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EFFECT OF EXTRACTIVES IN BIRCH KRAFT PULPING

Master´s Programme in Chemical, Biochemical and Materials Engineering

Major in Biomass Refining

Master's thesis for the degree of Master of Science in Technology submitted for inspection, Espoo, 26th of September, 2022.

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Abstract of master's thesis

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Abstract

This thesis investigated the role of extractives in birch kraft pulping. In the experimental part saw dust was produced from frozen birch wood and extracted with acetone. Some saw dust was dried prior to the extraction. Extracted saw dust samples were pulped along with non-extracted fresh and dried saw dust samples. The effect of extractive removal was assessed by analysing pulp and black liquor for pulp yield, viscosity, kappa number, carbohydrate content, lignin content and residual alkali. Acetone extracts of fresh and dried samples were also analysed by FT-IR spectrometry to study possible drying induced changes in their chemical composition.

The acetone-extracted saw dust samples demonstrated higher pulping yield, higher alkali consumption and higher kappa number when compared to the non-extracted samples. Carbohydrate analysis indicated higher xylose content of pulp and lower xylose content of black liquor in the acetone-extracted samples. Proposed explanation for these chemical differences is the behaviour of dissolved xylan, which partially readsorbs from black liquor back to cell wall. Lignin analysis indicated that the lignin content was very similar in all the pulp samples. The higher kappa number level of the acetone-extracted samples may be due to higher hexenuronic acid content of the pulps. FT-IR -analysis revealed only minor drying induced changes in the extract composition.

The results indicate that extractives present in pulping might inhibit xylan readsorption and thus effect pulp yield and alkali consumption.

Keywords birch, extractives, kraft pulping, saw dust, acetone extraction

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Tiivistelmä

Tässä opinnäytetyössä tutkittiin uuteaineiden merkitystä koivun sulfaattisellukeitossa. Kokeellisessa osuudessa tuotettiin sahanpurua jäisestä koivusta, jonka jälkeen sahanpurua uutettiin asetonilla uuteaineiden poistamiseksi. Osa tuotetusta sahanpurusta kuivattiin ennen asetoniuuttoa. Uuteaineiden poiston vaikutusta tutkittiin analysoimalla sellusta sekä mustalipeästä keiton saantoa, viskositeettiä, kappalukua, hiilihydraattipitoisuutta, ligniinipitoisuutta sekä jäännösalkalia. Asetoniuutteet analysoitiin FT-IR-spektrometrillä mahdollisten kemiallisten muutosten havaitsemiseksi.

Tuloksista voitiin nähdä, että asetonilla uutetut sahanpurunäytteet olivat keittosaannoltaan suurempia, kuluttivat enemmän alkalia keiton aikana ja niiden kappaluku oli korkeampi. Hiilihydraattianalyysi osoitti sahanpurun uuton nostavan sellun ksyloosipitoisuutta ja alentavan mustalipeän ksyloosipitoisuutta. Mahdollinen selitys tähän on polymeerisen ksylaanin adsorptio mustalipeästä takaisin kuituun. Ligniinianalyysi osoitti ligniinipitoisuuksien olevan samalla tasolla kaikissa sellunäytteissä. Kappaluvun nousu asetoniuutetuissa näytteissä saattoi johtua sellun sisältämästä heksenuronihaposta. FT-IR-analyysin mukaan uuteaineiden kemiallinen koostumus ei eronnut merkittävästi tuoreen ja kuivatun sahanpurun välillä.

Tulokset osoittavat, että uuteaineiden läsnäololla saattaa olla vaikutus ksylaanin readsorptioon ja sitä kautta keiton saantoon sekä alkalikulutuksen.

Avainsanat koivu, uuteaineet, sulfaattisellu, sahanpuru, asetoniuutto

Preface

This thesis was carried out in the Spring and Summer of 2022 in the research group of Tapani Vuorinen at Aalto University. The work was funded by FinnCERES, which I am thankful for. Raw material for the experimental work was provided by Mikko Vuohelainen from Helsinki city construction services, Stara. I would like to thank my advisor Kyösti Ruuttunen for supporting me and my work throughout the thesis project as well as providing me valuable knowledge and viewpoints. I would also like to thank my thesis supervisor Tapani Vuorinen for his expertise and insights. This thesis project has been challenging yet intriguing and there have been many people guiding me with different analyses in the laboratory, from which I am grateful for. I would also like to thank my fellow students for valuable conversations and peer support.

Finally, I want to say special thanks for my life-companion Anna for providing me invaluable support. Without you this thesis would still be in progress.

Mikko Hakala

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Abbreviations

L/S	Liquid-to-solids ratio
L/W	Liquor-to-wood ratio
AA	Active alkali
EA	Effective alkali
S	Sulfidity
DP	Degree of polymerization
$KmNO_4$	Potassium permanganate
o.d.	oven-dry
HexA	Hexenuronic acid

1 Introduction

Wood extractives, lipophilic and hydrophilic, are important compounds in wood. They function as an energy source and protect wood against insects and microbiological and physical damage (Alén, 2000). Although extractives represent only a minor proportion of wood dry mass, they have a significant impact on wood properties, e.g., durability, color and usability as a raw material for pulp (Pensar, 1977).

Wood extractives are reported to have a negative effect on pulp yield and in increased consumption of sodium hydroxide in alkaline pulping processes (Gardner & Hillis, 1962). Also experiments by Shin *et al.,* (2004) have indicated that residual extractives in kraft pulp led to higher kappa number when compared to extractive-free pulp. Preliminary results obtained from birch kraft pulp analysis conducted in laboratory contradict with these results by yielding higher kappa numbers for pulp that was produced from acetone-extracted saw dust.

The focus of this thesis is on extractives of birch (*Betula sp.*) and the impact of extractives on delignification during kraft pulping. Since wood extractives are known to oxidise readily dried and fresh saw dust samples were prepared and extracted with acetone. Extractive-free samples are pulped along with non-extracted dry and fresh samples and the comparison is made between the samples. The pulped material as well as black liquor and acetone-extracted extractives are analysed using various methods to determine the effect of extractive removal.

The goal of this thesis was to get understanding on how birch extractives affect birch kraft pulping. The effect was studied for both fresh and dried saw dust. Key parameters were determined from the pulps and black liquors obtained.

2 Wood structure and morphology

The primary part of a tree used for pulping is the stemwood. The stemwood, or the trunk, has three distinct physiological functions: to provide structural support, to transport water and to store nutrients. It can be histologically divided into three parts: xylem, cambium, and bark (Rydholm, 1965). Since wood is anisotropic material, the different structures can be best illustrated when observed in longitudinal, radial, and tangential planes, along with the cross-sectional view. This is illustrated in Figure 1.

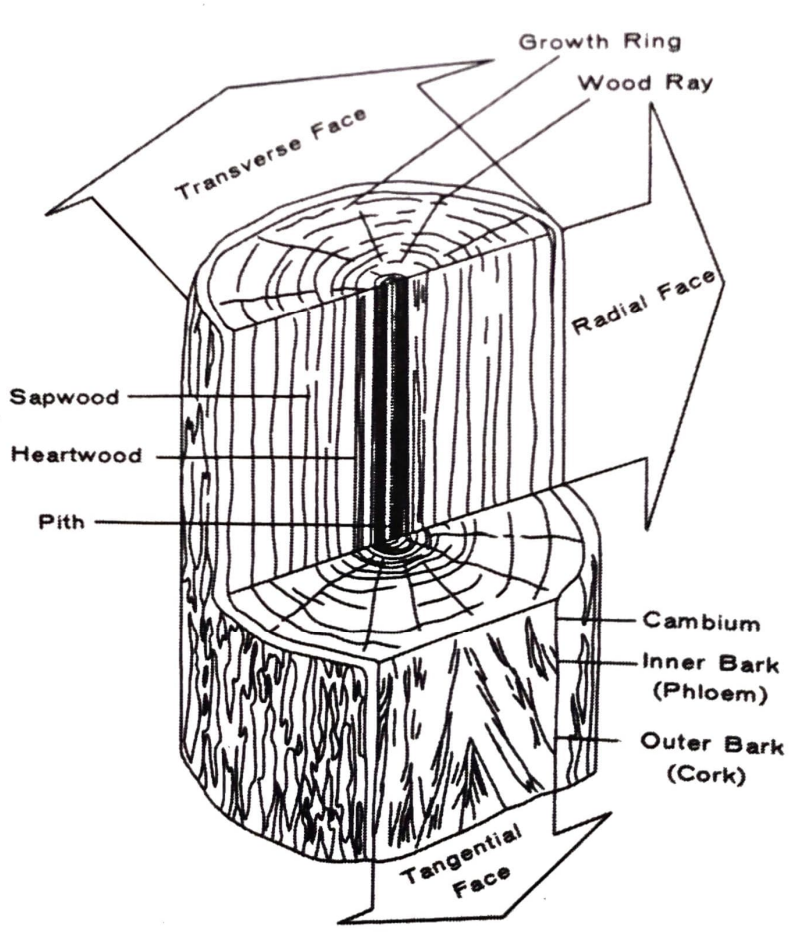


Figure 1. Transversal, tangential, and radial views of a tree stem illustrating anisotropic nature of wood (Smook, 2002).

Xylem, or wood, is formed by sapwood and heartwood. Sapwood is physiologically active part of the wood, and it is responsible for the structural support, water transport and nutrient storage. The inner part of wood is known as heartwood. Heartwood consists of dead cells and function mostly as a supporting structure for the tree. When observable, the darker color of hardwood compared to sapwood is due to the storage of extractives (Alén, 2000). According to Sixta *et al.,* (2006), birch (*Betula sp.)* does not form heartwood in normal growing conditions, and therefore the distinction of birch heartwood and sapwood is not made in this thesis.

Hardwood xylem is formed by four different elements which are needed for a tree stem to carry out its functions: parenchyma cells, fibres, tracheids, and vessel elements. Parenchyma cells function as storage and transport cells for nutrients and water. Fibres are elements which give wood its structural support. Tracheids and vessels function in a structural support and water transfer management (Rydholm, 1965). In softwoods, tracheids have the role of conducting and support, whereas in hardwoods, as in birch, vessels are the conducting cells and fibres provide structural support (Sjöström, 1993).

Cambium is a thin layer of tissue between the bark and the xylem. It contains living cells which annually during growth season form new layer for xylem known as growth ring. The living cells of cambium also form cells outwards towards phloem (Ilvessalo-Pfäffli, 1977). The rate of growth depends on the seasons and the light-colored growth ring, springwood, is formed in the first part of growing season. Latewood, which is the darker part, is formed at the latter part of the growing season. The difference in colors is due to difference in cell structures (Alén, 2000).

Bark is the outermost layer of the trunk, and it amounts to about 7-20% of the total mass of the wood (Miranda *et al.,* 2013). Bark has a complicated structure compared to wood, but it can be roughly divided into two parts: outer bark or rhytidome and inner park or phloem. Outer bark consists of dead cells which provide wood

protection against mechanical damage. It also preserves wood from humidity and temperature variation. Inner bark consists of sieve elements, parenchyma cells and sclerenchymatous cells. Sieve elements act as a transporter of water and nutrients, parenchyma cells function as a nutrient storage and sclerenchymatous cells function as a structural element (Sjöström, 1993).

3 Wood extractives

Wood extractives, which are low-molecular non-structural compounds of wood, comprise a minor fraction of wood mass compared to major structural polymers cellulose, hemicelluloses, and lignin. Although the typical extractive content is in the range of 1-5% of the wood dry solids, the number of different substances is large (Alén, 2000).

The extractive content varies not only between different wood species, but also between individual trees and different parts of the tree. Other causes of variation are e.g., the tree's age, growth conditions and geographical location. Table 1 compiled by Hillis, (1962) exhibit difference in *Eucalyptus regnans* heartwood extractives content of different aged trees in different parts of a tree.

Table 1. Total extractives content as weight percent of the xylem of *Eucalyptus regnans* in relation to tree's age and given position of the tree. Reproduced from Hillis (1962).

Age of tree (years)	Butt (%)	Center (%)	Top (%)
30	2.0	2.6	0.9
	5.2	-	-
50	3.3	2.6	2.7
	-	4.2	5.0
	4.8	-	-
	6.6	-	-
110	4.5	-	-
	6.8	-	-
	7.9	-	-
120	6.6	-	-
	8.0	10.2	18.1
	14.0	6.0	11.6

There is a substantial difference between softwood and hardwood extractive types and content. The most evident difference is the absence of resin acids in hardwood. Resin acids are major component in e.g., pine and spruce resin canals and generally account for 30-40% of the weight of the extract. This resin acid, or oleoresin is a viscous liquid which exudes from the wood after physical damage (Mutton, 1962).

Both hardwoods and softwoods contain resin, located in parenchyma cells. This resin, also known as physiological resin, is a mixture of saponifiable fatty acids and unsaponifiable triglycerides, sterol, steryl esters and triterpenyl alcohols. In addition, the greater proportion of unsaponifiable compounds in hardwoods, especially in birch (*Betula sp.)* is noteworthy (Ekman & Holmbom, 2000).

Different extractives have different distribution across the stem of wood. Figure 2 illustrates the variations in the content and composition of wood extractives across the radial axis of Scots pine (*Pinus sylvestris).* The highest total extractive contents are found towards the inner and outer parts of the stem. In all pines the heartwood contains more resin acid than sapwood, but for *Picea* species the sapwood is rich in resin acids (Sjöström, 1993).

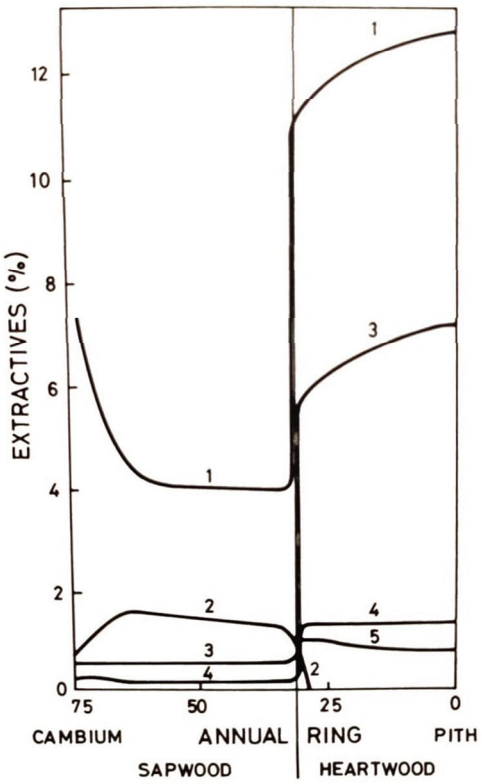


Figure 2. Variations of different wood extractives in radial axis in *Pinus sylvestris*. 1. Total extractives, 2. trigylcerides, 3. resin acids, 4. fatty acids. 5. pinosylvin and monomethyl ether (Sjöström, 1993).

Highest extractive content in trees can be found in bark and knots. Bark, which is the outermost layer of the wood, is susceptible to damage and knots are vulnerable for fungal attack when a branch is broken (Pietarinen *et al*., 2006). Therefore, the high content of fungicidal phenolic compounds in bark and knots is beneficial in a case of damage (Björklund Jansson & Nilvebrant, 2009). The extractive content in knots, especially in softwoods, is relatively high compared to other wood parts. For example, Norway spruce knots contain 6-24% of polyphenol lignan and the lignan content in hardwood knots can be 30-500 times higher than in stem hardwood (Routa *et al.,* 2017). In kraft pulping these parts of the tree are not utilized but removed from the raw material stream during the process, and therefore they are left outside of the scope of this thesis.

Felling of a tree influences the extractives. After felling the resin content starts instantly to decrease, and the chemical composition alters. Ambient air affects the carbon-carbon double bonds and free radicals are generated in chain reaction. These free radicals are particularly strong oxidants, which will react further on. Transition metal ions and light are known to accelerate this autoxidation, along with certain enzymes present in the wood (Alén, 2000).

According to Ekman (2000), the major chemical changes in wood extractives after felling and in storing are:

- Rapid hydrolysis of triglycerides accompanied by slower hydrolysis of steryl esters
- Oxidation/degradation/polymerization of resin acids and liberated fatty acids
- Evaporation of volatile terpenoids

Along with the above-mentioned compounds, also phenolic extractives undergo reactions in tree after felling. Eilamo (2020) has studied the oxidation of phenolic compounds in fresh birch wood sawdust by observing the discoloration. By drying sawdust prior to acetone extraction, he found the correlation between the color change and changes in the chemical composition. By extracting the sawdust with 80% acetone, wood discoloration was hindered. Eilamo (2020) suggested that acetone-extraction prevented enzymatic and autoxidative reactions, leading to a considerably hindered discoloration during drying.

3.1 Classification of extractives

Extractives can be divided into hydrophilic and lipophilic extractives, depending on their solubility in neutral organic solvents or water (Alén, 2000). Neutral organic solvents can dissolve lipophilic resin acids, fatty acids, and sterols, whereas water

dissolves hydrophilic compounds, e.g., sugars, phenols, and inorganic salts (Nisula, 2018). Sjöström (1993) divides extractives into 4 distinct categories:

- terpenoids and steroids
- fats and waxes
- phenolic constituents
- inorganic components

These different types of extractive compounds serve a variety of functions in wood. Terpenoids and steroids protect the wood against insects and physical and microbiological damage. Fats and waxes function as an energy source for wood cells (Alén, 2000). Phenolic compounds have an influence on color, odor, and taste of wood (Nisula, 2018). Palo (1984) has suggested that toxicity of phenolic compounds give protection against depredation.

Oleoresin consists of a solution of resin acids in a volatile oil, or turpentine. Both resin acids and turpentine are terpenoids. Terpenoids are made up of isoprene units (C_5H_8), which have molecular formula of some multiple of the isoprene unit. Some terpenes are e.g., diterpenes ($C_{20}H_{32}$) and triterpenes ($C_{30}H_{48}$) (Mutton, 1962). Sterols are derivatives of terpenes and closely related to triterpenoids. These compounds have hydroxyl group in C-3 position and are typified by β-sitosterol, an abundant sterol found both in softwoods and hardwoods (Sjöström, 1993).

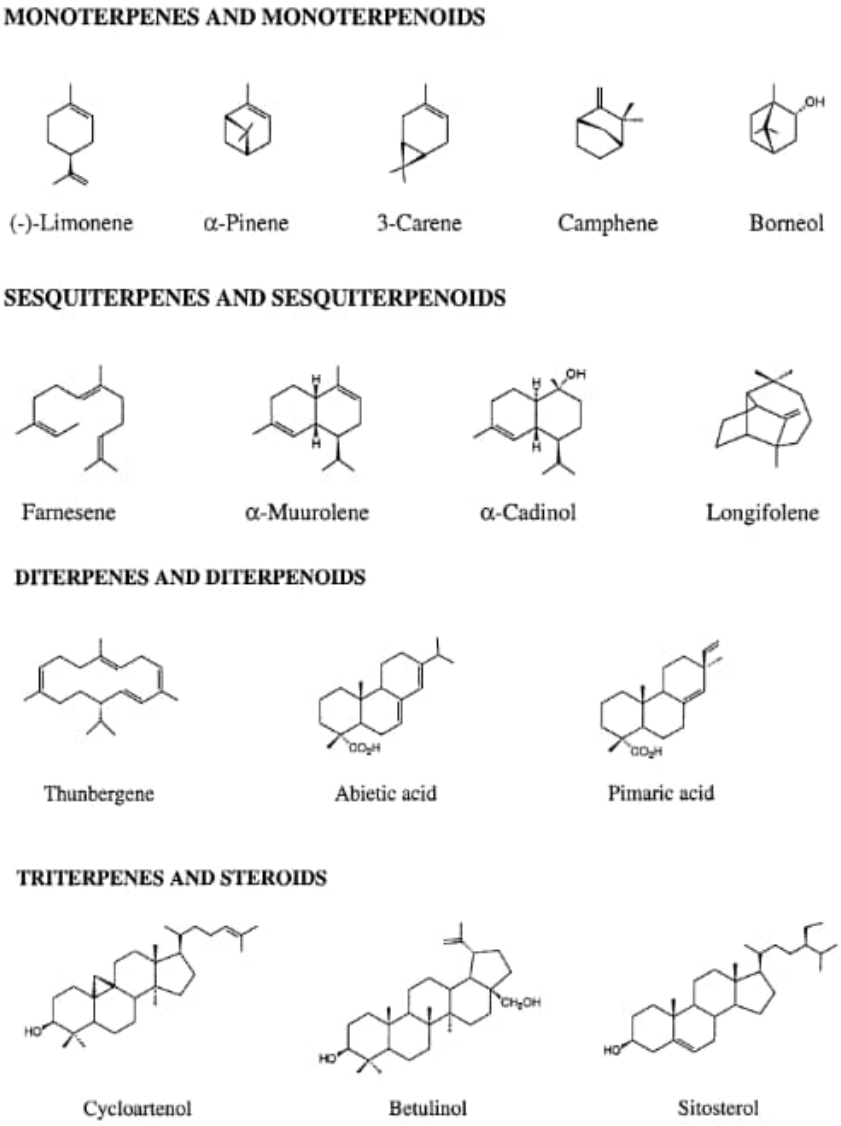


Figure 3. Structures of several terpenes found in wood (Alén, 2000).

Fatty acids are the major component of parenchyma cell resin in softwoods and hardwoods. Fatty acids are long-chained non-branched aliphatic carboxylic acids, which act as a reserve energy for tree. Usually, fatty acids occur either in esterified form, when they are called oils or fats or in esterified monohydric alcohol form, when they are called waxes (Mutton, 1962).

Phenolic constituents are a vast group of compounds found in wood. These components, widely present in heartwood, bark, and knots, are not significantly found in

sapwood. Phenolic compounds constitute a large variety of chemical structures from simple phenols to complex polyphenols and their derivatives. Core structure is benzene ring, in which one or more hydroxyl groups are bonded (Routa *et al*., 2017). Sjöström (2017) groups these compounds as:

- Stilbenes
- Lignans
- Hydrolysable tannin
- Flavonoids
- Condensed tannins

Stilbenes are derivatives of 1,2-diphenylethylene and possess a conjugated double bond. Typically, stilbenes such as pinosylvin are found in the heartwood of *Pinus* species. On the contrary, lignans are found widely in the stemwood of both hardwoods and softwoods. Lignans are formed by oxidative coupling of two phenylpropane units (Alén, 2000). Hydrolysable tannins are esters of D-glucose, which upon hydrolysis yield gallic and ellagic acid. These tannin components are not widely common in wood. Flavonoids are found in stemwood of hardwoods and softwoods. The flavonoid skeleton is formed by oxidative coupling of phenylpropane units. Condensed tannins are polymers of flavonoids and can be found widely in the stemwood of many wood species (Sjöström 1993).

Inorganic materials of softwoods and hardwood are mainly of potassium, calcium, and magnesium. These make up around 80% of the total inorganic constituents. Some of the organic elements are essential for wood growth but cause issues in pulping. For example, trace amounts of manganese, iron and copper accelerate pulp degradation during bleaching stages and silica is known to scale evaporator process equipment (Alén, 2000).

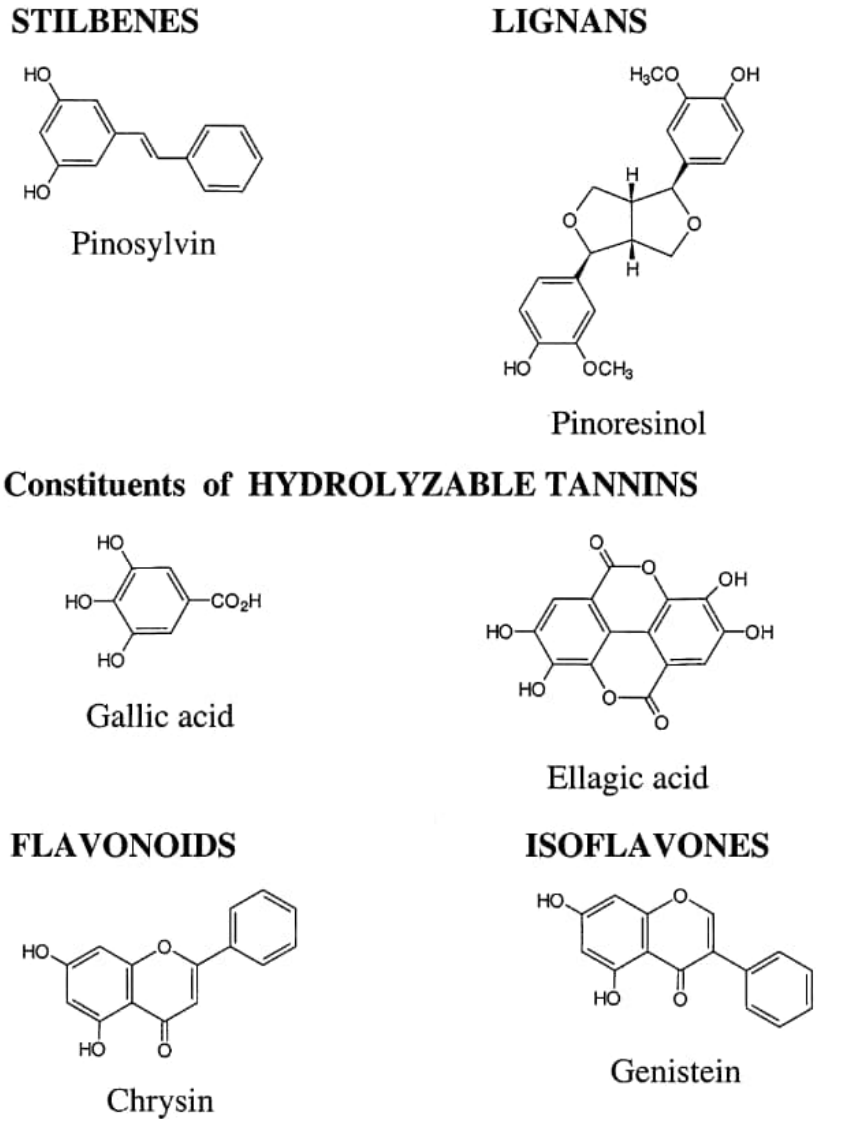


Figure 4. Various phenolic extractives and their chemical structures (Alén, 2000).

4 Extractives in birch

Typical content of birch extractives varies between 1.0 to 3.5% of the wood dry solids (Alén, 2000). The variation of extractive content between different birch species is considered to be moderate and the contents of most individual extractive components are relatively low, less than 1%. These components include fatty acids, sterols, steryl esters, triglycerides and lignans. Only exception is betulinol in bark with content up to 12.7% (Roitto *et al.,* 2015). The variation of different *Betula pendula* extractive components in comparison with *Pinus sylvestris* is illustrated in Table 2. The importance of birch extractives in kraft pulping is of the lack of resin acids, which hinders deresination. This makes birch difficult to pulp without experiencing pitch problems (Ekman & Holmbom, 2000).

Table 2. Variation of different extractives in *Pinus sylvesteris* and *Betula pendula* stemwood (w/w%). Adapted from Routa *et al.,* (2017).

	Pinus sylvestris	***Betula pendula***
Resin acids	0.21–6.34	-
Fatty acids	0.22–1.8	0.03–0.25
Sterols	0.01	-
Steryl esters	0.05–0.14	0.18–0.50
Triglycerides	0.03–0.1	0.2–0.68
Lignans	0.01	0.06

4.1 Extractives in birch xylem

Total amount of silver birch (*Betula pendula)* xylem extractives range from 0.8 to 5% of the wood dry solids (Roitto *et al.,* 2015). Extractives comprise both lipophilic and hydrophilic substances, but the term 'resin' is used as a collective term for lipophilic extractives (Alén, 2000).

Major extractives in birch xylem are resins, located almost entirely in parenchyma cells. These resins are composed mainly of fatty acids, triglycerides, steryl esters and sterols (Ekman & Holmbom, 2000). Hardwood resin composition is not qualitatively different of softwood resin, except for pinolenic acid, which is found exclusively in *Pinacea* family in softwoods. It is noteworthy that resin acids, which are found in resin canals in softwoods, are not present in hardwoods such as birch (Mutton, 1962). A group of polyterpenoids found solely in birch wood are betulaprenols (Sjöström, 1993). Betulaprenols are formed of 6-9 isoprene units and are difficult to remove from the pulp suspension due to hydrophobic nature (Pensar, 1977). Different birch species are rich in wood resin content, when compared to other hardwoods. Table 3 shows different birch species and the content of diethyl ether-soluble resin.

Table 3. Content of diethyl ether-soluble resin in different birch species (Ekman & Holmbom, 2000).

Species	**Ether-solubles of whole wood (%)**
Betula lutea	0.43-1.43
Betula papyrifera	1.5-3.52
Betula pendula	1.12-2.7

Seasoning of birch decreases the lipophilic extractive content substantially. In birch roundwood the dominating reaction is the hydrolysis of triglycerides into free fatty acids. During the storage of birch chips triglyceride hydrolysis is fast during the first weeks. Upon longer period of storage, the total amount of resin will decrease and steryl esters and fatty acids degrade (Ekman, 2000).

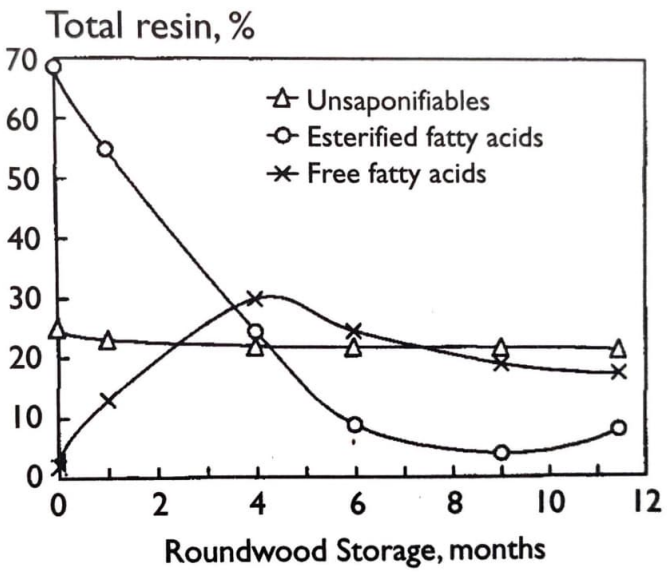
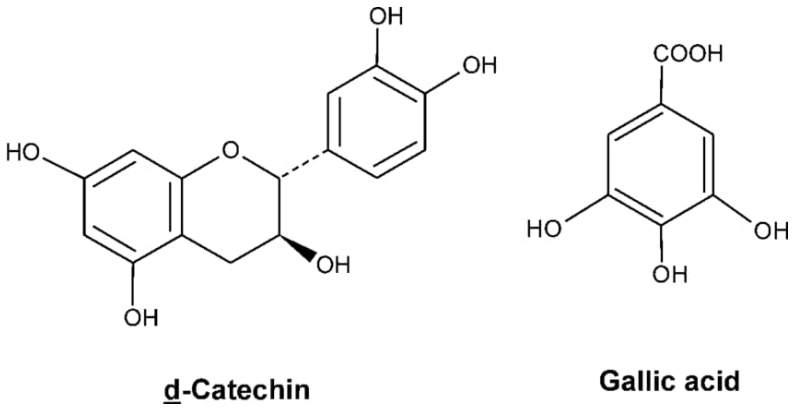


Figure 5. Changes of silver birch (*Betula pendula)* wood resin content during storage (Ekman, 2000).

Besides resins, birch xylem contains many phenolic compounds from simple phenols to complex polyphenols and their related compounds (Alén, 2000). Polyphenols are known to discolor wood material under different conditions, such as exposure to ambient air and sunlight. This is partly dependent on the vicinal hydroxyl groups in the molecule. Polyphenols can be divided into groups containing a vicinal trihydroxy grouping such as gallic acid, and those containing an *ortho* dihydroxy grouping such as catechin (Hillis & Swain, 1962).



d-Catechin **Gallic acid**

Figure 6. Structures of d-Catechin and Gallic acid, illustrating the *ortho* dihydroxy grouping and vicinal trihydroxy grouping (Zhou *et al.,* 2003).

Yamamoto *et al.,* (*2013*) have studied the color development of fresh squeezed birch xylem sap and by applying mechanical compression to wood disc, they were able to collect birch sap. The color development of the birch sap was suggested to be from formation of quinonoid intermediates by enzymatic activity of polyphenol oxidase (PPO). The major phenol acting as substrate for PPO was identified as (-)-epicatechin. The enzymatic activity was observed to occur even in the absence of oxygen.

This phenomenon was also studied by Eilamo (2020) and Aso (2021). Eilamo concluded that (-)-epicatechin polyphenol is a key component in wood discoloration after felling. Aso (2021) experimented isolating birch xylem sap prior kraft pulping and concluded that it yields no effect on pulping parameters such as kappa number, viscosity, or carbohydrate content.

4.2 Extractives in birch bark

Birch bark, especially outer bark, has a high extractive content. According to Miranda *et al.,* (2012) total extractive content of inner and outer birch (*Betula pendula*) bark is 17.6%, which is ten times the amount of extractives compared to birch (*Betula pendula)* wood. From this amount 75-85% is betulinol (Back, 2000b).

Betulinol is a triterpenoid, which is mainly responsible for the white color of birch outer bark. It has high melting point and is known for causing co-deposits with fatty acids in pulp and paper making and accumulating with hydrophobic substances in the process (Bergelin *et al.,* 2009). The content of betulinol in birch outer bark is around 10-30% of dry weight (Ekman & Holmbom, 2000). This is exceptional for a single extractive compound (Norin & Kremer, 1977). Therefore, efficient debarking is needed for mitigating issues with betulinol during pulping and papermaking (Ukkonen, 2020).

Inner bark of birch is known to be rich in suberin. Suberin is a polymeric substance which is not fully identified, but it is suggested to have similar cross-linked structure as lignin (Björklund Jansson & Nilvebrant, 2009).

Lappi *et al.,* (2014) have studied the changes in chemical composition of birch bark during a storage of 24 weeks. Figure 7 illustrates the significant decrease of compounds, not only tri-and diglycerides but also betulinol and lignans. Similar change is observable in storage of silver birch roundwood, as seen in Figure 5.

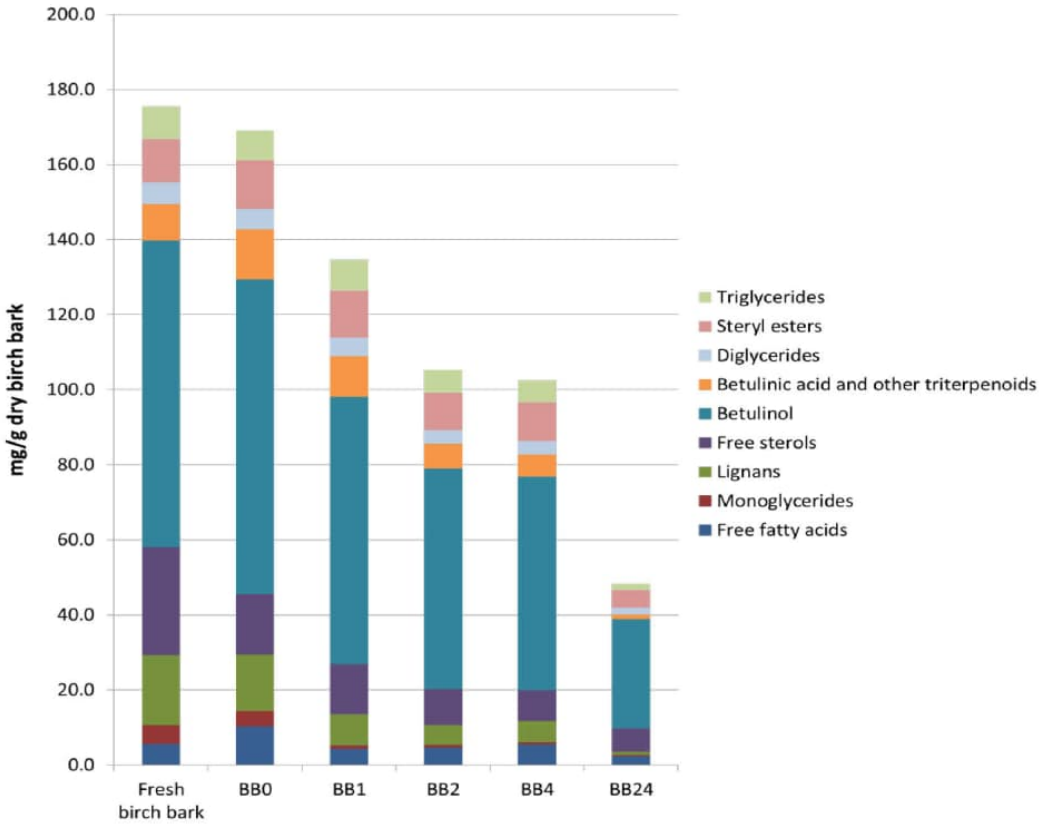


Figure 7. Amount of different extractives in birch bark. BB0 = sample before storage BB1 = after 1 week BB2 = after 2 weeks BB4 = after 4 weeks BB24 = after 24 weeks (Lappi *et al.,* 2014*).*

Since the wood is debarked prior to pulping process and the raw material in this thesis is saw dust produced from the sapwood of birch, the effect of bark extractives in delignification is left outside of the scope of this thesis.

5 Kraft pulping

Kraft pulping or sulfate pulping is the dominating pulping process today. According to Bajpai (2018), 91% of chemical pulps and 75% of all pulps are produced by kraft pulping. The advantages of kraft pulping are the high strength of the pulp, applicability to different wood species and efficient energy and chemical recovery cycle (Biermann, 1996).

Raw material for kraft pulping is chipped wood. The wood is chipped to particles with a length and width of 15-25 mm and thickness of 2-4 mm. This is done to aid the cooking liquor penetration during the chemical process (Rydholm, 1965).
The cooking liquor in kraft pulping is known as white liquor. White liquor is a strongly alkaline mixture of different chemicals, but the active cooking chemicals are sodium hydroxide (NaOH) and sodium sulfide (Na_2S). In water these compounds dissociate into main cooking agents, hydroxide (OH^-) and hydrosulfide (HS^-) ions, which will then react with the pulping material. This process is known as delignification (Sixta *et al.,* 2006).

The delignification can be divided into three phases: initial, bulk, and residual phase. The initial phase takes place at temperatures below 140 °C. OH^- and HS^- ions react with lignin and the lignin content is reduced by 15-25%. The amount of hemicelluloses decrease by 40% and the predominant carbohydrate losses occur. At this stage, the reaction is controlled by the diffusion of cooking chemicals into the chips (Alén, 2000).

During the bulk phase the temperature is over 140°C and the rate of delignification becomes controlled by the chemical reactions. These reactions accelerate with the rising temperature. At this stage 90% of lignin is removed and carbohydrate losses are minor.

The final phase is the residual phase, where the delignification occurs at a much lower rate than in the bulk delignification phase. If the residual phase prolongs and delignification proceeds, the dissolution of carbohydrates increases. Therefore, to obtain high quality pulp, delignification is limited to a certain degree. At this degree, the kappa numbers indicating the bleachability of pulp are around 15-20 for hardwoods and 25-30 for softwoods (Sixta *et al.,* 2006).

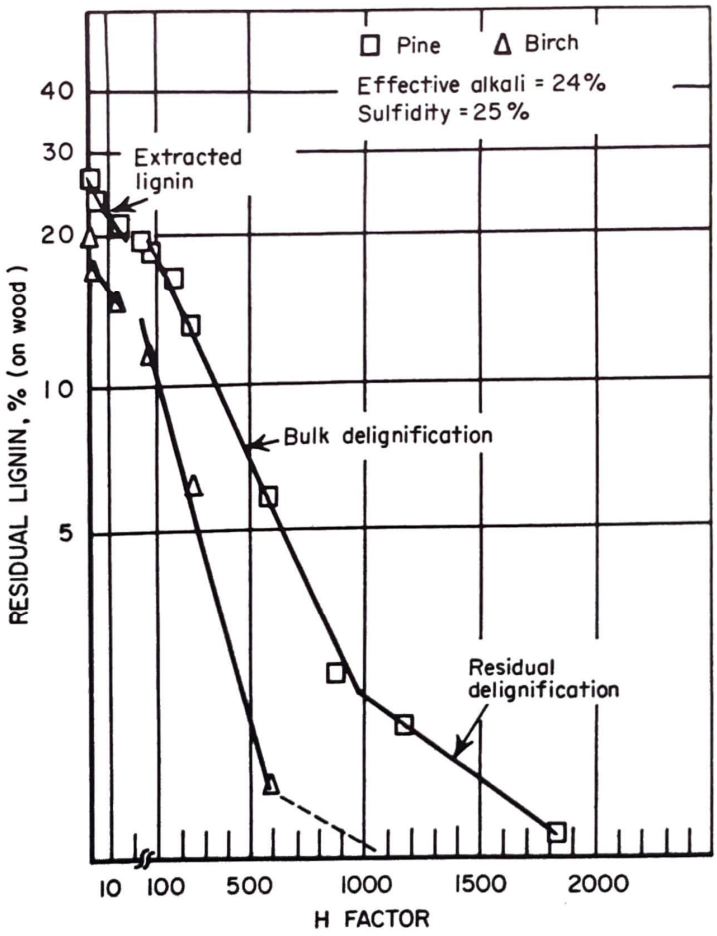


Figure 8. Bulk, and residual delignification phases. Initial phase is indicated as "extracted lignin" phase (Smook, 2002).

Reactions in kraft cooking can be divided into reactions of lignin, carbohydrates, and extractives. In pulping the lignin macromolecule degradation and solubilization is a wanted reaction but the carbohydrate degradation must be mitigated. Extractive

dissolution is important, to avoid issues such as pitch problems in the product, inferior delignification, reduced penetrability of cooking chemicals and toxicity of effluents (Sixta *et al.,* 2006). The reactions of these components can be analyzed with a variety of different analysis methods. Results of these analyses provide information on the effectiveness of pulping, as well as the qualitative and quantitative attributes of the pulp. These methods are reviewed in subchapter 5.3.

In kraft pulping the effect of cooking time and temperature can be expressed with a single variable, H-factor (Equation 1). The H-factor is used to estimate the cooking time needed at certain temperature to reach the desired kappa number. For example, if the cooking time or maximum temperature differs from the target value, the cooking time can be corrected by utilizing the H-factor (Rydholm, 1965).

$$H = \int_0^t e^{43.2-\frac{16113}{T}}\, dt \qquad (1)$$

Where T is temperature in K and t is time in h. Typically, the accumulated final H-factor value is between 1000 to 1500 (Alén, 2000).

Other important parameters in kraft cooking are:

- Effective alkali (EA)
- Active alkali (AA)
- Sulfidity (S)

Effective alkali is the concentration of alkaline constituents in the white liquor (Equation 2). In practice it is considered as concentration of OH^- -ions, including hydroxyl ions formed from sulfides by hydrolysis.

$$EA = NaOH + 0.5 * Na_2S \quad (2)$$

Active alkali is the total concentration of alkaline constituents, except carbonates. It is used to express sulfidity, which is the ratio between sodium sulfide and active alkali used (Equations 3 & 4) (SCAN-N:2 88).

$$AA = NaOH + Na_2S \quad (3)$$

$$S = \frac{Na_2S}{AA} * 100\% \quad (4)$$

These parameters are used in kraft cooking to express and calculate concentrations of active cooking chemicals (Sixta *et al.,* 2006).

5.1 Lignin and carbohydrates in kraft pulping

Lignin depolymerization and solubilization due to cleavage of β-O-4 -bonds is the most desired reaction during delignification. In lignin new carbon-carbon -bonds can also be formed, which will have effect on solubility and reactivity. This is referred to as condensation reaction (Brunow, 1977). To have pulp with acceptable brightness level, lignin must be either removed with delignification or residual lignin freed from light absorbing groups with bleaching (Sjöström, 1993).

Carbohydrates in pulp consist of cellulose and hemicelluloses. In the alkaline conditions of kraft pulping, carbohydrates undergo multiple reactions, which influence the

degree of polymerization and therefore pulp quality (Biermann, 1996). The degree of carbohydrate degradation is highly dependent on the morphology, crystallinity, and degree of polymerization. Cellulose, which has a high crystalline nature and degree of polymerization, is more resistant to degradation than hemicelluloses. Most carbohydrate losses during kraft pulping are due to hemicelluloses (Alén, 2000).

The carbohydrate degradation can be divided into end-wise peeling, oxidative peeling, and alkaline hydrolysis. In end-wise peeling reaction the terminal sugar unit is peeled off, creating a new reducing end group. Depending on the conditions, the reaction peels off 50-60 sugar units before saccharinic acid group forming stopping reaction occurs. Oxidative peeling takes place when keto or aldehyde groups are present in the polysaccharide chain. The cleavage of glycosidic bond via β-elimination forms a new reducing end group. The reducing end group peeling reaction will eventually be stopped by formation of stable non-reducing end and stable acid group (Sixta *et al.,* 2006).

Alkaline hydrolysis is an important reaction at higher temperatures of 160 -170 °C. It is a relatively slow reaction where glycosidic bonds are randomly cleaved forming new reducing end-groups. These reducing end-groups can lead to secondary peeling reactions (Alén, 2000).

Most of the carbohydrate losses occur during the heating-up period of cooking. The hemicelluloses, which are much more susceptible to peeling, will go through deacetylation. These acids formed from the carbohydrates will influence the alkaline content on cooking liquor (Sixta *et al.,* 2006). Hexenuronic acid groups (HexA), which are formed from 4-O-methylglucuronic acid groups of xylan in certain cooking conditions, are known to increase bleaching chemical consumption as well as contributing to the kappa number of pulps (Alén, 2000).

Besides carbohydrate degradation, xylan is known to readsorb at certain conditions from black liquor to fibre (Sjöström, 1993). Ribe *et al.,* (2010) have studied sorption

of birch black liquor xylan into unbleached softwood kraft fibres and found that at high cooking temperature (167 °C) xylan precipitated into the fibre surface.

5.2 Extractives in kraft pulping

According to Gardner & Hillis, (1962), the high content of extractives in kraft pulping process is unwanted due to reduction of yield, increased chemical consumption, inhibition of pulping reaction and corrosion of equipment. Therefore, an efficient removal of extractive-rich bark is mandatory. Still, extractive problems are typical in kraft pulp mills due to difficulties in debarking and extractives control in the process (Ukkonen, 2020). Common resin-related issue encountered in kraft pulp mill is the deposition of wood resin and other compounds on the surfaces of process equipment. These deposits may end up in final pulp product causing defects in pulp quality (Allen, 2000).

Most of the wood extractives are known to dissolve fast in the cooking liquor and retained to only a slight extent by the produced pulp. Therefore, pulpwood with unusually high extractives content and normal lignin content will result in lower pulping yield on weight basis (Gardner & Hillis, 1962).

Even though extractives are considered impurities, they are utilized in kraft process as valuable by-product of pulp production (Pensar, 1977). These products are e.g., crude turpentine and raw tall oil from softwood. For example, the yield of tall oil obtained from resinous woods is around 30-50 kg per ton of pulp (Alén 2000).

Ström (2000) divides extractives into two categories according to their behaviour in aqueous environment: organic acids and neutral components. Organic acids include fatty and resin acids and neutral components include glycerides and steryl esters of fatty acids. Organic acids have high solubility in water at higher pH values, but neutral components tend to remain insolubilized in aqueous environment.

Extractives in softwood kraft pulping can be divided into two groups according to their behaviour in kraft process: a volatile fraction (crude turpentine) and non-volatile fraction (tall oil soaps). Turpentine and tall oil are the two most important by-products in softwood kraft pulping (Alén, 2000).

Crude turpentine is a volatile compound that is recovered from the digester relief condensates. It is composed primarily of monoterpenes α-pinene and β-pinene but contains also minor amounts of 3-carene and other terpenes. Crude turpentine is purified by distillation to remove impurities such as methyl mercaptan and dimethyl sulfide (Sjöström, 1993).

Tall oil soap is composed of sodium salts of resin and fatty acids and unsaponifiable components. (Drew & Propst, 1981). These components include alcohols, aldehydes, fatty alcohols, and sterols (Ekman & Holmbom, 2000). The tall oil soap is recovered from the black liquor by skimming. Because of the salt content, the soap separates from the water phase and can be collected from the top of the black liquor. Sulfuric acid is added to tall oil soap to create crude tall oil (CTO). CTO must be vacuum distilled to obtain distilled tall oil (Pensar, 1977).

Purified tall oil is used in a wide range of applications, e.g., soap, lubricants, surface active agents and paper sizings. The yield and chemical composition of tall oil depends on the wood species, the method and duration of chip storage and the maturity of raw material when harvested (Smook, 2002).

Birch is a hardwood species that has high extractive content, and it has been considered a challenging wood to pulp due to its high content on unsaponifiable extractives and the lack of resin acids (Ekman & Holmbom, 2000). In alkaline conditions the saponifiable organic acids dissociate and dissolve into the cooking medium forming soaps. These soaps can form micelles, which are able to solubilize other non-soluble components, e.g., sterols. (Ström, 2000).

In birch the saponifiables-unsaponifiables – ratio is around 2:1, when e.g., pine has a ratio around 10:1. This ratio is used as an index for predicting pitch problems. It is estimated that to completely solubilize unsaponifiables in kraft pulping, the ratio should be about 3:1. Therefore softwood tall oil or black liquor is added as an additive in hardwood kraft cook to promote the soap formation by the presence of resin acids. During the cooking it is crucial to maintain alkalinity of the pulp suspension to allow saponification to occur. If at the end of the cooking, there is no residual alkali, the deresination is hindered and pulp quality is compromised (Ekman & Holmbom, 2000).

5.2.1 Extractive control in pulping process

Extractive control in kraft pulp mills starts from the seasoning of wood. During the seasoning the extractive content decreases, which has advantages and disadvantages. In the case of softwoods, decreased extractive content leads to decreased yield of tall oil (Allen, 2000). A few weeks' storage of pine chips lead to about 50% decrease in turpentine yield due to evaporation of volatile terpenes. Even though the evaporation is slower for roundwood than chipped wood, it is beneficial to pulp the material after felling as soon as possible without seasoning (Ekman, 2000). Wood will also undergo microbiological degradation, where micro-organisms invade wood and degrade polysaccharides. This leads to reduced pulp yield (Sjöström, 1993).

Aspen and birch have high resin content, with high unsaponifiables to saponifiables ratio. These species benefit from seasoning and should be seasoned for about six months as roundwood to have better pitch control in the process (Allen *et al.,* 1991). Figure 9 illustrates the amount of dichloromethane extractives of pulp as a function of storage time of chips.

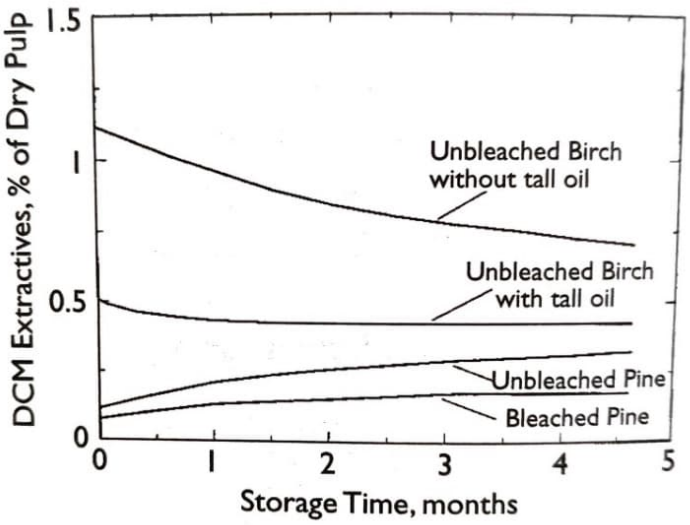


Figure 9. Dichloromethane-soluble extractives content of pulps as a function of storage time of chips prior to pulping. Addition of tall oil to digester improves deresination of birch (Allen, 2000).

The effect of wood extractive removal prior to kraft pulping has been studied by Baptista *et al.,* (2006) and the results indicate that pulping after extraction with organic solvents shows better results in terms of ISO brightness. When using acetone and mixture of ethanol-toluene (1:2), the ISO brightness reflectance factor improved by 7% compared to kraft-pulped reference material.

Shin *et al.,* (2004) have studied the effect of residual extractives on lignin determination of kraft pulps. By analysing the effect of residual extractive content contribution to kappa number and acid-soluble lignin content, they concluded that significant amounts of extractives were present in hardwood kraft pulps. They concluded that the contribution of residual extractives on kappa number of unbleached birch kraft pulps were 11.3-13.8%. The main residual components are sterols and sterol esters, which were not extractable by chosen ethanol-benzene (1:2, v/v) solvent. This indicates that ethanol-benzene can extract mainly lipophilic substances. According to Nisula (2018), acetone can extract both lipophilic and hydrophilic components.

5.3 Pulp and black liquor analysis and characterization

The most relevant parameters for characterizing the pulped material and black liquor in this thesis are:

- Unscreened yield
- Kappa number
- Intrinsic viscosity
- Residual alkali

The unscreened yield indicates the amount of material degraded during the pulping process. Screened yield on the other hand is used to calculate yield after reject screening. Kappa number is used to indicate the residual lignin content or bleachability of the pulp by oxidizing lignin structures. It is notable that all compounds, especially HexA in a case of birch pulp, oxidized by potassium permanganate ($KMnO_4$) will increase the consumption of $KMnO_4$ and therefore increase the kappa number (ISO 302:2015).

Intrinsic viscosity gives an indication of the average degree of polymerization of cellulose and hemicelluloses. Therefore, it can be used for indicating the degree of carbohydrate degradation in the pulping process. (Sixta *et al.,* 2006).

Residual alkali content in black liquor is an important process parameter. It measures the alkali left at the end of the cook and indicates the amount of alkali consumed during pulping (Milanova & Dorris, 1994). Sufficient alkali concentration at the end of the cook is required to avoid e.g., precipitation of lignin but excessive alkali should be avoided to maintain the economic feasibility of the process (Ulmgren *et al.,* 1994). Typical range for residual alkali varies between 7-9 NaOH g/l (Ribeiro *et al.,* 2018).

These analyses are conducted in the experimental part to assess the effect of extractive removal on birch kraft pulp.

6 Experimental

The structure of experimental part of this thesis is illustrated in the Figure 10. The raw material for the experiments was birch (*Betula sp.*), which was felled in Helsinki in December 2020. After felling the birch was cut into 1 m long logs and wrapped in plastic to prevent any reactions with ambient oxygen. These pieces were stored in freezer (-18 °C).

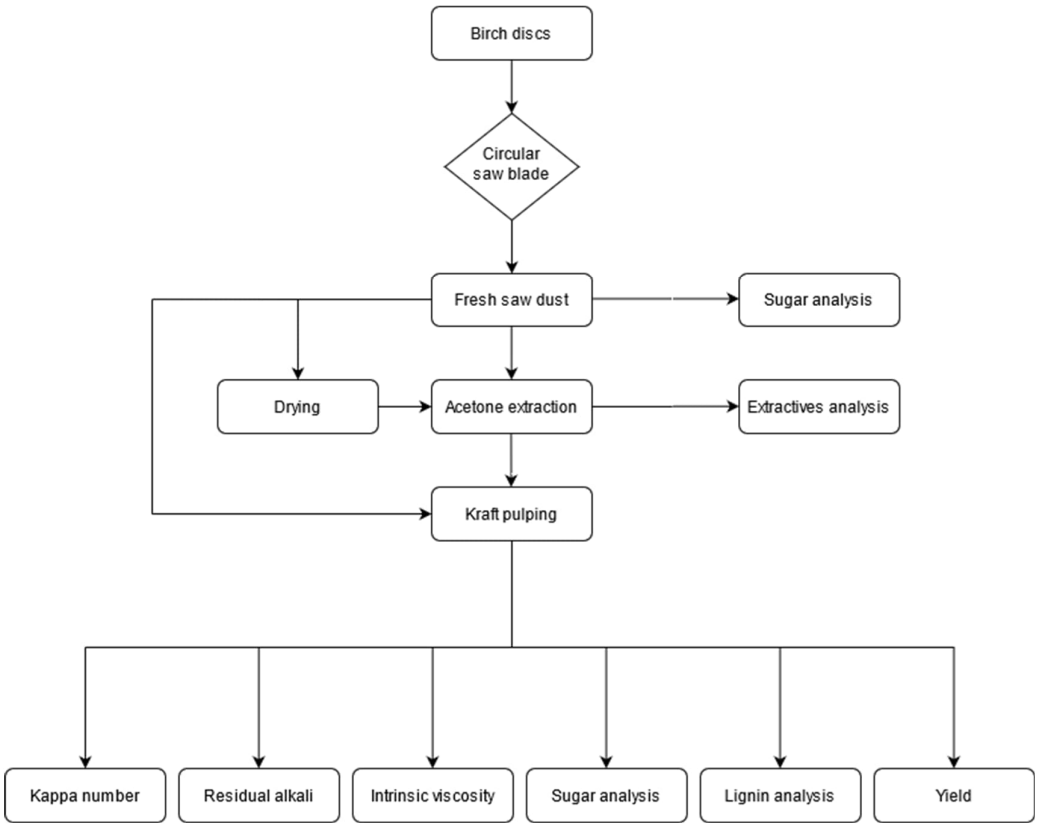


Figure 10. Flow chart of the experimental work.

6.1 Wood pretreatment

One birch (*Betula sp.*) log with diameter approximately 20 cm, *ca.* 6 m from the ground, was cut into 5 cm thick discs with chainsaw. The chainsaw blade was lubricated with synthetic chain oil, and it was assumed that some of the oil may have transferred into the birch discs. Discs were exposed to ambient air for 10 minutes, until they were sealed air-tightly in plastic bags to avoid reactions between extractives and oxygen. Sawn discs were stored in freezer (-18 °C).

For determining the dry-matter content and to produce material for pulping, birch discs were sawn with Strands S53L pillar drill to produce saw dust. The particle size was not determined but the material was closer to wood dust than chipped wood. Dry-matter content was determined according to standard SCAN-CM 39:94. Due to the low density of saw dust material, dry-matter content was determined by having two samples of 5-10 o.d. g each.

6.2 Extraction

Part of the saw dust was put into freezer as a fresh material and part was dried for 72 h in a fume hood. Dry matter content of the dried material was determined prior to the extraction. It is notable that saw dust was produced in batches according to the need of saw dust in experiments.

Chosen solvent for the extraction was acetone, since Baptista *et al.* (2006), concluded that extractions with acetone were the most efficient. Both fresh and dried saw dust were extracted with acetone to assess the effect of drying to pulping. Table 4 illustrates the chosen methods of extraction and possible pre-treatments.

Table 4. Sample names with corresponding pre-treatments.

Sample name	Pre-treatment	Solvent extraction
Dry_None	Air drying	None
Fresh_None	None	None
Dry_Acetone	Air drying	Acetone
Fresh_Acetone	None	Acetone

Extraction was run in two different batches for 24 hours in a closed container in a fume hood in room temperature. Magnetic stirrer was utilized to allow good mixing and uniform impregnation of solvent. Solvent extractions were performed for 100 g of oven-dry wood with acetone/dry wood ratio of 20:1 (ml/g). Different water content in fresh and dried saw dust was compensated in latter batch by adding water in dried birch saw dust extraction. After 24 hours, acetone was removed from sawdust samples with Büchner funnel. Small amount of acetone sample from each extraction was stored for further extract analysis. Pure acetone was used for washing the extracted sawdust to enhance extractive removal. Extracted sawdust was left to dry in a fume hood for 24 hours, after which the sawdust was stored in airtight plastic bags at room temperature.

Figure 11. Acetone-extraction for dried and fresh birch saw dust. Extractions were carried out in a closed containers to avoid evaporation of acetone.

6.3 Pulping

Pulping was carried out in two separate experiments, using Haato Air Bath Digester. The digester was equipped with six identical autoclaves with volume of 2.5 litres each. The amount of saw dust pulped was 40 o.d. g per each autoclave. Only one autoclave was equipped with thermometer, but the same temperature was assumed to be in all autoclaves. The number of parallel samples was 4 for acetone-extracted samples and 2 for non-extracted samples. Same pulping parameters were used in both experiments, which are illustrated in Table 4. Actual H-factors were recorded according to realised values calculated by computer connected to the digester thermometer.

Table 4. Pulping parameters for the pulping experiments.

Parameter	Experiment 1 and 2
L/S	10:1
Sulfidity	38%
Active alkali	30%
Cooking temperature	168 °C
Desired H-factor	1000

Prior to the pulping experiments, a preliminary pulping experiment was conducted for determining suitable level of active alkali. The parameters of preliminary experiment can be seen in Table 5. The goal was to have high enough residual alkali content to reach a kappa number range of 10-20.

Table 5. Pulping parameters for the preliminary pulping experiment.

Parameter	Preliminary experiment
L/S	10:1
Sulfidity	38%
Active alkali	26.4%
Cooking temperature	168 °C
Desired H-factor	1000

After pulping, autoclaves were left to cool in water bath before opening. Black liquor samples were taken from each autoclave by draining the pulped material in a wire cloth bag. The black liquor samples were stored in plastic bottles from which air had been squeezed off to avoid the oxidation of black liquor. Drained pulp samples were washed with 3 litres of deionized water prior to homogenization and weighing. Both pulp and black liquor samples were stored at 4 °C for further analyses.

6.4 Characterization of pulp and black liquor

6.4.1 Raw material analysis

Dry-matter content was determined for produced saw dust for extraction and pulping calculations. Untreated sawdust was analyzed to determine content of extractives according to SCAN-CM 49:03 standard method (Soxhlet extraction with acetone). To determine possible residual extractives content, Soxhlet extraction was performed also to the dried and fresh saw dust samples, which had been extracted with acetone in room temperature. The isolated extractives of dried and fresh saw dust samples were analyzed with PerkinElmer Spectrum Two FT-IR spectrometer to assess possible differences in chemical compositions.

6.4.2 Black liquor analysis

Black liquor samples were analyzed for residual alkali with Metrohm OMNIS titrator by titrating samples with 1 M hydrochloric acid (HCl). The analysis was carried out according to the standard method SCAN-N 33:94. Black liquor pH values were measured with the same equipment at the same time as the residual alkali analysis. Method NREL/TP-510-42618 (Sluiter *et al.,* 2008) was used to analyze carbohydrates of black liquor with Dionex ICS-3000 anion exchange chromatography system.

6.4.3 Pulp analyses

Total yield of pulping was determined by weighing the wet pulp and calculating the dry-matter content. Pulped material was analyzed to determine kappa number, viscosity, structural carbohydrates, and lignin. Kappa number was analyzed according to SCAN-C 1:00 standard, viscosity according to SCAN-CM 15:99 standard and structural carbohydrates and lignin according to method of NREL/TP-510-42618 (Sluiter *et al.,* 2008). Carbohydrate analysis was performed with Dionex ICS-3000 anion exchange chromatography system.

7 Results and discussion

7.1 Raw material

The composition of birch (*Betula sp.)* raw material is shown in Figure 12. Minor hemicelluloses galactose, arabinose and mannose are all included in other carbohydrates. Other compounds, which include inorganic material and acetone-insoluble compounds, are determined by subtracting all other components from 100%.

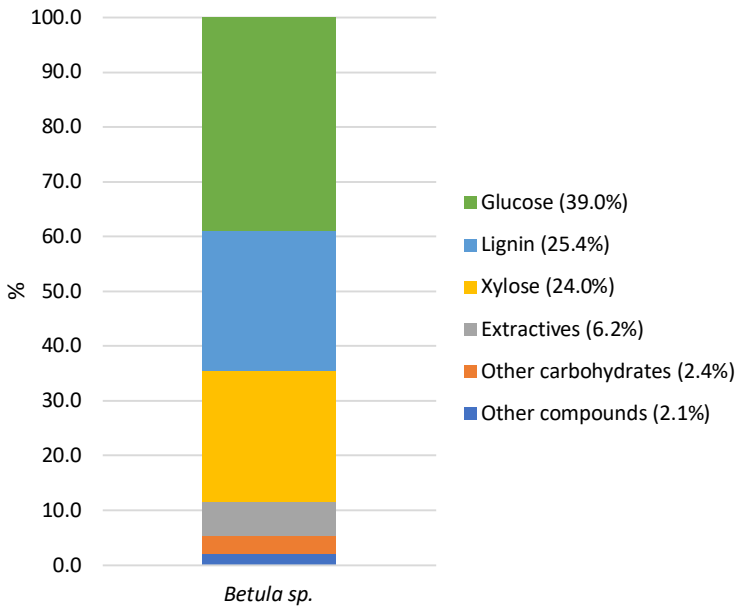


Figure 12. Composition of birch (*Betula sp.*) used as a raw material in the experiments.

According to Sixta *et al.,* (2006), silver birch (*Betula pendula*) carbohydrate content of wood dry solids is 73.6%, from which glucose and xylose contents are 39.7% and 22.1%, respectively. The lignin content is 23.3% and dichloromethane-extractable extractives content 1.9%. Results obtained from experiments are consistent with the values from literature except for the extractives content. Unlike dichloromethane, acetone is known to dissolve lignans and monosaccharides along with extractives

(Björklund & Nilvebrant, 2009); therefore, it is reasonable that the values from this experiment are higher.

Content of extractives determined from non-extracted and extracted samples with standard SCAN CM-49:03 are illustrated in the Table 6.

Table 6. The amount of acetone-soluble extractives of saw dust samples.

Sample	**Extractives content (w/w%)**
Dry_None	6.20
Fresh_None	5.22
Dry_Acetone	1.11
Fresh_Acetone	1.18

As the typical amount of extractives in silver birch extractives range from 1.0 to 3.5% of the wood dry solids (Alén, 2000), the amount of extractives in dried and fresh non-extracted saw dust samples are distinctly high. Because the standard method used is applicable for wood chips and pulp, the results obtained for saw dust are likely to differ from the values obtained from the literature. Since the lower limit of quantification in standard CM-49:03 is 0.5%, some residual extractive material is likely to still be present in the acetone-extracted samples. Nonetheless, results indicate that 24-hour pre-extraction with acetone lowered the amount of extractives in saw dust approximately 4 to 5%. Minor amount of extractives may still be present in the already acetone-extracted samples.

Gravimetric analysis of extracted compounds in acetone indicate that dried and fresh acetone-extracts obtained in 24-hour acetone-extraction contain 3.56% and 3.53% of acetone-soluble extractives, respectively. As the extraction was carried out in room temperature, it is likely that the extraction process is not as efficient compared to the standard method SCAN CM-49:03.

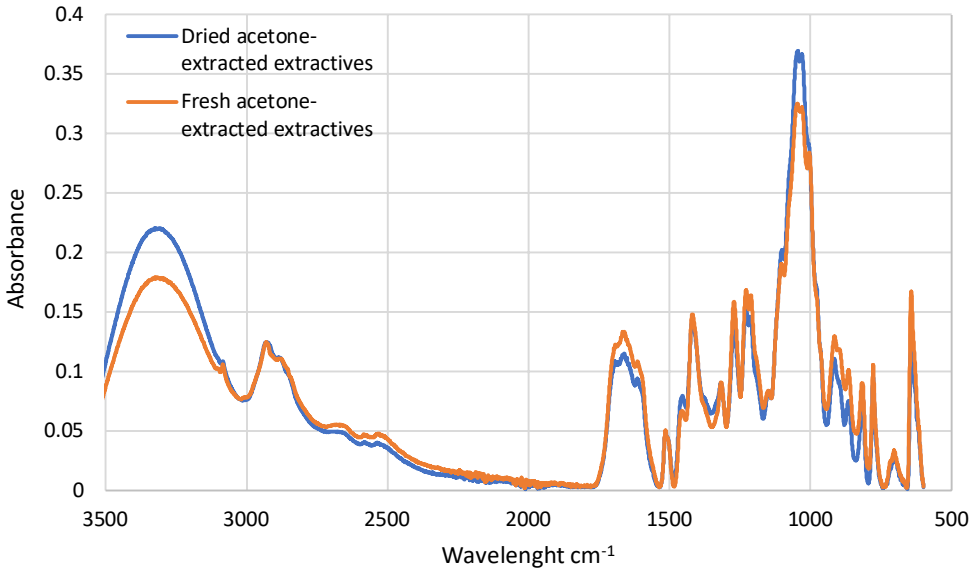


Figure 13. FT-IR spectra of extractives.

FT-IR spectra of the extracts are illustrated in Figure 13. Since both samples were filtered in identical procedure of using vacuum filtration and filtering paper with particle retention value of 11 µm, resulting filtrates were considered to be free from solid material.

The focus is on the fingerprint region between 1800 cm^{-1} and 800 cm^{-1}, where most of the molecular bond vibration variations occur (Pandey & Pittman, 2003). In both spectra, multiple absorbance peaks are observable between wavelengths 1700 cm^{-1} and at 600 cm^{-1}. Outside fingerprint region, a notable absorbance peak can be observed at 3300 cm^{-1}. Comparison of both spectra reveals no major peak differences at any specific wavelength, but further chromatographic analysis would be needed to identify compounds present and to quantify the actual amounts. However, this type of analysis is beyond the scope of this thesis.

7.2 Pulping

Sulfidity, cooking temperature and desired H-factor were chosen based on previous experiments done in the laboratory. The highest recorded temperature in the autoclave was 169.7 °C in experiment 1 and 169.4 °C in experiment 2. The recorded H-factors were 1023 and 1005, respectively. Table 7 shows the pulping conditions and realized temperatures and H-factors. Even though the thermometer was only measuring one autoclave, it is assumed that the same temperature and H-factor can be applied to all autoclaves. Temperature and H-factor profiles of pulping experiments are presented in Appendix I.

Table 7. Pulping conditions and recorded H-factors.

	Experiment 1	**Experiment 2**
Sawdust (o.d. g)	40	40
L/S	10:1	10:1
Sulfidity %	38	38
Active alkali %	30	30
Cooking temperature °C	169.7	169.4
H-factor	1023	1005

After the pulp was washed, total yield was determined gravimetrically. As seen in Figure 14, the highest yields were obtained in pulp samples produced from dried and fresh acetone-extracted saw dust. According to Alén (2000), the total cooking yield of conventional birch (*Betula pendula/Betula pubescens)* kraft pulping is 47% of the dry wood material. The yields reported below are relatively close to the values found from the literature. The accuracy of yield results has to be considered since the manual work involved included emptying wire cloth, homogenizing sample in mixer and transferring sample to plastic bag.

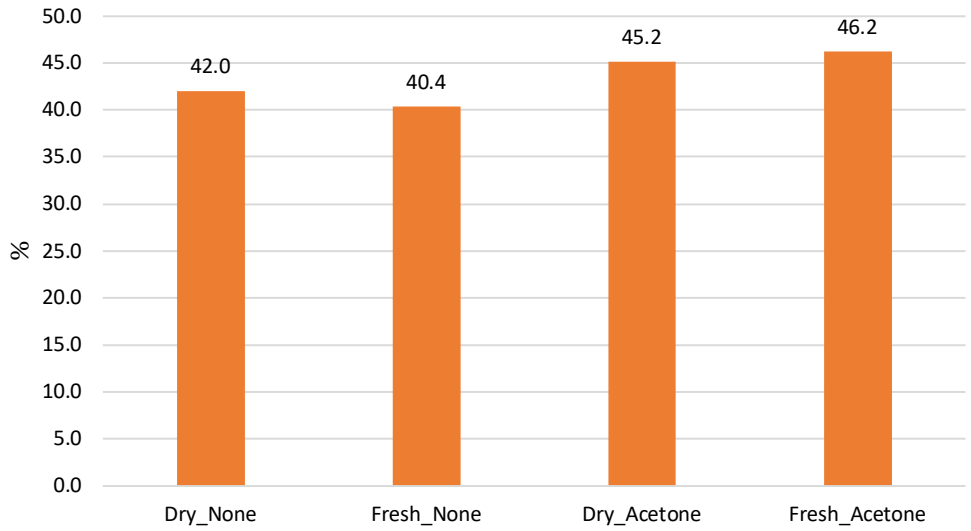


Figure 14. Pulping yields of the experiments

As the quantitative analysis of extractives indicated the extractive content to be around 6%, the increase in the pulp yield can be explained to some extent by the absence of extractives. The obtained values from the extraction analysis must be carefully interpreted, since the variation of extractives content in different tree parts can be substantial (Hillis, 1962). Routa *et al.,* (2017) had determined total extractive content of birch stemwood to be 0.5-1.5% and Alén (2000) reports silver birch (*Betula pendula*) extractives to range between 1.0 to 3.5% of the wood dry solids. This could indicate that the absence of extractives may not fully explain the higher pulping yield in pulp produced from acetone-extracted saw dust. One hypothesis for higher yields is the presence xylan, which would have dissolved in black liquor in polymerized form. Hardwood kraft pulp is known to have relatively higher yield compared to softwood kraft pulp due to readsorbtion of xylan back to fibre (Sjöstrom, 1993). Other reason for higher for higher hardwood yields is the stability of xylan against peeling reactions when compared to softwood hemicellulose glucomannan. Xylan dissolved in black liquor as polymerized form would not only enhance pulping yield but also decrease alkali consumption in pulping since the amount of alkali-consuming carbohydrates in pulping medium would be lower. This is covered in subchapter 7.3., where the alkali consumption is discussed.

7.3 Black liquor

Analyses of black liquor were done day after the pulping to minimize the effect of oxygen during the storage. All the results were converted to g/l of NaOH.

As can be seen in the Figure 15, alkali consumption is highest in the samples where extractives have been removed.

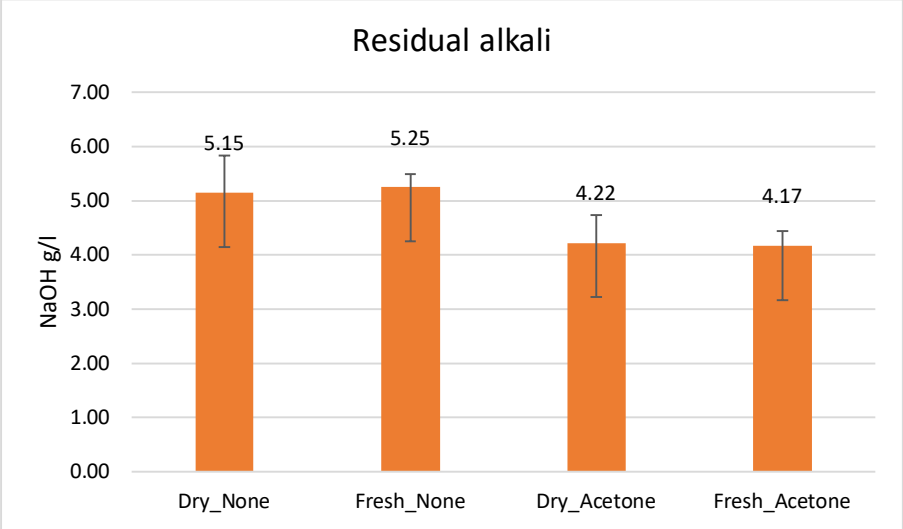


Figure 15. Results from residual alkali analysis with corresponding standard deviations.

Gardner & Hillis (1962) state that extractives present in the wood increase the consumption of sodium hydroxide in kraft pulping, along with the reduced lignin solubility and reduction on yield. The contradictory results presented here suggest that the increased consumption of alkali may not be due to presence of extractives. The possible explanation for increased alkali consumption might be linked to carbohydrates. Experiments by Ribe *et al.*, (2010) suggest that at higher temperatures (167 °C) xylan from birch black liquor most likely precipitates on the unbleached softwood kraft fibre surface as globular xylan aggregates. This may indicate that the xylan forms globular aggregates in the black liquor. Figure 16, which illustrates the carbohydrate composition of black liquor, indicates lower xylose concentrations in black liquor of acetone-extracted samples. This may indicate that the polymerized xylan could be readsorbed in the pulp and thus decrease the amount of xylose in black liquor.

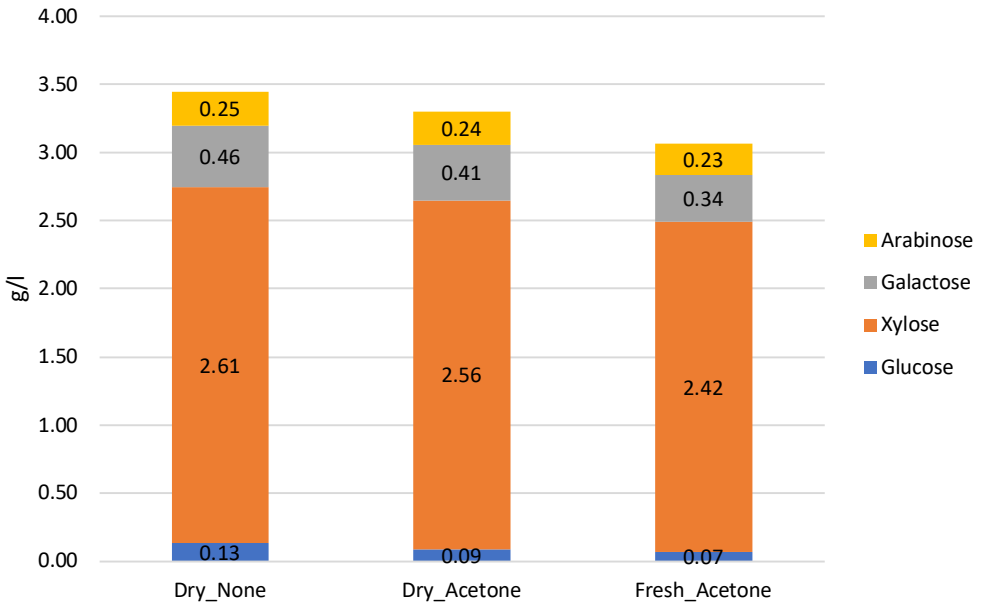


Figure 16. Carbohydrate content of black liquor samples. Absence of Fresh_None sample results is due to breakage and maintenance of analysis device.

If the absence of extractives in pulping would promote peeling reactions in xylan and at the same time enhance xylan readsorbtion back to fibre, it would lead higher alkali consumption as well as lower xylose content of black liquor. The presence of xylan in pulped material is discussed in subchapter 7.6.

7.4 Kappa number

After the preliminary pulping experiment which yielded high kappa numbers as seen in the Appendix II, kappa number of Dry_None sample was set between 13-25, which is almost in the range of typical unbleached hardwood kraft pulp (Roudier *et al.*, 2015). With the chosen pulping parameters, the highest kappa numbers were obtained for pulps prepared from acetone-extracted saw dust.

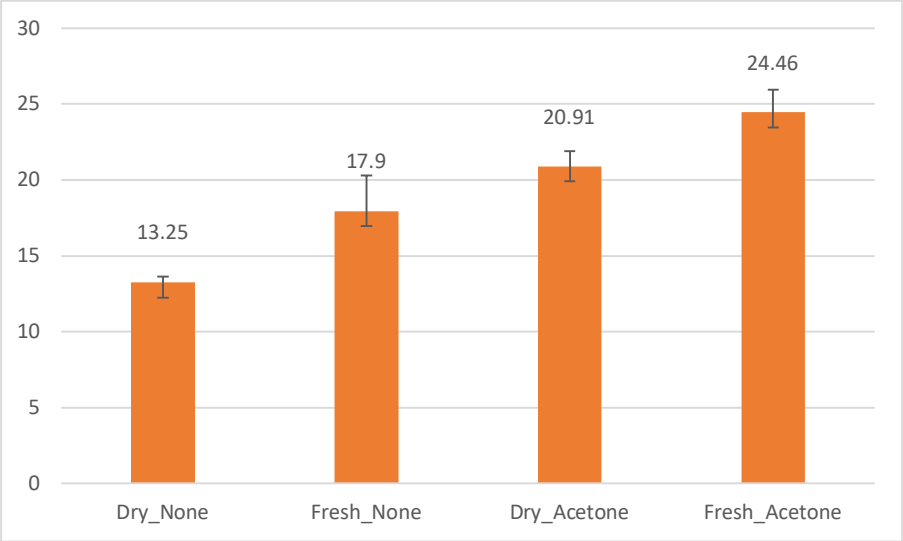


Figure 17. Results from kappa number analysis with corresponding standard deviations.

The higher kappa numbers indicate that the pulps prepared from acetone-extracted saw dust contain more oxidizable components compared to the pulps prepared from saw dust containing extractives. Since there is no unambiguous correlation between kappa number and lignin content, the rise in kappa number values may be due to presence of hexenuronic acid.

Since the permanganate is known to oxidize HexA which would therefore contribute to the kappa number. According to study of Li & Gellerstedt (1997), kappa number contribution for unbleached kraft pulps per 10 µmol of hexenuronic acid is between 0.84-0.86 units. To have better understanding of hexenuronic acid content of pulps, a chromatographic analysis would be needed.

7.5 Viscosity

In the alkaline pulping process, majority of hemicelluloses dissolve in the pulping liquor. Since the hemicelluloses have lower degree of polymerization than cellulose, the presence of hemicelluloses in pulp would decrease the average degree of polymerization and thus decrease the viscosity. Cellulose is also degraded to some extent, but the crystalline structure of cellulose is more resistant towards alkaline media than hemicelluloses (Sixta *et al.*, 2006).

Viscosity results for sample Fresh_None are unexpectedly low when compared to results of other samples. Most likely the cause of low viscosity for fresh non-extracted sample is due to faulty chemical dosage in the particular autoclave. Therefore, the reported results for Fresh_None -sample are not entirely comparable to other samples. Viscosity analyses compiled in Figure 18 illustrate lower viscosity in Fresh_Acetone sample when compared to dried non-extracted sample. Since the coefficient of variation for the standard method used is 2.1% at viscosity level 1150 ml/g, viscosity value for Dry_Acetone sample does not significantly differ from the value of Dry_None sample. Possible explanation for lower viscosity of Fresh_Acetone sample might be due to readsorbtion of xylan from black liquor to fibre. The presence of xylan is discussed more in subchapter 7.6.

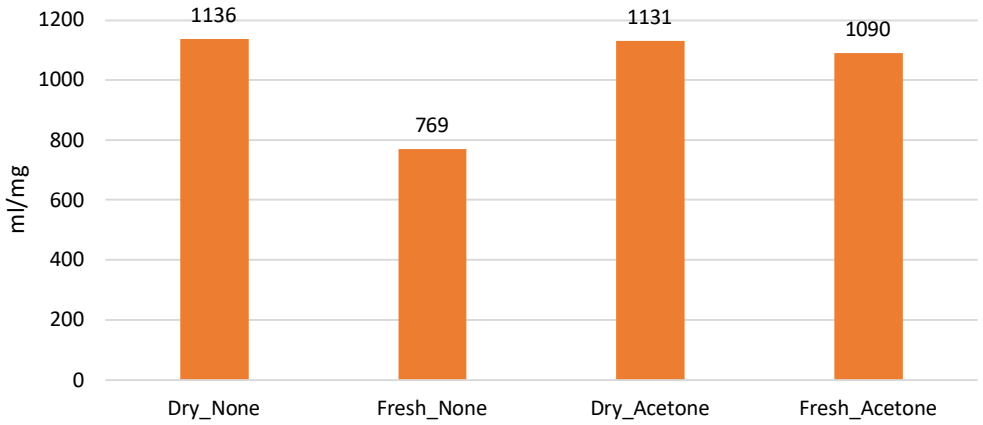


Figure 18. Compiled results from viscosity analyses.

7.6 Carbohydrate and lignin analysis

The composition of fresh wood and pulped samples is presented in Figure 19. Major components are presented individually but hemicelluloses rhamnose, galactose and mannose are presented as other carbohydrates. Other compounds, which are

determined by substracting all other compounds from 100% consist mainly of inorganic compounds. Due to inaccuracies in carbohydrate, extractives and lignin analyses, the amount of other compounds is quite high. Typical amount of inorganics in wood is typically 0.1 to 1% (Alén, 2000).

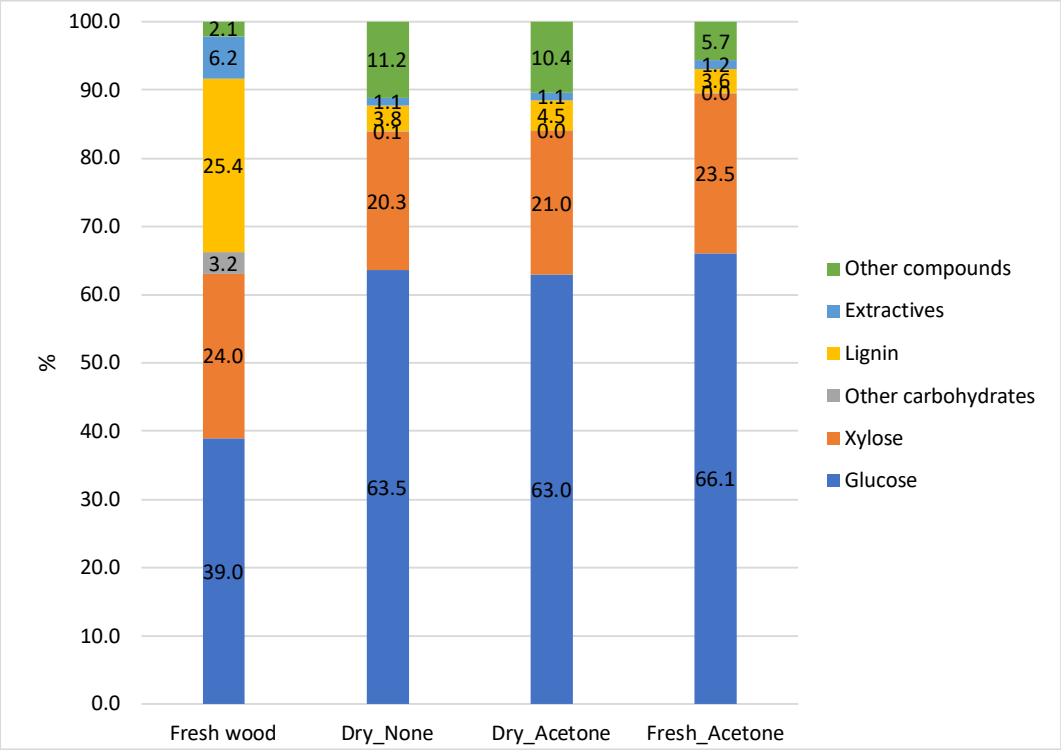


Figure 19. Composition of the original birch sample and the kraft pulps produced. Absence of Dry_Fresh -sample results is due to breakage and maintenance of the analysis device.

As can be seen (Figure 19), the amount of glucose is highest in Fresh_Acetone -sample. The higher amount of xylose compared to samples Dry_None and Dry_Acetone most likely influences the pulp viscosity. As the degree of polymerization for xylan is lower than cellulose, the relatively higher amount of xylose in pulp may lead to lower viscosity level. At the same time, when the amount of consumed alkali and pulping yield are high for acetone-extracted samples, it is likely that xylan readsorbtion has taken place.

The results from lignin analysis are illustrated in Figure 20. Level of acid-soluble lignin is relatively same for all the pulp samples, but the result for birch saw dust is

questionable. Since the typical amount of acid-soluble lignin in birch (*Betula pendula*) is around 4% (Sixta *et al.,* 2006), the value obtained is rather low. Since in this thesis only one individual wood was used, it is likely that there is variation in acid-soluble lignin content between individual trees.

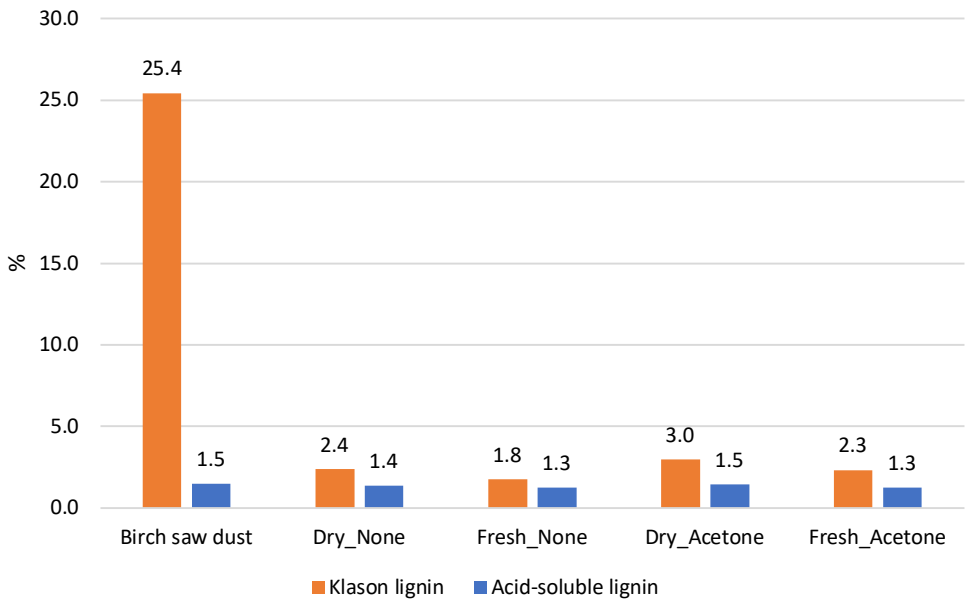


Figure 20. Acid-soluble lignin and Klason lignin contents of the samples.

Total lignin content of birch saw dust is close to the values represented in the literature, which range from 23 to 25% (Fagerstedt, 2015). The results for pulped samples are ambiguous. Typically, the total lignin content of unbleached pulp is less than 5%, but if the measured kappa values were justified only by lignin content, highest Klason lignin content in pulped samples would be in acetone-extracted samples. However, kappa number is determined by all compounds oxidized by potassium permanganate. Possible explanation for this inconsistency might be HexA formed from xylan during cooking, which would contribute to the kappa number of pulps.

8 Conclusions

The goal of this thesis was to study the effect of extractives on kraft pulping of birch wood. By having fresh and dried saw dust samples, both acetone-extracted and non-extracted, comparative analysis was made to assess the effect on pulping yield, viscosity, kappa number, residual alkali and carbohydrate content of pulp and black liquor. Also, the effect of acetone-extraction on extractives was analysed with infrared spectroscopy.

Acetone-extraction influenced measurable parameters of pulp and black liquor. As the 24-hour acetone extraction lowered the extractive-content of saw dust samples 4 to 5%, the total pulping yields of dried and fresh acetone-extracted samples were approximately 42.9 and 44.4%, respectively. The difference in non-extracted saw dust samples were 1 to 4%, average being approximately 2.5.%. This can be at some extent explained with higher xylan content in the pulps. The effect of 24-hour acetone extraction to lignin content of pulps was approximately 0.6%, or 0.3% when calculated from the saw dust. Differences in kappa numbers account approximately 1% difference in lignin and hexenuronic acid content of the pulps.

Possible explanation for higher kappa numbers for the pulp samples prepared from extractive-free wood was proposed to be the presence of hexenuronic acid. Since the determined lignin content did not unambiguously correlate with the obtained kappa number values, it is possible that hexenuronic acid contributes to the kappa number.

Higher xylose content of pulp produced from dried acetone-extracted saw dust is suggested to be the reason for higher yield, lower consumed alkali, and lower viscosity. If the xylan would readsorb back to fibre as polymer, the yield of pulp would increase. At the same time, consumed alkali as well as pulp viscosity would decrease, since the xylan with lower degree of polymerization would not consume alkali of black liquor. Most of the alkali is consumed by the cleavage of polysaccharides. This

is most likely because the 24-hour acetone extracted saw dust samples had higher polysaccharide content.

These observations suggest that birch extractives enhance the dissolution of xylan. The dissolved xylan, as well as cellulose, is cleaved more rapidly. At some extent this can be explained with Donnan's effect. The higher xylan content increases the anionic nature of cell wall, which would lower the alkali content in the Donnan-phase.

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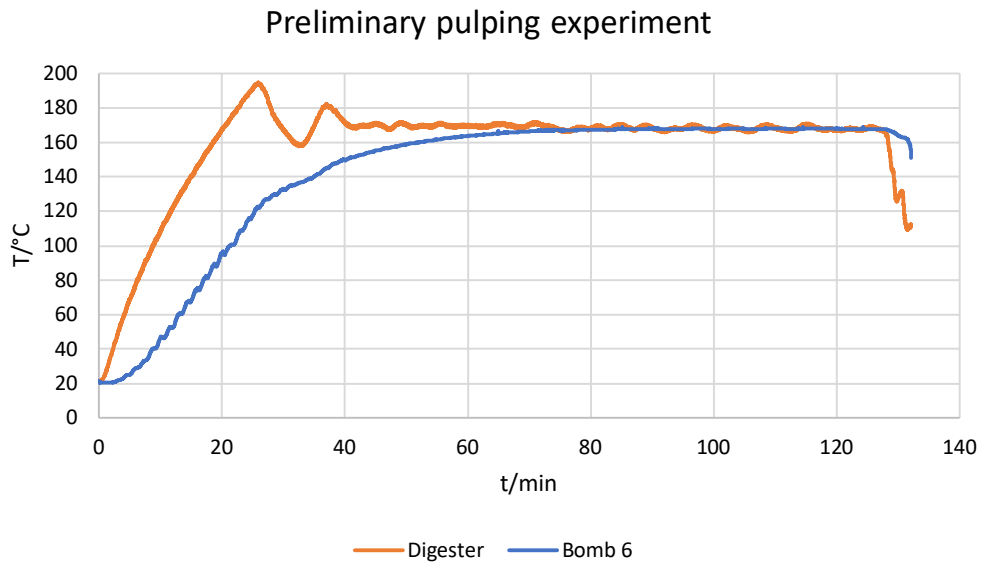
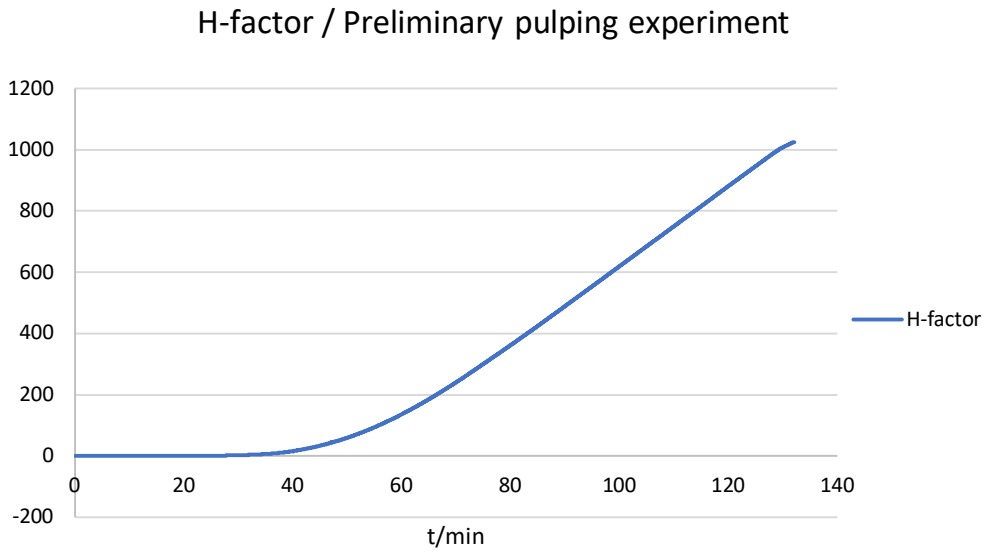
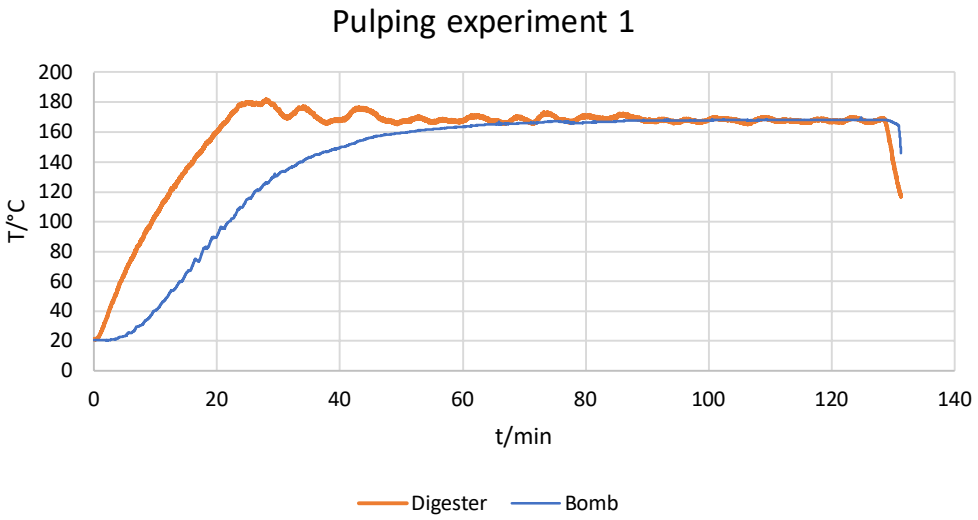
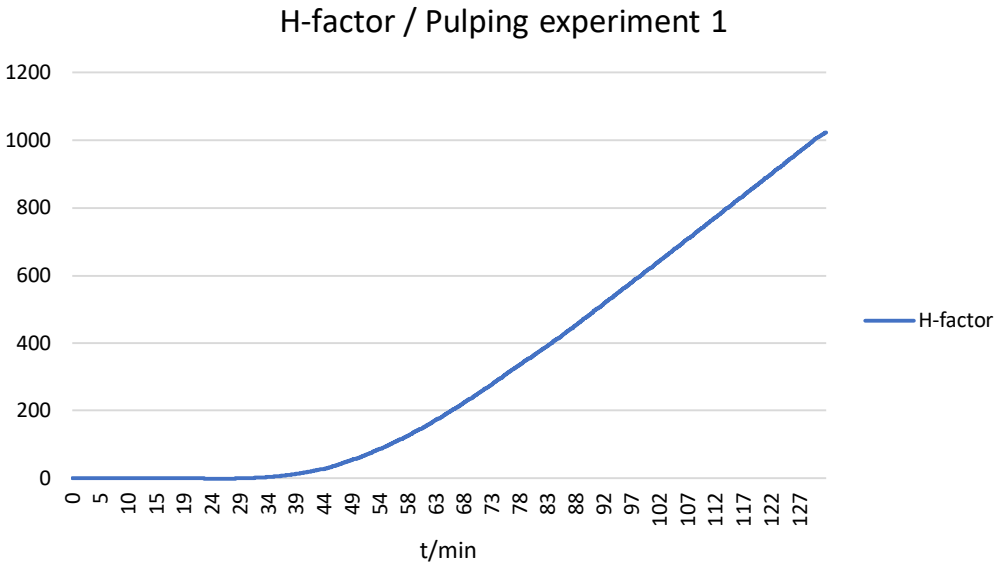
Appendix I

Temperature and H-factor profiles of pulping experiments






Pulping experiment 1
T/°C
200
180
160
140
120
100
80
60
40
20
0
0
20
40
60
80
100
120
140
t/min
Digester
Bomb


H-factor / Pulping experiment 1
1200
1000
800
600
400
200
0
0
5
10
15
19
24
29
34
39
44
49
54
58
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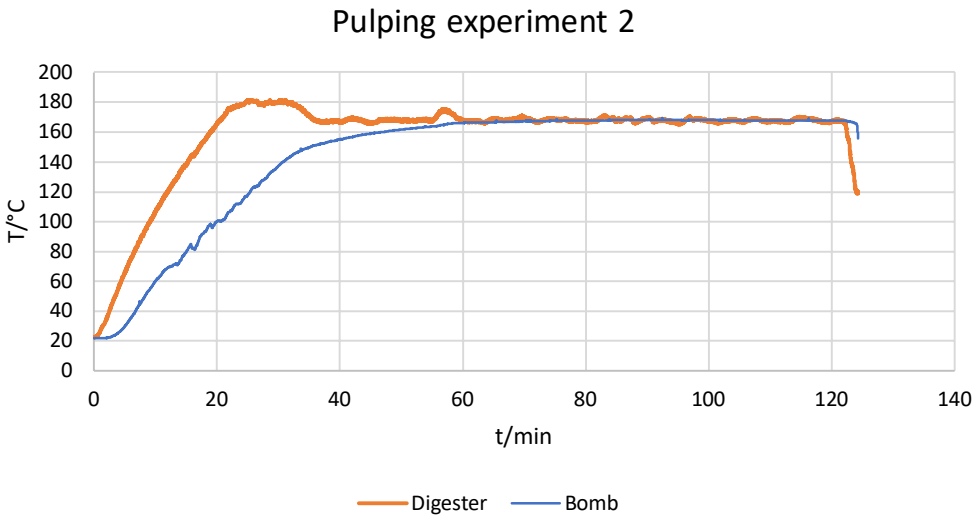
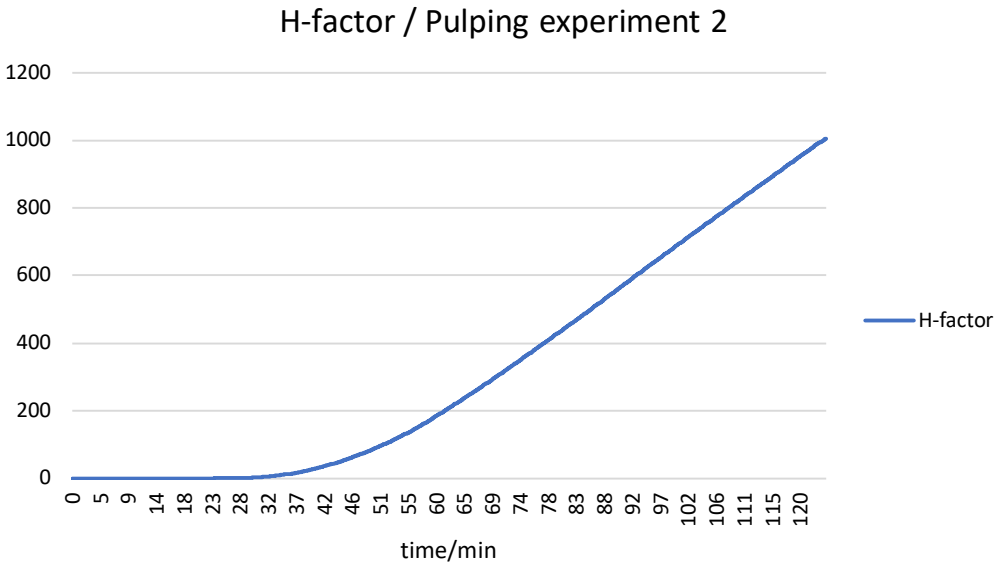
73
78
83
88
92
97
102
107
112
117
122
127
t/min
H-factor


Pulping experiment 2
T/°C
t/min
Digester
Bomb


H-factor / Pulping experiment 2
time/min
H-factor

Appendix II

Measured kappa number, residual alkali and intrinsic viscosity for the preliminary pulp and black liquor samples

	Dry_None	Dry_Acetone	Fresh_Acetone
Kappa number	33.06	27.88	44.77
Residual alkali NaOH g/l	2.24	2.47	1.40
Intrinsic viscosity ml/mg	1146	1082	1071