa metoder användes för att identifiera och kvantifiera extraktivämnena, och bestämma hur sammansättningen varierade under tillverkningsprocessen. Tolv olika ämnen identifierades och den substans som visade sig vara svårast att tvätta bort var björkbark hartset, betulinol. Stort sett så var steroler och triterpenoler svårast att bli av med, medans avhartsingen av hartssyror, fettsyror och fettalkoholer var mer effektiv. Det visade sig även att PO-reaktorerna hade en sönderdelande effekt på substanser såsom squalen och betulaprenoler, dessa består av långa kolkedjor med många dubbelbindningar mellan kolatomerna.

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1. Introduction

1.1 Background

Many paper mills are having problems with extractives remaining in the pulp and the finished paper product. Resins, one type of the extractives, are especially undesired in the process. These substances can leave pitch deposits on the production equipment, leading to process disturbances such as production stops and spots on the paper product. Process stops are expensive due to default revenues and the spots are undesired and therefore resulting in less valuable products. Resins can also remain in the furnish leading to weakened mechanical properties for the paper product. Problems with high amounts of resins are especially large in the processes using birch as a raw material. [1, 2] Due to this the project took form.

The company *SCA Packaging Munksund* are interested in seeing how the amount of resins are changing during the pulp process and which steps that affect the content the most. They are also interested in how the resin amount varies in the wood chips entering the digester.

At the paper mill in Munksund the process starts when the raw material, wood, goes into the rotary drum barker where bark is removed. Then the wood enters the chippers, here it is cut into approximately 20x7 mm thick chips. Afterwards the wood chips are transported to the digester where the cooking step occurs. Chemicals called white liquor, consisting of sodium hydroxide and sodium sulfide, is also added to the digester. The temperature in the digester varies depending on raw material and desired quality, but is about 160°C. After the cooking step the fibers are chemically released. Remaining cooking chemicals and other wood components than cellulose are washed away from the pulp in steps, and then regained. The birch pulp is bleached to get desired whiteness. Beating is done to the pulp to improve the paper quality. Then the furnish is prepared, and sprayed onto a wire. The kraftliner is formed and water is pressed out between felts and pressing rolls. Remaining water is removed by drying the sheets on hot cylinders. Finally the kraftliner is rolled onto huge rolls, tambours. They are later parted into smaller ones; the size depends on the customer's choice. [3]

1.2 Goal

One goal was to get a better understanding in how the resin content in the birch pulp during the *White top kraftliner* process changes, why it does change, if some process steps are much preferred from the resin cleaning perspective, and if some cleaning steps does not contribute to the resin removal at all.

Another goal is to get more information from the literature about how the amount of resins can be lowered; the addition of tall oil in the process is one area to consider.

1.3 Purpose

The purpose was to investigate how the resin amount, and the composition of different components in the resin, varies in the birch pulping process producing *White top kraftliner* at the pulp and paper mill *SCA Packaging Munksund*. The variation in amount of resin, from chips to fully bleached pulp, is going to be compiled in a resin profile. As a result of this a better understanding of the deresination can be achieved. It is also of interest to evaluate the variation in resin amount in the chips which enters the digester.

It would be of economical value for the company if the resin amount can be lowered. Consequently the manufacturing process and paper quality could be improved.

2. Theoretical section

2.1 *White top kraftliner*

White top kraftliner is an organic material belonging to the paper quality liners. These kinds of papers have very good mechanical properties and are mainly used for the production of corrugated cardboard. *White top kraftliner* has a white and a brown side. At *SCA Packaging Munksund* the brown side is primarily made from pine fibers, but sometimes also recycled fibers are added. The pine fibers are long and strong, which contributes to a stronger paper. The white side is often made from birch fibers and fillers like calcium carbonate. Birch fibers are a better choice than pine/spruce fibers when a bleached paper with a good formation is desired. The birch fibers are shorter than the pines and the amount of fibers per gram of pulp is much higher, thus the material gets a smoother and nicer surface. Birch is also relatively easy to cook to low kappa values (low amounts of remaining lignin in the pulp), hence, lower amounts of bleaching chemicals is needed to obtain preferred brightness. When a print is desired on a box, corrugated cardboard made from *White top kraftliner* is a good choice. [2, 4]

2.2 Resins and deposits

2.2.1 Extractives

Wood consists of different kinds of extractives. Almost all substances in wood except the cellulose, lignin and hemicelluloses are extractives. It can be everything from inorganic salts to fats. Extractives can be extracted from wood with neutral or polar solvents. [5] Extractives can also be found in the bark where the amount can be very significant. [6]

2.2.2 Resins

One type of the extractives in wood are called resins. Resins are lipophilic substances which are soluble in solvents with a low polarity. The resins can be divided into 4 groups:

- Fats and Fatty acids
- Steryl esters and sterols
- Terpenoids including terpenes and polyisoprenes.
- Waxes

Wood resins can leave deposits on the paper or the equipments used during the process. These deposits are referred to as pitch. [5]

2.2.3 Wood resins in birch

Parenchyma cells, which act as storage places for reserving nutrition in the wood, represent 10 % of the total weight of birch wood. Dissimilar from softwoods and some other hardwood species, birch does not have any resin canals. Instead the main part of the resin content is located in the parenchyma cells. Birch does not produce any pathological resins, which function is to seal mechanical injuries, nor does birch wood contain any volatile turpentine like softwoods do. Thus, birch resins are not as visible as softwood resins. Instead birch resins contain of free fatty acids and a lot of neutral components like sterols, triterpenols and fatty alcohols. No free resin acids can be found in birch wood. In the pulping process the neutral components contribute to the most problems because of their hydrophobic properties. [7]

When producing paper products with birch as a raw material the problems with wood resins are especially large. The reason for this is that the resins are situated in the small parenchyma cells which have a mean pit size of 1.5 μm, on the contrary this value is ten times higher for pine. In birch it is difficult for the black liquor, which contains some resin and fatty acid soaps, to diffuse through the pit and into the cell. In the cell the desired saponification reaction occurs and micelles are formed (reactions are presented in section *2.4.1 Digester*, under *Resin removal during the kraft pulping process at SCA Packaging Munksund*). The reason for micelle formation is that resin and fatty acids often consists of a head and a tail, the head is polar and the tail non-polar. Similar parts attract each other, the tail likes tails and vice versa. Furthermore the polar heads form a shell surrounding the tails (*Figure 1*), this reduce the resins contact with water but does not eliminate it totally because the heads do not cover the surface area completely. The micelles diffuse out from the cells, this is good for the resin removal, but the process is slow because of the pit size. Hence, the parenchyma cells contain more than 60 % of the remaining pulp resin after digestion. [7]

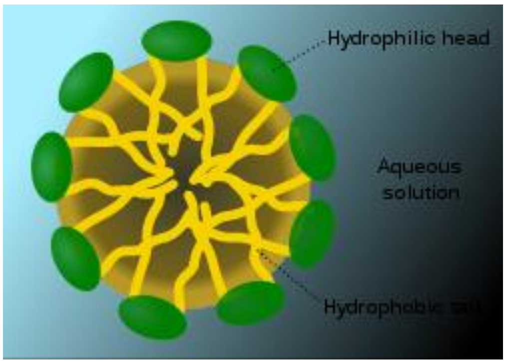

Figure 1. *A micelle.*[1]

2.2.4 Resin in birch bark

The birch bark consists of a lot of extractives, about 20-40 % [6]. Especially the outer layer of the bark contains a high amount of extractives, 80 % of these generally consists of the neutral component betulinol. The removal of betulinol shall preferably be done during the debarking step. This is because it is hard to eliminate the substance later in the process. Betulinol has a melting point of 261 °C and is insoluble in water [8]. The birch wood does not contain any betulinol at all [9]. Lupeol, sitosterol, betulinic acid, and oleanolic acid are examples on some other components that can be found in the birch bark [10].

2.2.5 Resins affect on the paper products and production

Resins contain London-van der Wahl's forces; their energy contribution is only 20 % of the energy in the hydrogen bonds which cellulose produces. Therefore, as a result of lower amounts of hydrogen bonds, the total bond strength in the sheet will be reduced with an increasing number of resin layers between the cellulose. Consequently the material's mechanical properties will be reduced. [1]

The paper strength is primarily increased during the process steps where the main parts of the hydrogen bonds are developed; these are the forming, compacting and drying steps. The hydrophobic components (resins) which remain in the paper product interfere the hydrogen bonding and therefore reduce the total bonding energy. The amount, size and physical state of the resins are of great meaning for the outcome. [1]

Also the wet web strength (the ability of the never dried paper to resist breakage) is reduced as a result of present resin molecules. As mentioned earlier the hydrogen bonded areas are reduced also in this state, but the contraction forces are affected as well. [1]

Pitch can affect the production badly. Production stops as a result of pitch deposits on washers and forming wires are usual [11]. At the Munksund mill where this project has been performed, the main problem with pitch deposits causing production stops are at the press rolls and felts in the paper machine. [2] Overall, their biggest problem with pitch is the marks they leave on the paper products. Spots on the product make it less valuable, the customer wants a clean paper with a white surface. [4]

2.2.6 Calcium soaps

The main components in deposits in kraft mills are calcium soaps and calcium carbonate. Calcium soaps are formed from calcium ions and fatty or resin acids, the reaction takes place on the surface of calcium carbonate particles. Calcium comes into the process with both the wood and the recovered cooking liquor. [7] In addition calcium carbonate often is one of the main components in the fillers used at the paper machine [4].

2.2.7 Methods to prohibit pitch deposits

A good result after the debarking step (i.e. a low amount of bark in the wood) is an important parameter for prohibiting pitch. Bark consists of a lot of extractives, therefore as little bark as possible should enter the digester. [9]

Storage of birch wood improves the deresination in both the digester and washing steps during kraft cooking. During the seasoning of chips triglycerides are hydrolyzed during the first time, later also fatty acids and steryl esters are degraded. Seasoning of roundwood is dominated by hydrolyzing of triglycerides. A similar method to decrease the amount of pitch deposits during the paper making is to treat the chips or pulp with biological treatments. For example the chips can be treated with fungi, and pulp with a special type of enzymes. The fungi reaction with the chips is similar to the reactions happening during seasoning, but the reaction rate is faster with fungi. The main reactions in both cases are triglyceride hydrolysis and degradation/oxidation of resin components. The enzyme treatment is tested in different studies and the degree of triglyceride hydrolysis was around 80% in many of them. This can decrease many pitch problems. [12]

Tall oil is often added during the digesting to improve the resin removal. To get a good result the amount should be about 3 % of the dry wood. [8] At the paper mill in Munksund approximately 60 kg tall oil is added for each ton pulp. Tall oil is a spin-off from the pulping process, and all tall oil used in Munksund is regained from the mill's own production. The usage of tall oil is necessary; otherwise the resin content after the digester would be too high and cause enormous problems. [4] Tall oil is added because it contains of a lot of resin acids which are necessary for the reactions during the kraft cooking (reactions are presented in section *2.4.1 Digester*, under *Resin removal during the kraft pulping process at SCA Packaging Munksund*). Another advantage with tall oil is that is contains of little unsaponifiables (substances that fail to form soaps during the digesting and therefore are insoluble in black liquor). [7]

To get an effective removal of fatty and resin acids during the cook it is important to keep the temperature and pH in the digester as high as possible. [8]

To add dispersing agents during the kraft pulping can often be an advantage. These are often anionic on nonionic surface active compounds which operate by stabilizing and dispersing the pitch particles. [13] Today *SCA Packaging Munksund* uses a dispersing agent from the company *BIM Kemi*. The main reason is to prevent pitch deposits in the bleaching process. The agent is designed to keep the pitch particles small, and thus avoid issues. When the particles get larger they can stick to the equipment and cause problems. [4]

Talc can be added to the process to reduce pitch problems by making the resins less sticky. This is recommended at the end of the bleaching sequence because resins which are adsorbed onto talc particles are hard to wash out. [14]

A lot of resin can also be washed out in the different washing steps. Washing steps like screw presses have the capacity to remove resin by breaking parenchyma cells. As a result of this parenchyma resin can be deresinated. [15]

Problems with pitch on the paper machine can be reduced by keeping the pH below six. At higher pH-values hard water soaps are formed, these can cause pitch deposits. Resin and fatty acids are protonated at pH-values below six and cannot form calcium soaps (calcium is added with the fillers) in such environment. [7] At *SCA Packaging Munksund* a weak acid is used at the paper machine to prohibit pitch deposits. [4]

2.3 Washing and bleaching steps at *SCA Packaging Munksund*

The birch pulp is going to be used for white paper applications in *White top kraftliner*. Hence, it is important to expose it for a number of washing and bleaching steps. The steps at the paper mill in Munksund can be seen in *Figure 2*.

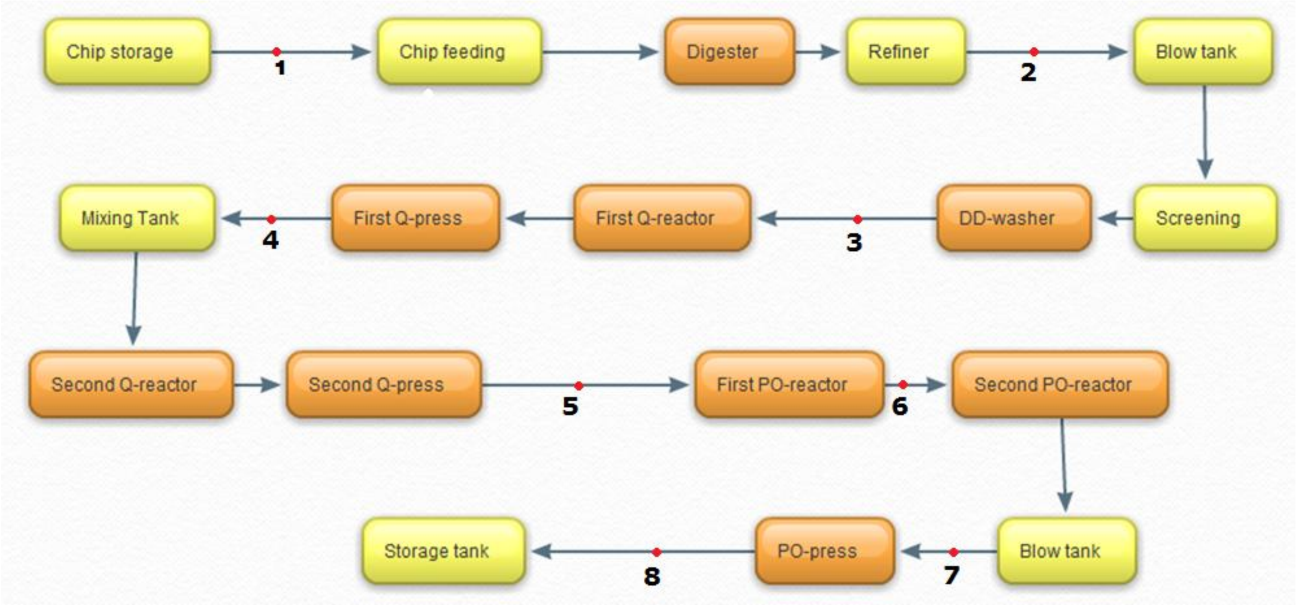

Figure 2*. The bleaching and washing steps in Munksund, an overview. The orange positions are the ones described in this report.*[2]

2.3.1 Digester, washing zone

In the lower parts of the digester, the first washing takes place. Washing liquor is introduced into the bottom of the digester, in a counter-current way, i.e. the chips/pulp is going down in the opposite direction compared to the liquor. Thus, some of the dissolved wood substances and cooking chemicals are displaced. [16]

2.3.2 Drum displacement washer (or DD-filter)

In the drum displacement washer more chemicals and undesired dissolved wood substances are washed out from the birch pulp.

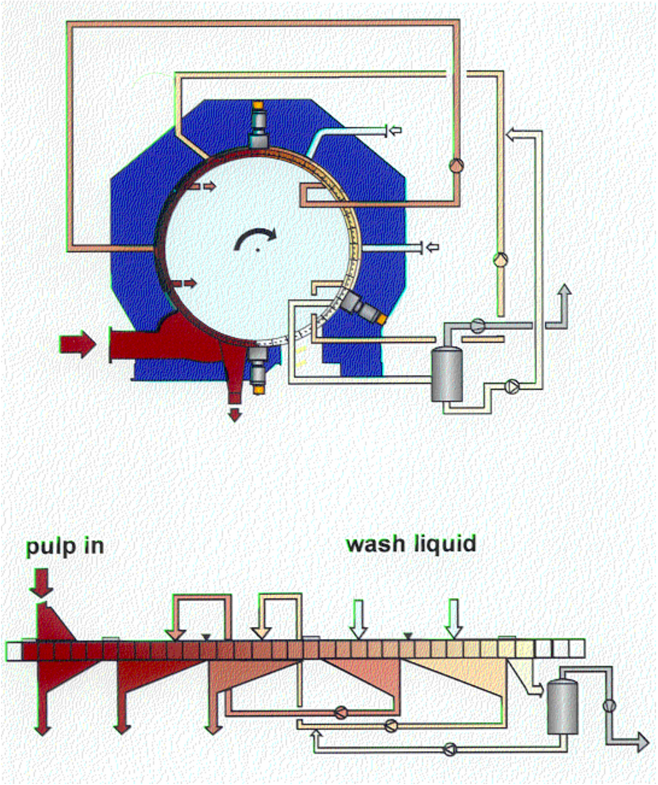

Figure 3. *Operating principle for a DD-Washer (Andritz).*[3]

The drum rotates like the arrow in the upper part of *Figure 3* shows. Pulp is transported into the machine to the left and then it travels around the drum until it reaches the right side. During this time warm washing liquor (about 90°C) is sprayed onto the top of the pulp layer, through the pulp and into the perforated drum. The liquor is reused in two steps, the dirtiest liquor wash the dirtiest pulp. In Munksund they can reuse the liquor in four steps instead of two, but this would limit the production. At the place where the cleanest liquor is washing the pulp a vacuum is applied to help the removal of liquor, this contributes to a more solid pulp. To be able to transport the pulp to the next step air is used; it is blown out from the drum, making the pulp release. [16]

2.3.3 First Q-step

The first Q-step mainly consists of a reactor where the reactions get time to happen, and a screw press (Q-press) for washing (*Figure 4 and Figure 5*). First chelating agents are added and the pH is lowered to five by addition of sulphuric acid to give the reaction optimal environment. The aim is to get rid of the undesired metal ions in the pulp, like for example manganese, which would disturb the upcoming bleaching in the PO-steps. The removal is done by the forming of stable complexes consisting of many metal ions which are easy to wash out. When the time for the reaction is enough, the pulp enters the first screw press. Due to a decrease in volume liquor is displaced from the pulp, and a lot of metals with the liquor. The pulp is then diluted with liquor again. [16]

Figure 4* and *Figure 5. *Inner part of a screw press (left) and screw press in use (right)* [4]

2.3.4 Second Q-step

To remove more metal ions there also is a second Q-step. It is similar to the first step; chelating agents are used once more. The difference is that also magnesium is added here. Without magnesium the hydrogen peroxide, which are going to be added in a later step, can lead to a high degree of depolymerization. Magnesium is believed to protect the carbohydrates during the hydrogen peroxide bleaching [17]. When magnesium is added in this step the amount into the PO-steps are correct because spill-over is displaced in the second screw press together with other metals. Too much magnesium can contribute to magnesium oxides and deposits in the equipments. [16]

2.3.5 PO-steps

Before the PO-steps hydrogen peroxide, oxygen and sodium hydroxide are added. Sodium hydroxide contributes to a higher pH-value which makes the environment for the reactions more favorable. Oxygen delignify the pulp and hydrogen peroxide bleaches. The reactions take place in two reactors subjected to pressure. Especially the hydrogen peroxide treatment is severe for the fibers, thus, to be gentler to the cellulose fibers, the treatment is done in two steps with lower amounts of chemicals in each step. [16]

To get a higher temperature, and benefit the reactions, hot steam is added with the oxygen gas into the second PO-step. This is not needed in the first because the temperature is already high from the washing liquor. The reaction rates can be controlled by the temperature and pH-value. The dosage of chemicals is done automatically with the amount of residual hydrogen peroxide and the whiteness of the pulp as controlling parameters. [16]

2.3.6 Washing press (PO-press)

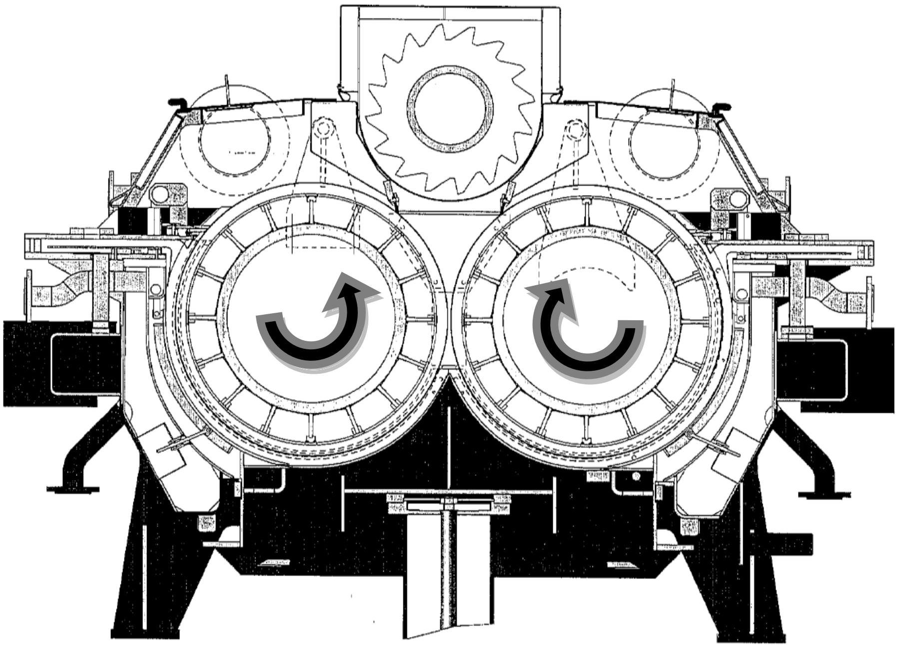

Figure 6. *The washing press in Munksund (Metso).*[5]

The last washing step in Munksund is the washing press which can be seen in *Figure 6*. Pulp is introduced in the sides and the pulp continues into a space which surrounds the two rotating perforated drums. This space becomes smaller and smaller and more and more water is pressed out. At the same time clean liquor (condensate) is washing the pulp. The tightest space for the pulp is between the two drums, after the pulp has passed the drums it is very solid and a screw is needed for transportation. [16]

The birch pulp at *SCA Packaging Munksund* is now washed and bleached. Until the papermaking process takes place, it is diluted and stored in towers. [16]

2.4 Resin removal during the kraft pulping process at *SCA Packaging Munksund*

2.4.1 Digester

At *SCA Packaging Munksund* the digester used for birch is a continuous stream liquor phase digester. During the process alkali (white liquor) is added, the largest part is added in the beginning with the chips, some is added in the trim circulation and some in the washing zone in the bottom. Also tall oil is inserted in the bottom. The white liquor which is added in the trim circulation and the bottom of the digester is heated with the rest of the cooking chemicals to regulate to preferred cooking temperature. Because the liquor in the washing zone is heated the cooking time is extended. The reactions occur in the whole digester and not only in the cooking zone (the digester is often divided into a cooking and a washing zone). The tall oil which is added is produced at the mill and consists of components from both birch and pine, but it is basically the components from pine which are desired. [16]

The reactions with resin components (both from the wood and the added tall oil) which take place during the kraft cooking are:

$$\text{Free (fatty and resin) acids} \rightarrow \text{sodium soaps (reaction rate } K_1\text{)}$$
$$\text{Fats (mainly di- or triglycerides)} \rightarrow \text{sodium soaps + glycerol (reaction rate } K_2\text{)}$$
$$\text{Steryl (fatty) esters} \rightarrow \text{sodium soaps + sterols (reaction rate } K_3\text{)}$$

Where $K_1 >> K_2 > K_3$

Important factors during the kraft cooking are; alkali concentration, chip size and distribution, temperature and liquor impregnation rate. [12]

As can be seen in the reactions above the triglycerides are saponified faster than the steryl esters. When the concentration in solution is above a certain value micelles or resin/fatty acid mixed micelles are formed from the dissolved fatty and resin acid soaps. These can solubilize other resin components which cannot be solved in water otherwise. Therefore an additional reaction takes place. The reactions in the digester can be summarized with:

Soap anions → Micelles

Unsaponifiables → Solubilized into mixed micelles

The reactions above are depending on the salt concentration, pH and temperature, but also on the physical accessibility of the resin. [12]

The saponified resins are soluble in the black liquor and can be removed during the washing steps. The remaining unsaponified resins, which are insoluble in black liquor, are the problem. [7]

2.4.2 Washing and bleaching

When the resin has been removed from the parenchyma cells it is dissolved in the black liquor solution. At the high temperatures in the digester, 150-170°C, the resins appears like fine droplets of a lamellar crystalline phase. If the temperature decreases a large amount of the earlier dissolved resins precipitate onto the fibers. Thus, to get a better deresination, it is preferable for the washing to take place at high temperatures. [7]

Foaming can occur during the washing steps. The amount of added tall oil is one parameter which affects the quantity of foam. Foaming can lead to lowered washing effects during the washing steps. Defoaming chemicals can be used if this is a problem, but also these can result in deposits and the defoamer feed rate should be kept low. [7, 18]

During the bleaching the main idea is to brighten the pulp, but some extractives can also be removed. Deresination during the bleaching with oxygen and hydrogen peroxide, which are the chemicals used at the mill in Munksund, can be obtained by oxidation. The chemical modification obtained by oxidation of the resin components can convert them into a hydrophilic form. The more hydrophilic compounds can dissolve in the liquid phase and be washed away from the pulp. [7]

Another deresination mechanism occurs when parenchyma cells are broken in washing steps like presses. Hence, then resins can be dispersed and desorbed from the broken parenchyma cells and fibers. The dispersion and desorption can also be improved by adding surfactants. [7]

The paper mill in Munksund got washing equipments and two steps combining the addition of oxygen, hydrogen peroxide and alkali (sodium hydroxide), here resins can be removed. In the washing steps resins can be dispersed, and even neutral components like betulinol can be washed out. Theoretically the oxygen can oxidize resins and make them easier to remove in the following washing steps, but oxidation of unsaturated resins is complicated and does not happen in any large extend. Hydrogen peroxide does not penetrate the resin aggregate but it can react with the already dissolved resin components. Especially with substances containing conjugated double bonds, like abietic type acids. The result of the dispersion is a higher concentration of colloidal resin. The alkali can dissolve and hydrolyze remaining resin components to sodium soaps which act as dispersing and solubilizing agents. As a consequence the amount of neutral components can be reduced by the sodium soaps. [7]

2.5 Analyze methods

2.5.1 Soxtec

Soxtec is a modern extraction method used for determining the amount of soluble material in for example pulp. The system is automatic and consists of an extraction unit, control unit and a drive unit. The sample that is going to be analyzed is weighed into thimbles and inserted in the extraction unit. The solvent is added to the extraction cups in a closed system, and the cups are heated by an electric heating plate. The extraction is done during four steps; boiling, rinsing, solvent recovery and pre-drying. Different solvents can be used and the recovery is about 80 %. [19]

SCA Packaging Munksund performs regularly analyzes on the washed and bleached pulp (the last sampling point in this project) in their Soxtec device, and the method is based on the standard method SCAN-CM 49:03. The other partly washed and bleached samples are going to be treated in the same way during this study, but the two first samples; wood chips and unwashed pulp, need special treatment. The treatment for wood chips is also described in the earlier mentioned standard method, SCAN-CM 49:03, but for the unwashed pulp an additional method is necessary. The reason for this is to prevent high amounts of lignin and sugars from disturbing the extraction. These substances are soluble in acetone just like the extractives, and will therefore also remain in the final sample. By using both acetone and petroleum ether as solvents the undesired substances can be removed from the sample. The method for this is invented by Karin Pettersson [20].

2.5.2 GC-MS

This device consists of two parts, the Gas Chromatography (GC) and the Mass Spectrometer (MS). The gas chromatograph separates the molecules based on their volatility and the mass spectrometer identifies the compounds based on their structure. [21]

The gas chromatograph basically consists of an injection port, an oven and a column. The molecules that are going to be identified is solved and then injected with the solvent. To get the chemicals into gas phase the inject port is heated to about 300˚C. The molecules are usually carried through the device by the inert gas helium. In the column, which is a 30 meter thin tube with a special polymer coating on the inside, the molecule mixtures are separated based on their votality. The transportation through the column is done faster for molecules with high votality, than for those with low. During the transportation through the column the chemicals are heated, this is done by an oven surrounding the column. This oven is specialized and the temperatures often are between 40˚C to 320˚C. [21]

The mass spectrometer consists of an ion source, a filter and a detector. When the molecules have passed the gas chromatograph the ion source is reached. Here they are blasted with electrons. As a result of this the molecules break into pieces and form ions. To pass through the following filter the particles have to be charged. The filter is based on an electromagnetic field and it filters the particles because of differences in mass. What kinds of particles that are allowed to pass the filter are determined by the person who runs the test. Finally the remaining particles reach the detector, here the number of ions with a specific mass is counted and the computer creates a mass spectrum. The mass spectrum shows a graph based on the number of ions with different masses preceding the test. [21]

2.5.3 GC-FID

The Gas Chromatography-Flame Ionization Detector can be used to quantify the substances in a sample containing molecules made from mainly carbon. An electrical current is generated when carbon particles are burning, the FID measures this and creates a chromatogram. The gas phase output from the column is directed into a hydrogen flame and a voltage of 100-200 V is applied between the flame and an electrode which is located a distance away. Due to the burning carbon particles, electrons are emitted. The emitted electrons causes an increased current, the variation in current is measured. [22]

The FID detects almost all carbon containing compounds, only a few organic compounds, like for example carbon monoxide, cannot be detected. [22]

3. Experimental section

3.1 Aim with the laboratory work

The aim was to determine the amount of extractives in pulps and chips sampled from different positions in the process, and how it changes with position in fiberline and time. To evaluate how the composition of different components in the extractives changes during the process is also of great interest.

3.2 Samples

3.2.1 Sampling

A time schedule and description of both the sampling and project was written and sent to the operators. They were instructed to keep the production even during the whole period. *Appendix A* includes graphs showing some important operation parameters for the production and how they changed during the period. Fortunately the production was very stable, this was important for the time table to be correct. The aim with the schedule was to estimate the time it took for the same wood chips/pulp to pass trough different steps in the process. If this was done correct, the wood chips that entered the digester at the first sampling time should also be the wood chips that was transformed into pulp and sampled in the coming positions.

The operators sampled six samples from eight different positions in the process. The time between each sample at the same position was four hours, hence the time period for sampling was 24 hours at each position. The estimated times of stay between the sampling points and the final schedule for the operators can be seen in *Appendix B.*

3.2.2 Sampling positions

1. Chip silo
2. Refiner (closest to the digester)
3. DD-washer
4. First Q-step
5. Second Q-step
6. First PO-reactor
7. Second PO-reactor
8. PO-press

In addition bark from the chip samples were analyzed to get an idea of what kinds of extractives which came into the process with the bark, and therefore could be represented in the pulp. The reason for this is that the wood was not totally debarked. Laboratory results at *SCA Packaging Munksund* gave a bark content of 1.0 – 1.1 % during the sampling period. The bark was not mixed with the wood chips before the extraction analyze because the amount of bark was not expected to be proportional during the whole process.

3.2.3 Preparation

All pulps were stored in a freezer until about 16 hours before the extraction. Then they were moved to room temperature for unfreezing before the treatment started.

3.2.3.1 Washed and bleached, to partly washed pulps

Pulps from sampling points 3, 4, 5, 6, 7 and 8 were acidified according to *SCA Packaging Munksund´s* own method (*Appendix C*) which is based on SCAN-CM 49:03. The pulps were diluted to a degree of dryness of approximately 3-5 %. Then the weight of the sample needed for analyze was calculated and weighted in. A solution of acetic acid and de-ionized water was added to the sample. The sample was mixed for 1 minute and then the pH was controlled, it should be 3 or less. Otherwise more acetic acid was added and the sample was mixed again. When the pH was 3 or less the sample was allowed to react for 8 minutes and after that mixed for 1 minute again. Subsequently the pulp was washed and disintegrated to small parts (approximately 10-5 mm in diameter). The sample was dried over night at 40°C.

3.2.3.2 Unwashed pulps

The whole method including preparation for pulps from sampling point 2 is described in section *3.3.1.2 Unwashed pulps* under *Methods, Extraction.*

3.2.3.3 Wood chips

The wood chips were transported to a freezer after the sampling. Later they were sent to Stockholm where they were disintegrated in a Wiley mill. Approximately 5 g of each sample were disintegrated. The reason for the small amount was that the disintegration process was hard to perform because of wet samples. The disintegrated wood chips were frozen again and transported to Munksund, Piteå by flight. The chips were dried in room temperature for about 3 hours before the extraction. The dry content of the sample was analyzed.

3.2.3.4 Bark

Bark from all wood chips samples were combined and dried in an oven at 40°C for 28 hours. The dry bark was disintegrated with a Wiley mill. The bark was frozen between sampling and drying.

3.3 Methods

3.3.1 Extraction

In this analyze the samples were extracted with acetone in a Soxtec device, the reason for choosing this method for extraction is that the company uses it, and a comparison with earlier values is desired. The chosen method is also a quite easy method which gives good results.

An extraction procedure with acetone gives a value of the acetone soluble matter in the samples, this substances are here assumed to be all the extractives.

The following settings were used at the Soxtec:

- <u>Pulp</u>: temperature 130°C, boiling time 15 minutes, rinsing time 1 hour, recovery time 7 minutes and drying time 1 minute.
- <u>Chips and Bark</u>: temperature 130°C, boiling time 30 minutes, rinsing time 2 hours, recovery time 7 minutes and drying time 1 minute.

This is according to the company's usual method (*Appendix C*), and the standard method SCAN-CM 49:03.

3.3.1.1 Washed and bleached, to partly washed pulps

The acidified pulps were extracted in a Soxtec device with acetone according to SCAN-CM 49:03.

3.3.1.2 Unwashed pulps

The unwashed samples which were taken closest to the digester (sampling point 2) were analyzed according to a method which was invented by Karin Pettersson [20]. In *Appendix D* the original description is attached. This method was used to get a sample including only extractives. If the samples would have been treated like the other samples a lot of other components like lignin and sugars, which remain in the unwashed pulp, could have been extracted with the resin and therefore disturbed the result. The reason why this only concerned the first pulp is that it consists of a lot of other substances, and the pH is very alkaline. During the analyze the pH is converted to acidly and the substances can precipitate.

An amount of 15-17 g unwashed pulp was weighted in accurately. At the same time an amount of about 30 g sample was analyzed for dry content determination. The pulp should have a dry content of about 10-20 %, if the dry content is less the sample can be dried in an oven with a temperature of maximum 40°C. It does not matter if the already weighed in sample is dried; the important thing is that the first dry content is the one used in the calculations. Thereafter the pulp is mixed with for example an electric mixer or just a spoon (depending on the consistency of the pulp) and the pH is corrected to a value of 3-3.5 with acetic acid. Then the pulp is transferred to a pre-extracted extraction thimble. Electric mixer or spoon, pH-electrode, beaker and other equipment which has been in contact with the sample are cleaned with a clean pad of glass fiber wool drenched in acetone, this is extracted together with the pulp in the thimble. The extraction was done in the Soxtec device with the same program as for the other pulp samples in this study.

After the extraction the extract is transferred to a separating funnel, and the flask from the extraction procedure is rinsed with some acetone which also is added to the funnel. Methanol and de-ionized water are also added to the extract, a relation of 1:2:1 for the water/acetone/methanol is desired, but it does not have to be exact. Too much acetone prohibits phase separation, too much water results in emulsions. If the determination of this relation is hard, the acetone can be evaporated and a solution with an exact relation can be added. The amount of solution should be around 100 ml in total. The solution is mixed with 50 ml petroleum ether four times. The petroleum ether phases are separated from the rest of the solution between each mixing, and the phases are collected in a common beaker. If water is left in the petroleum ether phases it is removed with a pipette and the petroleum ether is evaporated.

Remaining extractives are weighted in and amount of extractives are calculated due to the dry content of the pulp.

3.3.1.3 Wood chips

The wood chips were extracted in a Soxtec device with acetone according to SCAN-CM 49:03.

One difference from the method was that the samples had a dry content of about 70 %, in SCAN-CM 49:03 a dry content of 90 % was recommended. Because of the long storage time of both the wood chips and the disintegrated samples, it was believed to be better to keep the samples in a freezer and to not dry the disintegrated wood chips because of the risk of great extractive loses (the disintegrated wood gets a lot of surfaces where emissions can occur). Instead the dry content of the wood chips was taken in consideration when the calculations were done.

According to the method about 50 g of each wood chip sample should be disintegrated, however, as mentioned before, only 5 g of each sample was disintegrated in this study.

3.3.1.4 Bark

The bark was extracted in a Soxtec device with acetone according to the instructions for wood chips in the standard method SCAN-CM 49:03.

3.3.1.5 Date and place of testing

<u>Pulps and wood chips</u>: March 19 – 28, 2012
<u>Bark</u>: April 11, 2012
The laboratory at SCA Packaging Munksund, Piteå.

3.3.2 GC-MS and CG-FID

The execution was based on method A in the NSP-report No 3: "Two methods for extraction and GC-analysis of lipophilic wood extractives", convenor: Marianne Björklund Jansson.

In this study the extractives were dissolved in 300 µl, 1000 µl or 3000 µl acetone depending on the samples ability to dissolve (this was taken in consideration in the calculations). Then 100 µl of the solution was moved to a small vial with a screw cap. To the 100 µl solution in the vial 50 µl BSTFA was added and everything was mixed. The sample was heated at 80˚C in 30 minutes (this time and temperature was recommended by Marianne Björklund Jansson and Pierre Ljungquist who were a part of the project resulting in the NSP report). The samples were thereafter cooled to room temperature and 20 µl of an internal standard (hexacosane) was added. Now the derivatisation was done and the samples were inserted into the GC-MS and GC-FID. To GC-MS 1 µl was injected and to GC-FID 2 µl.

After 41 minutes the program was finished and the spectra were done.

GC-column: DB-5ms, Phenyl Arylene polymer (virtually equivalent to a (5 %-Phenyl)-methylpolysiloxane), 30 m x 0.32 mm, 0.25 µm film thickness.

Temperature program: 120°C in 1 minute, 6°C per minute, 300°C in 10 minutes.

Injector: Split, with a split ratio of about 1:20.
Injector temperature: 230°C.
Ion-source: 70 eV
The factor for relative abundance for each substance was assumed to be one in this study.

3.3.2.1 Date and place of testing

April 11 – 20, 2012
The laboratory at KTH, Teknikringen 58, floor 5.

Comment: Between the times for extraction and GC analyze the extractives were stored in a freezer.

4. Results and Discussion

4.1 Total resin content

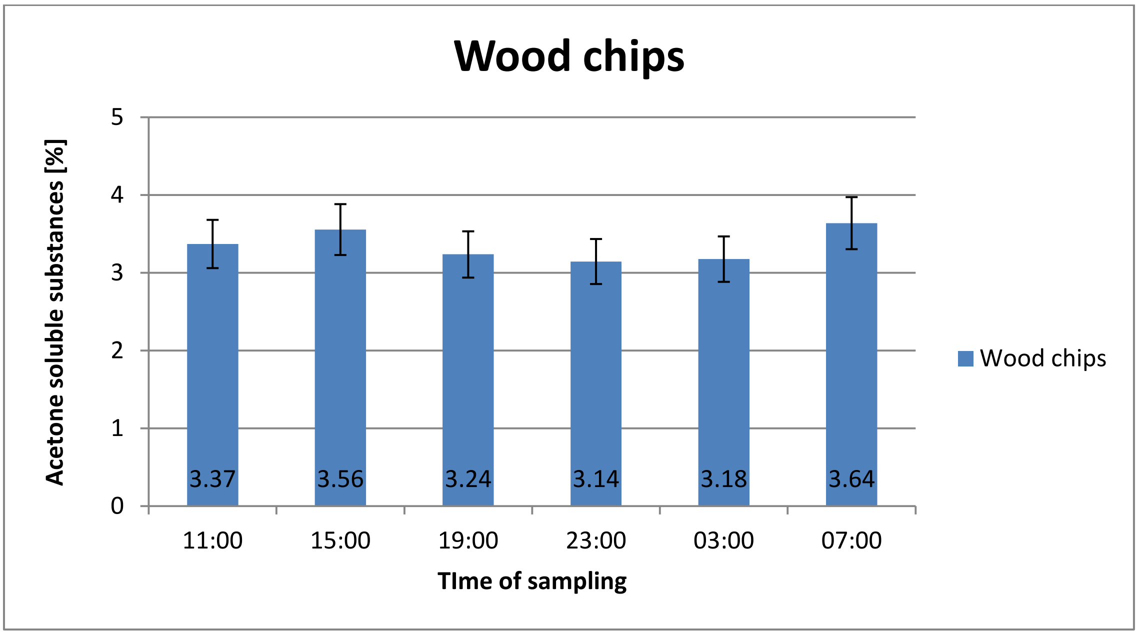

Figure 7. *The percentage of acetone soluble substances in birch chips taken at different times during 24 hours. The four first samples are from March 12, 2012, and the remaining two from March 13, 2012. The error bars are based on a coefficient of variation which is ±9.2 %, this value comes from the reproducibility in SCAN-CM 49:03.*

As *Figure 7* shows the variation of extractives in the birch chips was low during 24 hours. If the coefficient of variation is considered, there is no significant difference in the amount of acetone soluble substances between the samples.

According to test results from the standard method SCAN-CM 49:03 the content of acetone soluble matter in birch is 2.20 % ± 0.20 (95 % confidence interval). The amount of acetone soluble matter turned out to have mean value of 3.35 % in this study. This is slightly higher but in the same size of order as in the earlier study mentioned, and therefore these result is reasonable. The coefficient of variation gives the following result: 3.35 % ± 0.31 (95 % confidence interval).

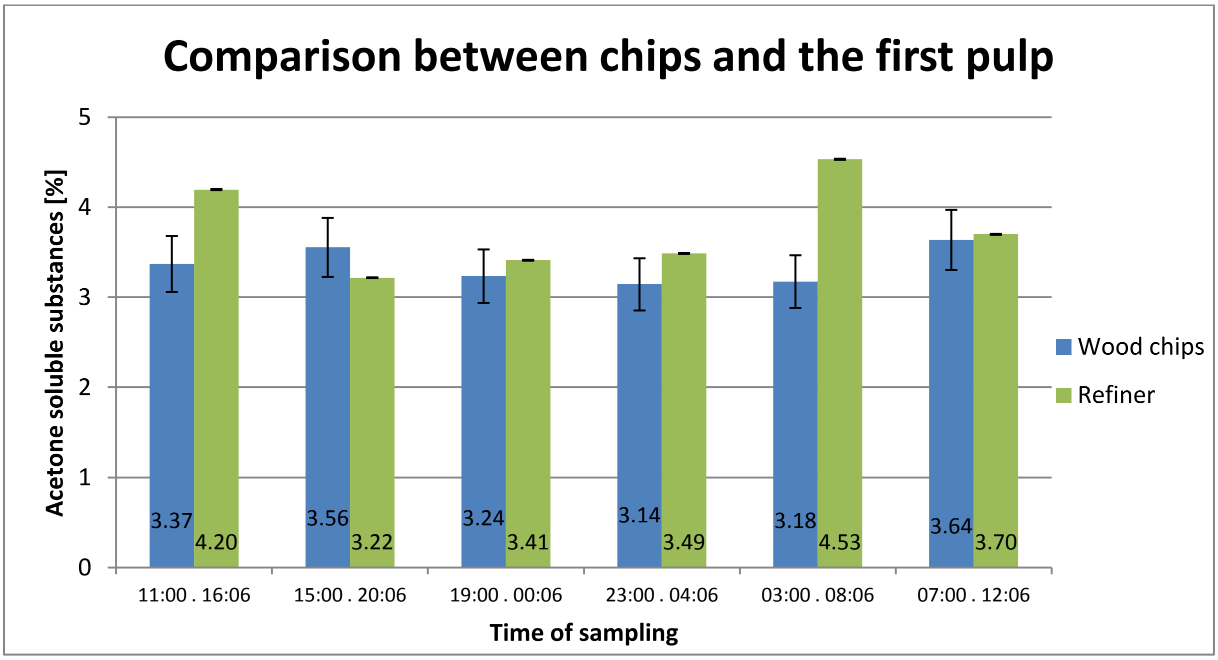

Figure 8. *The percentage of acetone soluble substances in samples from position 1 (wood chips) and 2 (refiner) taken at different times during 24 hours. Note that for the sample from the refiner also petroleum ether was used as solvent. The four first chips samples are from March 12, 2012, and the remaining two from March 13, 2012. The two first pulp samples are from March 12, 2012, and the remaining four from March 13, 2012. The error bars for the wood chips are based on a coefficient of variation which is ±9.2 %, this value comes from the reproducibility in SCAN-CM 49:03. For the refiner pulps the error bars are based on one sample which was analyzed in duplicate, the coefficient of variation is ±0.15 %.*[i]

If a comparison is made between samples from position 1 and 2 (*Figure 8*), wood chips and pulp directly after the digester, the total resin amounts seem to be somewhat higher after the digester than in the wood chips. The mean value from the wood chips are 3.35 % ± 0.31 (95% confident interval) which can be compared with 3.76 % ± 0.01 in the pulp. Some things have to be taken in consideration in this case. The reason for the higher resin amounts after the digester is believed to be that bark was excluded from the wood chips. In addition tall oil is added in the digester, tall oil contributes with important substances for the resin removal, but also a lot of resins. After the digester all of these resins might not have been removed. The washing in the digester is performed with dirty wash liquor, hence, resins which are washed out in another step in the process can be added to this pulp.

Another factor is that some substances does not exist in extractable forms in the wood, but are

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[i] To obtain a good value for the coefficient of variation more than one sample should be analyzed in duplicate, however, this was not possible in this study.

transformed and released during the cook (this is discussed further in *4.2 Identification and quantification*).

The variation in resin amount for the samples from the refiner indicates an uneven resin removal in the digester washing zone.

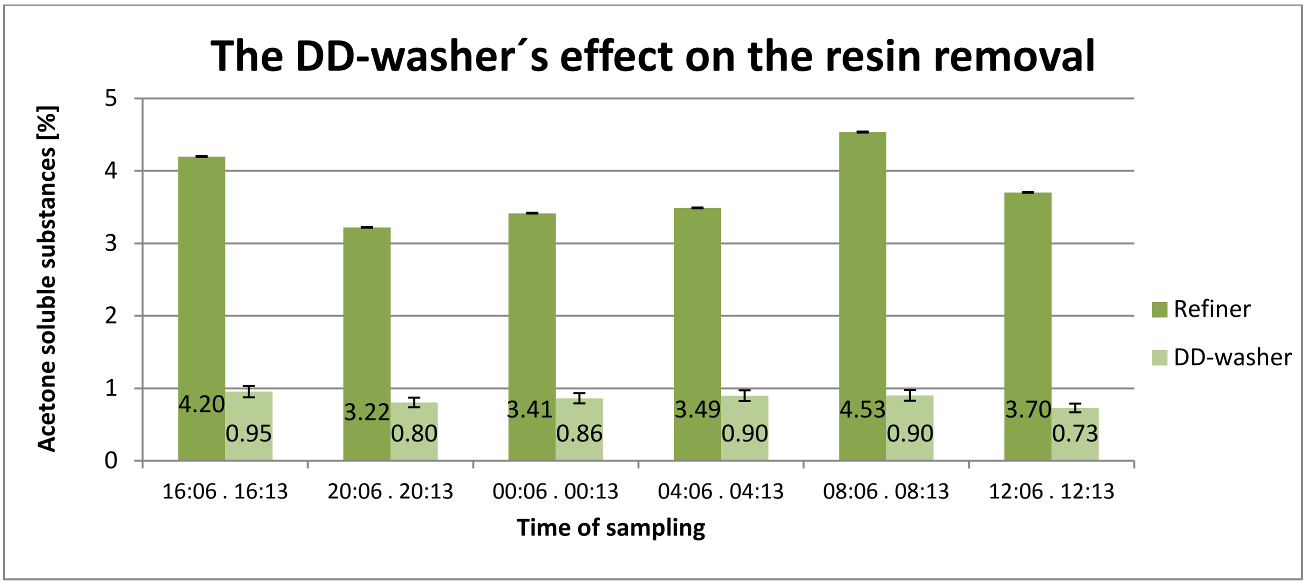

Figure 9. *The percentage of acetone soluble substances in samples from position 2 (refiner) and 3 (DD-washer) taken at different times during 24 hours. Note that for the sample from the refiner also petroleum ether was used as solvent. The two first samples are from March 12, 2012, and the remaining four from March 13, 2012. For the refiner pulp the error bars are based on one sample which was analyzed in duplicate, the coefficient of variation is ±0.15 %.*[ii] *The error bars for the DD-washer pulps are based on a coefficient of variation which is ±8.2 %, this value comes from the reproducibility in SCAN-CM 49:03.*

According to *Figure 9* the acetone soluble matter decreased with a mean value of 77 % during the washing in the DD-washer. In this study this is the greatest removal of resins during the whole process.

The four middle samples from the DD-washer have values within the mean value of 0.86 % ± 0.07 (95 % confidence interval), even though the amount after the digester varies between 3.22 % and 4.53 %. The first and the last sample are not in the same interval but the difference is small.

[ii] To obtain a good value for the coefficient of variation more than one sample should be analyzed in duplicate, however, this was not possible in this study.

This indicates that the DD-washer compensates for the uneven removal of extractives in the digesters washing zone.

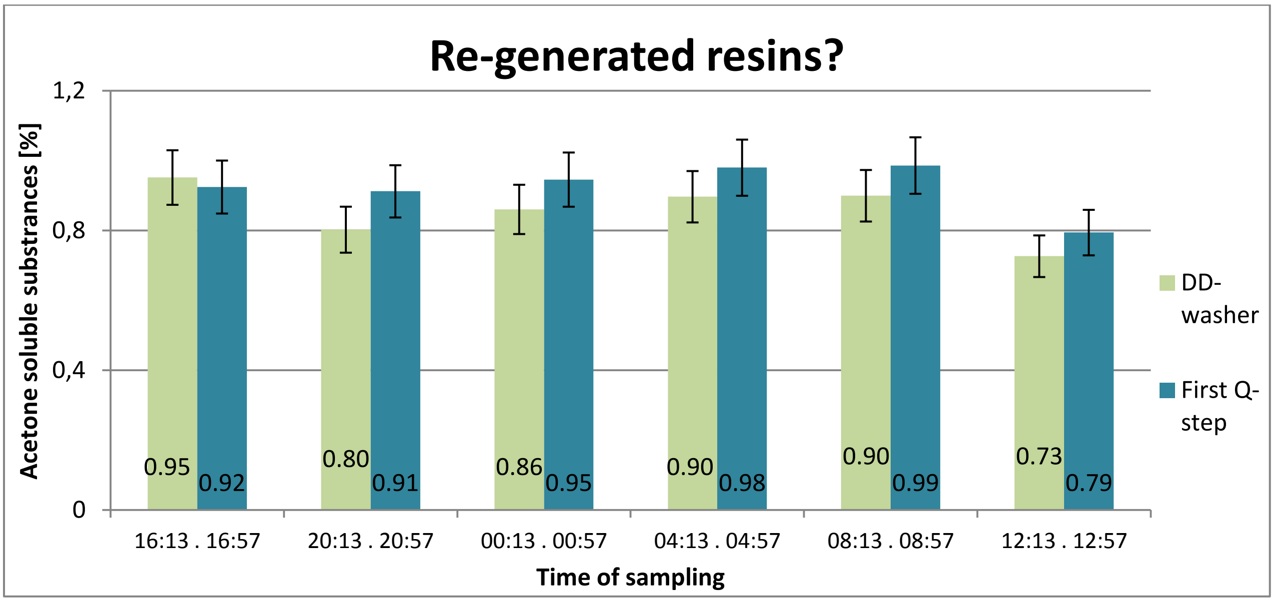

Figure 10. *The percentage of acetone soluble substances in samples from position 3 (DD-washer) and 4 (first Q-step) taken at different times during 24 hours. The two first samples are from March 12, 2012, and the remaining four from March 13, 2012. The error bars for the pulps are based on a coefficient of variation which is ±8.2 %, this value comes from the reproducibility in SCAN-CM 49:03.*

As can be seen in *Figure 10* the pulp after the first Q-step seems to get a higher resin content, all samples but one indicates that. This could happen if the liquor used for dilution is reused and taken from a later process steps. Because of this resins which are washed out somewhere else can be added to this pulp, especially if the pH is going from alkaline to acidly. Nevertheless, all the samples after the first Q-step are in the within the range of variation of the samples from the DD-washer, and no such conclusion could be drawn. Most likely nothing happens with the extractive content.

The mean value from the first Q-step is 0.92 % ± 0.08 (95% confidence interval), if this is compared with the results from each time, it seems like there is no significant change at this point during the 24 hours.

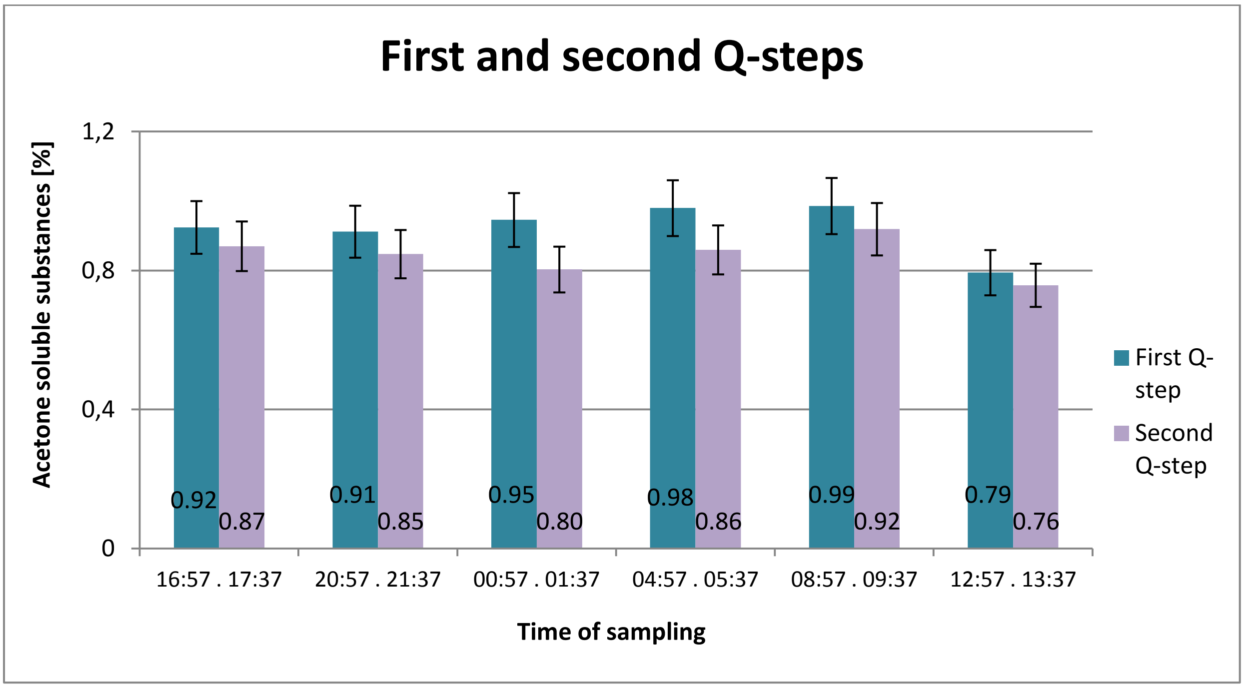

Figure 11. *The percentage of acetone soluble substances in samples from position 4 (first Q-step) and 5 (second Q-step) taken at different times during 24 hours. The two first samples are from March 12, 2012, and the remaining four from March 13, 2012. The error bars for the pulps are based on a coefficient of variation which is ±8.2 %, this value comes from the reproducibility in SCAN-CM 49:03.*

According to *Figure 11* it seems like there is a small decrease in resin content over the second Q-step, but all samples are within the range of variation and no such conclusion can be drawn. The variation over the 24 hours is small as well.

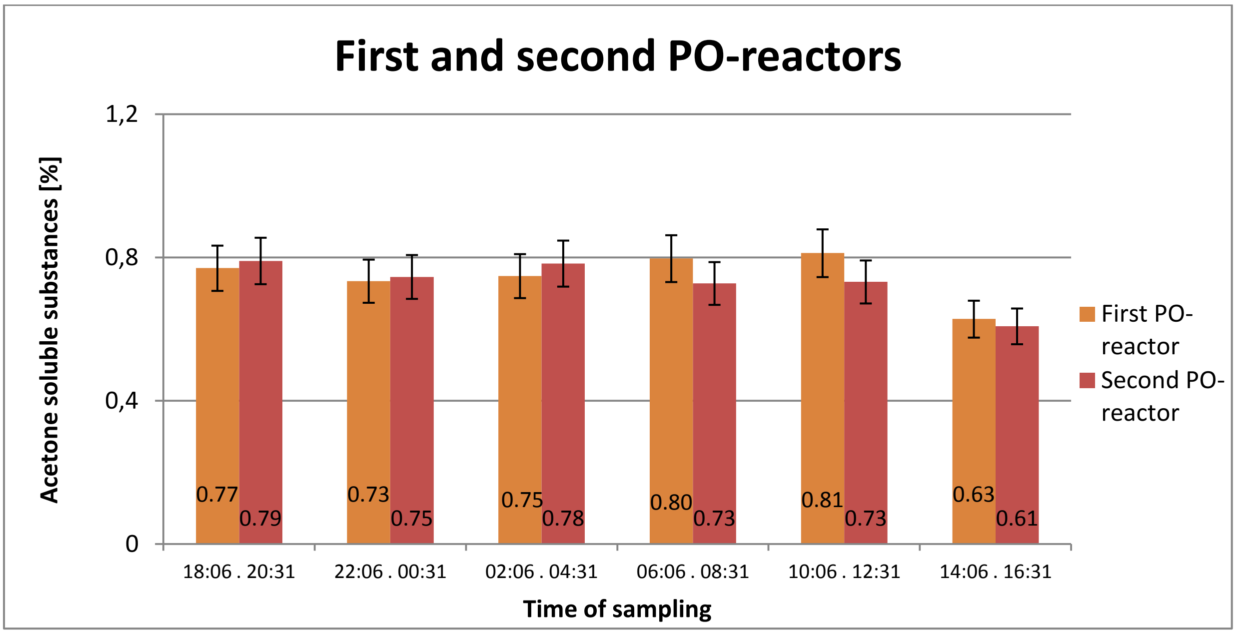

Figure 12. *The percentage of acetone soluble substances in samples from position 6 (First PO-reactor) and 7 (Second PO-reactor) taken at different times during 24 hours. The two first samples from the first PO-reactor, and the first sample from the second PO-reactor are from March 12, 2012, and the remaining ones from March 13, 2012. The error bars for the pulps are based on a coefficient of variation which is ±8.2 %, this value comes from the reproducibility in SCAN-CM 49:03.*

As *Figure 12* shows the amount of resins is about the same after the first and second PO-reactor, and the variation between the samples from different times are low.

If the second Q-step and the first PO-reactor are compared instead, the following result is obtained:

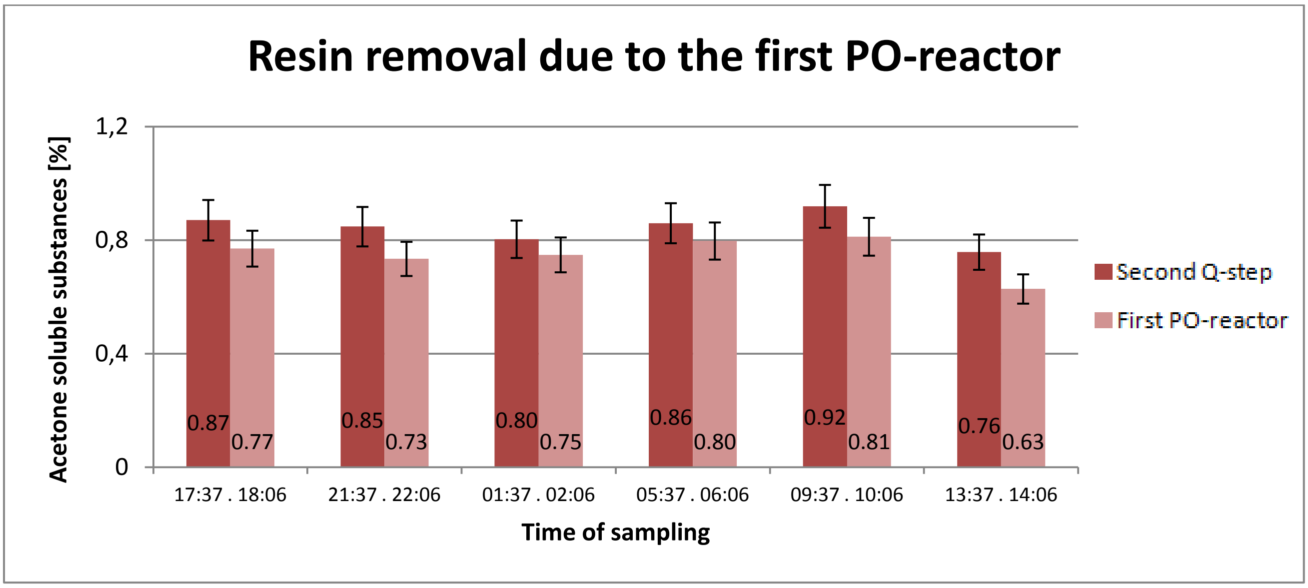

Figure 13. *The percentage of acetone soluble substances in samples from position 5 (second Q-step) and 6 (First PO-reactor) taken at different times during 24 hours. The two first samples are from March 12, 2012, and the remaining four from March 13, 2012. The error bars for the pulps are based on a coefficient of variation which is ±8.2 %, this value comes from the reproducibility in SCAN-CM 49:03.*

Figure 13 shows that all samples got a lower amount of acetone soluble substances after the first PO-reactor. However, almost all of the samples are within the range of variation and there is no significant difference between the samples. Despite this there could be a small lowering of resin content after the first PO-step. According to the theory oxygen and hydrogen peroxide can oxidize resins, even though there is a complex reaction. A conclusion which can be made according to *Figure 12* and *Figure 13* is that the resins which are easy to oxidize are removed during the first PO-step, but in the second PO-step only components which are hard to oxidize is left, and there is no change of the resin content. Also the addition of alkali can improve and benefit the resin removal.

Another factor to consider is that there is no washing step between the reactors. Even though some resins have been oxidized to more hydrophilic forms, they are not washed out. During the extraction analyze the pulps are washed under acidic conditions, but an alkaline washing may be needed for complete deresination.

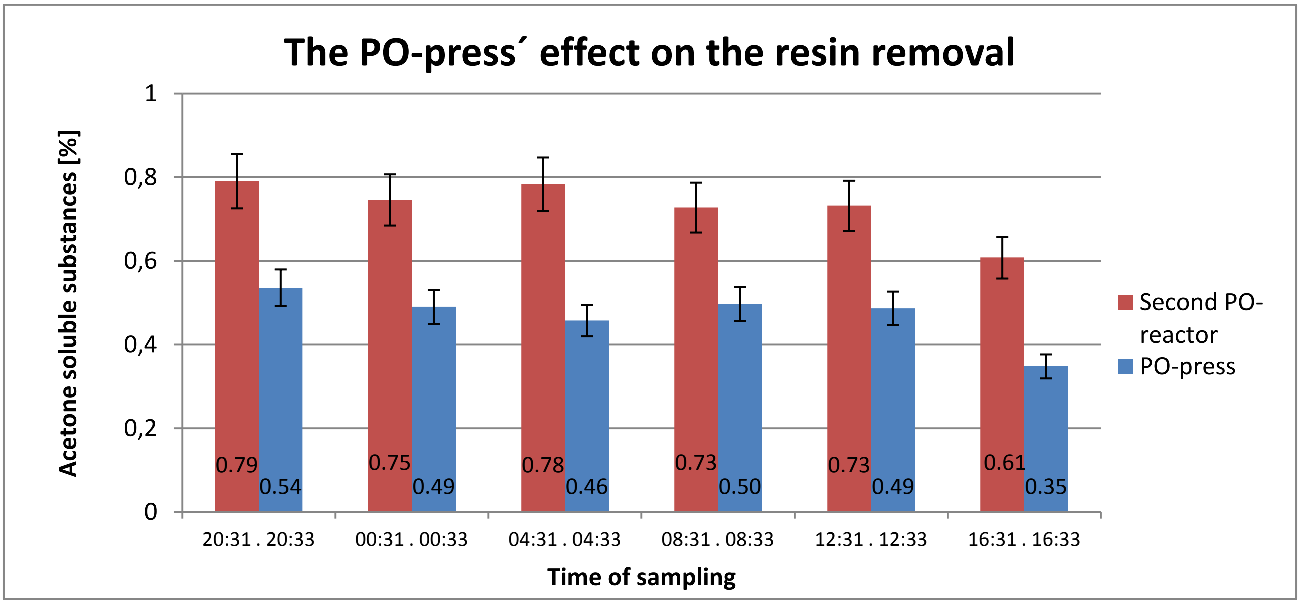

Figure 14. *The percentage of acetone soluble substances in samples from position 7 (second PO-reactor) and 8 (PO-press) taken at different times during 24 hours. The two first samples are from March 12, 2012, and the remaining four from March 13, 2012. The error bars for the pulps are based on a coefficient of variation which is ±8.2 %, this value comes from the reproducibility in SCAN-CM 49:03.*

As *Figure 14* shows, it is clear that resin is removed over the PO-press. Mean values gives a decrease of 36 % in resins content. The theory about resin removal in presses which was described earlier in this report seems to be correct. Another possibility is that resins which have been modified in the earlier PO-steps are left in the pulp until the PO-press where they are removed during the washing.

There is no significant change in resin amount over the 24 hours, but the last sample is slightly lower.

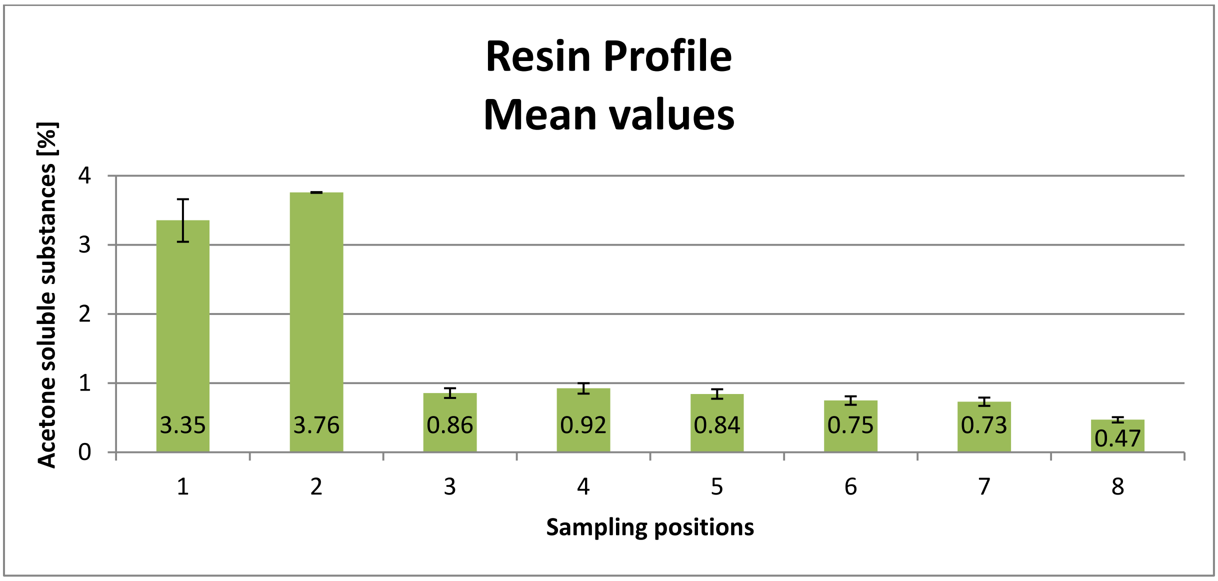

Figure 15. *Mean values of the percentage of acetone soluble substances in samples from all positions included in this study. Note that for the sample from position 2 also petroleum ether was used as solvent. Samples are from March 12 and 13, 2012. The error bars for the pulps from sampling points 3-8 are based on a coefficient of variation which is ±8.2 %, for the wood chips the coefficient of variation is ±9.2 %, theses values come from the reproducibility in SCAN-CM 49:03. For the pulp from sampling point 2 the error bars are based on one sample which was analyzed in duplicate, the coefficient of variation is ±0.15 %.*[iii]

According to *Figure 15* it is clear that the biggest difference in resin content is between position 2 and 8. A removal of 88 % is observed between these points.

According to Bjarne Holmbom (see reference [14]) oxygen pre-bleaching is very beneficial with respect to the deresination, and a removal of 50-90 % is often obtained. The value is lower for hardwood than softwood. [14] These values can be compared with this mills process too, the steps between sampling point 5 and 8 deals with oxygen bleaching and the removal here are 44 %. The steps the pulp has to go through are two reactors with oxygen, hydrogen peroxide and alkali treatment, and one washing press.

A removal of 44 % is less than the values mentioned in the earlier study. The reason for this could be that oxygen is added in two different reactors with a smaller amount in each instead of a large amount in one reactor. This is gentler to fibers, but maybe also to the resin. The main reason is probably that oxygen is not used in the beginning of the washing sequence. When

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[iii] To obtain a good value for the coefficient of variation more than one sample should be analyzed in duplicate, however, this was not possible in this study.

oxygen is added at this mill a lot of resin already has been removed, and there is less left to react with.

The bark sample consisted of 20.0 % ± 1.84 (95 % confidence interval) extractives (the coefficient of variation for the reproducibility of wood chips has been used). If this is compared with values mentioned in *2.2.4 Resin in birch bark* it seems to be valid.

Compared with the company's earlier results on the acetone soluble matter in the finished pulp the values in this study are in the range of their earlier values, but in the upper range. In the earlier studies it often varies between 0.2 % and 0.4 % but the result in this study had a mean of 0.47 %. The value should preferably be below 0.2 % or as low as possible.

4.2 Identification and quantification

In the extracts the following substances were identified:

Resin acid:

- Abietic acid

Saturated fatty acids:

- Anteisoheptadecanoic, C17:0 (anteiso-branched)
- Stearic acid, C18:0
- Behenic acid, C22:0
- Arachidic acid, C20:0

Unsaturated fatty acid:

- Linoleic acid, C9, 12 - 18:2

Sterols and triterpenols:

- Squalene
- Sitosterol
- Lupeol

- Betulinol

Fatty alcohols:

- 7-Betulaprenol
- 8-betulaprenol

4.2.1 Bark

The bark sample which was analyzed consisted of 83.1 % ± 3.70 betulinol. This is a normal value if comparisons are made with other studies mentioned earlier in the section *2.2.4 Resin in birch bark*. Also lupeol which was found in the pulps came from the bark, the extractives consisted of 14.7 % ± 4.41 lupeol. Sitosterol was found in small amounts and corresponded to 1.39 % ± 0.42 of the extractives. These substances have been found in birch bark also in earlier studies [10]. (The variation limits are based on one sample which was analyzed in duplicate.)

4.2.2 Resin acid

The resin acid, abietic acid, was identified in the sample from position 2, but nowhere else. This indicates that the resin acids come from the tall oil, but are washed out in the DD-washer. The fact that resin acids come from tall oil is expected because birch wood does not contain any resin acids naturally. The amount of abietic acid was 0.83 mg/g pulp, oven dried.

The resin acids are needed for the saponification reaction in the digester. It is good to see that they are washed out early and not contributes to resin problems later in the process.

4.2.3 Fatty acids

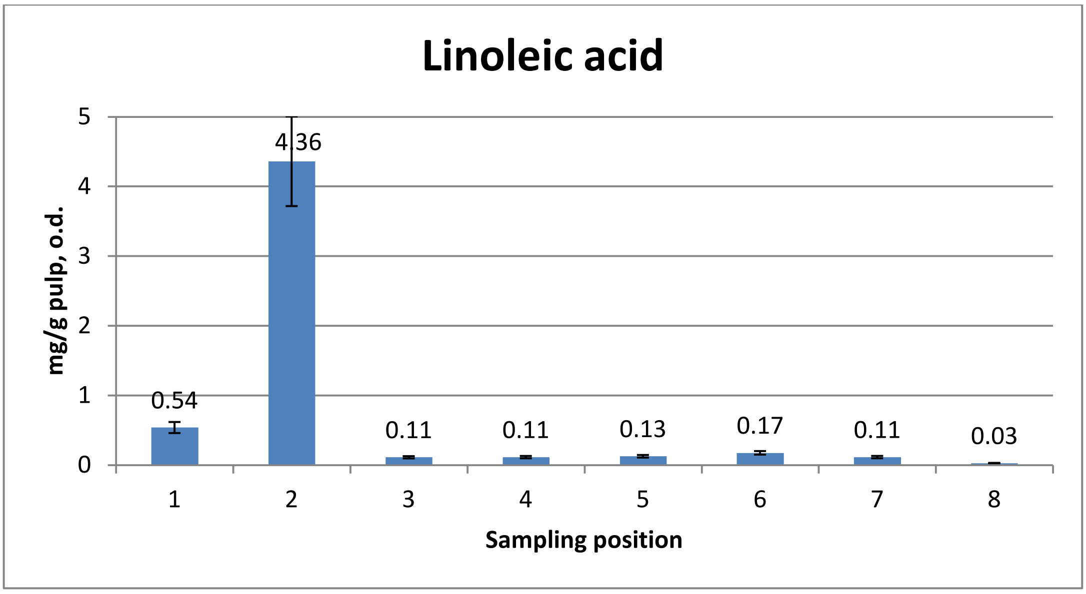


Figure 16. *The variation of the unsaturated fatty acid, linoleic acid, during the process. Mean values from four samples are complied. The coefficient of variation for the reproducibility was determent to 15.4 % based on six samples which was analyzed in duplicate. (o.d. = oven dried)*

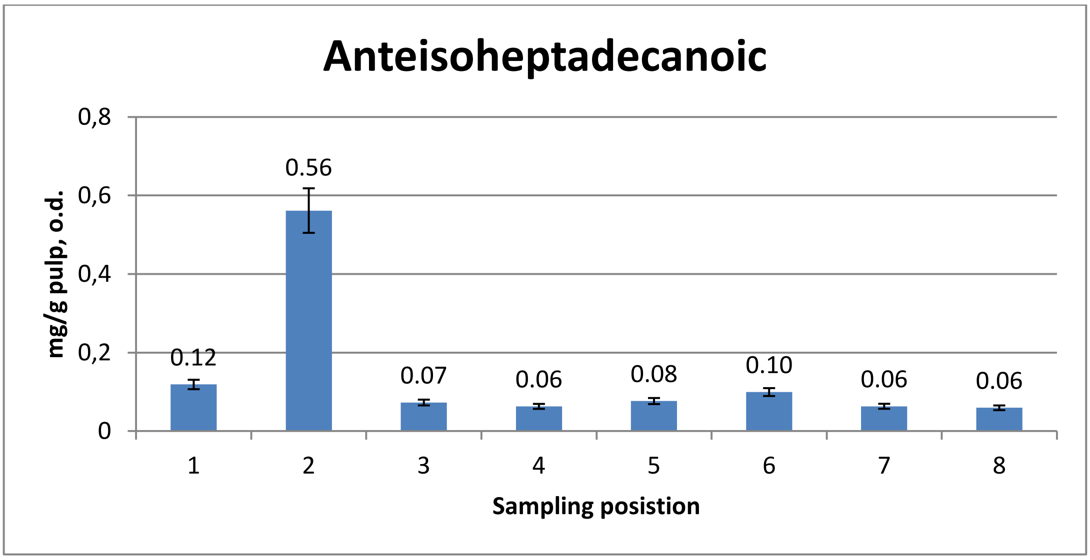


Figure 17. *The variation of the saturated fatty acid, anteisoheptadecanoic, during the process. Mean values from four samples are complied. The coefficient of variation for the reproducibility was determent to 10.1 % based on seven samples which was analyzed in duplicate. (o.d. = oven dried)*

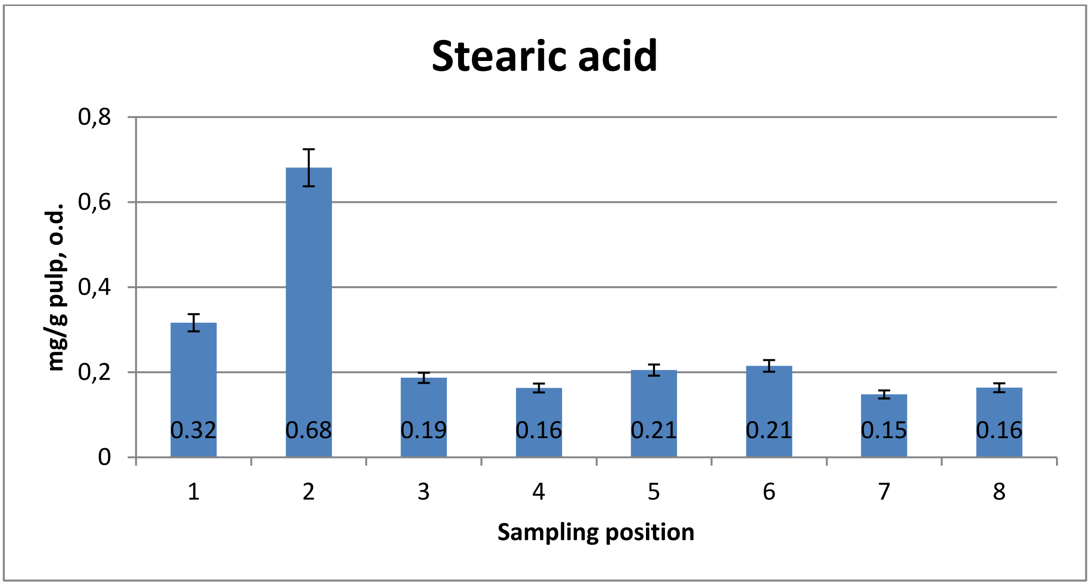


Figure 18. *The variation of the saturated fatty acid, stearic acid, during the process. Mean values from four samples are complied. The coefficient of variation for the reproducibility was determent to 6.4 % based on seven samples which was analyzed in duplicate. (o.d. = oven dried)*

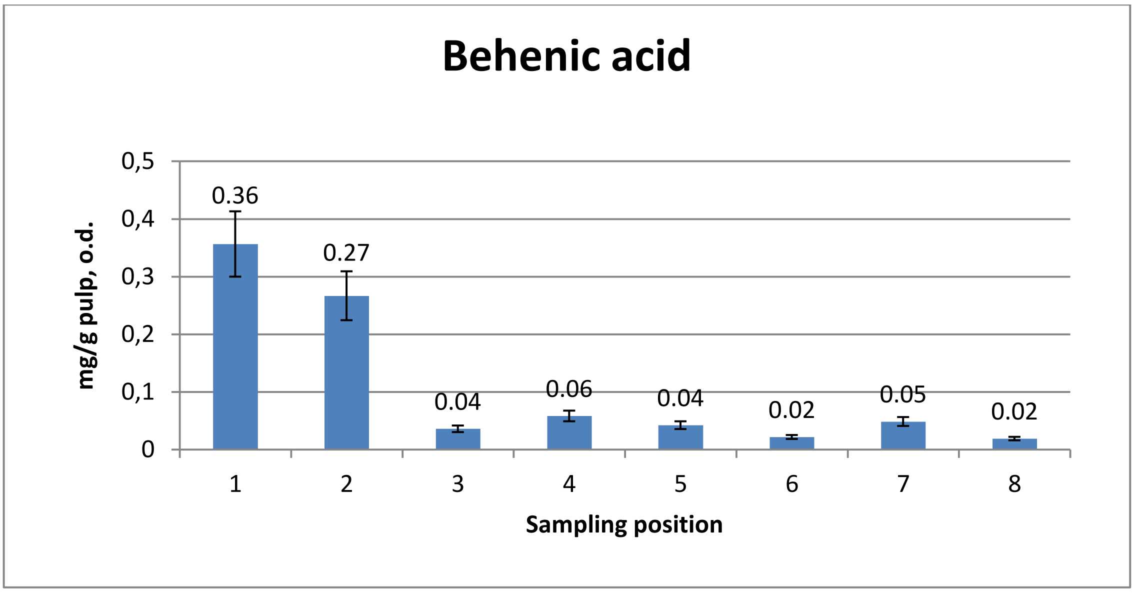


Figure 19. *The variation of the saturated fatty acid, behenic acid, during the process. Mean values from four samples are complied. The coefficient of variation for the reproducibility was determent to 15.9 % based on seven samples which was analyzed in duplicate. (o.d. = oven dried)*

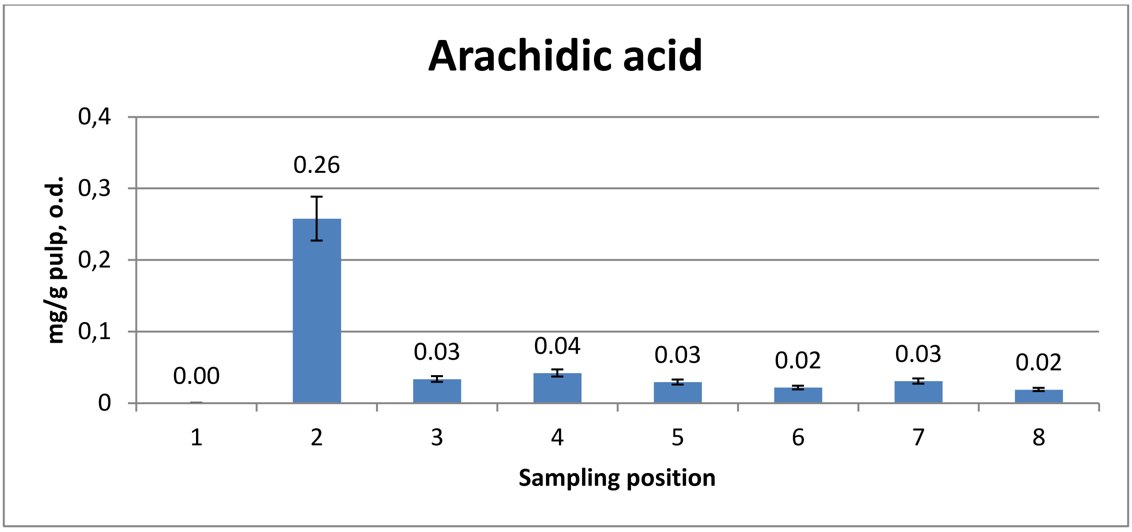


Figure 20. *The variation of the saturated fatty acid, arachidic acid, during the process. Mean values from four samples are complied. The coefficient of variation for the reproducibility was determent to 11.9 % based on six samples which was analyzed in duplicate. (o.d. = oven dried)*

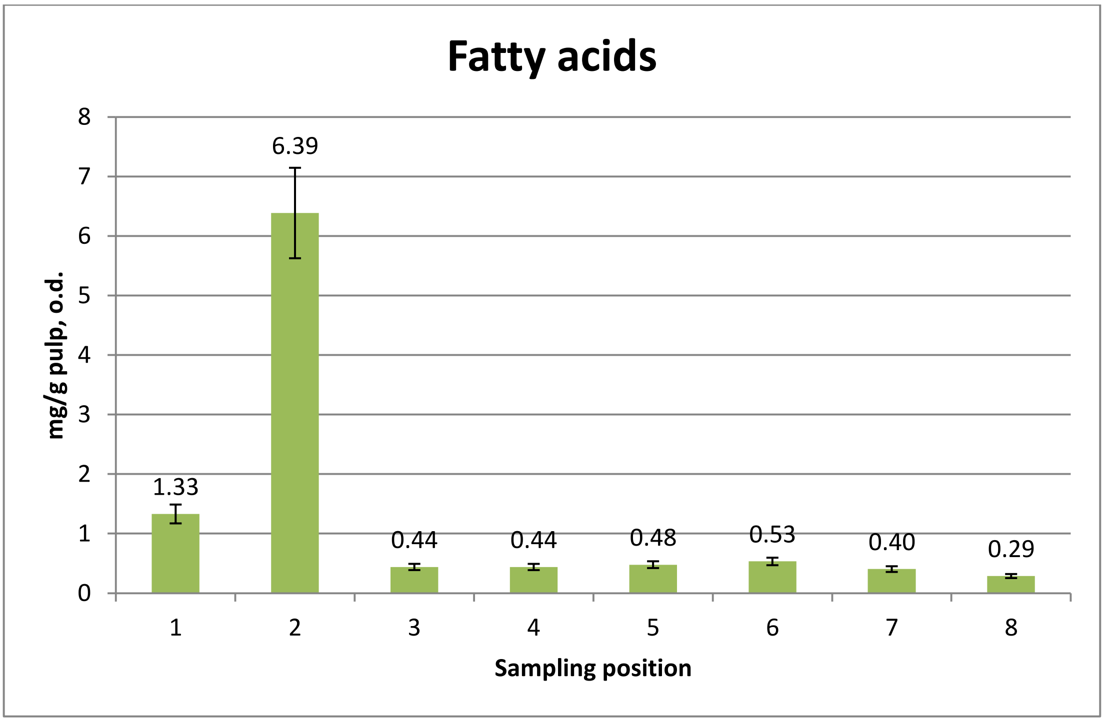


Figure 21. *The variation of the fatty acids during the process. Mean values from all earlier mentioned fatty acids are complied. The coefficient of variation for the reproducibility was determent to 11.9 %, and is a mean value from all the fatty acids´ coefficients of variation. (o.d. = oven dried)*

As *Figure 21* shows the most significant deresination occurs during the washing in the DD-filter.

The unsaturated fatty acid which was found in the samples was linoleic acid. It is often a lot of unsaturated fatty acids in birch wood, especially this C18 fatty acid is usual [23]. The amount of this linoleic acid decreased from the highest amount of all fatty acids to low values very fast, and there was very small amounts left after the final step (the PO-press). The good removal of this resin could be due to its reactive double bonds. Reactions with the double bonds can cause fragmentation of the fatty acid to smaller groups.

Arachidic acid could not be found in the wood like the other fatty acids, neither in the bark sample. According to earlier studies this acid can be found in both pine and birch wood [23]. However, in this case it seems like the main part of this substance is added with the tall oil. This means that some substances can be added with the tall oil and remain in the pulp over the whole process, even though the main idea with the tall oil is to help the deresination.

All fatty acids which were found in the pulps have been found in both pine and birch in earlier studies. [23]

The pulps was acidified before the extraction, this converts saponified fatty acids to water insoluble forms to make them extractable. Therefore the fatty acids here should contain both free and saponified fatty acids.

4.2.4 Sterols and triterpenols

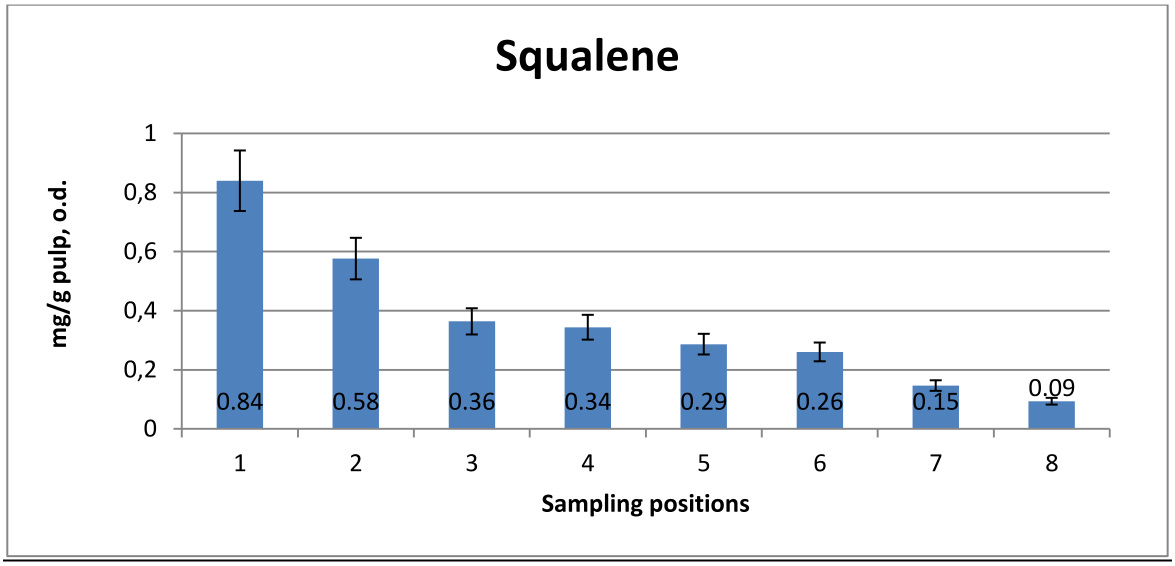


Figure 22. *Squalenes variation during the process. Mean values based on four samples are complied. The coefficient of variation for the reproducibility was determent to 12.2 % and is based on eight samples which were analyzed in duplicate. (o.d. = oven dried)*

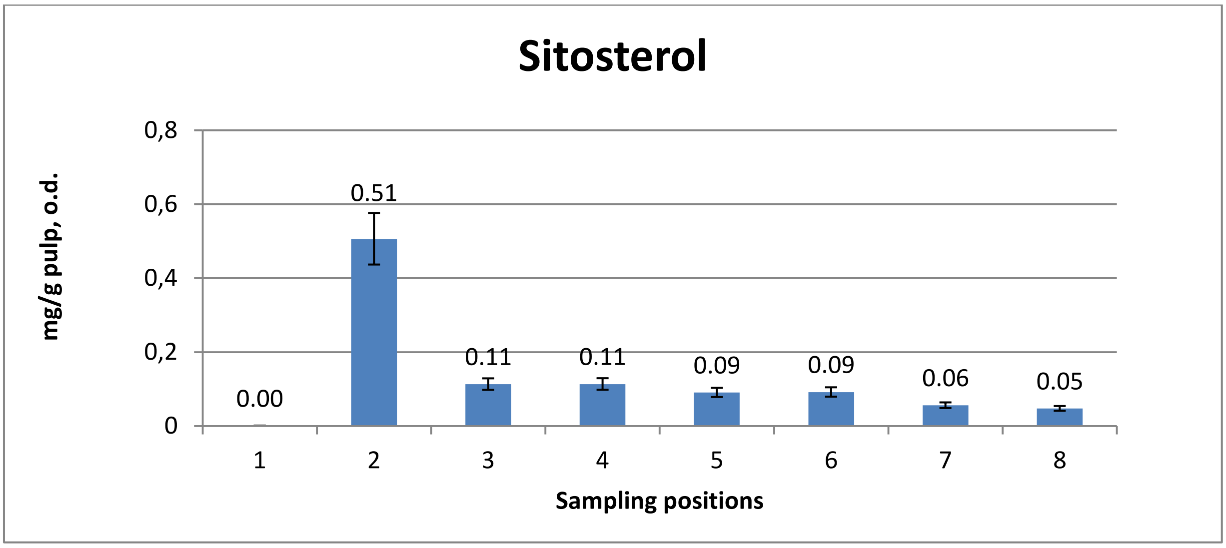


Figure 23. *Sitosterols variation during the process. Mean values based on four samples are complied. The coefficient of variation for the reproducibility was determent to 13.8 % and is based on seven samples which were analyzed in duplicate. (o.d. = oven dried)*

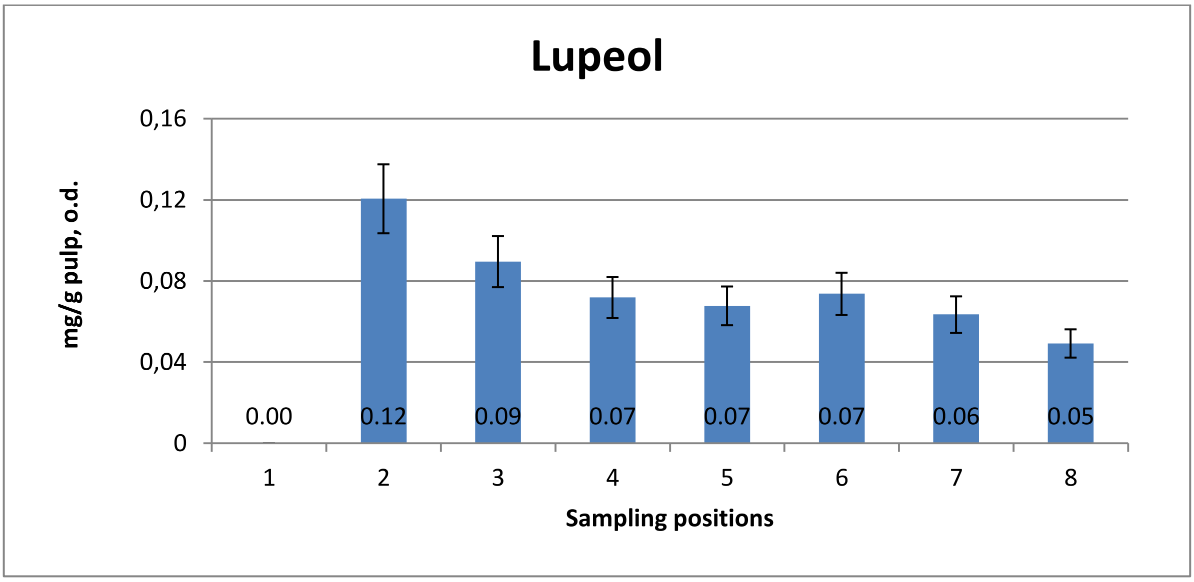


Figure 24. *Lupeols variation during the process. Mean values based on four samples are complied. The coefficient of variation for the reproducibility was determent to 14.1 % and is based on six samples which were analyzed in duplicate. (o.d. = oven dried)*

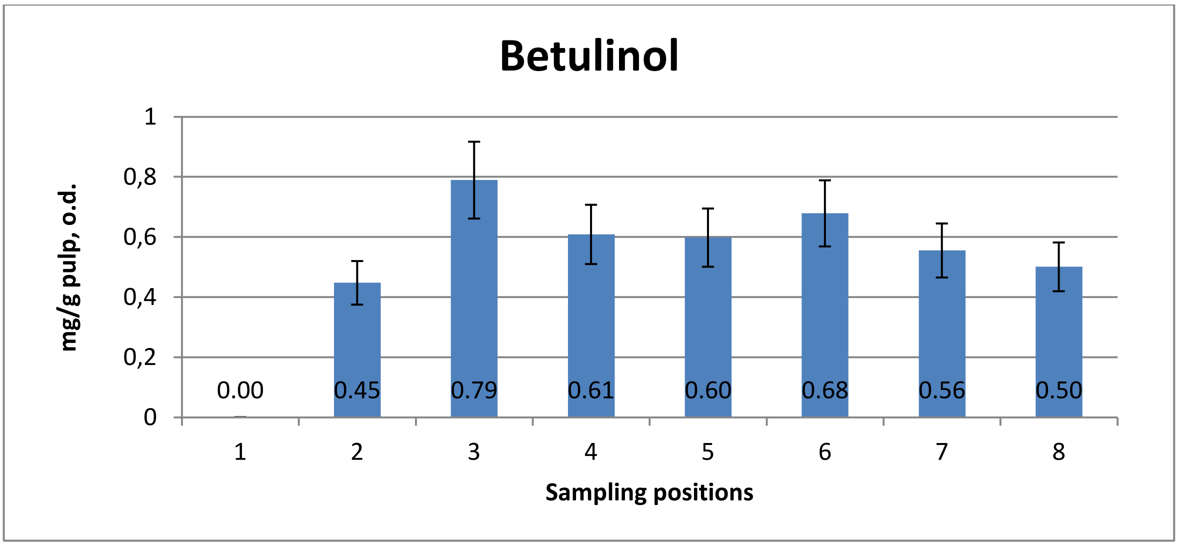


Figure 25. *Betulinols variation during the process. Mean values based on four samples are complied. The coefficient of variation for the reproducibility was determent to 16.2 % and is based on six samples which were analyzed in duplicate. (o.d. = oven dried)*

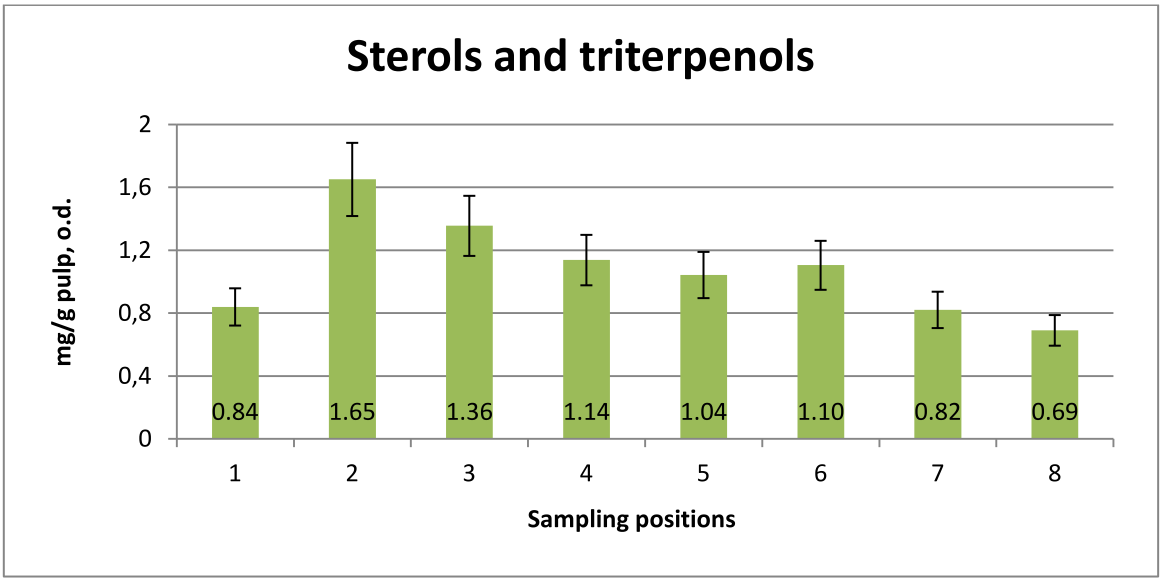


Figure 26. *The variation of the sterols and triterpenols during the process. Mean values from all earlier mentioned compounds are complied. The coefficient of variation for the reproducibility was determent to 14.1 %, and is a mean value from all the compounds´ coefficients of variation. (o.d. = oven dried)*

Squalene is a neutral component that was found in all samples, and the amount decreased during the whole process. According to *Figure 22* the second PO-reactor had a significant effect on the final removal. Squalene consists of a lot of double bonds and the effective removal in the PO-step indicates fragmentation due to oxidation.

Sitosterol comes partly from the birch wood but was not detected in the chips samples. This can be due to the fact that sitosterol is bound as esters to fatty acids in the wood, but during the cook these sitosterols are released [24]. Sitosterol was also detected in the bark, and since the tall oil is a mix of components from both pine and birch all resin components can be added with the tall oil as well. Lupeol and betulinol enters the process with the bark.

The melt point varies between the compounds, sitosterol melts at 140˚C, lupeol at 215˚C and betulinol at 261˚C [24]. This seems to have a significant effect on the deresination. If these three compounds are compared it is clear from *Figures 23, 24 and 25* that betulinol are the most difficult to wash out and sitosterol the most easy one. There are equal amounts of lupeol and sitosterol left in the final pulp, but if it is taken in consideration that there was more than four times as much sitosterol than lupeol at position 2 the removal of sitosterol can be considered as easier.

The low amount of betulinol in the pulp from position 2 is hard to explain, probably there was something during the analyze that affected the result from this position. The GC analyzes are sensitive and something could have happened there. Another factor that could matter is that these samples were extracted with another method, and not the SCAN-CM 49:03 like the other samples. Perhaps some betulinol was lost during the extraction. The amounts of betulinol in samples from position 3, 4, 5, 6, 7 and 8 were all within the range of variation, therefore no obvious removal occurred.

The sterols and tritepenols turned out to be the most difficult component to remove in the process. In this study the amount of these neutral components remaining in the final pulp are highest, especially the betulinol content is high. That neutral components are hard to wash out has been proved in other studies as well, and is mentioned in under *2.2.3 Wood resins in birch*, in the *Theoretical section*. Their hydrophobic properties are unfavorable for the deresination.

4.2.5 Fatty alcohols

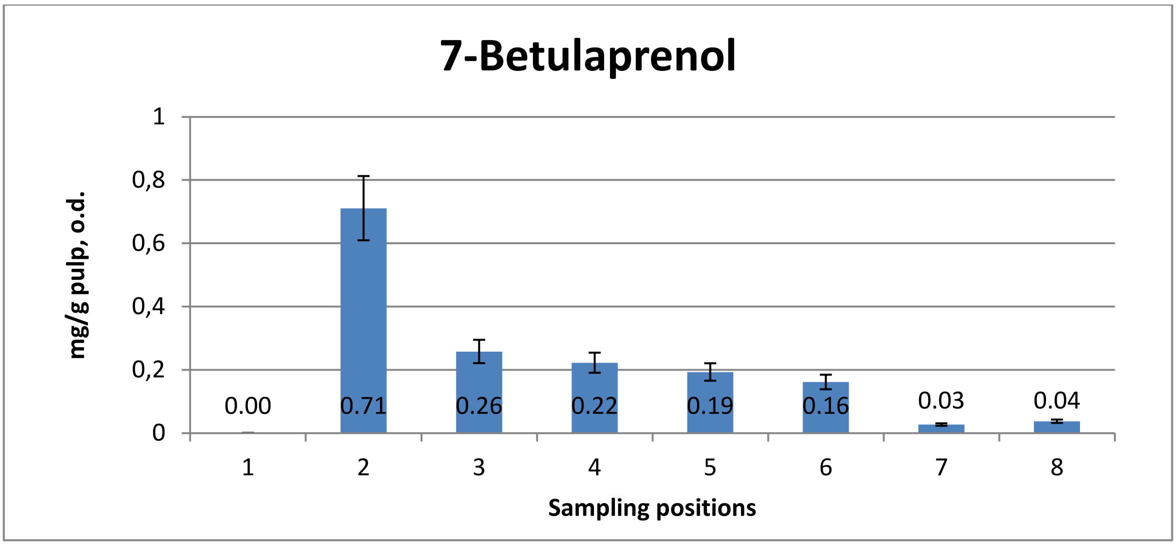


Figure 27. *The fatty alcohol, 7-betulaprenols variation during the process. Mean values from four samples are complied. The coefficient of variation for the reproducibility was determent to 14.3 % and is based on five samples which was analyzed in duplicate. (o.d. = oven dried)*

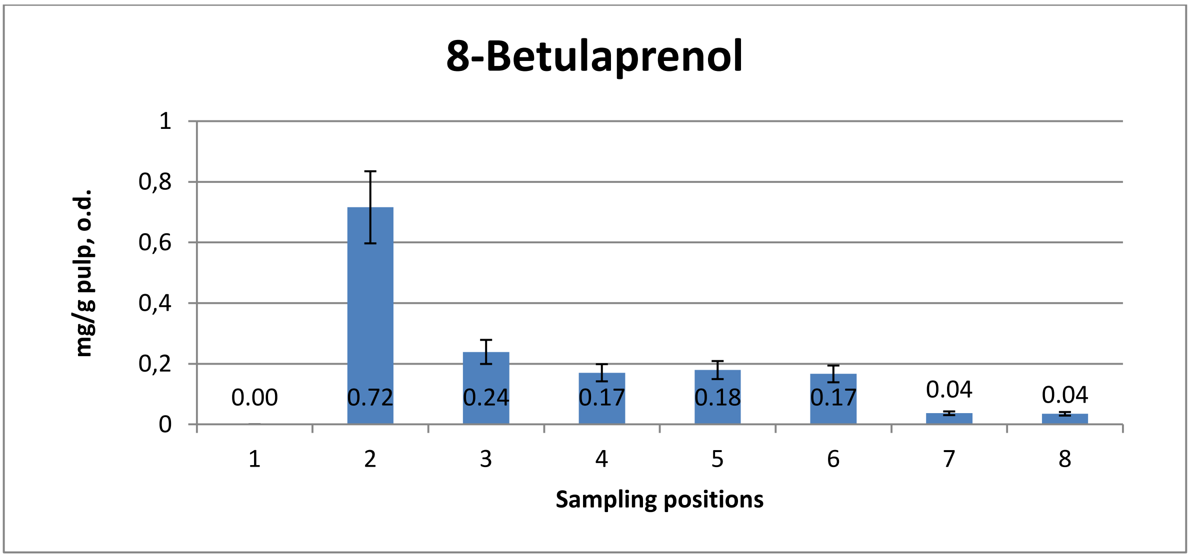


Figure 28. *The fatty alcohol, 8-betulaprenols variation during the process. Mean values from four samples are complied. The coefficient of variation for the reproducibility was determent to 16.6 % and is based on seven samples which was analyzed in duplicate. (o.d. = oven dried)*

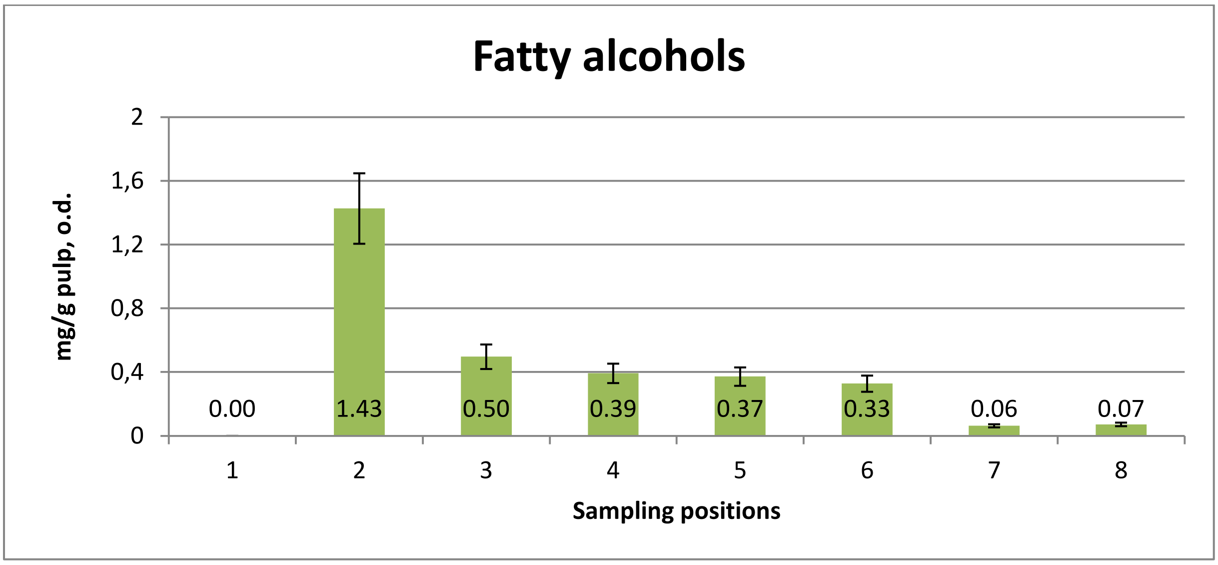


Figure 29. *The variation of the fatty alcohols during the process. Mean values from the two betulaprenols are complied. The coefficient of variation for the reproducibility was determent to 15.5 %, and is a mean value from all the betulaprenols´ coefficients of variation. (o.d. = oven dried)*

The both betulaprenols which was found in the pulp samples could not be found in the wood chips. The reason is probably that betulaprenols are formed during the cook, as described by Lauri Laamanen [24]. In the same study betulaprenols are said to be very difficult to wash out and cause large problems, but that was not the case in this study, here these substances were washed out in large extend. A lot easier than the sterols and triterpenols, and about in the same range as the fatty acids. The mean decrease in percent is calculated to 95.5 % for the fatty acids and 95.1 % for the fatty alcohols.

According to *Figures 27, 28 and 29* the large removal occurs during the DD-washer and in the second PO-reactor. The removal in the DD-washer is expected because a lot of the resin is believed to be saponified in the digester. The decrease in the PO-step indicates oxidation and betulaprenols consists of a lot of double bonds. The molecular structure is similar the one for squalene but betulaprenols also got an alcohol groups.

The reason for the low difference after the first PO-reactor compared with after the second one is unknown. This is the opposite situation compared to the result from the total content of resins, there the amount seemed to be lowered mainly in the first PO-reactor. Perhaps the time is an important factor for the reactions with substances like betulaprenols, but not for other components that could not be observed in this study.

4.2.6 Chromatograms

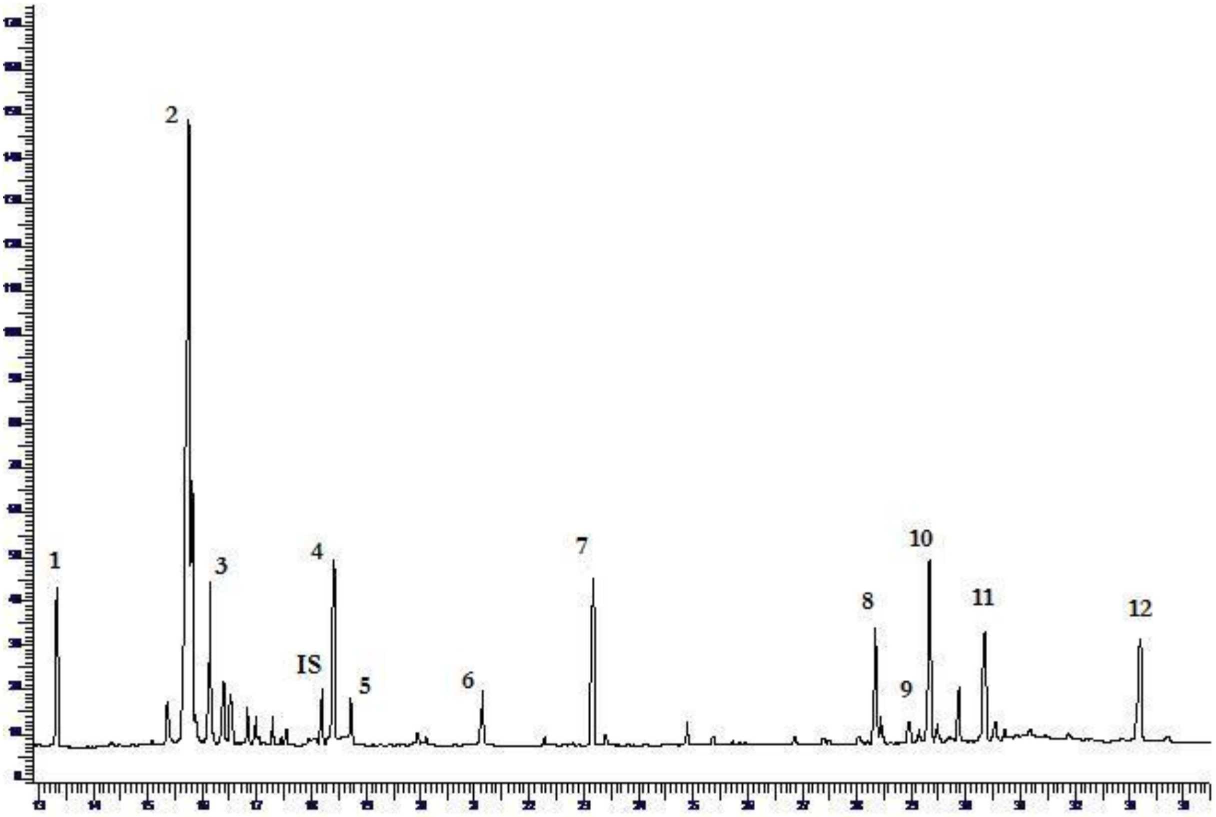


Figure 30. *A chromatogram from one of the samples from position 2, pulp after the digester. The x-axis is the retention time, and the y-axis the response. (IS = Internal Standard)*

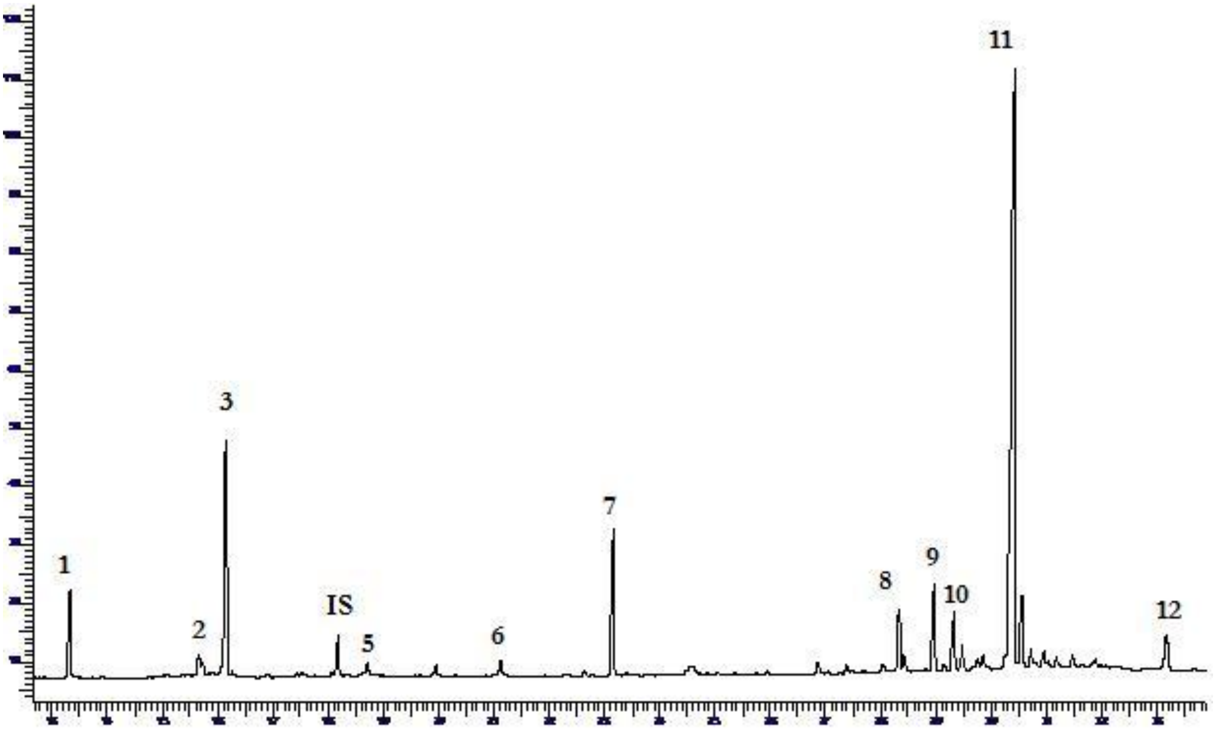


Figure *31.* *A chromatogram from one of the samples from position 8, the final pulp. The x-axis is the retention time, and the y-axis the response. (IS = Internal Standard)*

Where:

1 Anteisoheptadecanoic, C17:0 a.i.
2 Linoleic acid, C9, 12 - 18:2
3 Stearic acid, C18:0
4 Abietic acid
5 Arachidic acid, C20:0
6 Behenic acid, C22:0
7 Squalene
8 Sitosterol
9 Lupeol
10 7-Betulaprenol
11 Betulinol
12 8-Betulaprenol

Figure 30 and 31 are two of the chromatograms which were obtained during the CG-FID analyze. The amount of the different compositions was calculated due to a number of factors (described in the NSP-report), among these the areas of the peaks and concentration of extractives in the analyzed solution was considered. There was not exactly the same concentration of extractives in each sample, therefore the chromatograms cannot be compared to each other. The calculated values shown in *Figures 16 – 29* are the correct comparison. However, it is obvious from the chromatograms that there is a large deresination of the unsaturated fatty acid, linoleic acid, which is represented by peak number 2.

As mentioned earlier and showed in *Figure 30*, the amount of betulinol is low in the sample from position 2, this value should probably be higher.

5. Conclusions

- This study showed no variation in resin content in the wood chips over the 24 hours for sampling. On the other hand the samples taken after the digester showed variations. This indicates that the resin removal in the digester is uneven, however, this is compensated by the DD-washer. All other samples showed small variations in total resin content over the 24 hours.

- In this study 88 % of the resins were washed out during the different steps. The largest resin removal occurs during the washing in the DD-washer. The reason for this is believed to be that many important reactions occurs in the digester, but the washing zone is quite inefficient. The DD-washer on the other hand, is effective and washes out much of the dissolved resins. The PO-press is also effective in removing resins. This could be due to the fact that presses has shown a good resin removal ability, but another reason could also be that resins reacts with the oxygen, sodium hydroxide and hydrogen peroxide in the PO-reactors, and that these are left in the pulp until the washing in the press. The Q-steps has not proved to affect the resin content. Neither the PO-reactors showed any large effects on the total resin content if they was not followed by the washing press.

- Twelve different compounds were identified in the samples. These were fatty acids, sterols and triterpenols, fatty alcohols and one resin acid.

- The sterols and triterpenols turned out to be the most difficult to remove from the pulp, and especially the birch bark component betulinol. This is believed to be due to their hydrophobic properties, and particularly betulinol also got a high melting point. The resin acid was removed early in the process. The fatty acids and fatty alcohols were deresinated to about 95 % if the final pulp and the pulp from the digester are compared. The highest deresination for these substances occurs during the washing in the DD-washer.

- The PO-reactors turned out to have a favorable effect on the removal of resin components like betulaprenoler and squalene, which consists of long carbon chains with many reactive double bonds.

6. Process considerations

6.1 Deresination

One part of the goal with this project was to study the different ways to improve the resin removal, this is included in the *Theoretical section*. After doing this, combined with the analyzes, some conclusions about the company´s process and deresination can be drawn.

A big part of the substances which were the hardest to remove came into the process with the bark. Therefore an improved debarking step would be a good way to get rid of much of the resins. It would especially keep substances like betulinol and lupeol out from the process.

Seasoning of the wood is another method that can be tried to lower the amount of resins entering the digester, especially triglycerides.

The DD-washer and PO-press showed a good effect on the resin removal, but not the screw presses. One reason for this could be that the DD-washer is situated directly after the digester where a lot of reactions take place. The PO-press is also placed after steps with chemical reactions which can affect the resin content. The screw presses on the other hand, are situated after the reactors where chelating agents are added. According to this the conclusion that chelating agents do not affect the resin content can be drawn, or that the screw presses are ineffective for the deresination. If the chelating agents do not affect the resin content, the screw presses lack of contribution could depend on the DD-washer. If the DD-washer is very effective and remove all accessible resin components after the digester, the screw presses have less to remove. Another factor is that in both in the PO-press and DD-washer liquor is added to help the washing, the screw presses only displace liquor which was added for dilution. Also the pH could have an effect, the pH is alkaline in the PO- and DD-washer, but in the screw presses the environment is more acidly.

The PO-reactors showed effect on the deresination of some substances with reactive double bonds. Therefore it would be interesting to do a project where the dosing of chemicals in the PO-reactors is varied, and see how this affects the resin content and composition.

6.2 Environment

To put an environmental perspective on this project the effects of high amounts of extractives are considered. If large amounts of extractives would pass through the washing and bleaching steps, and continue further in the process problems with higher amounts of resins in the waist water can arise. Emissions of resins into the nature contribute to higher COD values (chemical oxygen demand), this is an important parameter for the waist water and it is controlled daily at the mill. Some extractives are hard to degrade and stay in the receiving waters for a long time. [25] Because of this the surrounding nature and organisms may be affected. Extractives like for example resin acids and sterols have been proved to affect fishes in a negative way [26].

If the resins are removed in the washing and bleaching steps the liquor finally end up in the evaporation plant. Here the resins are taken care of and converted into tall oil. The tall oil is then used in the digester to prohibit resin problems, but parts of the tall oil are also sold to a company, *SunPine*, that produces biodiesel. [25] Biodiesel is a more environmental friendly product than many other fuels. Therefore a good deresination in the washing and bleaching steps are of great importance for the environment in more than one aspect.

6.3 Economy

It is of economic beneficial to separate as much of the extractives as possible, and for sending the extractives to the evaporation plant and convert them into tall oil. The tall oil gives incomes when it is sold to *SunPine* and default expenditures when the company does not have to by tall oil from others.

Another economical aspect can be considered. If a lot of resins are left in the pulp, this can cause deposits. Deposits can lead to spots on the paper product, and process stops to remove the deposits from the equipment. Process stops are influencing the company's economy because of default revenues from products that could have been produced during this time. If the white paper products made from birch get a lot of spots on it, the paper cannot be sold to the customer. In this case the paper is reused in the process producing brown paper products. These brown paper is a cheaper product than the white paper. Due to this, it is unfavorable for the economy to use white papers in the brown ones, compared with selling the white paper. [27]

Another scenario can also be considered; what if the paper product gets a lot of spots but happens to go through the quality controls? The customer gets a product with bad quality and will probably make a complaint, this is also expensive. If a customer is exposed to this more than once a consequent could be that they will buy the product from some other manufacturer instead.

Hence, it is very important to keep the extractive content as low as possible, both from environmental and economical aspects.

7. Suggestions for future studies

- An investigation in how the resin amount varies in the wood chips over a longer period than 24 hours is suggested. In this study the resin content in both wood and pulps varied only slightly. Therefore, the earlier problems with big variations in resin content in the pulp cannot be connected to variations in the wood.

- The PO-reactors which indicated an effect on the resin content, but was inside the area for accepted variation, could be further evaluated to get a reliable result. The chemical dosing can be varied to see if for example larger amounts of oxygen would improve the deresination.

- More research could be made on the digesters affect on the resin content. Thus the reason for the unevenness in resin removal can be discovered, and as a result arrangements can be done to improve the deresination in the digester and make it more stable.

8. References

[1] - *Pitch Control, Wood Resin and Deresination*, Ernst L. Back, Lawrence H. Allen, 2000, p. 343

[2] - Tommy Berglund (Production Engineer), SCA Packaging Munksund, Private communication 2012-02-16

[3] – Information paper about SCA Packaging Munksund, written by the company, 2012

[4] - Kenneth Johansson (Department Engineer), Anna Wiksten (Laboratory Manager) and Tommy Berglund (Production Engineer), SCA Packaging Munksund, Private communication 2012-02-16

[5] - *Pitch Control, Wood Resin and Deresination*, Ernst L. Back, Lawrence H. Allen, 2000, p. vii

[6] - *Organic extractives in wood and paper pulp: Occurrence, properties and analyses*, Jon Reimo Heum, NTNU, 2005-12-21, p. 5

[7] - *The Behaviour of Birch Resin During Kraft Cooking*, Simon Fagerudd, Umeå University, May 2002, p. 11-28

[8] - *Optimerad hartsuttvättning ur björksulfatmassa (Optimized resin removal from birch kraft pulp)*, K. Pettersson, M. Björklund Jansson, A. Rutqvist, 1986, p. 9 and 31

[9] - *Lipophilic Extractives of Inner Bark of Birch, Betula verrucosa*, R. Ekman, Finn Chem. Letters, no. 7/8, 1983, p. 162-165

[10] - <http://www.fpl.fs.fed.us/documnts/fplgtr/fplgtr18.pdf>, *Extractives in eastern hardwoods, a review*, 1979, p. 11

[11] - *A New Method of Analyzing Pitch Deposits in Pulp and Paper Processes*, H. Zheng, M. C. Uhing, D.R Cosper, 2002, p. 204-210

[12] - *Pitch Control, Wood Resin and Deresination*, Ernst L. Back, Lawrence H. Allen, 2000, p. 197-208

[13] - *Resin and fatty acids in kraft pulp washing. Physical state, colloid stability and washability*, M. Lindström, L. Öberg, P. Stenius, 1988 Nordic Pulp & Paper Res. J. 3(2), 1988, p. 100-106

[14] - *Pitch Control, Wood Resin and Deresination*, Ernst L. Back, Lawrence H. Allen, 2000, p. 239

[15] - *Pitch Control, Wood Resin and Deresination*, Ernst L. Back, Lawrence H. Allen, 2000, p. 217

[16] - Tommy Berglund (Production Engineer), SCA Packaging Munksund, Private communication 2012-02-27

[17] - *Ullman Encyclopedia – Pulp*, Ragnar, Henriksson, Lindström, Wimbly, To be published (version 2012-02-09), Wiley 2012, p. 101

[18] - *Pitch Control, Wood Resin and Deresination*, Ernst L. Back, Lawrence H. Allen, 2000, p. 271-272

[19] - <http://www.foss.dk/~/media/Files/Documents/Industry%20solution%20documents/Brochures%20and%20data%20sheet/Soxtec/Soxtec2050/Soxtec%202050%20datasheet_GB.ashx>, 2012-02-26, p. 1-2

[20] - *En ny metod för hartsbestämning i våt sulfatmassa och liknande prov (A new method for determination of resin content in wet kraft pulps and similar samples)*, K. Pettersson, STFI, SCAN-Forsk, report 520, October 1988, p. 15

[21] - <http://www.unsolvedmysteries.oregonstate.edu/MS_05>, 2012-03-10

[22] - <http://www.chromatography-online.org/directory/methdcat-2/page.html>, 2012-04-11

[23] - *Pitch Control, Wood Resin and Deresination*, Ernst L. Back, Lawrence H. Allen, 2000, p. 57-62

[24] - *Björkextrakt I kok och vid blekning, forskningsresultat från projektet "Extrakten vid blekning"*, Lauri Laamanen, SCAN-Forsk , report 437, 1998, p. 14-15

[25] - Anna Wiksten (Laboratory manager), SCA Packaging Munksund, Private communication 2012-05-08

[26] - *Pitch Control, Wood Resin and Deresination*, Ernst L. Back, Lawrence H. Allen, 2000, p. 245-249

[27] - Tommy Berglund (Production Engineer), SCA Packaging Munksund, Private communication 2012-05-08

Figures:

1 - <http://en.wikipedia.org/wiki/Micelle>, 2012-03-10
2 - Author's own work, 2012-02-18
3 - Ljungberg textbook, chapter 25*, Pulp Washing*, Lars Miliander, Karlstad University
4 - Author's own work. Pictures taken at the pulp and paper mill SCA Packaging Munksund AB, 2011-10-01
5 - Sunds defibrator, Metso. Handbook for washing press DBP-915, 1999

Appendix A1. Important operation parameters during the production.

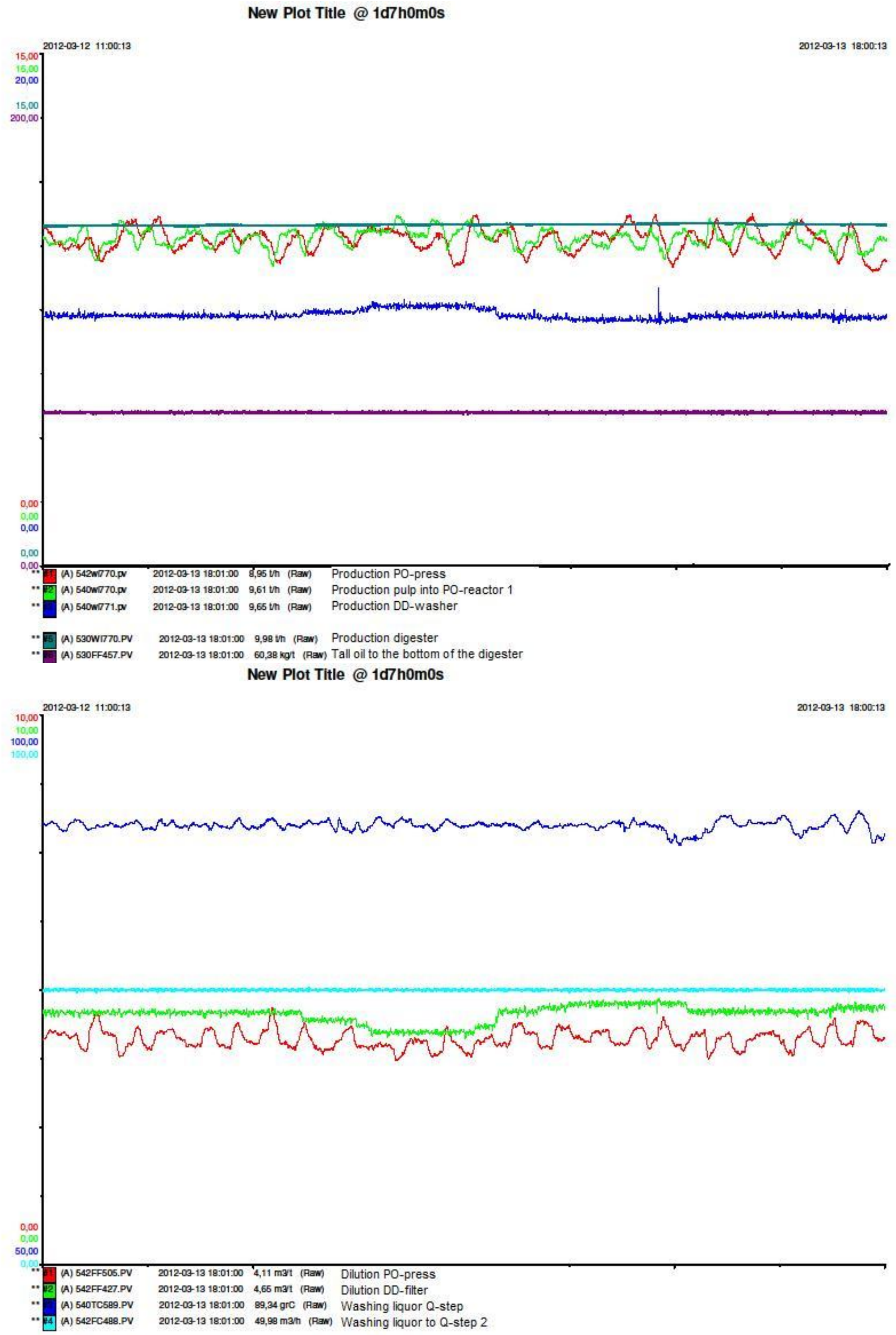
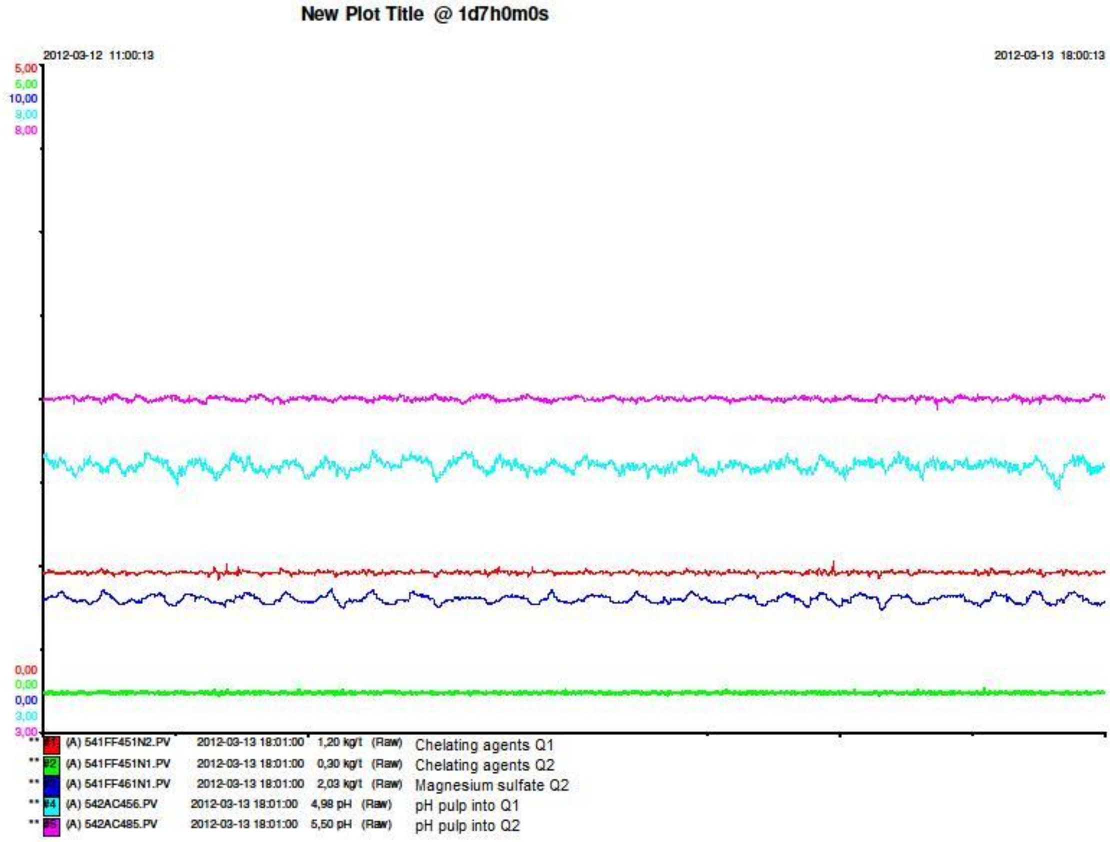


Figure A1 and Figure A2. *Variation of process parameters in the digester, DD-washer, first PO-reactor, PO-press and Q-steps.*

Appendix A2. Important operation parameters during the production.



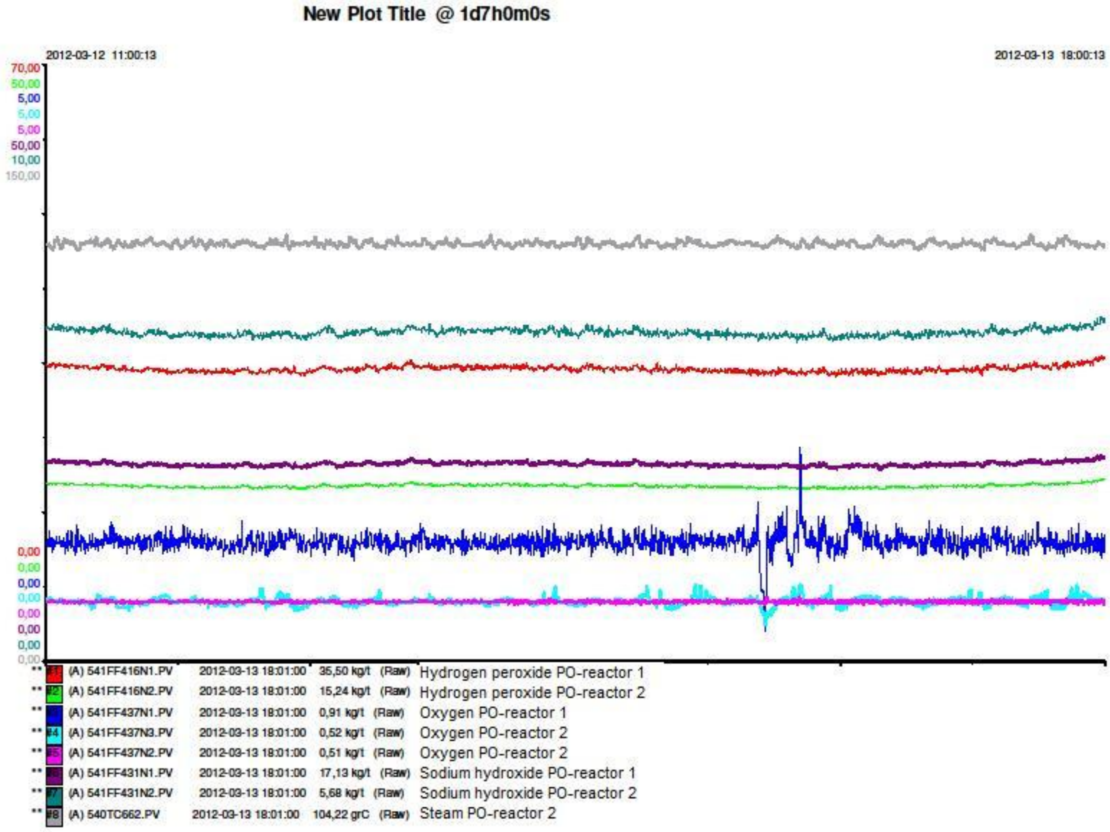


Figure A3 and Figure A4. *Variation of process parameters in the Q-steps and PO-reactors.*

Appendix B1 – Schedule for sampling, sampling position 1, 2 and 3.

Production = 10 t/h in the digester. (9.4 t/h in the washing and bleaching steps):

1. WOOD CHIPS:

Sample number:	**Day and time:**
1.1	Monday 11:00
1.2	Monday 15:00
1.3	Monday 19:00
1.4	Monday 23:00
1.5	Tuesday 03:00
1.6	Tuesday 07:00

2. REFINER:

(5 hours and 6 minutes after sample 1)

Sample number:	**Day and time:**
2.1	Monday 16:06
2.2	Monday 20:06
2.3	Tuesday 00:06
2.4	Tuesday 04:06
2.5	Tuesday 08:06
2.6	Tuesday 12:06

3. DD-WASHER:

(7 minutes after sample 2)

Sample number:	**Day and time:**
3.1	Monday 16:13
3.2	Monday 20:13
3.3	Tuesday 00:13
3.4	Tuesday 04:13
3.5	Tuesday 08:13
3.6	Tuesday 12:13

Appendix B2 – Schedule for sampling, sampling position 1, 5 and 6.

4. FIRST Q-STEP:

(44 minutes after sample 3)

Sample number:	**Day and time:**
4.1	Monday 16:57
4.2	Monday 20:57
4.3	Tuesday 00:57
4.4	Tuesday 04:57
4.5	Tuesday 08:57
4.6	Tuesday 12:57

5. SECOND Q-STEP:

(40 minutes after sample 4)

Sample number:	**Day and time:**
5.1	Monday 17:37
5.2	Monday 21:37
5.3	Tuesday 01:37
5.4	Tuesday 05:37
5.5	Tuesday 09:37
5.6	Tuesday 13:37

6. FIRST PO-REACTOR:

(29 minutes after sample 5)

Sample number:	**Day and time:**
6.1	Monday 18:06
6.2	Monday 22:06
6.3	Tuesday 02:06
6.4	Tuesday 06:06
6.5	Tuesday 10:06
6.6	Tuesday 14:06

Appendix B3 – Schedule for sampling, sampling position 7 and 8.

7. SECOND PO-REACTOR:

(2 hours and 25 minutes after sample 6)

Sample number:	**Day and time:**
7.1	Monday 20:31
7.2	Tuesday 00:31
7.3	Tuesday 04:31
7.4	Tuesday 08:31
7.5	Tuesday 12:31
7.6	Tuesday 16:31

8. AFTER PO-PRESS:

(2 minutes after sample 7)

Sample number:	**Day and time:**
8.1	Monday 20:33
8.2	Tuesday 00:33
8.3	Tuesday 04:33
8.4	Tuesday 08:33
8.5	Tuesday 12:33
8.6	Tuesday 16:33

Appendix B4 – Schedule for sampling, all times in one table.

Sample number:	**Day:**	**Time:**
1.1 - WOOD CHIPS	Monday	11:00
1.2 - WOOD CHIPS		15:00
2.1 - REFINER		16:06
3.1 - DD-WASHER		16:13
4.1 - FIRST Q-STEP		16:57
5.1 - SECOND Q-STEP		17:37
6.1 - FIRST PO-REACTOR		18:06
1.3 - WOOD CHIPS		19:00
2.2 - REFINER		20:06
3.2 - DD-WASHER		20:13
7.1 - SECOND PO-REACTOR		20:31
8.1 - AFTER PO-PRESS		20:33
4.2 - FIRST Q-STEP		20:57
5.2 - SECOND Q-STEP		21:37
6.2 - FIRST PO-REACTOR		22:06
1.4 - WOOD CHIPS		23:00
2.3 - REFINER	Tuesday	00:06
3.3 - DD-WASHER		00:13
7.2 - SECOND PO-REACTOR		00:31
8.2 - AFTER PO-PRESS		00:33
4.3 - FIRST Q-STEP		00:57
5.3 - SECOND Q-STEP		01:37
6.3 - FIRST PO-REACTOR		02:06
1.5 - WOOD CHIPS		03:00
2.4 - REFINER		04:06
3.4 - DD-WASHER		04:13
7.3 - SECOND PO-REACTOR		04:31
8.3 - AFTER PO-PRESS		04:33
4.4 - FIRST Q-STEP		04:57
5.4 - SECOND Q-STEP		05:37
6.4 - FIRST PO-REACTOR		06:06
1.6 - WOOD CHIPS		07:00
2.5 - REFINER		08:06
3.5 - DD-WASHER		08:13
7.4 - SECOND PO-REACTOR		08:31
8.4 - AFTER PO-PRESS		08:33
4.5 - FIRST Q-STEP		08:57
5.5 - SECOND Q-STEP		09:37
6.5 - FIRST PO-REACTOR		10:06
2.6 - REFINER		12:06
3.6 - DD-WASHER		12:13
7.5 - SECOND PO-REACTOR		12:31
8.5 - AFTER PO-PRESS		12:33
4.6 - FIRST Q-STEP		12:57
5.6 - SECOND Q-STEP		13:37
6.6 - FIRST PO-REACTOR		14:06
7.6 - SECOND PO-REACTOR		16:31
8.6 - AFTER PO-PRESS		16:33

Appendix C1 – The company´s method for the extraction analyze.

METODBESKRIVNING ACETONLÖSLIG SUBSTANS I MASSA

Denna metod är identisk med SCAN-CM 49:03

Skyddsutrustning: Skyddsglasögon, (glasögon) och skyddshandskar (Använd alltid skyddshandskar när massan hanteras.) Dragskåp används vid hantering av ättiksyra och aceton.

Syfte:
Kontrollera halten extraktivämnen (acetonlöslig substans) i massaprov. Halten extraktivämnen i massa ska vara så låg som möjligt för att motverka utfällningar av kladdiga substanser på pappersmaskinen, fläckar i färdig liner etc.

Kemisk beskrivning av analys:
Acetonlöslig substans - Den mängd fett- och hartssyror i ett massaprov som kan extraheras ut. Surgörning av massa före extraktion innebär att vattenlösliga natriumtvålar av fett- och hartssyror överförs till vattenlöslig syraform och blir extraherbara.

Utrustning:
2050 Soxtec Avanti **(Metodbeskrivning M 116)**
Analysvåg
Ventilerat torkskåp ca 40° C, och ca 105° C
Kokstenar av porslin eller liknande material
Glasfiberull
Aluminiumformar för engångsbruk
Glasfiltertratt, porositet 3 (Art.nr.511-1313 Lev. VWR)
Büchnertratt
Nylonvira (50µm)

Kokstenar ,glasfiberull och extraktionshylsor, tvättas före användning genom extraktion med aceton.
Följ beskrivning M 116 PROGRAM 3 = TVÄTTNING Temp 130° / Kokning 30 min / Sköljning 120 min / Återvinning 15 min / Torkning 1 min

Analys Kemikalier:
Aceton PA
Ättiksyra 99%
Utförligare information finns i SÄKERHETSDATABLADEN för dessa kemikalier **(Sökväg:** börja med Start, SCA Packaging Munksund AB , Gemensamma Program, Välj Kemikaliedatabas Munksund (Chemsoft), skriv in kemikalien(ovanför avancerad sök) tryck Sök, VÄNTA, välj fliken Säkerhetsdatablad)

Appendix C2 – The company´s method for the extraction analyze.

Utförande:

1. Blanda två nävar torr massa i en 3 litershink tillsätt ca 1 liter destvatten till ca 3 % konc. **Använd skyddshandskar.** Bestäm den exakta koncentrationen på våtlab enligt Metod .

Surgörning av massa före extraktion

2. Uträkningen för den mängd massa man ska tillsätta i mixerskålen är: (20×100/konc.)/2
3. Mät upp 160 ml destvatten i ett mätglas tillsätt 15 ml ättiksyra i mätglaset. **Hantering av ättiksyra sker alltid i dragskåp.**
4. Mixa provet 1 minut, mät pH, det skall vara under 3, tillsätt mera ättiksyra om pH är över 3. Låt stå 8 minuter och mixa sedan ytterligare 1 minut.
5. Avskilj ättiksyralösningen från provet med hjälp av Bῠchnertratt (nylonvira (50um) i botten!!) och samla upp filtratet i en ren sugflaska.
6. Skölj mixerskålen med filtratet. Låt filtratet passera genom massakakan fyra gånger med mellanliggande avsugning.
7. Riv det surgjorda provet i små bitar, **använd engångshandskar** och låt massan torka i ventilerat torkskåp (ca 40^{o}C) över natten. (Används blöt massa, måste man göra en torrhaltsbestämning för att kunna göra beräkningar på torrt prov).

Extraktion

8. Lägg några tvättade kokstenar i en aluminiumkopp
9. Väg in ca 7.xxx g av den **torra surgjorda** massan. **Använd engångshandskar**. Anteckna exakt vikt med tre decimaler.
10. Sätt massan i den tvättade extraktionshylsan. Täck hylsan med en tuss tvättad glasfiberull innan den placeras i Soxtec.
11. Tillsätt 110 ml aceton i aluminiumkoppen. **Hantering av Aceton sker alltid i dragskåp**. **Följ beskrivning M 116** och använd **PROGRAM 1** **=** Temp 130^{o} / Kokning 15 min / Sköljning 60 min / Återvinning 7 min /Torkning 1 min
12. Efter kokning filtreras extraktionsåterstoden genom ett glasfilter porositet 3. **Utförs i dragskåp**.
13. Skölj aluminiumbägaren med 3 x 5 ml aceton och filtrera genom samma filter.
14. Överför extraktionsåterstoden till en torkad och vägd aluminiumform. Avdunsta innehållet i aluminiumformen på vattenbad ca 80˚C i dragskåp.

15. Sluttorka extraktionsåterstoden i ett torkskåp 30 min**.** vid ca 105^{o}C. Låt aluminiumformen svalna i excikator och väg den sedan.
16. Töm acetonen ur Soxtec i en mätkolv och avdunsta i en kristallationsskål i dragskåp på vattenbad, ca 80˚C
17. Beräkna acetonlöslig substans enligt nedan

Appendix C3 – The company´s method for the extraction analyze.

$$\textbf{Acetonlösligt i \%} = \frac{\mathbf{(A - B) \times 100}}{\mathbf{C}}$$

A = Alumimiumform **efter** extraktion, g
B = Alumimiumform **före** extraktion, g
C = Torrt **prov**, g
100 = för att få resultatet i %

Rapportera värden under 0,05 % som <0,05 %

Appendix D. Karin Petterson´s method for extracting unwashed pulps. [20]

Acetonextraktion av våt massa

15-20 g otvättad massa eller 30-40 g tvättad massa vägs in noggrant. En mindre mängd prov tas ut för torrhaltsbestämning. Massan som skall analyseras bör ha en torrhalt av 10-20 %. Om massan har lägre torrhalt än 10 % bör den torkas i vakuumexsickator eller i torkskåp vid 40°C efter invägning. Massan slås upp i en bägare med t ex elvisp, pH justeras till 3-3,5 med ättiksyra. Därefter placeras massan med sked i en förextraherad extraktionshylsa och extraheras med aceton. Harts kan fastna på glas- och metallytor. Bägare, visp, pH-elektrod och sked bör därför torkas med acetonindränkt, förextraherad bomull som sedan extraheras tillsammans med massan.

Efter extraktionen tillsätts metanol och avjoniserat vatten till extraktet så att förhållandet vatten/aceton/metanol, inklusive provets vatteninnehåll och kvarvarande aceton blir, ungefär 1:2:1. Förhållandet behöver inte vara exakt. Om acetonhalten är för stor får man ingen fasseparation, om vattenhalten är för stor kan det bildas emulsioner. Det är lätt att göra ett snabbt överslag hur mycket som skall sättas till. Exempel: 15 g massa med torrhalt 15% har använts. Fibermängden är då 2,25 g och vattenmängden 12,75 g. Detta kan rundas till 13 ml vatten. Om cirka 70 ml aceton använts för extraktion skall 35-13= 22 ml vatten och 35 ml metanol sättas till. Eventuellt kan istället aceton först drivas av och sedan tillsätts 100 ml vatten/aceton/metanol 1:2:1. Lösningen skakas fyra gånger med 50 ml petroleumeter i en separertratt. Petroleumeterfaserna, översta fasen, skiljs av och slås ihop.

Eventuellt kvarvarande vatten i de hopslagna petroleumeterfaserna sugs upp och skiljs av med en pasteurpipett. Efter indunstning och torkning vägs extraktet. Hartshalten i massan beräknas mot den torrtänkta vikten. När otvättad sulfatmassa analyseras utgörs torrsubstansen i provet till stor del av svartlutssubstans.