Roman Poschner, B.Sc.

Influence of pitch on paper properties

MASTER'S THESIS

to achieve the university degree of

Diplom-Ingenieur

Master's degree programme: Chemical and Pharmaceutical Engineering

submitted to

Graz University of Technology

Supervisor

DI Dr.techn. Jussi Antero Lahti

Univ.-Prof. Dipl.-Ing. Dr.techn. Ulrich Hirn

Institute of Bioproducts and Paper Technology

Graz, March 2020

STATUTORY DECLARATION

I declare that I have authored this thesis independently, that I have not used other than the declared sources / resources, and that I have explicitly marked all material which has been quoted either literally or by content from the used sources.

Graz, March 2020

Acknowledgments

At the beginning I want to mention that I am very grateful that I had the possibility to conduct my master’s thesis at the Institute of Bioproducts and Paper Technology (BPTI) at the Technical University of Graz. First of all, I would like to thank Prof. Dr. Wolfgang Bauer for giving me the chance to work in such an outstanding environment.

It was a privilege to work under the supervision of Prof. Dr. Ulrich Hirn. His professional advice and immense knowledge about fibre technology were more than helpful in various cases. I cannot imagine a better co-supervisor than Dr. Jussi Antero Lahti, who guided me throughout my thesis. It was a pleasure to work with him, therefore I want to express my sincere gratitude to him.

Furthermore, I want to thank Dr. Elisabeth Schwaiger from Mondi Frantschach as a representative for the industry partner. She, Dr. Matej Ravber and the lab team at Mondi Frantschach were more than supportive by providing advice, guidance and the necessary raw materials.

Additionally, I want to deeply thank Heidi and her lab team, consisting of Bianca, Kerstin, Manu, Sarah and Irmi, for supporting me with their knowledge and help during my laboratory work. Furthermore, I am grateful for the administrative and technical support by Claudia, Kerstin, Harry and Christian.

I am thankful for my work colleagues at the institute and the APV Activitas, who incorporated me into their social network and activities. The solidarity and team spirit of those people is inspiring. Special thanks go out to my friends that accompanied me throughout my university studies and made my student life as delightful as it was.

In the end, I hardly find any words to express how grateful I am for my family and my girlfriend Daniela. They have always supported me and had my back, whenever something did not work out as planned. After all the time I have learned that if everything breaks down, you can always count on your family!

Abstract

Carry-over lipophilic organic compounds from the pulp mill cause severe problems in the paper production process. The influence of those pitch compounds on softwood kraft pulp handsheets through laboratory simulation was investigated in this thesis.

GCMS-analysis of carry-over pitch compounds was conducted, showing that a major part of the carry-over pitch compounds are fatty acids, fatty alcohols and sterols. The most abundant pitch components were oleic acid, docosanol and β-sitosterol. Pitch dispersions of selected compounds were directly added to pulp suspensions to produce handsheets. In addition, trials with a strength agent (cationic starch) and a fixative (alum) were performed. The retained amount and compound itself defined how much strength decreased. While oleic acid proved to be the most harmful component, all compounds were harmful for the paper strength when alum was present. Starch increased in general the tensile strength, especially when alum was present. Some components seemed to hinder the positive effect of starch (oleic acid, docosanol and β-sitosterol). Further purification of the pulp through alkaline washing yielded better tensile strengths of paper, when the pH was not too high.

Table of Contents

1. Introduction

1.1 General introduction to the topic

Nowadays consumers as well as the industry have a rising necessity for products which tend to be eco-friendlier while also maintaining or even enhancing beneficial properties. This current trend has already arrived in the packaging industry, leading the way to light weight packaging materials. Top priorities are the reduction of raw material use, transportation costs and waste as well as retaining substantial strength properties of the material. The demand for conventional plastic packages is on its downfall, therefore development of high-performance renewable materials is crucial for the growth of the packaging industry.
Wood-based materials have proven to be advantageous for packaging. The renewable resource exhibits a lower carbon footprint and meets the customer demand for environmentally friendly packaging. The final products of paper are recyclable and their low weight is beneficial for transportation. In contrast to plastic materials, the produced waste is degradable by itself in a reasonable time period. Paper materials produced from kraft pulp, especially from softwood, have proven to provide the strength and structure needed to meet the sophisticated requirements for packaging products. Therefore, kraft pulping represents the dominating pulp technology of this segment (Johansson *et al.*, 2012).

1.2 Dissolved colloidal substances

In the kraft pulping process, wood pulp is produced from wood by liberating the fibres through softening and dissolving lignin under hot alkaline conditions. During this alkaline cooking process there are also other dissolved colloidal substances (DCS) released from the wood matrix / fibres. These DCS consist of lignin, lignans, hemicelluloses, pectins, polysaccharides and extractives, also called pitch (Gutiérrez *et al.*, 1998, 2006).
The DCS are sought to be removed by the subsequent washing step, which separates the pulp from the black liquor including DCS and inorganic compounds (cooking chemicals). Crude tall oil can be produced by skimming off the saponifiable and unsaponifiable components from the removed black liquor and

subsequent acidification. The black liquor is burned in the recovery boiler to generate heat (organic DCS) and recover inorganic chemicals (Theliander, 2009). Despite the cooking and washing steps, the entire DCS cannot be removed completely (Hubbe *et al.*, 2012). Some of the DCS are stuck onto fibres or in the residual black liquor of the pulp suspension and are then carried over to the paper machine. As a result, they end up in the process water and may cause several problems in paper production. Since water is cycled for economic and environmental purposes, the DCS accumulate and further deposit in the machine which leads to dead times because of cleaning (Hubbe, 2007). Above all, compounds adsorb onto fibres and eventually interact with process chemicals in the water phase or the cellulose itself. This causes major constrains in paper performance concerning tensile strength, hydrophobicity, air permeance etc (Sundberg *et al.*, 2000).

1.3 Wood pitch compounds

Extractive lipophilic compounds of the DCS cause runnability problems through pitch deposition and affect the paper properties (Sundberg *et al.*, 2000). Due to the harmful effect of pitch on papermaking, this thesis focused mainly on the extractives as part of the DCS. In Figure 1, the major components of extractives/pitch are depicted, including fatty alcohols (a), fatty acids (b), steryl esters (c), triglycerides (d), terpenes (e), resin acids (f), sterols (g) and other diterpenoids (h) in the case of softwood. (Gutiérrez *et al.*, 1998, 2006) As a result of the alkaline cooking step, the triglycerides and steryl esters are hydrolysed and dissociate to saponifiable (fatty acids) and unsaponifiable (sterols) components (Tenkanen *et al.*, 2002). The composition of pitch model compounds may vary between different wood species and are also dependent on the season, in which the wood is harvested. According to literature the pitch composition of trees varies over the year (Blazey, Grimsley and Chen, 2002).

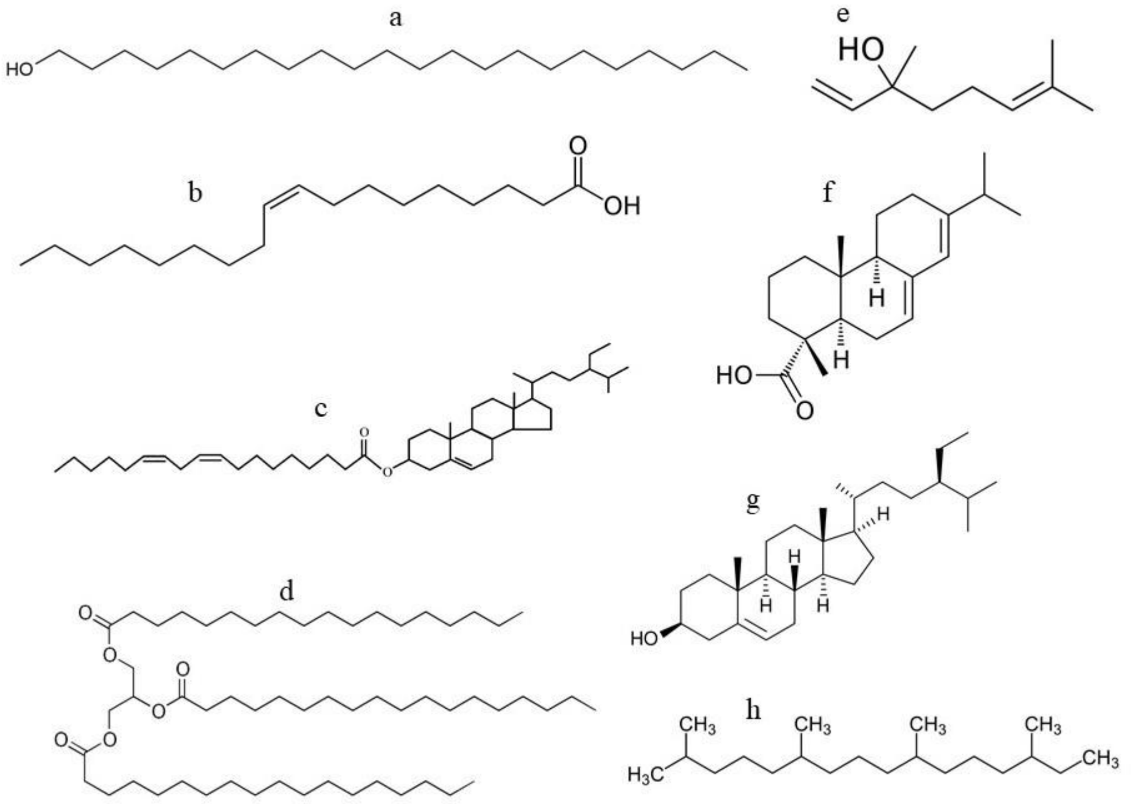

Figure 1: Chemical structure of the major compounds of softwood pitch: a)1-Docosanol (fatty alcohol); b) Oleic acid (fatty acid); c) sitosteryl linoleate (steryl ester) ; d) tristearin (triglyceride); e) linalool (terpene)l; f) abietic acid (resin acid); g) β-sitosterol (sterol); h) Phytan (diterpene)

1.4 Solubility behaviour of pitch compounds

The above-mentioned pitch compounds eventually end up in the papermaking process water. The behaviour of these extractives in water is primarily depends on the pH, shown in Figure 2. At a low pH around 3 the compounds form colloidal droplets, in which the hydrophilic part of the saponifiable substances, i.e. resin or fatty acids, is phasing towards the water while the lipophilic part and the unsaponifiable substances are located at the centre. At higher pH, starting around 8, the amphiphilic compounds become more and more ionically charged because of the dissociation of the carboxylic groups. As a result, they dissolve into the water phase as depicted in Figure 2 (Hubbe *et al.*, 2012).

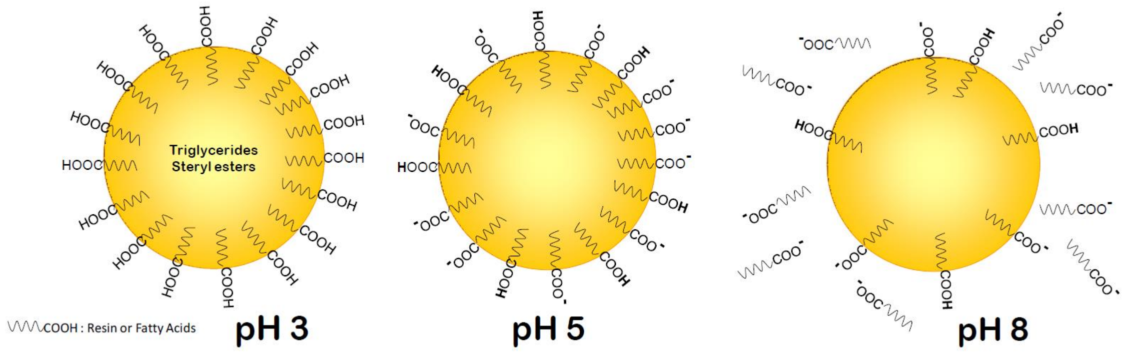

Figure 2: pH dependency of pitch behavior in aqueous phase (Hubbe et al., 2012)

Strand (2013) proved in his experiments, that resin acids dissolve more easily than fatty acids (as seen Figure 3). At alkaline conditions (Figure 2 -> pH8) dissolved fatty and resin acids form micelles which are electrostatically stabilized due to negative surface charge (DLVO theory). Unsaponifiables are only able to dissolve into these micelles. Due to negative surface charge these colloids are probably more stable (no coagulation) and smaller in comparison to colloidal particles at acidic conditions (Figure 2 -> pH3). Under acidic conditions the colloidal partices are uncharged and thus more prone to coagulate (Alén, 2000). They potentially remain in the pulp and get carried over by the process stream.

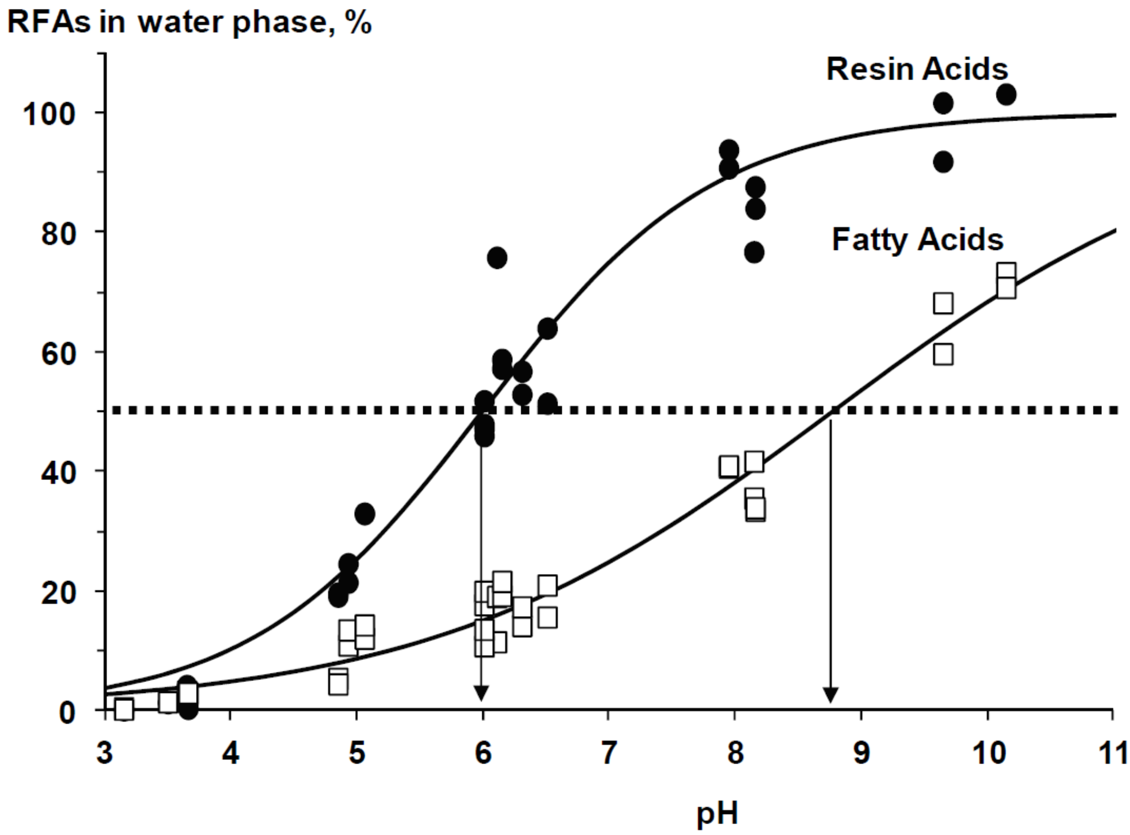

Figure 3: Effect of pH on the solubility of the extractive compounds: resin and fatty acids (RFAs) (Strand, 2013)

1.5 Influence of pitch on paper performance

These carry-over extractives in the process water lead to various problems like reduced paper machine efficiency through deposition and paper quality issues like decrease in paper strength (Sundberg *et al.*, 2000). Brandal and Lindheim (1966) added pitch model compounds in form of an aqueous dispersion directly into an acetone-extracted groundwood pulp suspension (Norway spruce) before producing hand sheets to investigate their influence on paper properties. Their influence on the breaking length of the hand sheets are depicted in Figure 4. The amphiphilic compounds, i.e. n-dodecyl alcohol followed by linoleic acid and oleic acid, exhibited the highest decrease in breaking length. In case of n-dodecyl alcohol (retention: 2 mg/g fibres), the decrease in breaking length was up to approximately 70%. The influence of abietic acid on the breaking length was much smaller compared to other substances (Brandal and Lindheim, 1966).

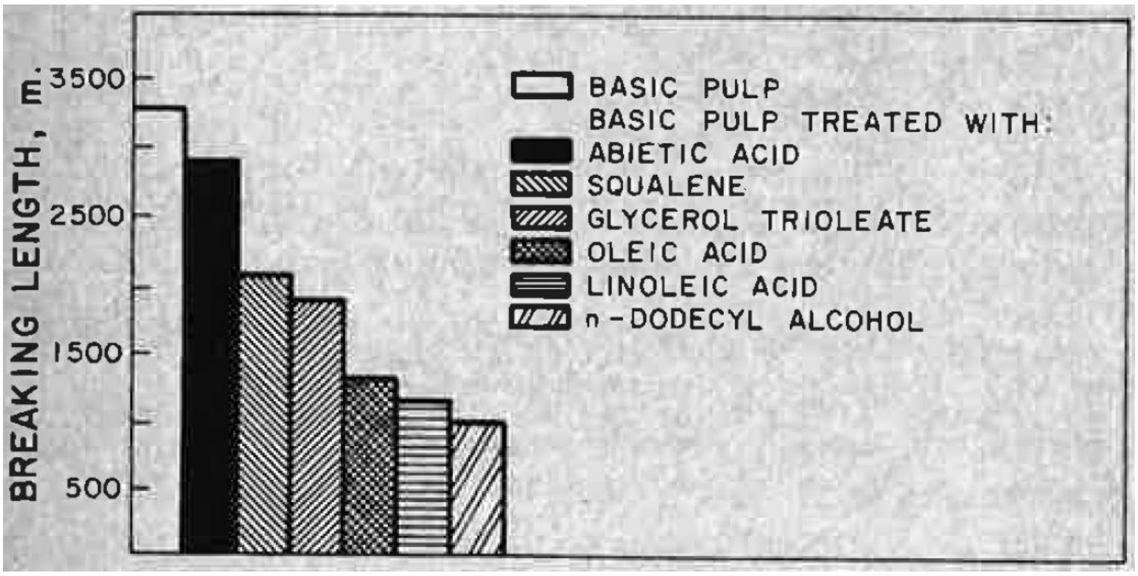

Figure 4: Influence of pitch compounds on the breaking length of acetone extracted groundwood pulp handsheets (Norway spruce) (Brandal and Lindheim, 1966)

Sundberg *et al.* (2000) also performed experiments to investigate the weakening of paper strength by wood resin. Similar to the experiments of Brandal and Lindheim (1966), the pitch dispersion was directly added to a fiber suspension before producing hand sheets from bleached softwood kraft pulp, bleached softwood kraft pulp with TMP and bleached softwood kraft pulp with TMP and kaolin. According to the results shown in Figure 5, the tensile index of the kraft pulp decreased almost by 50% upon reaching a pitch concentration of around 2 mg/g fibers. The decrease in tensile index was highest when only kraft pulp was present, i.e. pitch was most harmful in the case of kraft pulp. The tensile index decreased rapidly between a pitch content of 0.1 to 2 mg/g fibers, while increasing the concentration further exhibited no significant influence.

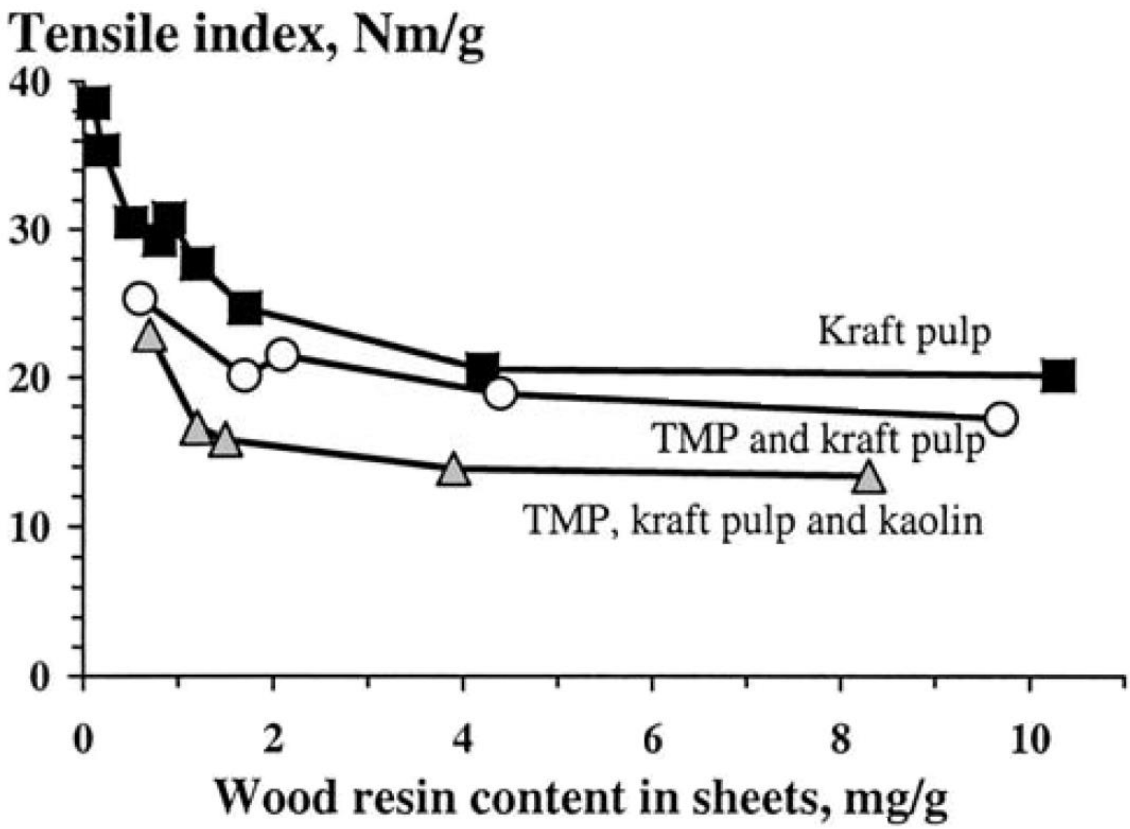

Figure 5: Influence of hexane-extracted TMP (Norway spruce) pitch on bleached softwood kraft pulp; bleached softwood kraft pulp with TMP; bleached softwood kraft pulp with TMP and kaolin (Sundberg et al., 2000)

Kokkonen et al. (2002 & 2004) investigated the effects of different types of lipophilic extractives on paper properties. Therefore, unbleached spruce thermomechanical pulp (TMP) was acetone extracted to remove the lipophilic compounds. The major model compounds of pitch were then dissolved in acetone and mixed together with the extracted pulp. The acetone was evaporated, leaving the model compounds adsorbed onto the fiber surfaces. Several tests were performed, amongst others a tensile test shown in Figure 6. The results revealed that, sitosterol and stearic acid (saturated fatty acid) did not influence the tensile index at all. Other compounds had a clear influence with increasing pitch concentration. The decrease of the tensile index was especially high in the case of oleic acid (unsaturated fatty acid). Oleic acid decreased the paper strength by approximately 25% at an extracted content of 7 mg/g fibers.

Fatty acids and sitosterol did not influence contact angle significantly, as shown in Figure 7. Other compounds increased it. Especially high increase in hydrophobicity was achieved with steryl esters and resin acids at high pitch concentrations.

The influence of pitch on the bulk and air permeance are depicted in Figure 8 and Figure 9 respectively. The addition of resin acids and oleic acid yielded higher bulk and air permeance. Steryl esters, stearic acid, sitosterol and triolein had no significant influence on both properties.

Kokkonen et al. (2002) concludes that at high pitch concentrations, oleic acid was the most harmful compounds for paper strength. In case of resin acids and steryl esters, the contact angle increased with increasing pitch concentration. The effect of the addition of pitch compounds on the air permeance and bulk was inconsistent and depended on the respective extractive used. Kokkonen et al. (2002) also concludes that the effect of model compounds on paper properties depends on chemical structure, surface coverage and distribution on the fiber surfaces.

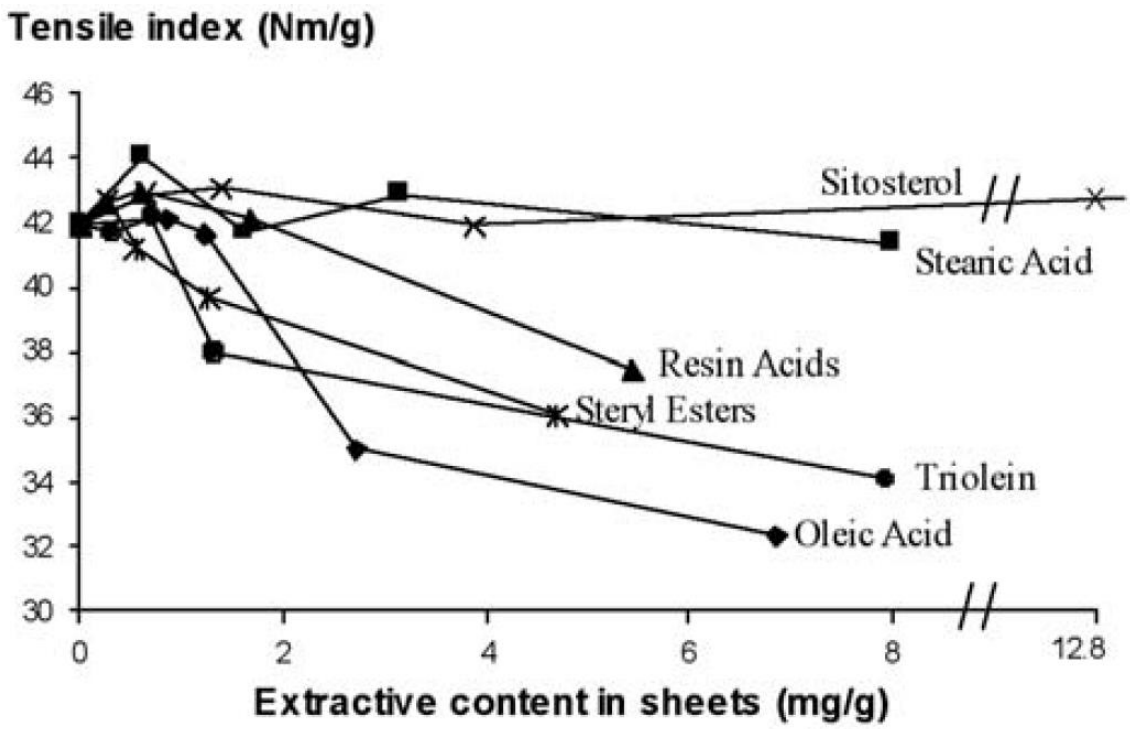

Figure 6: Influence of pitch model compounds on the tensile index of acetone-extracted TMP (Norway spruce) handsheets (Kokkonen et al., 2002)

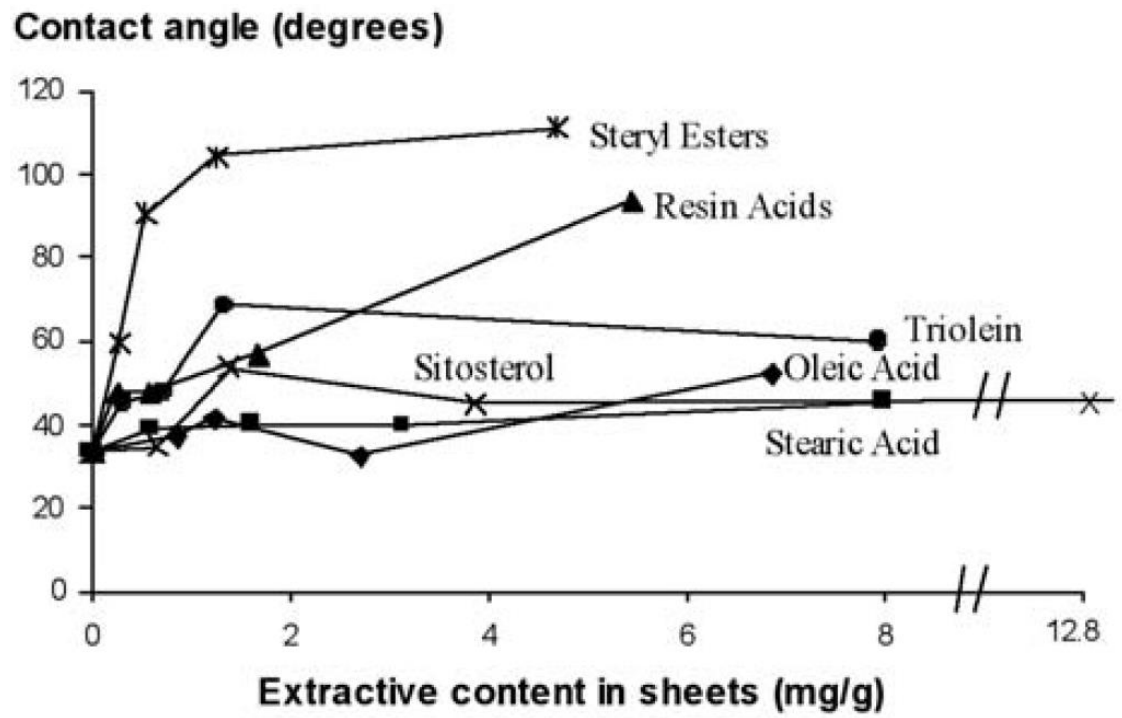

Figure 7: Influence of pitch model compounds on the contact angle of acetone-extracted TMP (Norway spruce) handsheets (Kokkonen et al., 2002)

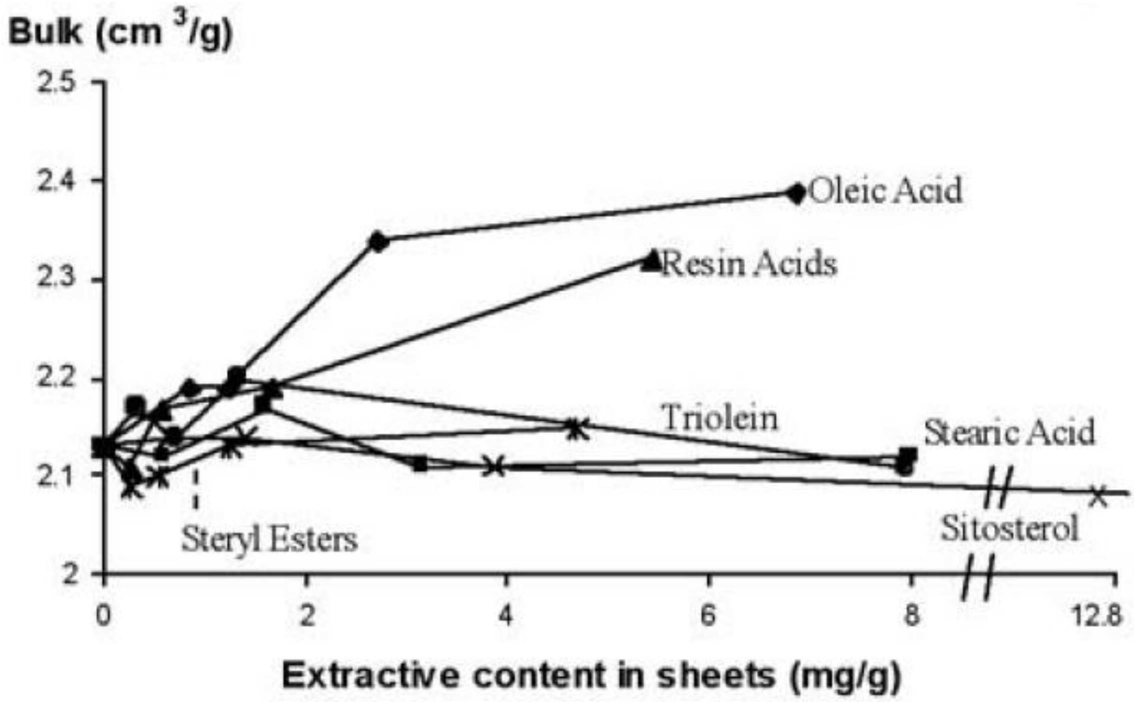

Figure 8: Influence of pitch model compounds on the bulk of acetone-extracted TMP (Norway spruce) handsheets (Kokkonen et al., 2002)

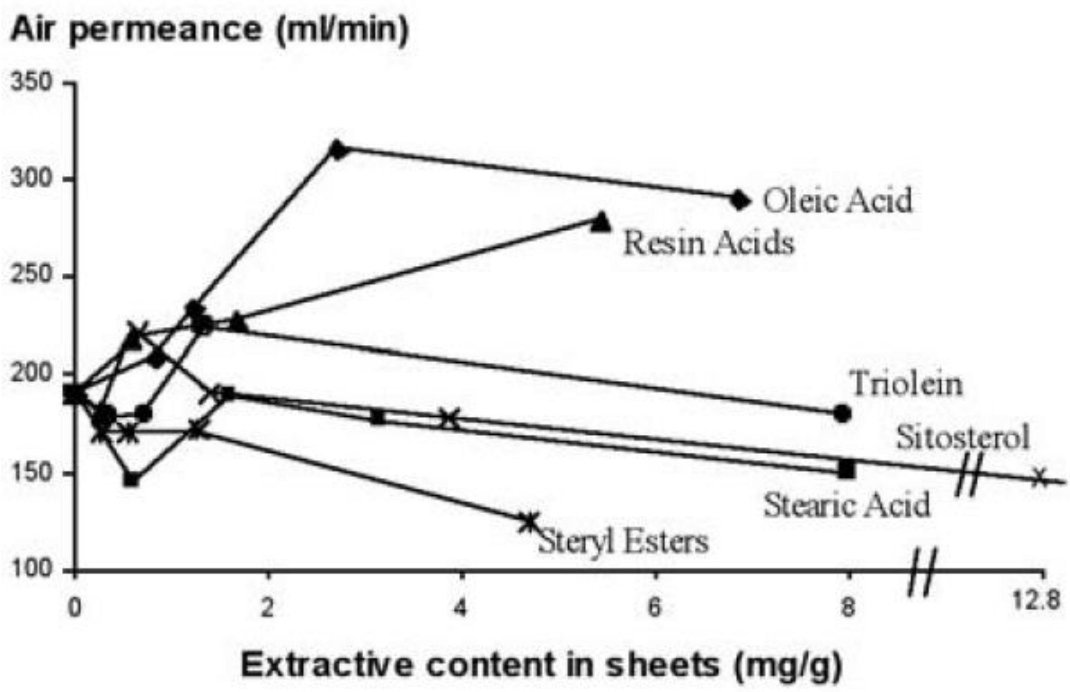

Figure 9: Influence of pitch model compounds on the air permeance of acetone-extracted TMP (Norway spruce) handsheets (Kokkonen et al., 2002)

According to Davison and Page, the interfiber bonding is a weak link for paper strength (Page, 1969; Davison, 1972). Lipophilic extractives adsorb onto the surfaces of the fibres. As a result, interfiber bonding is disturbed, leading to a decrease in the strength properties of the paper (Hubbe *et al.*, 2012).
Interfiber bonding can be enhanced through refining (beating) of the fibers (Abitz and Luner, 2018) or by the addition of dry strength enhancing agents. In addition, fixatives or electrolytes can also be used to agglomerate pitch extractives. The pitch extractives are adsorbed or precipitated onto the fiber surface and are removed from the water circulation with the paper product (Hubbe et al. 2006).

1.6 Dry-strength agents

Strengthening agents are in most cases cationic polyelectrolytes like starch, that improve interfiber bonding. They have several charged functional groups, that can interact with cellulose or other compounds like extractives. In solvents like water, they dissolve by shifting into their ionic form, which grands the ability to exchange their counter ions or interact with opposite charged substances. As a result, cationic polysaccharides may adsorb onto the anionic fibers of cellulose, eventually building a connection between two fibers and therefore strengthening the fibre network. (Möller, 1966) Cationic polyelectrolytes may also interact with anionic particles, e.g. pitch, suspended in aqueous phase, therefore those pitch compounds are reducing the positive effect of the strengthening agents (Hubbe *et al.*, 2012). Starches represent the most important group for strength agents. (Lindström et al., 2005)

Starches consist of amylopectin (70 – 80%) and amylose (20 – 30%). Amylopectin exhibits a linear structure of α(1-4)-linked glucopyranose units and has branches, which occur every 20-30 units by α(1-4)-linked bonds. Amylose is a straight chain of α(1-4)-linked glucopyranose units. (Lindström, Wågberg and Larsson, 2005) The molecular structures of both compounds are depicted in Figure 10.

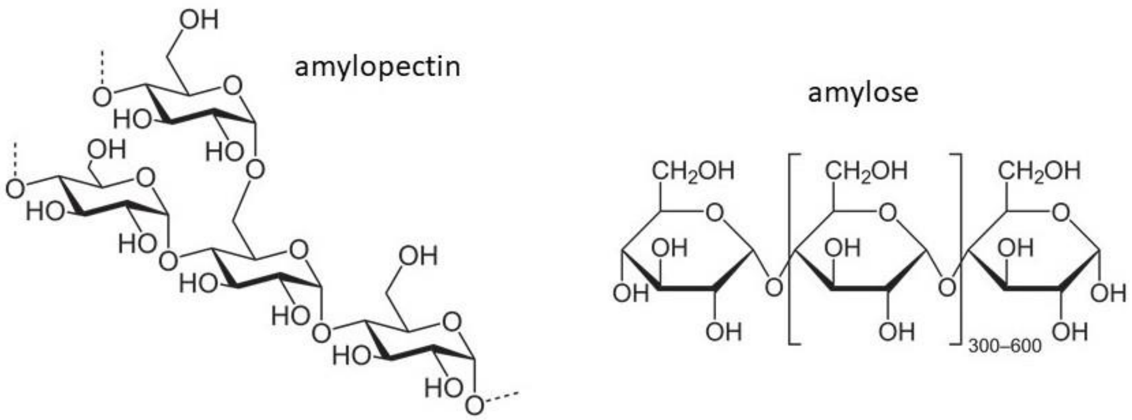

Figure 10: molecular structures of amylopectin (left) and amylose (right)

The relative content of starch depends on the source from which it is produced, e.g. potatoes, corn or wheat. The starch must be modified to cationic starch in order to efficiently interact with the cellulose fibers (Lindström, Wågberg and Larsson, 2005).

The adsorption of starch onto cellulosic fibres obeys in general the rules for adsorption of polyelectrolytes on negatively charged surfaces like cellulose itself (van de Steeg *et al.*, 1993). According to van de Steeg et al., the adsorption of starch increases slightly with increasing electrolyte concentration. However, at high electrolyte concentrations the adsorption decreases to zero.

The adsorption of starch is favoured by increasing surface area and surface charge density. (Márton and Marton, 1976) The performance enhancing properties of starch on the bonding strength are more pronounced for higher molecular weights of starch. Therefore, potato starch exhibits better enhancing abilities for paper strength than waxy maize starch. (Brouwer, 1997) The strength increasing potential of starch is higher when interfiber bonding is weak. (Lindström et al., 2005)

According to the review of Lindström, Wågberg and Larsson (2005), cationic starches enhance the strength properties of papers by:

- improving sheet consolidation, therefore increasing the sheet density
- increasing the specific bond strength
- decreasing stress concentrations in paper sheets

Other strength enhancing agents include:

- acrylamide – based polymers
- chitosan
- wood hemicelluloses
- latex additives
- gums

1.7 Deposit control agents

Deposition of lipophilic extractives in the paper machine cause undesired downtime and costs for cleaning, paper breaks, reduction of product quality and losses in productivity and efficiency. (Hubbe, Rojas and Venditti, 2006) Colloidal destabilization, charge neutralisation and hydrodynamic shear are often focused, when dealing with pitch deposit problems. (Allen, 1980) Several types of additives are used in paper industry, in order to control pitch deposition. Those include multivalent cations, adsorbent materials, various types of polyelectrolytes with different charge densities, surfactants, inorganic dispersants, solvents, biocides and enzymes. (Hubbe, Rojas and Venditti, 2006)

1.7.1 Multivalent inorganic cations

The most abundant substance used in papermaking industry is either aluminium sulfate (papermaker's alum) or poly-aluminium chloride (PAC). They are often applied in systems that deal with pitch problems. (Allen, 1980) Alum neutralizes the surface charge of critical substances and agglomerates them onto the surface of suitable adsorbent materials like fibers. If the dosage of alum is high enough, it strongly adsorbs onto negatively charged surfaces and gives them even a positive charge. Consequently, they may be retained onto the negative surfaces of cellulose fibers. This effect is highly pH-dependent as at neutral and higher pH values Al^{3+} interacts strongly with OH^- ions in water (Matijević and Stryker, 1966).

1.7.2 Adsorbent materials

Talc is the most important substance for adsorbent materials. It's a natural magnesium silicate with a high affinity to oleophilic materials. Talc has a platy structure with a lipophilic face and hydrophilic edges. (Doshi, 1994)
Tacky particles (pitch) get adsorbed onto the surface of talc, up to a count of 14 pitch particles on a single talc unit. (Allen, 1980)
A significant decrease in tackiness is expected, when the pitch gets stuck between talc plates, illustrated in Figure 11. (Gill, 1974)
Further important adsorbent materials are bentonite, kaolin clay, inorganic minerals with positively charged surfaces and synthetic/organic fibres (Hubbe, Rojas and Venditti, 2006).

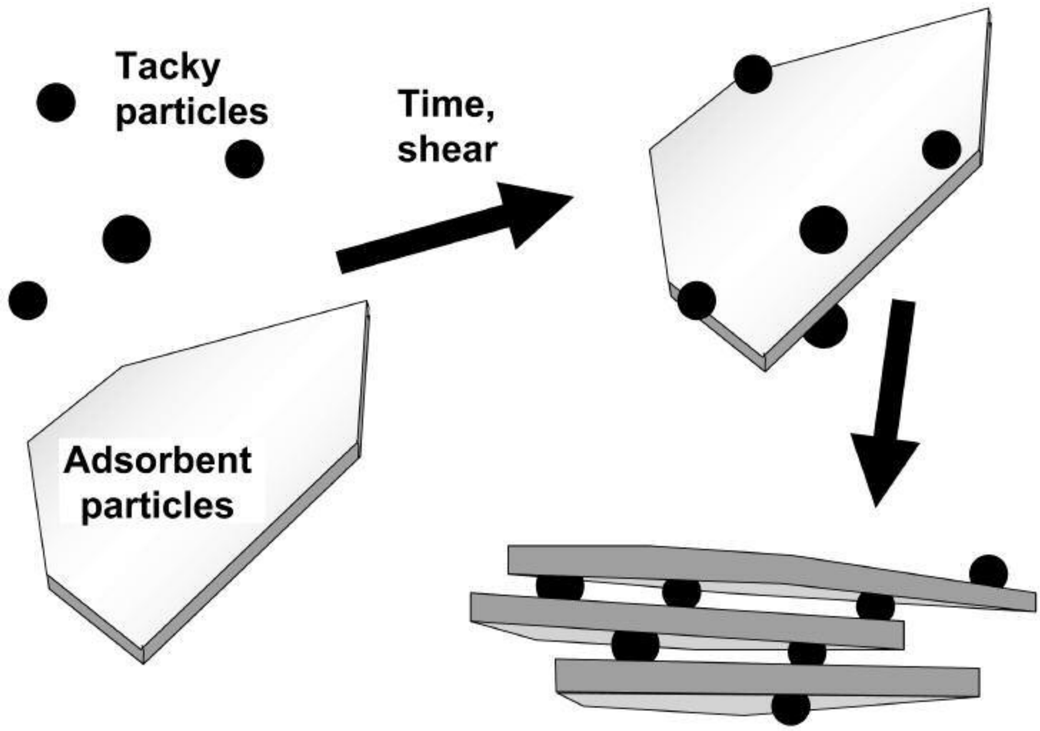

Figure 11: Model for the adsorption of tacky particles on talc (Hubbe, Rojas and Venditti, 2006)

Other important deposit control agents, which were not considered in this thesis, are:

- Organic polymers
- Dispersants
- Surfactants
- Solvents
- Enzymes

1.8 Influence of polysaccharides, electrolytes and fixatives on paper strength

The influence of polysaccharides, electrolytes and fixatives in combination with hexane-extracted pitch from TMP (Norway spruce) on kraft pulp handsheets (produced from the pulp suspensions described below) was tested by Sundberg et al. (2000). The extracted pitch was added in colloidal form to the pulp suspension of either bleached softwood kraft pulp or TMP with kraft pulp and kaolin. Figure 12 shows that there is no significant difference in tensile index of kraft pulp, whether pitch is aggregated and retained in the paper sheet with different electrolytes or fixatives. However, Figure 13 indicates that TMP, kraft pulp and kaolin hand sheets produced with electrolytes may have higher tensile strength than sheets produced with fixatives. Upon reaching a concentration around 2 mg resin/g pulp, no significant decrease of the tensile index is observed by the addition of further extractives in both figures.

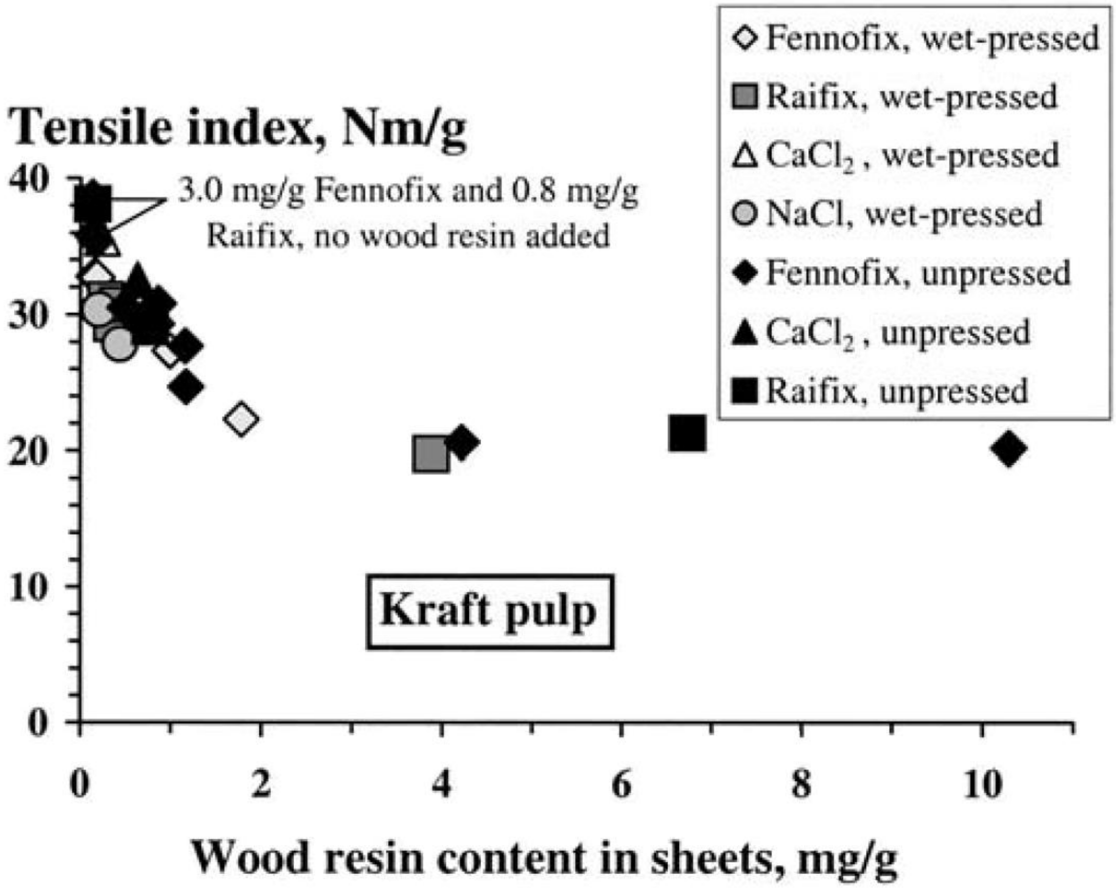

Figure 12: Influence of pitch retention substances, i.e. polysaccharides, electrolytes and fixatives, on the tensile index of hexane-extracted kraft pulp (Norway spruce) handsheets (Sundberg et al., 2000)

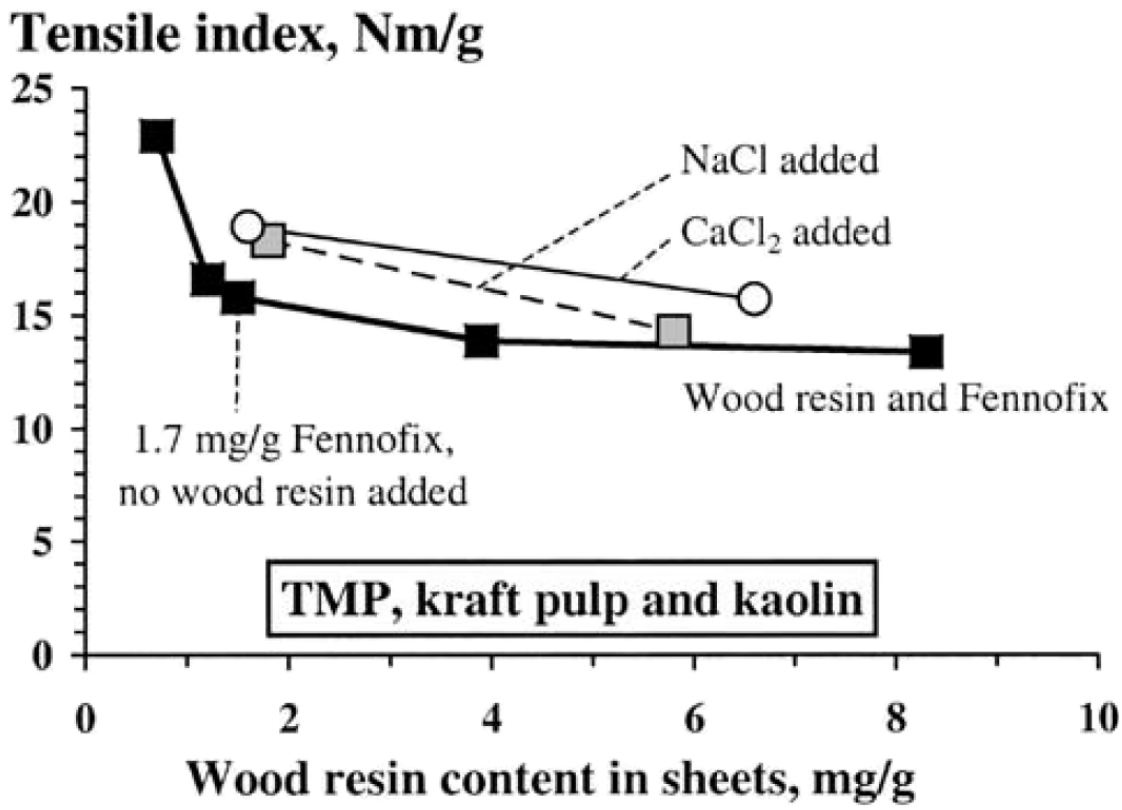

Figure 13: Influence of pitch retention with fixatives (pDADMAC - Fennofix) or electrolytes (NaCl or $CaCl_2$) on the tensile index of hexane-extracted TMP (Norway spruce), kraft pulp and kaolin handsheets (Sundberg et al., 2000)

In Figure 14 the results of using polysaccharides by Sundberg et al. (2000) are depicted. The values indicate that any polysaccharide proved to be beneficial for the tensile strength of TMP, kraft pulp and kaolin handsheets. Polysaccharides eventually adsorb onto the pitch droplets, increasing their hydrophilicity and therefore pitch aggregates, which are adsorbed onto the fibers, may still contribute to interfiber bonding (Sundberg *et al.*, 2000).

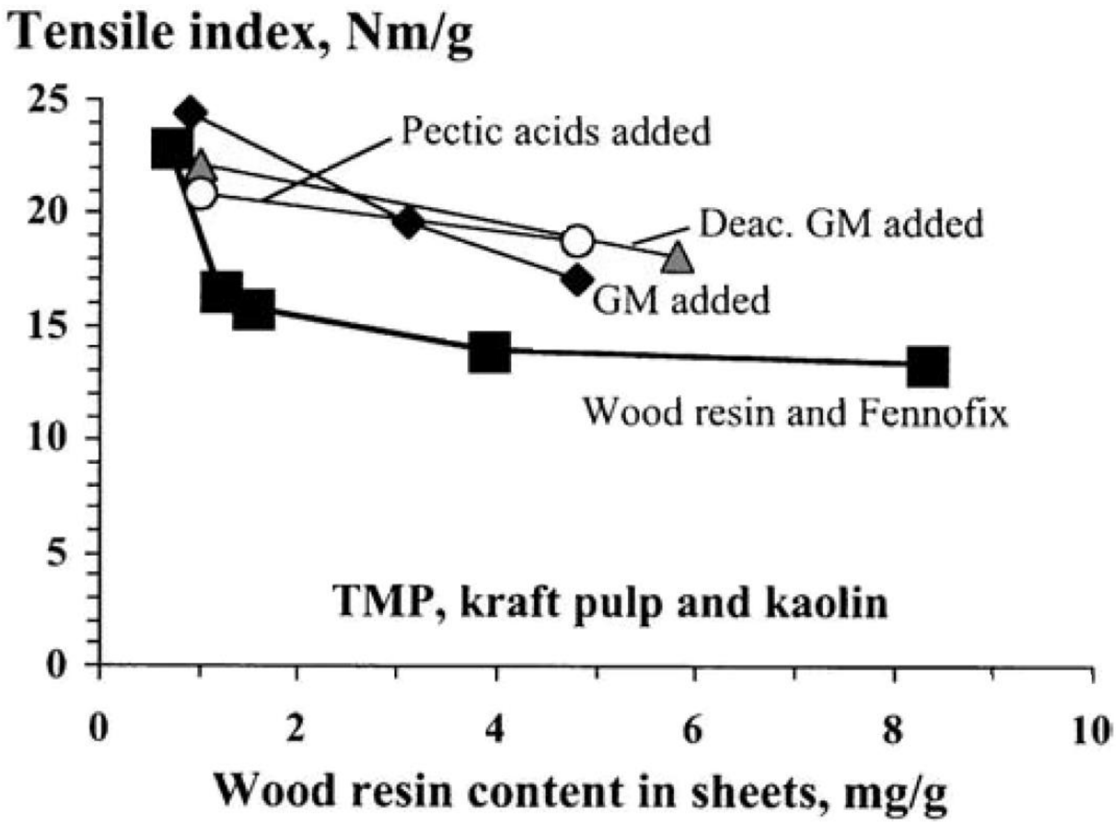

Figure 14: Influence of different polysaccharides on the tensile index of TMP, kraft pulp and kaolin handsheets with hexane-extracted TMP (Norway spruce) pitch (Sundberg et al., 2000)

According to previous studies, pitch potentially disturbs the functioning of cationic strength agents and paper strength.

The goal of this master thesis was to investigate the interaction of extractives, pulp and process chemicals in defined systems through laboratory simulation.

1.9 Trial objectives and investigations

- analysis of lipophilic extractives carried over by pulp to the paper making process of an integrated softwood kraft pulp and paper mill
- how extractive compounds directly influence the paper properties and how they influence the beneficial impact of polysaccharides like cationic starch
- how fixatives like alum assist in the removal of pitch compounds and how they affect the strength characteristics of paper by doing so
- how intensive alkaline cooking and washing may further help to minimize the pitch content and enhance paper properties

Gas chromatography-mass spectrometry (GC-MS)

-Analysis of extractives present in the paper making process with softwood kraft pulp

1st trial

-Investigation of sheet properties of reference and extracted kraft pulp from the paper mill

-Investigation whether model compounds have an influence on paper strength

2nd trial

-Investigation of the influence of different pitch model compounds on paper properties

-Investigation of the influence of starch in presence of pitch on paper properties

3rd trial

-Testing the influence of realistic pitch concentrations on paper properties

4th trial (production site Trial)

-Mimic process conditions at the production site (hardness of water, pH, alum etc.)

-Investigation of the influence of talc on dissolved and colloidal pitch and paper properties

-Investigation whether results of Graz Trials can be reproduced at the production site or not

5th trial

-Investigation of the influence of alum on paper properties

-Investigation of the influence of pH on paper properties (pH 10, 8 and 6,8; adjusted with alum)

6th trial

-Investigation whether the given pulp can be further purified from pitch by alkaline cooking/ washing

-Further investigation of the influence of alum on paper properties

7th trial

-Investigation of the influence of alum on paper properties by using the quantities of alum that occur during real process conditions

-Repeating whether pulp can be further purified by alkaline cooking/ washing

8th trial

-Further investigation of washing and alum on paper properties

2. Experimental

2.1 Analysis of seasonal pitch

Pitch was extracted from the pulp (after leaving the paper mill) using Soxhlet extraction with acetone and was further analysed by using GC-MS.

In order to analyse nearly every compound of pitch by GC-MS a sialylation reaction had to be done beforehand. Therefore, 10-15 mg of the sample/compound were dissolved in 1 ml of dry pyridine and 250 µl BSTFA (N,O-Bis(trimethylsilyl)-trifluoroacetamide) containing 1% TMSCl (trimethylchlorosilane). The solution was flushed with nitrogen gas and mixed for 2 h at 70 °C.

The final solution was heated up to 40 °C for 1 hour before an aliquot was injected into the GC-MS. The GC-MS consisted of a Trace GCUltra and a Polaris Q mass spectrometer (Thermo Fisher, USA). A full-scan mass spectrum (50-650 m/z) was applied by using electron-impact ionization with 70 eV. Single-ion-monitoring (SIM) was chosen for the MS to gain semi quantitative results and samples were injected manually (2 µl) in split-less mode. The fused-silica capillary column had a length of 30 m and a diameter of 90,25 mm. The capillary was coated with a 0,25 µm film of CP-Sil 8 CB low bleed/MS (Varian). Helium with a purity of 99.999% at a flow rate of 1 ml/min was used as carrier gas. Injector temperature was 275 °C. After injection the oven temperature was held at 60 °C for 1 minute and then raised to 130 °C with 30 °C/min. After 2 min at 130 °C, the temperature was raised to 205 °C with 20 °C/min, staying at level for 1 minute. Then temperature was risen to 275 with 30 °C/min for another 15 minutes. The transfer-lien temperature was 280 °C.

2.2 Materials for papermaking trials

-never dried unbleached softwood kraft pulp (after the last wash press step; Kappa number of 45; was provided by European kraft pulp mill)

-pitch model compounds from Merck (at least 80% purity): abietic acid, stearic acid, oleic acid, linalool, docosanol, β-sitosterol

-cationic starch

-alum

-talcum

2.3 Storage and conservation of pulp

For the trials performed in Graz, the never dried, wet pulp from the kraft pulp mill had to be stored and conserved. The pulp was spread over a plastic foil and dried by air over several days. The dry content of the pulp had risen to 93,167%. The air-dried pulp was then stored in a plastic bag.
For experiments performed at the production site, fresh, never dried pulp from the pulp mill was taken.

2.4 Preparation of pitch dispersions

The pitch dispersions of the model compounds were prepared in beakers. 24 mg of the desired compound was dissolved in approximately 10 ml acetone, depending on the solubility behaviour. The solution was mixed in an ultrasonic bath to dissolve components properly. The resulting liquid was slowly added to 600 ml of distilled water under intensive stirring to give a final concentration of 40 mg/l or 200 mg/l. Beforehand, the pH of the distilled water had been risen to approximately 8 - 9 with a sodium hydroxide solution. In order to get a stable dispersion further mixing in an ultrasonic bath was applied for 5 min. The amount of acetone was neglected since it has no significant influence on the deposition behaviour of pitch on the fibres (Stack *et al.*, 2012) and its amount was very small.

2.5 Preparation of cationic starch solution

The cationic starch solution was prepared by adding 2 g of cationic starch to 200 ml of distilled water in a small beaker to give a 1% mixture. The solution was stirred and heated up to a temperature of 90 °C for 20 minutes. After cooking, the solution was cooled down to room temperature and distilled water was added while stirring to compensate for evaporation.

2.6 Preparation of alum solution

30 g of Alum was dissolved via ultrasonic bath in approximately 500 ml of distilled water. The solution was then poured into a volumetric flask and the missing amount of distilled water was added to give 1 litre of a 30 g/l solution.

2.7 Preparation of handsheets

A schematic workflow is shown in Figure 15.

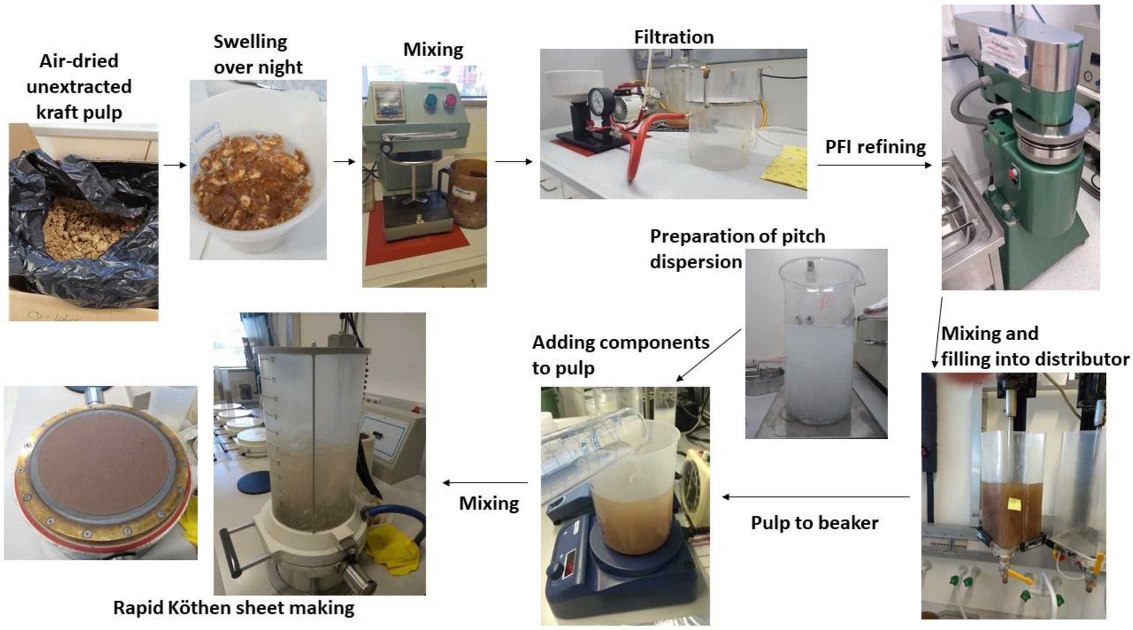

Figure 15: Schematic workflow of the preparation of handsheets

-PFI milling

The pulp was beaten with the PFI mill for 3000 rev according to ISO 5264-2 standard to give a Schopper Riegler degree of 15 (°SR). Before beating of the air-dried pulp, it was swelled overnight in a beaker with distilled water.

-Schopper Riegler

The refining degree tests for the milled pulp were performed according to ISO 5267-1 standard with a Schopper Riegler apparatus. The required amount of fibre suspension was taken from the distributors.

-Fibre suspension

The fibre suspensions were prepared in distributors with mixers. 30 g of refined pulp (ovendry basis) were mixed with 10 L of tap water and possible pH adjustment was done with a NaOH solution. The required amount of fibre suspension for paper production was taken from the distributors and filled into a beaker. In the beaker the desired chemicals were added.

-hand sheets production

The hand sheets were produced according to ISO 5269-2 standard with a Rapid Köthen apparatus to give 2,4 g pulp per sheet (oven-dry basis) (approximately 800 ml of fibre suspension was needed).

2.8 Paper testing

The produced hand sheets were brought to the climate room in order to condition under 50% relative humidity and 23 °C for at least 24 hours according to ISO 187 standard. Conditioned hand sheets were then weighted according to ISO 536 to get the basis weight. Thickness and density were measured according to ISO 534. The tensile properties were then determined by a tensile tester according to ISO 1924-3. The retention of model compounds on hand sheets was investigated by gravimetric measurements of the extracts from Soxhlet extraction, which was done according to ISO 14453 standard. Acetone of the extracted solution was evaporated, and the remaining extracted amount was then weighed. Contact angle measurements were performed with a dynamic contact angle and absorption tester (FIBRO system AB, Hägersten, Sweden). For the trials 1, 2 and 3, the contact angle was measured 1 second after the drop formed on the surface. In case of the trials 4 and 7, the contact angle was measured 0.1 second after the drop formed on the surface.

2.9 Trial procedures

1st trial - *influence of pulp extraction and model compounds*

Air dried pulp was Soxhlet extracted with acetone. Then sheets were produced with air-dried pulp and the extracted pulp, as described above.

The pitch dispersions of oleic- and abietic acid were prepared according to the described procedure but with a concentration of 200 mg/l. Approximately 120 ml of the dispersion was added in a beaker to 800 ml of fibre suspension (2,4 g air-dried pulp / L) while stirring. The resulting suspension was mixed for 1 minute to give a ratio of 10 mg pitch/ g dry pulp. The mixture was then processed to a sheet according to the standard procedures.

2nd trial - *influence of different model compounds on paper properties and starch*

The starch solution was prepared as described above.

The pitch dispersions (oleic acid, stearic acid, abietic acid, β-sitosterol, linalool, docosanol) were made with a concentration of 200 mg/l. In addition, a mixture of all model compounds was created, which mimicked the composition of the GC-MS analysed extracted industrial pitch sample. Furthermore, part of the extracted industrial pitch provided by the European pulp mill was used to create a 200 mg/l dispersion.

120 ml of the respective dispersion was added to a beaker with about 800 ml of fibre suspension (equals 10 mg pitch/ g dry pulp). The mixture was stirred for one minute before it was used for sheet making without cationic starch. In case of cationic starch samples, 3,6 ml of the 1% starch solution was added after stirring of the pitch containing mixture. After one minute of further mixing, sheets were produced.

3rd trial - *verification of results at realistic concentrations*

The procedure of this trial was the same as in the second trial but with a pitch component concentration of 1 mg pitch/g dry pulp. The trial was done for oleic acid, β-sitosterol and the mixture of model compounds.

***4th trial (production site Trial) -** mimicking of the process conditions of real paper production*

Pulp was directly taken from the pulp mill at the production site, after the last washing step.

In case of the pulp refining, PFI milling was done at 3010 rev and 50 ml of a sodium phosphate buffer, with a concentration of 100 g/l distilled water, was added. The buffer was used on the daily basis at the production site, therefore it was added.

Model compound dispersions (oleic acid, stearic acid, abietic acid, β-sitosterol, linalool, docosanol) with a concentration of 40 mg/l were made as described above. Black liquor carry-over (BL carry-over), provided by European kraft pulp mill, was separated from solids (fibers) by filtration and the water was evaporated. The required amount of residue was dissolved in acetone and used to create a dispersion with a concentration of 40 mg/l.

Alum- and the cationic starch solution were prepared as described.

A talcum suspension with 1 g/l was prepared by mixing 1.111 g (90% purity) with 1 l of tap water. The suspension was then stirred constantly to avoid deposition.

The produced sheets had a target weight of 2.35 g instead of 2.4 g.

The pH of the fibre suspension in the distributors was risen to 10 with a sodium hydroxide solution.

About 783 ml of fibre suspension was taken from the distributor to a beaker. The required amount of pitch dispersion (60 ml) was added while stirring, which was equal to 0.001 g pitch compound/g pulp. After one minute of mixing sheets were produced. In case of the pitch compound + starch samples, 3.6 ml of the 1% starch solution was added (0.015 g starch/g pulp) to the pitch containing suspension with subsequent mixing for one minute. Concerning the compound + starch + talcum samples, 2.4 ml of the talcum suspension (0,01 g talcum/g pulp) was put into the beaker after the addition of starch.

Prior to the production of sheets - but after the addition of compounds, the pH of the respective beaker was lowered to 7 with alum. The amount of alum added was approximately 6.6 ml of the 30 g/l solution. Subsequently the suspension was mixed for one minute and then used for paper production.

***5th trial -** Investigation of the influence of alum and pH on paper properties*

The pitch dispersion of oleic acid, the cationic starch solution and the alum solution were prepared as described.

The pH of the distributors was adjusted to 10 with a NaOH solution.

About 800 ml of fibre suspension was put into a beaker and the respective compound was added (0,001 g compound/g of pulp) while stirring for one minute. Afterwards, the equivalent of 0,015 g starch/g pulp was added, followed by a minute of mixing. Further pH adjustment was done with the alum solution until a pH of either 8 or 6,8 was reached. After one minute of stirring sheets were produced.

***6th trial -** influence of alum on paper properties and impact of pulp purification*

A NaOH solution was prepared with a concentration of 2 mol/l. The sulfuric acid solution was created with a concentration of 1 mol/l.

The cationic starch- and the alum solution were prepared as described.

The pulp swelled overnight and was put into a big beaker together with distilled water. The suspension was treated with NaOH solution during agitation to reach a pH of 12 at 25°C. While mixing, the suspension was heated up to 85 °C and held at this point for 20 minutes. The pH decreased with increasing temperature; further pH adjustment was done by adding NaOH solution. After the time passed the hot suspension was filtered and the residue was washed 6 times with 1 l of distilled water at a pH of 12. The alkaline pulp was then washed several times with distilled water to reach a pH of approximately 7-8.

The pulp was then put into a beaker with distilled water overnight for swelling and then further processed by PFI milling as mentioned.

The pH of the suspension in the distributors was adjusted to 10. 800 ml of either washed or unwashed suspension was taken to a beaker and the equivalent of 0.015 g starch/ g pulp was added while stirring for 1 minute. Afterwards the pH was lowered to 6.8 by either alum- or sulfuric acid solution and one minute of mixing was added. Then sheets were produced as described while the pH in the Rapid Köthen apparatus was adjusted to 6.8 by either alum- of sulfuric acid solution.

***7th trial -** influence of alum on paper properties using realistic quantities and impact of pulp purification*

The procedure was overall the same as for the 6th trial but with a minor adjustment.

A fixed amount of alum (0,015 g alum/ g pulp), corresponding to industrial setting, was added to the beaker and further pH adjustment to 6.8 was done with the sulfuric acid solution.

***8th trial -** further investigation of washing and alum on paper properties*

The procedure is the same as in trial 6th with minor adjustments.

The pH of the beaker for alkaline cooking was risen to 13 and held at approximately 12.5 during alkaline cooking. The residue after filtration was washed with distilled water at a pH of 13.

The sheets were prepared like in the 7th trial.

3. Results and Discussion

3.1 Analysis of carry-over pitch

In order to investigate the influence of different compounds on paper properties, the pitch, carried over with unbleached softwood kraft pulp to the paper mill, had to be analysed to gain information about the single compounds present in the process. As mentioned in the introduction, the composition of pitch entering the paper mill depends on wood species, seasons and pulp production process.
Analysis was done for pitch samples extracted during high capacity load (normal operation capacity) in summer and winter season to investigate differences in seasonal composition. Model compounds were also analysed as a reference. In Addition, winter pitch samples of 'good' and 'normal' washing (low and high capacity load of the washing line) from the paper mill were supposed to be analysed to gain an impression whether washing should be optimized.

3.1.1 Summer pitch

About 66.31% of all extractive compounds were classified by the GC-MS. Non-identified compounds are thought to be small organic molecules and fragments formed by ionization. In Table 1 the relative amounts of pitch compounds from the analysis are shown, in which compounds were grouped into classes. A major part of the extracted summer pitch consists of terpenes and fatty acids, followed by fatty alcohols.

Table 1: Relative amounts of different pitch compounds of the GCMS-analysis of the acetone extract, derived from unbleached softwood kraft pulp during summer at normal capacity load

classes	%	most abundant compounds	%
Fatty acids	15,24	oleic acid	4,71
Resin acids	3,05	dehydroabietic acid	2,02
Sterols	9,90	β-sitosterol	4,57
Fatty alcohols	11,21	docosanol	2,44
Terpenes	18,79	manoyl oxide	6,35
Acids	3,13	acetic acid	0,75
Sugars	0,88	-	-
BSTFA/pyridin derivates	4,09	-	-

The amount of fatty acids found is explicitly higher than the content of resin acids. Hydrolysis of the glycerides during kraft pulping leads to a rapid increase of fatty acids, since the glyceride content is considerably high in softwood according to Ekman and Holmbom (2000). The literature also points out the high amount of oleic acid, which is found as most abundant compound of fatty acids. Unsaponifiables like fatty alcohols, sterols and terpenes are hard to remove since they basically dissolve only into micelles formed by saponifiables. Their content in the carry-cover is therefore also considerably high.

3.1.2 Winter pitch

Normal washing

The first attempt to analyse the winter pitch for high capacity load of the washing line failed. The analysis proposed a total of 62.15% as TTMSS derivatives, which are by-products of the sialylation reaction. 23.06% were questionable or undetected substances, therefore only 14.79% of the compounds were classified by GCMS. As a result, this outcome does not represent a reasonable analysis and was therefore repeated.

On the next attempt the sialylation reaction was done more carefully, especially because there was only little left over of the pitch sample. After the reaction took place, the sample was taken to the analysis lab. Unfortunately, the GCMS device had been broken the day before and needed maintenance, which took another 2 weeks. During this time period, the ongoing sialylation reaction would’ve dismantled most of the compounds, making the results unusable. Thus, the second attempt to analyse the winter pitch at high capacity load also failed.

Therefore, the comparison of summer and winter pitch had to be done with the low capacity load (good washing) of the winter sample.

Good washing

Table 2 contains the results of the winter pitch analysis at low capacity load, in which substances are grouped into classes. A total of 89.33% of all compounds were able to be analysed, in which 14.69% are derivatives of the silylation reaction. The missing 10.67% were either non identified or questionable compounds. The majority of substances analysed appear to be fatty acids with a total of

41.14%, in which oleic acid is the most abundant compound with 16.98%. The content of the unsaponifiable substances like sterols, terpenes and fatty alcohols is also fairly high.

Table 2: Results of the GCMS-analysis of the acetone extract, derived from unbleached softwood kraft pulp during winter at low capacity load

classes	%	most abundand compounds	%
Fatty acids	41,14	oleic acid	16,98
Resin acids	1,83	dehydroabietic acid	0,86
Sterols	10,51	β-sitosterol	5,94
Fatty alcohols	6,94	docosanol	3,15
Terpenes	7,64	manoyl oxide	7,64
Acids	5,69	3-hydroxyisocaproic acid	3,25
Sugars	0,89	-	-
BSTFA/pyridin derivates	10,68	-	-

The relative amounts of fatty acids drastically increased, when comparing the analysis results of the summer and winter pitch. However, the amount of resin acids decreased. This may be due to the fact, that fatty acids are not easily dissolved in moderate alkaline conditions in comparison to resin acids, as mentioned in literature. The low capacity load might have enhanced the alkaline cooking and washing efficiency, effectively removing substances like resin acids but leaving behind long chain fatty acids (Strand, 2013). Another reason for this could be the seasonal composition of pitch (Blazey, Grimsley and Chen, 2002). The amount of non-identified compounds was higher in case of the summer pitch analysis. These non-identified substances might include some fatty acid compounds. Nevertheless, the content of fatty acids was higher for the winter pitch sample compared to the summer sample. Since the attempt to analyse the high capacity load during winter failed, pointing out the exact reason for these phenomena is impossible.

3.2 1st trial

Non-extracted and extracted kraft pulp

Figure 16 shows the results of the first trial for the reference and extracted pulp sample. The extracted pulp yielded weaker paper strength than the reference, although components that may harm the tensile index were extracted. The TEA-index (see Figure 17) mimics overall the results of the tensile index. The reduced tensile index of the acetone extraction sample occurs most probably due to the reduced swelling capacity of the fibers after the extraction.

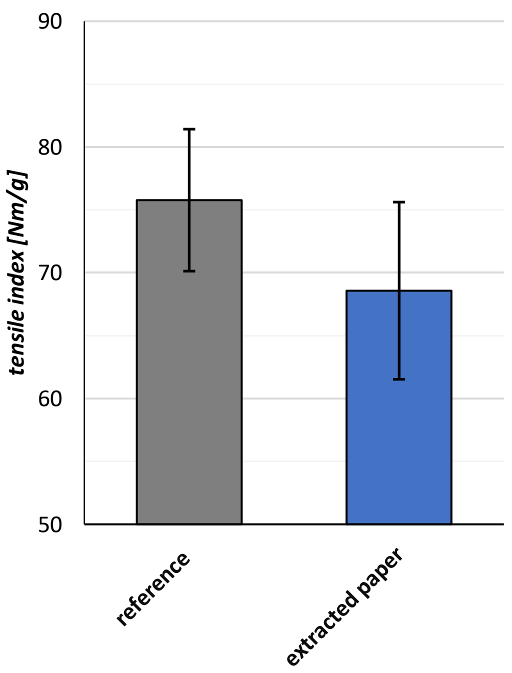

Figure 16: Influence of acetone extraction on the tensile index of unbleached softwood craft pulp

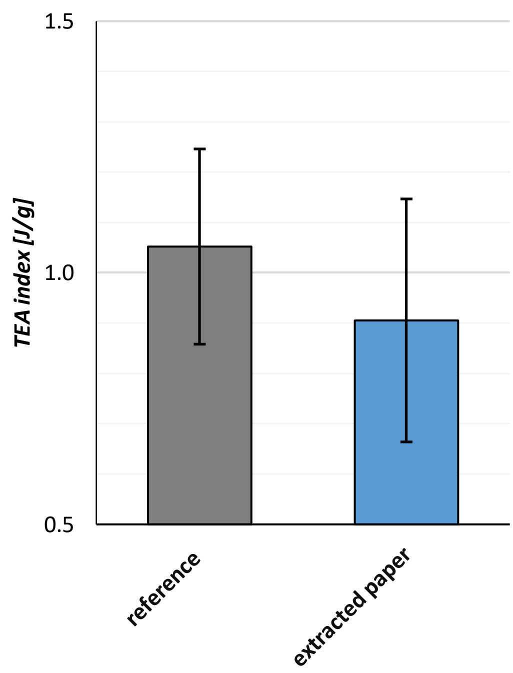

Figure 17: Influence of acetone extraction on the TEA index of unbleached softwood craft pulp

According to Figure 18 the air permeability of the extracted pulp was lower than the reference. The extracted pulp seemed to have a higher tendency to absorb water than the non-extracted pulp which is shown in Figure 19. Due to the removal of hydrophobic extractives, the hydrophilicity of the extracted paper is higher compared to the reference sample.

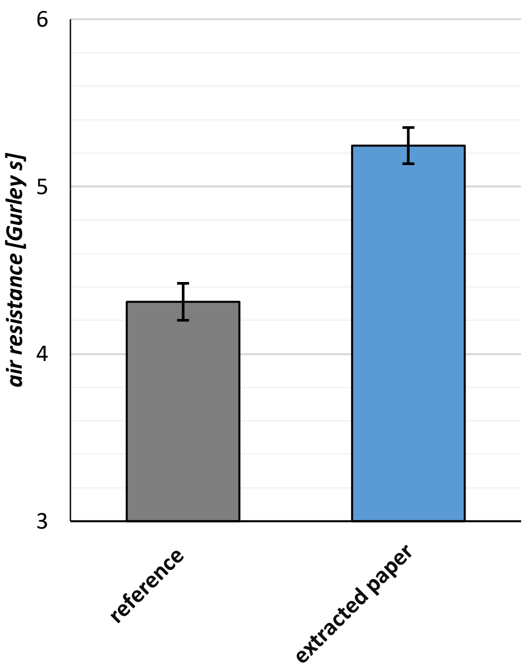

Figure 18: Influence of acetone extraction on the Gurley value of unbleached softwood craft pulp

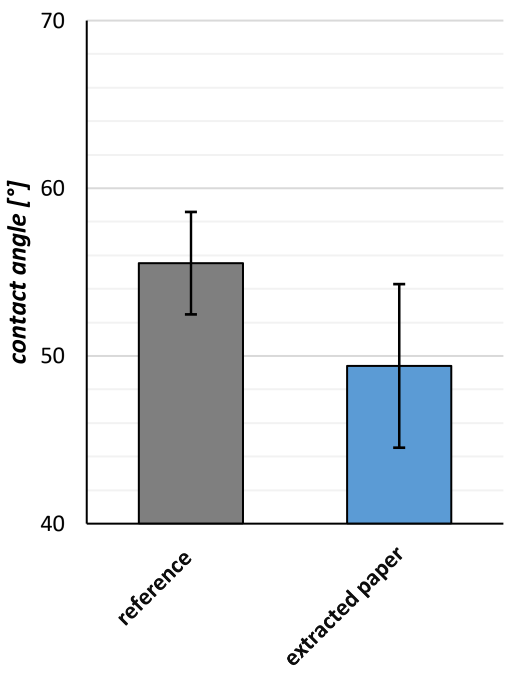

Figure 19: Influence of acetone extraction on the contact angle of unbleached softwood craft pulp

Figure 20 shows the extracted content of the papers via Soxhlet extraction. In contrast to our expectation, extracted content from the extracted paper was still half of the amount of the untreated pulp. This means that full removal of extractives, even with solvent (acetone), is very difficult.

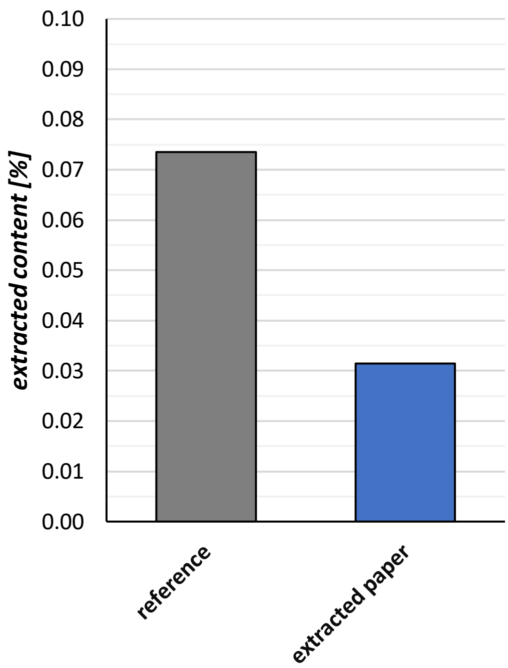

Figure 20: Influence of acetone extraction on the extracted content of unbleached softwood kraft pulp

The cause of these results might be the deswelling of the pulp fibres due to the acetone extraction which may lead to lower paper strength and higher air resistance. The swelling ability is not recovered after acetone extraction despite the prolonged stay in water. The outcome indicates that the acetone extraction had a negative influence on the produced paper. Although confidence intervals between reference and extracted sample are partly overlapping, there is a statistically significant difference.

Influence of model compounds

In Figure 21 and Figure 22 the tensile- and TEA index are depicted of the paper treated with the model compounds. In the case of abietic acid the strength properties of the paper barely changed which indicates that resin acids may not be harmful. However, the addition of oleic acid had a big impact on the strength of the paper. Oleic acid (unsaturated fatty acid) seemed to have a negative influence on paper strength while abietic acid (resin acid) had no significant impact, which was also described by Kokkonen et al. (2002).

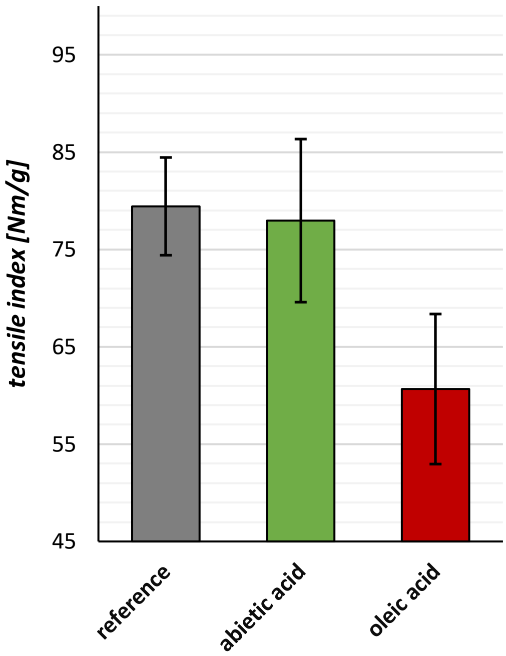

Figure 21: Influence of oleic- and abietic acid on the tensile index of kraft paper

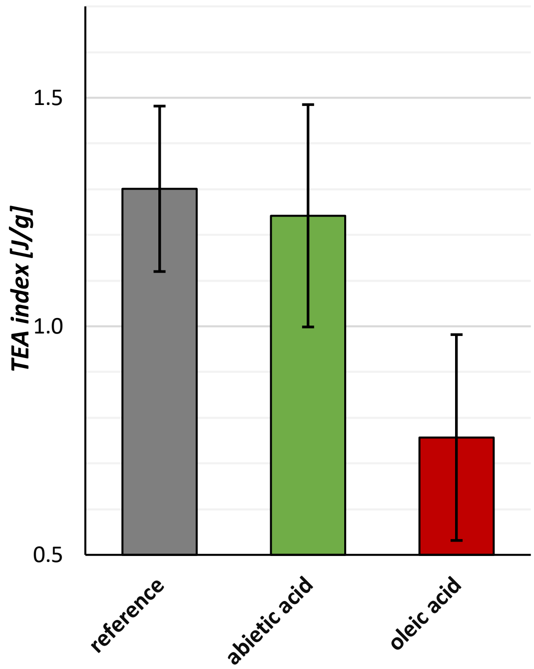

Figure 22: Influence of oleic- and abietic acid on the TEA index of kraft paper

In contrast to the results of Kokkonen et al. (2002), the air permeability of paper was slightly reduced by the addition of the resin acid. The fatty acid had no influence in comparison to the reference sheets which is depicted in Figure 23. The hydrophilicity of the paper was slightly lower in case of abietic acid samples, which is in line with Kokkonen et al. (2002). However, the oleic acid seemed to have a higher attraction to water. This instance is shown in Figure 24. According to Kokkonen et al. (2002) oleic acid did not really have an influence on the contact angle.

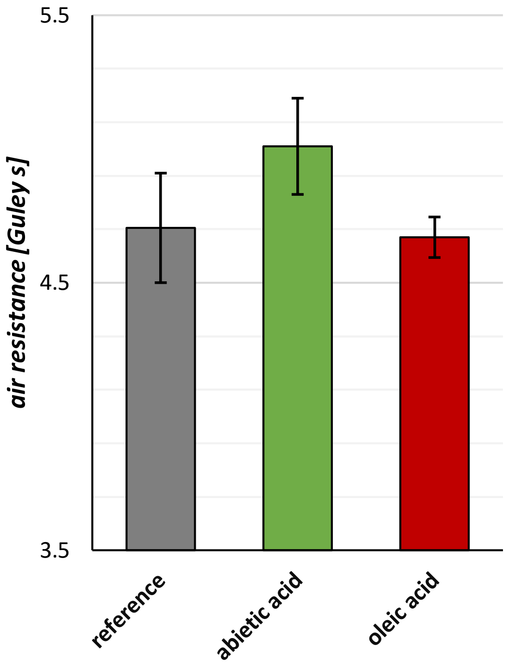

Figure 23: Influence of oleic- and abietic acid on the air permeance of kraft paper

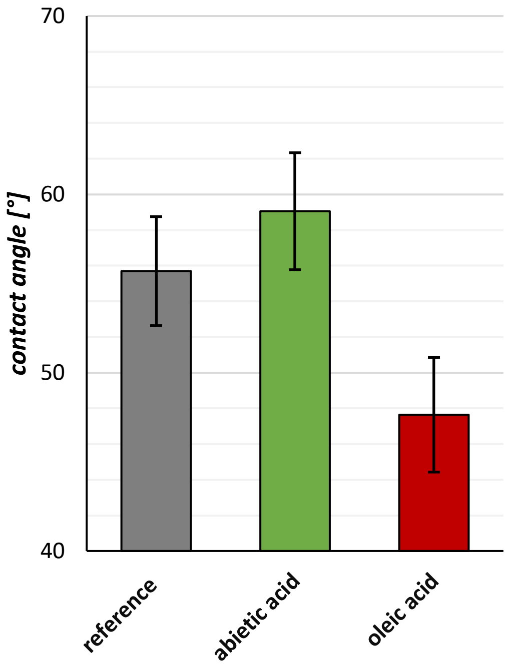

Figure 24: Influence of oleic- and abietic acid on the contact angle of kraft paper

The extracted amount from the paper was higher in both cases of resin- and fatty acids, depicted in Figure 25. This indicates that added compounds are adsorbed or precipitated on the pulp fibres used for paper production and are not just washed away by water.

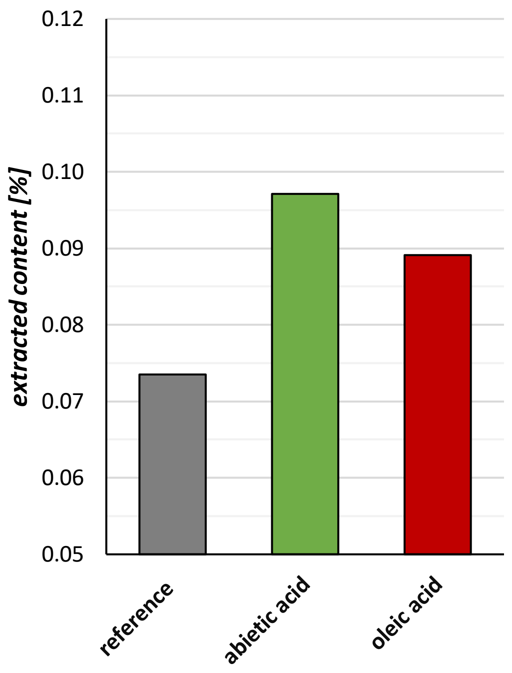

Figure 25: Influence of oleic- and abietic acid on the extracted content of kraft paper

The results show that model compounds had an influence on paper properties. While abietic acid had no major influence on paper strength, the addition of oleic acid certainly had. The different components of pitch seem to have dissimilar influence on the quality of paper which was further investigated in subsequent trials. While the reduction of the tensile index through oleic acid was also described by Kokkonen et al. (2000), the results for air permeance or contact angle were not in complete agreement with the literature.

3.3 2nd trial

Influence of different model compounds on paper properties and starch

Oleic acid and abietic acid had different impacts on paper properties in the 1st trial, therefore other model compounds of pitch were tested in the second trial to gain information about their effects. In addition, cationic starch was added to gain an impression how single components may interact with it and to get closer to process conditions as it is frequently used as a strength enhancing agent in industry.

Figure 26 contains the results for the tensile index of papers produced with and without starch. The bars in the front represent the samples without starch. Paper strength was lowest with oleic acid, similar to the papers with pitch model compound mixture. Although stearic acid is a fatty acid as well, there was a significant difference in tensile strength compared to oleic acid. This is the same as in the case of Kokkonen et al. (2002), i.e. unsaturated fatty acids are more harmful for strength than saturated ones.

The other pitch compounds didn't have a major influence on paper strength, except docosanol which lowered the value slightly.

The bars in the rear of the diagram indicate the paper samples with pitch and starch. Overall the mixtures, i.e. model compound mixture and extracted pitch, and the oleic acid had the lowest tensile index. In this trial, the increase in paper strength due to addition of starch seemed to be inhibited by docosanol, β-sitosterol, stearic acid and oleic acid when compared to the reference. Especially the β-sitosterol exhibited barely any increase in tensile index in comparison to the sample without starch. This may indicate an interaction between starch and pitch molecules. In case of the pitch model mixture with starch sample the results were similar to the oleic acid. Abietic acid and linalool were the same as the reference.

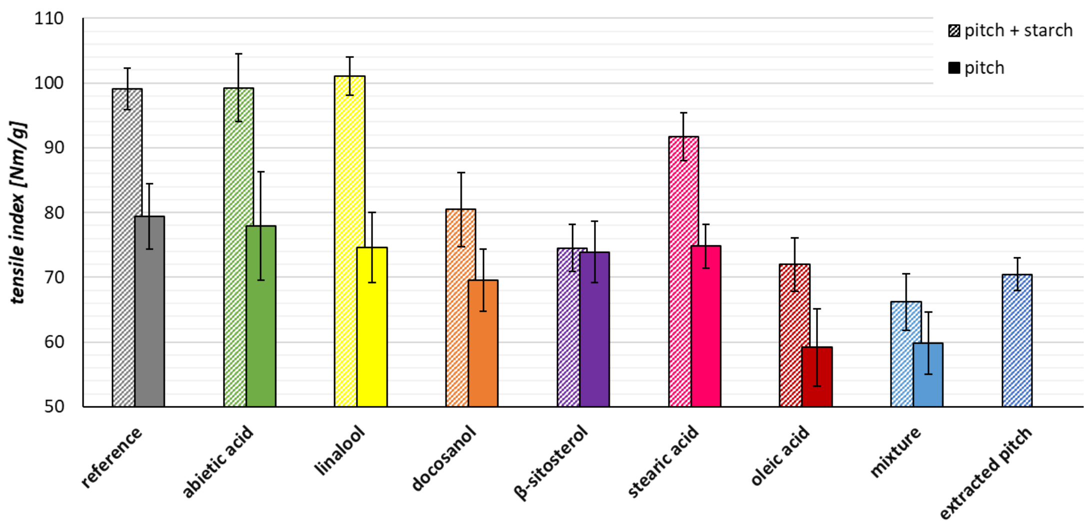

Figure 26: Influence of pitch model compounds on the tensile index of unbleached softwood kraft pulp handsheets with and without starch

In Figure 27 the TEA index of this trial is depicted. The results appear to be nearly identical to the tensile index of this experiment. Every compound with starch, except the resin acid and the terpene, lowered the value of the TEA index compared to the reference. Docosanol and stearic acid in combination with starch only exhibited a slight increase in strength compared to the sample without starch. β-sitosterol showed a very small decrease with overlapping confidence intervals, therefore the difference is not statistically significant.

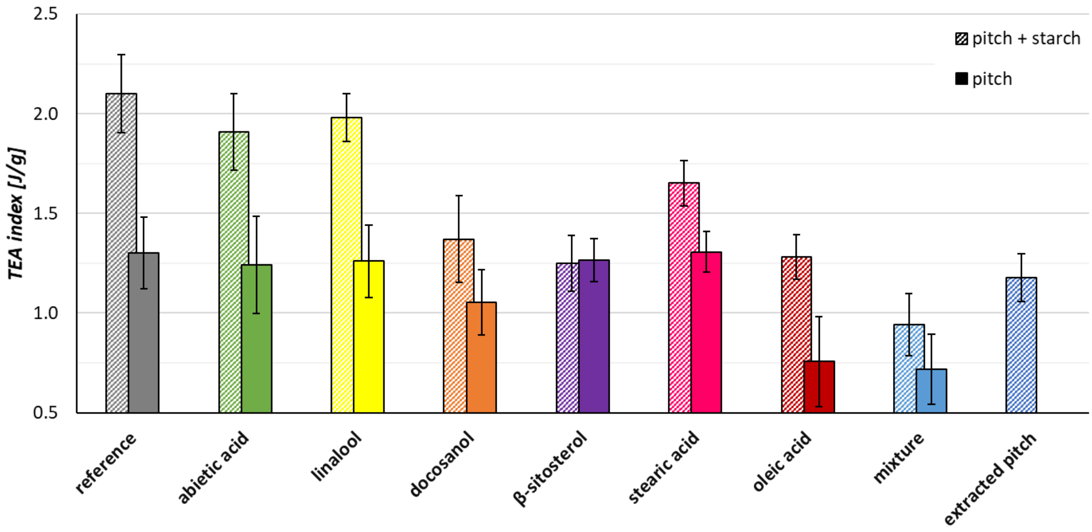

Figure 27: Influence of pitch model compounds on the TEA index of unbleached softwood kraft pulp handsheets with and without starch

The air permeance of paper increased due to every component except abietic acid (Figure 28; front bars). The mixture of compounds shows especially high air permeance which might be caused by the combination of the influence of the different compounds. Air permeance increased while paper strength decreased due to disturbed interfiber bonding which led to a more porous sheet. The air permeance of paper was increased in by the addition of starch for many samples shown by the rear bars of the diagram. Starch may have worsened the formation and thus the sheet became more permeable.

However, the reference and oleic acid had the same air permeance with and without starch. In case of docosanol and stearic acid the air permeances were more or less the same due to overlapping error bars.

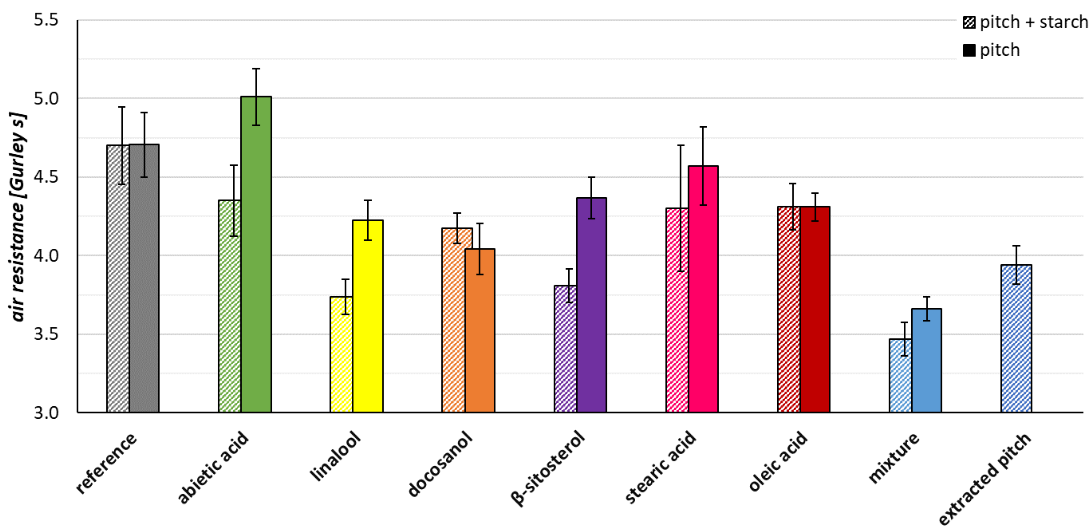

Figure 28: Influence of pitch model compounds on the air permeance of unbleached softwood kraft pulp handsheets with and without starch

The wettability of the papers produced is depicted in Figure 29. The bars in the front indicate that water resistance was lower for the added compounds than the reference sample. However, in case of abietic acid and stearic acid the contact angle seemed to have approximately the same value as the reference.

The addition of starch had a positive effect on the water resistance for every compound except for docosanol, β-sitosterol and the mixture. Somehow, the contact angle for the process water sample with starch was very high compared to the other components.

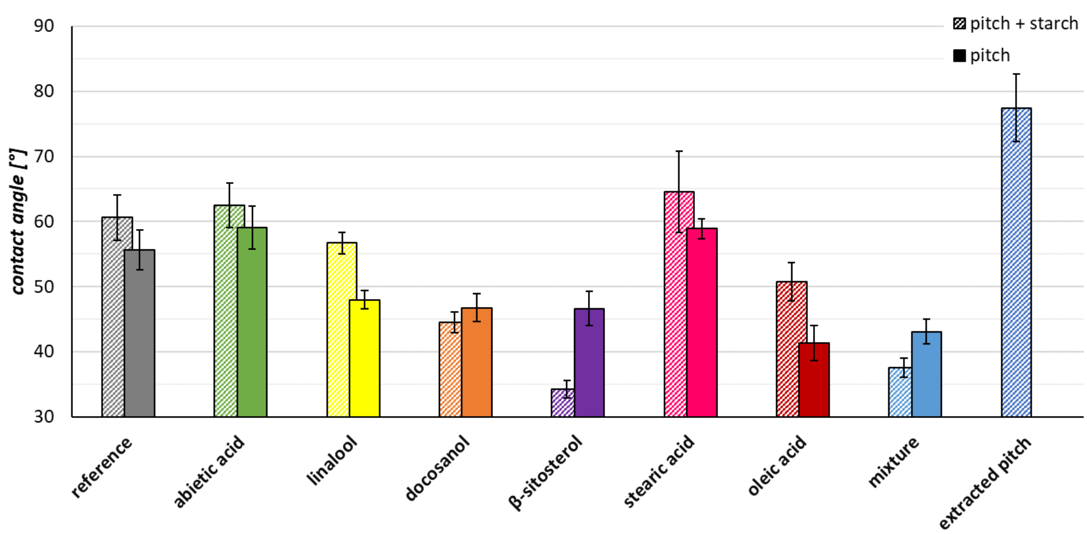

Figure 29: Influence of pitch model compounds on the contact angle of unbleached softwood kraft pulp handsheets with and without starch

As expected, pitch content of paper sheets increased for every compound shown in the front bars in Figure 30. The extracted content of the mixture was very high. Oddly in case of linalool the extracted amount decreased. The gravimetric measurement of the extracted amount could only be done once, therefore the result might be an outliner.

The bars in the rear depict the extracted amounts of compounds with starch. Docosanol and β-sitosterol had a very high retention with starch. Both compounds are unsaponifiable, i.e. they don't dissolve easily and thus starch was probably capable of binding or agglomerating them to the fibres. Especially in the case of β-sitosterol the starch was not able to increase tensile index. The fatty acids and the mixture also exhibited higher retention. The extracted content for the resin acid and terpene decreased by the addition of starch.

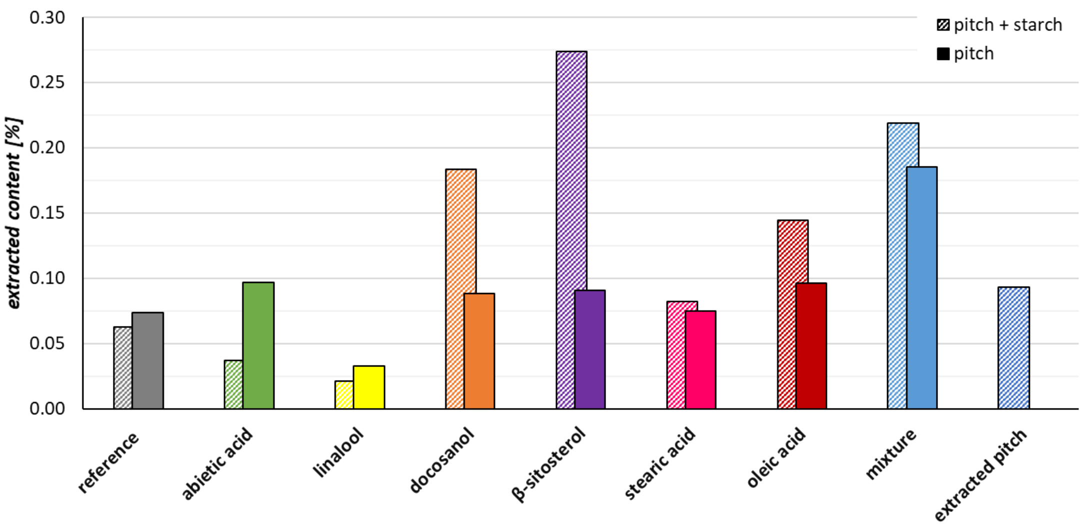

Figure 30: Influence of pitch model compounds on the extracted content of unbleached softwood kraft pulp handsheets with and without starch

The results of this trial show that oleic acid had a negative influence on the paper strength with and without starch. Stearic acid and the fatty alcohol (docosanol) lowered the tensile strength too, but at a lower magnitude. β-sitosterol was also harmful for the paper strength without starch. It was especially harmful witch starch due to blocking the positive effect of starch. The air permeance of paper samples was improved by nearly every compound. The water resistance however suffered by the addition of pitch components except for abietic acid and stearic acid.

3.4 3rd trial

Verification of results

The results of the second trial were very interesting, therefore another trial was done to check for their validity at realistic pitch concentrations (1 mg compound / g pulp).

The tensile index of the papers with oleic acid and the mixture was overall the same as the reference and β-sitosterol without starch, shown by the front bars of Figure 31.

The bars in the rare show that the tensile strengths of papers with β-sitosterol and pitch mixture in combination with starch were lower compared to the reference. The tensile index of papers with oleic acid and starch was not significantly lower compared to the reference. The relative increase in strength through starch for the papers with pitch mixture and β-sitosterol wasn't as low as in the previous trial with higher pitch concentration. The effect of starch was not so much hindered when the pitch amount was lower.

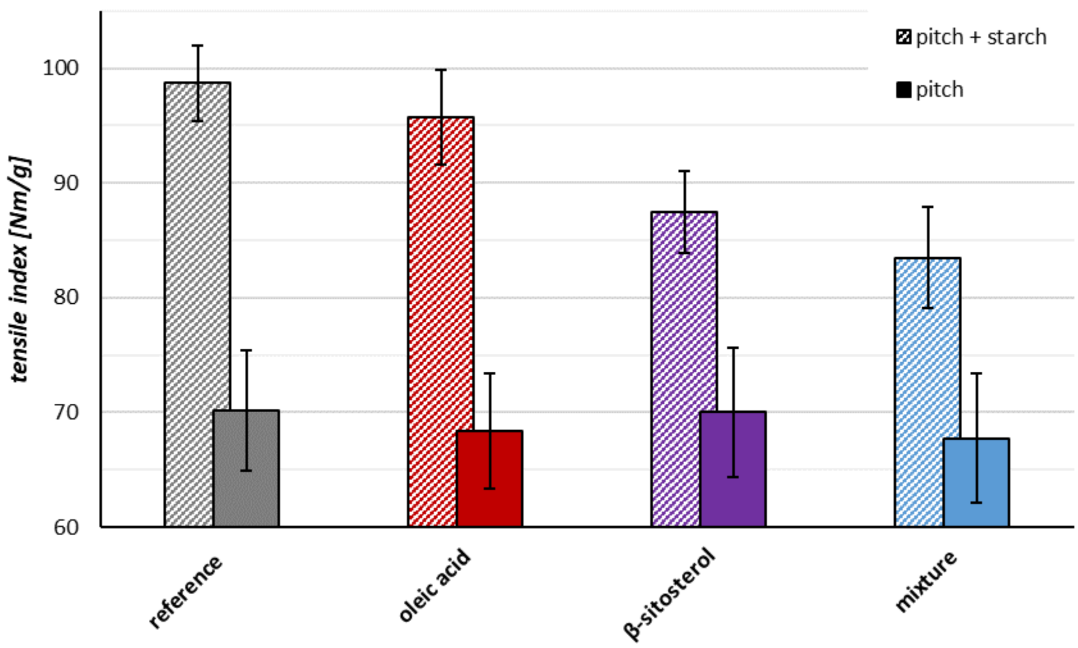

Figure 31: Influence of pitch model compounds with realistic concentrations on the tensile index of unbleached softwood kraft pulp handsheets with and without starch

The TEA index of the front bars in Figure 32 shows overall the same outcome as the tensile index. The papers with β-sitosterol, mixture and oleic acid without starch had approximately the same values as the reference. The error bars for the TEA index are relatively big and overlap, therefore the mean values of those results are not differentiable.

The bars in the rare (TEA index of pitch with starch) mimic overall the results for the tensile index. All compounds were lower in energy absorption than the reference though in case of oleic acid the difference was not significant. β-sitosterol and the mixture lowered the positive effect of the starch.

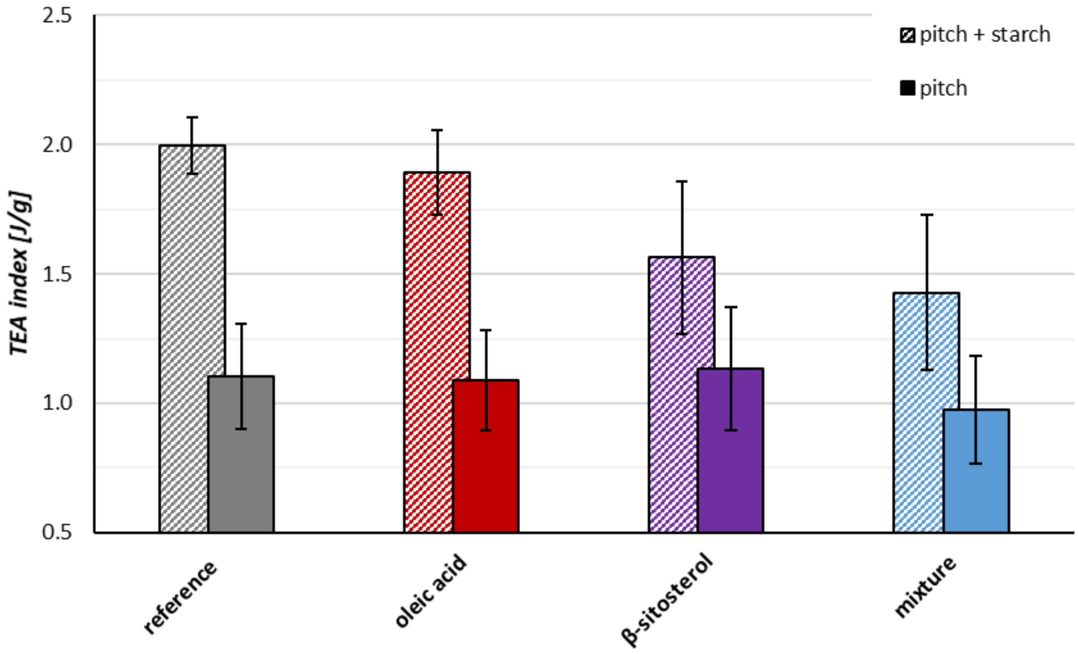

Figure 32: Influence of pitch model compounds with realistic concentrations on the TEA index of unbleached softwood kraft pulp handsheets with and without starch

The air permeance of papers with β-sitosterol and oleic acid without starch, shown by front bars in Figure 33, was higher than the reference. This was also noticed in the second trial. In contrast to the second trial, the paper with pitch mixture had approximately the same Gurley value as the reference.

The addition of starch lowered the air permeance of all samples which is indicated by the rare bars. Starch probably improved interfiber bonding and thus densified the papers which led to lower air permeance. The Gurley value was slightly higher for the reference and papers with β-sitosterol and mixture. In case of papers with oleic acid, the air permeance decreased a lot by the addition of starch.

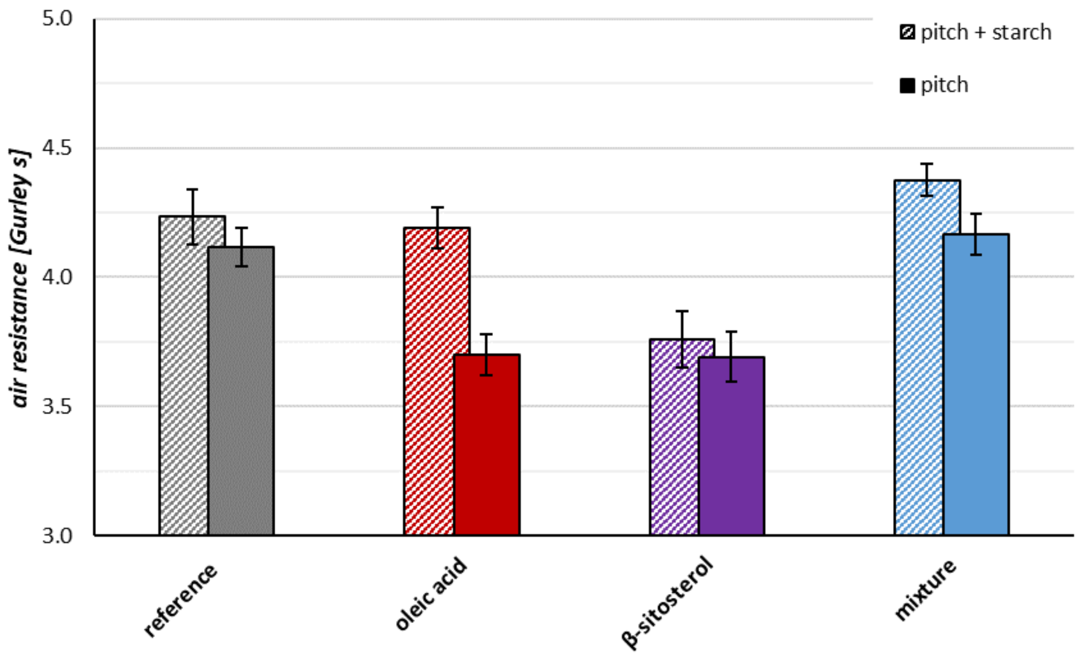

Figure 33: Influence of pitch model compounds with realistic concentrations on the air permeance of unbleached softwood kraft pulp handsheets with and without starch

In contrary to the second trial the water resistance of papers with oleic acid and β-sitosterol was approximately the same as the reference. (front bars in Figure 34) The results are in line with Kokkonen et al. (2002). The mixture had a lower contact angle compared to other samples.

The addition of starch increased the water resistance of papers with all the different compounds except with oleic acid, which exhibited the same values as without starch. When starch was added, the contact angle was lower for papers with pitch in comparison to the reference sample.

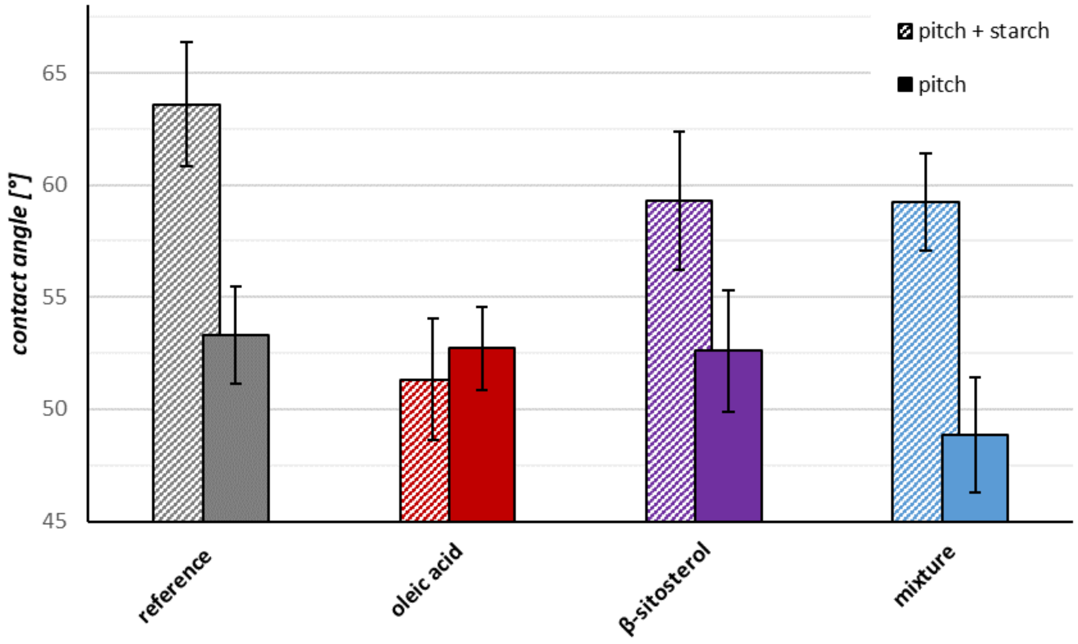

Figure 34: Influence of pitch model compounds with realistic concentrations on the contact angle of unbleached softwood kraft pulp handsheets with and without starch

As expected, the extracted content increased with every compound without starch, shown by the front bars in Figure 35. The addition of starch increased the extracted amount of papers with all the different substances depicted by the rare bars in the diagram. Papers with oleic acid in combination with starch had the highest increase.

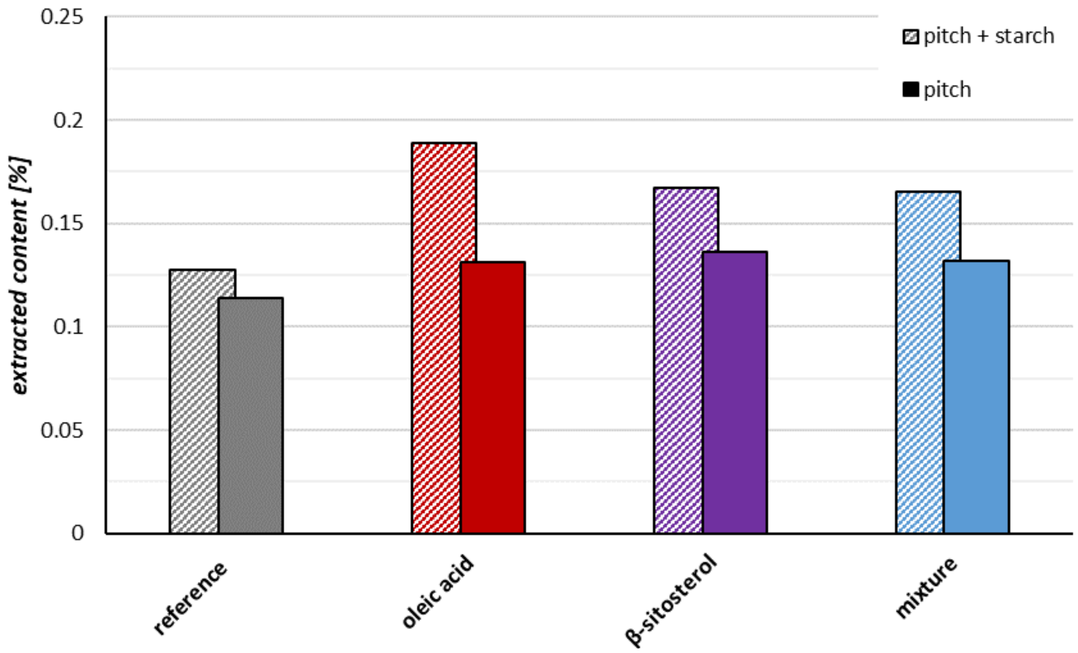

Figure 35: Influence of pitch model compounds with realistic concentrations on the extracted content of unbleached softwood kraft pulp handsheets with and without starch

The lower concentration of compounds had an impact on the magnitude of the results. However, the values still exhibit a certain pattern, similar to the second trial. Oleic acid seemed to slightly lower the tensile index with and without starch, but not significantly in this trial. β-sitosterol hindered the positive effect of starch. On the other hand, the strong retention of β-sitosterol measure with the extracted content was not observed. The water resistance increased with starch whereas in the previous trial it didn’t. Furthermore, the starch didn’t increase the air permeance of paper with β-sitosterol.
The next step was to mimic the process conditions of the real industrial paper making process as close as possible in the laboratory in order to observe the behaviour and influence of the pitch compounds under these circumstances.

3.5 4th trial

Mimicking the process conditions of real paper production

The results of previous experiments showed that oleic acid and β-sitosterol may have negative influences on paper production. The fourth trial was designed to mimic the real process conditions as close as possible to get an impression, how pitch compounds behave under these circumstances. Therefore, the trial was executed in an industrial laboratory at the process plant. A major reason for this was the hardness of the water which has an influence on paper production. In Graz the water is quite “hard” with approximately 16.7 dH, which is a much higher value than at the production site, where the water is considered to be soft with about 6.2 dH.
Before paper production, the pH in the distributor was increased to 10, which mimicked the pH value of the incoming pulp to the paper production.
Alum was added to all samples because it is used as a retention aid in industrial paper making process. Alum was used to lower the pH of the pulp suspension to a value of 6.8 before sheet forming which mimics the process conditions. Furthermore, handsheets with talcum were produced to see if there is an effect on paper strength and pitch retention. As described in the literature part of this thesis, talcum is added in paper production to prevent pitch agglomeration and deposition within the production machine, enhance pitch control and increase in general the quality of finished paper products. Related to the previous experiment, the

concentration of pitch was regulated to 1 mg pitch / g pulp. This is in the same order of magnitude as the pitch content in the paper mill process waters.

The results for the tensile index of this trial are represented by Figure 36. The solid bars in the front show the samples with added pitch compounds. In contrast to previous experiments the tensile index rapidly decreased for every pitch component when compared to the reference sample. While oleic acid had a very negative influence on the strength, stearic acid and docosanol showed even worse results. Abietic acid and linalool exhibited also a low tensile index although in the previous experiments they didn’t seem to have such a negative impact. The results for papers with mixture and BL carry-over are approximately the average of the values of all compounds. It seems that the alum effectively agglomerated and retained all pitch compounds at the cost of tensile strength.

The striped bars in the middle represent the papers with pitch compounds and starch. The tensile index of papers increased when the pitch compounds were added together with the strengthening agent. The positive effect of starch was more pronounced than in the previous trials. Oleic acid exhibited the lowest strength followed by stearic acid. Oleic acid and β-sitosterol had the lowest increase with starch. The tensile strengths of papers with model compounds, BL carry-over and mixture together with starch were approximately in the same range. The papers with oleic acid and starch exhibited the lowest tensile index.

The dotted bars in the rare represent the papers with pitch compounds, starch and talcum. Talcum doesn’t seem to have a big influence on the paper strength itself. The error bars overlap with the results of papers with pitch compounds and starch. In case of the reference, the addition of talcum had a noticeable negative influence on the strength when compared to the reference paper with starch. Nonetheless, the result was still in the range of the compound with starch and talcum samples.

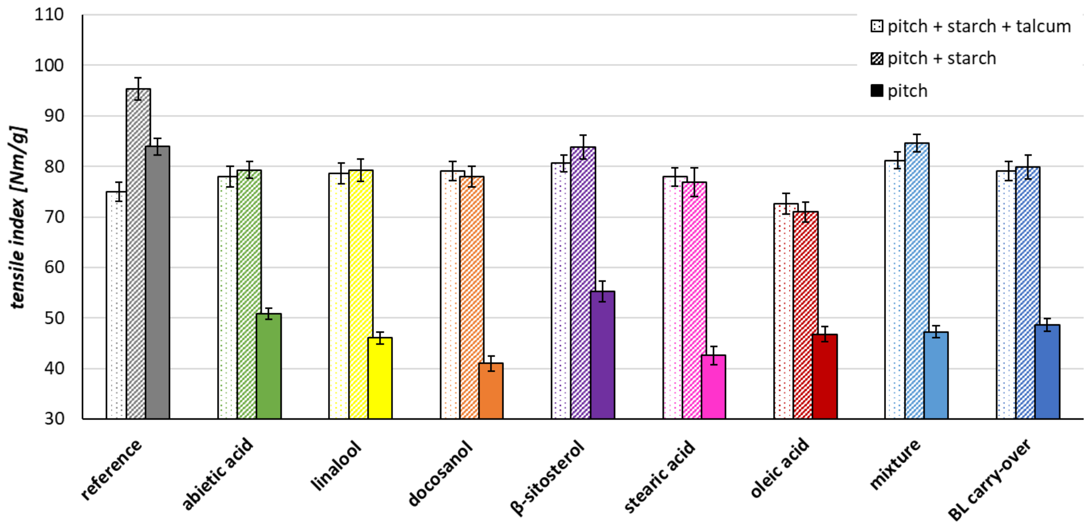

Figure 36: Influence of pitch model compounds under laboratory simulated process conditions on the tensile index of unbleached softwood kraft pulp handsheets without starch / with starch / with starch and talcum

The TEA index of this trial is depicted in Figure 37. The values mimic overall the results of the tensile index.

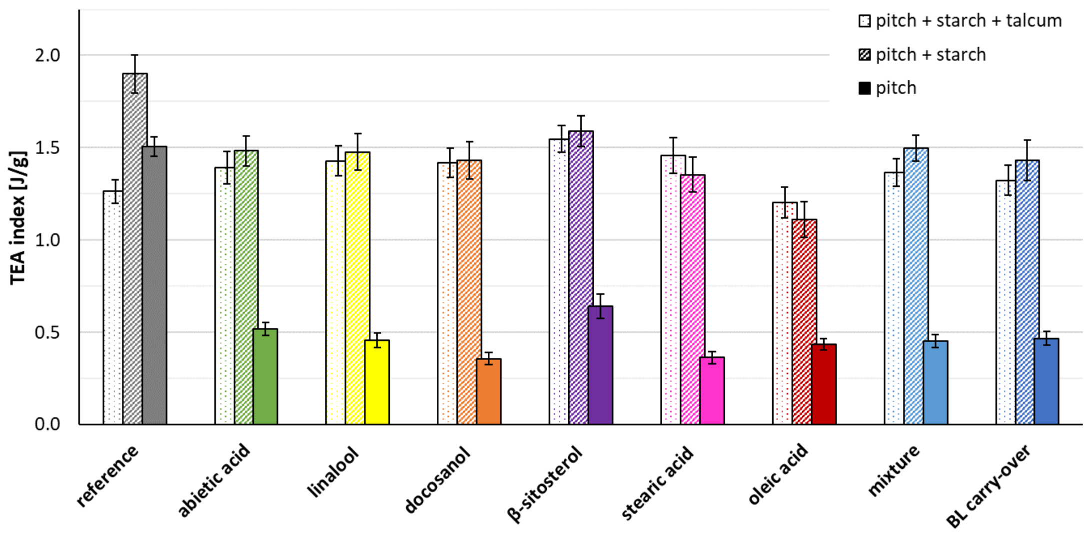

Figure 37: Influence of pitch model compounds under laboratory simulated process conditions on the TEA index of un-bleached softwood kraft pulp handsheets without starch / with starch / with starch and talcum

The air permeance of the paper samples was improved by every pitch compound, even more than in previous trials as depicted by the solid front bars in Figure 38. Docosanol exhibited the lowest Gurley value followed by linalool and stearic acid. These high air permeance values in combination with low tensile index indicates

that the interfiber bonding between fibers was disturbed, and consequently the porosity became high and tensile index low. The values of the other compounds were approximately in the same range including the mixture and BL carry-over.
The addition of starch decreased air permeance in general as shown by the striped bars in the middle. Starch improved the interfiber bonding of the sheets, and thus decreased porosity (which was high without starch due to pitch) and improved tensile index. The reference exhibited no difference in air resistance with and without starch due to overlapping error bars. There was no pitch present without starch to reduce air resistance and tensile index, i.e. interfiber bonding without pitch was much better. Consequently, the starch influenced much less on porosity and tensile index. Linalool followed by abietic acid had the highest air permeance while the mixture and the BL carry-over showed at least the same Gurley value as the reference. No correlation between air resistance and tensile index can be seen here.
The talcum had not a big influence on the air permeance overall with exception of the reference sample as represented by the dotted bars in the rare. Only the reference showed higher air permeance when talcum was added.

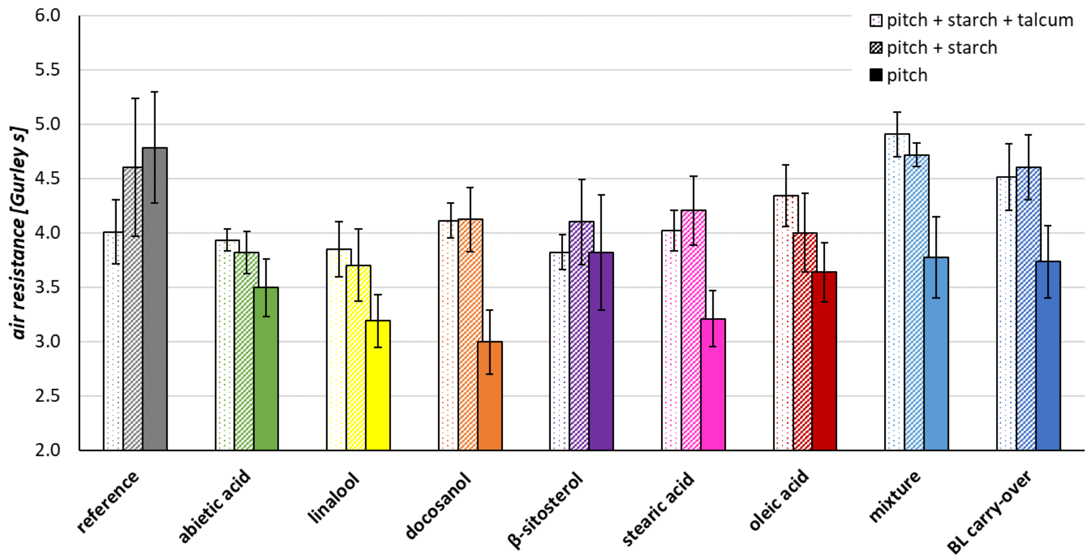

Figure 38: Influence of pitch model compounds under laboratory simulated process conditions on the air permeance of un-bleached softwood kraft pulp handsheets without starch / with starch / with starch and talcum

The water resistance of the produced samples is depicted in Figure 39. The papers of each pitch substance had approximately the same contact angle which is shown by the solid front bars. Oddly, the contact angle decreased in comparison to the reference, when pitch was added.

By adding starch, the hydrophobicity in general increased as illustrated by the striped bars in the middle. While the contact angles of papers with oleic acid, stearic acid and β-sitosterol were high, the reference papers and papers with BL carry-over exhibited the lowest values. Other compounds in the BL carry-over (e.g. hemicelluloses) eventually reduce the hydrophobic effect of pitch.

The dotted bars in the rare indicate that the addition of talcum had not a big impact on the contact angle. Only the reference paper with talcum and starch exhibited a significant lower value compared to the reference paper with starch. For papers with all other compounds the value of the contact angle stayed in the same range as the results for the samples with starch.

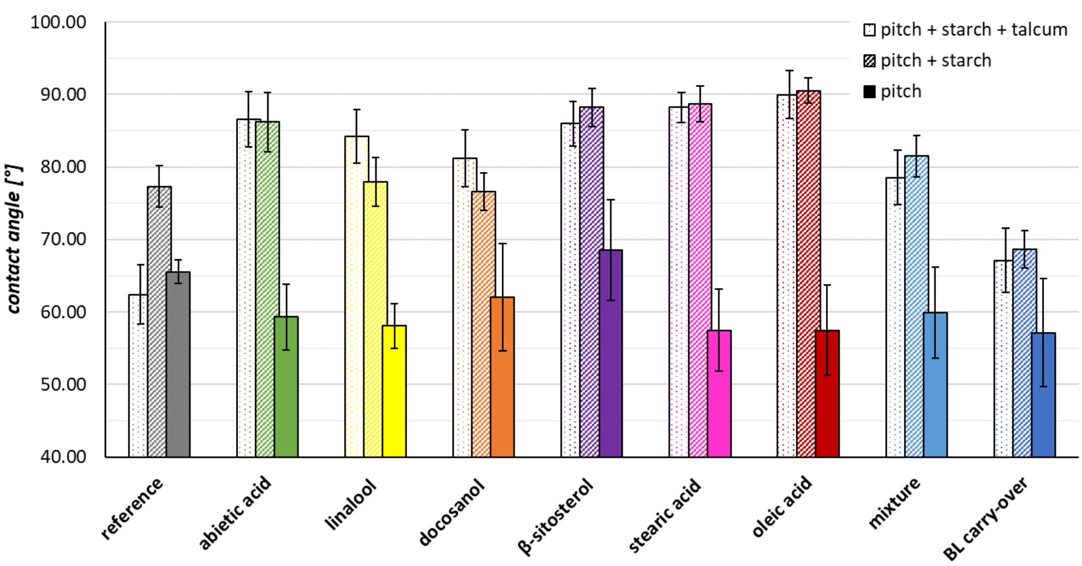

Figure 39: Influence of pitch model compounds under laboratory simulated process conditions on the contact angle of un-bleached softwood kraft pulp handsheets without starch / with starch / with starch and talcum

Figure 40 illustrates the extracted content from the samples of this trial. The solid bars in the front show that the extracted amount in comparison to the reference increased by the addition of compounds which was expected. The relative masses of the extracts from the samples are approximately in the same range from 0.1% to 0.15% with exception of the mixture, linalool, docosanol and of course the reference.

The addition of starch increased a bit or did not change the extracted amount of all compounds as depicted by the striped bars in the middle. Docosanol and the BL carry-over had a slight decrease in relative mass.

Talcum had not a big influence on the extracted amount of produced handsheets. The extracted amount stayed roughly the same compared to the papers with compound and starch samples. This is shown by the dotted bars in the rare. The extracted content of papers with oleic acid and linalool decreased a little bit while papers with abietic acid exhibited a slight increase.

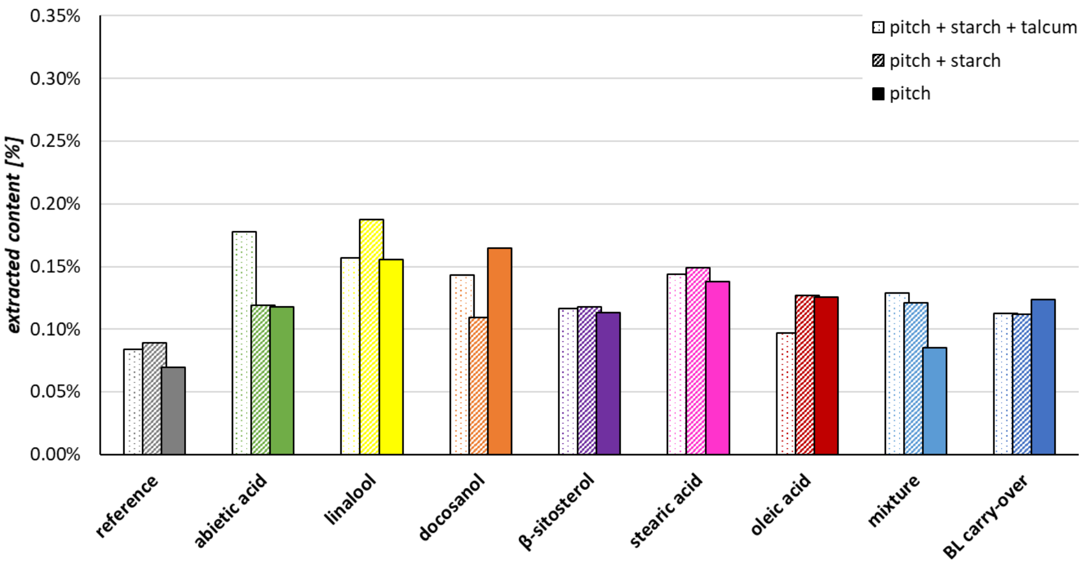

Figure 40: Influence of pitch model compounds under laboratory simulated process conditions on the extracted content of un-bleached softwood kraft pulp handsheets without starch / with starch / with starch and talcum

The trial in the industrial laboratory demonstrated that every compound of pitch is harmful for paper production in contrast to the previously performed trials. Papers with fatty acid and fatty alcohol (stearic acid and docosanol) without starch exhibited the lowest tensile index. Abietic acid and linalool without starch had a significant negative influence on the tensile index of papers.

The air permeance increased in general and the water resistance decreased overall by the addition of pitch compounds without starch. Both conclusions were also extracted from the previous trials. Perhaps the interfiber bonding was disturbed and thus porosity increased. Therefore, the increased porosity may have enhanced the air permeance and decreased the water resistance of the paper.

The extracted amount from Soxhlet extraction increased by the addition of compounds which was also true for other performed trials.

In combination with starch every compound showed a good increase in strength properties, although the relative increase was the lowest for oleic acid and β-sitosterol. In combination with starch, oleic acid had the lowest tensile index. In contrast to the second trial, the addition of starch decreased the air permeance in general. The water resistance was increased by starch overall which was also observed in other trials. The interfiber bonding was eventually improved by the addition of starch, decreasing the porosity and therefore enhancing air- and water resistance.

The effect of talcum was not really pronounced in this trial. It had little to no effect on nearly every paper property. Therefore, talcum is probably beneficial for reducing pitch deposit problems within the paper machine but had no noticeable impact on paper performance, at least not in the lab scale.

While papers with saturated fatty acid (stearic acid) or fatty alcohol (docosanol) exhibited the lowest tensile index without starch, the unsaturated fatty acid (oleic acid) was the most harmful compound for paper strength, when starch was present. According to the GC-MS analysis, the relative content of fatty acids in carry-over pitch was very high. In combination with the significant negative influence on the tensile index, fatty acids seemed to be especially harmful for paper performance.

Nevertheless, the outcome of this trial showed that every pitch compound had a remarkable negative influence on the paper strength which contrasts with previous trials. Besides the hardness of the water, the major difference to other experiments was the addition of the retention aid alum. Therefore, alum aroused suspicion to be in general harmful for paper production which was investigated in the following trials together with the influence of pH on paper performance.

3.6 5th trial

Investigation of the influence of alum and pH on paper properties

The fourth trial delivered interesting results, first and foremost that every compound had a negative influence under laboratory simulated industrial conditions. Since the addition of alum was one of the few things that changed as opposed to the previous trial, this experiment focused primary on the effects of alum on paper properties. In addition, the pH during paper making was investigated because it should've an influence on the state of dissolved substances. The pH was solely changed through the addition of alum in this trial, leading to samples produced at a pH value of 10, 8 and 6.8. The latter is the typically used pH for paper production at the production site. In case of the pH 10 sample no alum was added at all.

Every compound was harmful for tensile strength in the previous experiment. Therefore, only oleic acid was used in this trial as it has proven to be the most harmful component of pitch when starch was present. In this experiment all papers were produced with starch.

In Figure 41 the results of this trial are depicted. The solid bars in the front indicate that there was no significant difference between the reference and the papers produced with oleic acid.

The striped bars in the middle represent the samples produced at pH 8. Lowering the pH yielded lower tensile index for the reference and higher tensile strength in case of oleic acid. Since the error bars overlap with each other, there might not have been any difference.

The tensile strength of the produced samples at pH 6.8 was significantly lower compared to other samples. Oleic acid exhibited higher strength properties than the reference sample under these circumstances.

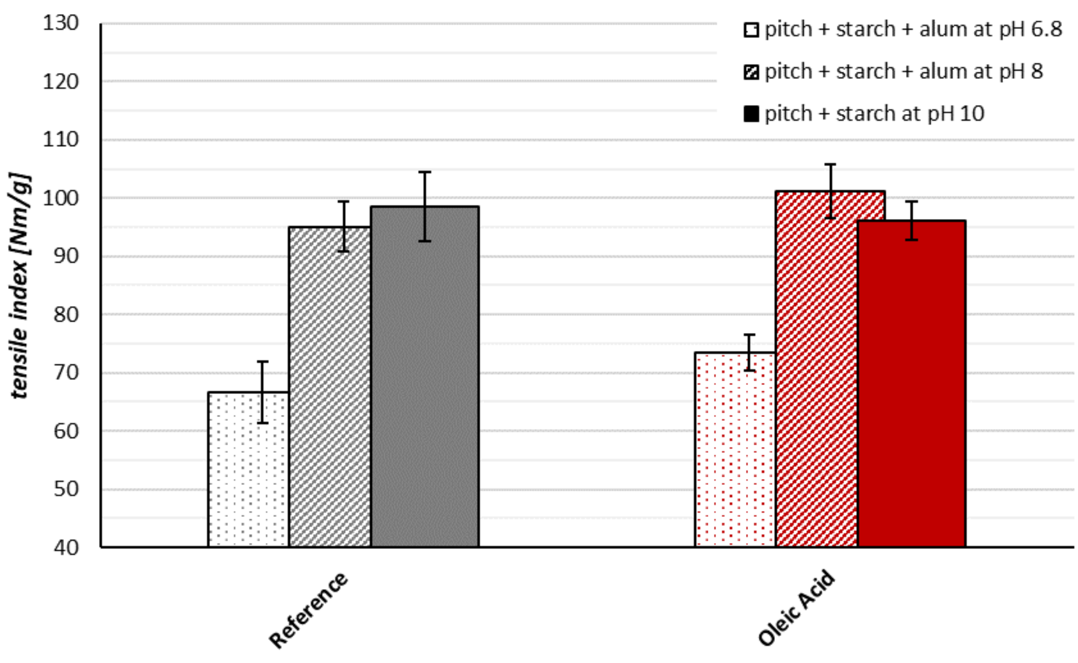

Figure 41: Influence of different pH levels during papermaking on the tensile index of unbleached softwood kraft pulp handsheets: papers with starch at papermaking pH 10 / with starch and alum at papermaking pH 8 / with starch and alum at papermaking pH 6.8

The results of this trial show that there was a huge impact on tensile strength by lowering the pH. Nevertheless, there were still uncertainties whether the alum or the pH itself contributed to these values of tensile index. The following trial was designed for clarification of these factors. Furthermore, it was investigated whether the pulp can be further purified by alkaline washing.

3.7 6th trial

Further investigation of the influence of alum on paper properties and impact of pulp purification through alkaline washing

In this experiment all samples were produced at a pH 6.8 to mimic process conditions. The pH was adjusted either with alum or sulfuric acid to see if alum has an influence on paper strength.

In addition, the given pulp from the industrial partner was further washed under alkaline conditions. The further purified pulp was then used for production of handsheets at pH 6.8 which was adjusted with alum. This was done to gain an impression whether the pulp can be further purified and whether this purification yields better strength properties.

In Figure 42 the results for the tensile index of this experiment are depicted, the bars in the front indicate the samples without starch. The unwashed sample adjusted with sulfuric acid had a much higher tensile index than the unwashed sample adjusted with alum. Alum seems to be quite harmful for paper strength when used in such high quantities (approximately 0,435 g of alum was needed to bring the pH down to 6.8 in the beaker). Although the difference between the further purified (washed) sample with alum and the unwashed sample with alum is only small, the results show a significant statistical difference, i.e. washing improved the tensile index.

The striped bars in the rare show similar trends for the samples in combination with starch. Adjusting the pH with sulfuric acid yielded a much higher tensile strength in comparison to the unwashed reference sample adjusted with alum. The washed reference sample with starch also exhibited a higher tensile strength than the unwashed reference sample with starch.

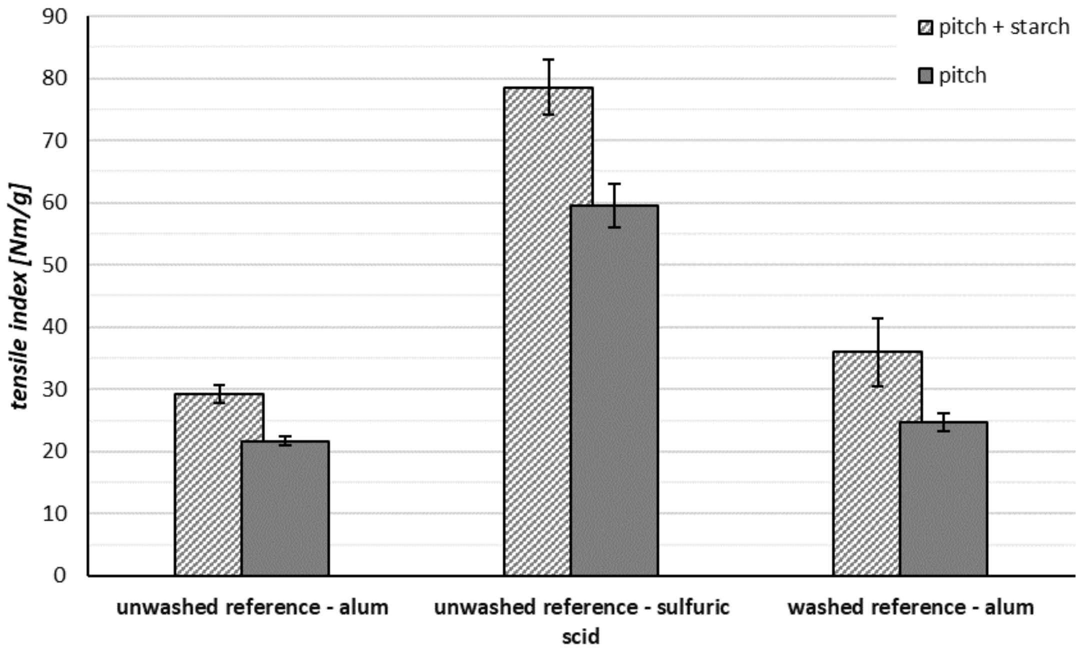

Figure 42: Influence of excessive addition of alum and further purification of the pulp on the tensile index of un-bleached softwood kraft pulp handsheets with and without starch at realistic papermaking pH 6.8

The TEA index depicted in Figure 43 shows the same trend as the tensile index but much more pronounced.

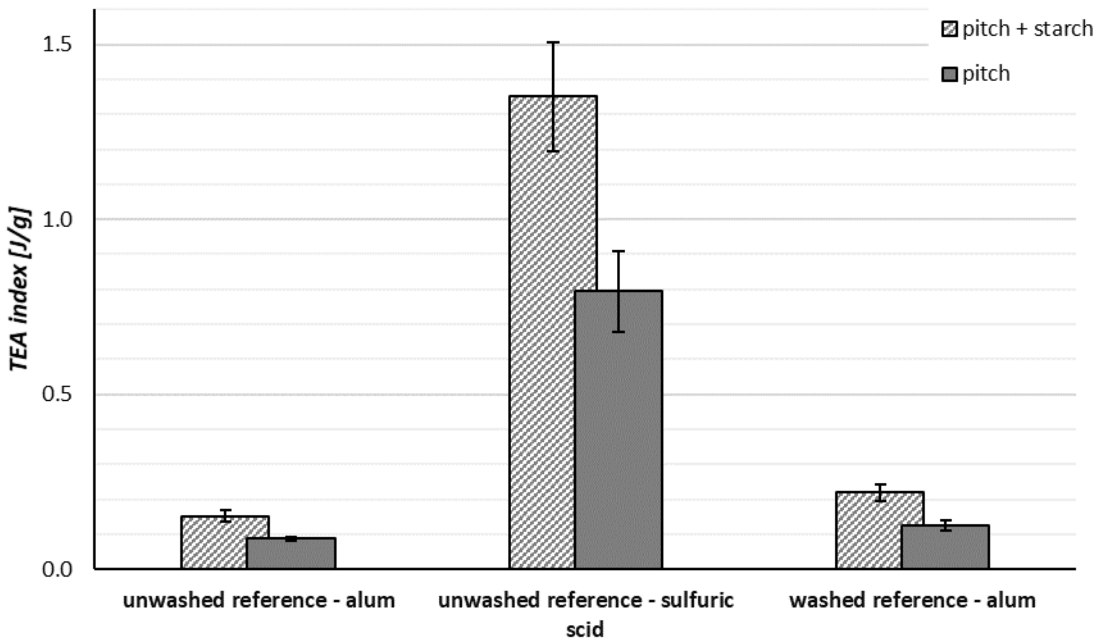

Figure 43: Influence of excessive addition of alum and further purification of the pulp on the TEA index of un-bleached softwood kraft pulp handsheets with and without starch at realistic papermaking pH 6.8

The air permeance of the unwashed reference with alum is higher than the unwashed reference adjusted by sulfuric acid. The unwashed reference with alum also had a lower Gurley value than the washed reference with alum as shown by the solid front bars in Figure 44.

The striped bars in the rare represent the samples in combination with starch which also show a similar trend. Only the unwashed reference with sulfuric acid showed a statistically significant difference with and without starch. Perhaps the addition of starch made the formation worse and thus air permeance slightly increased.

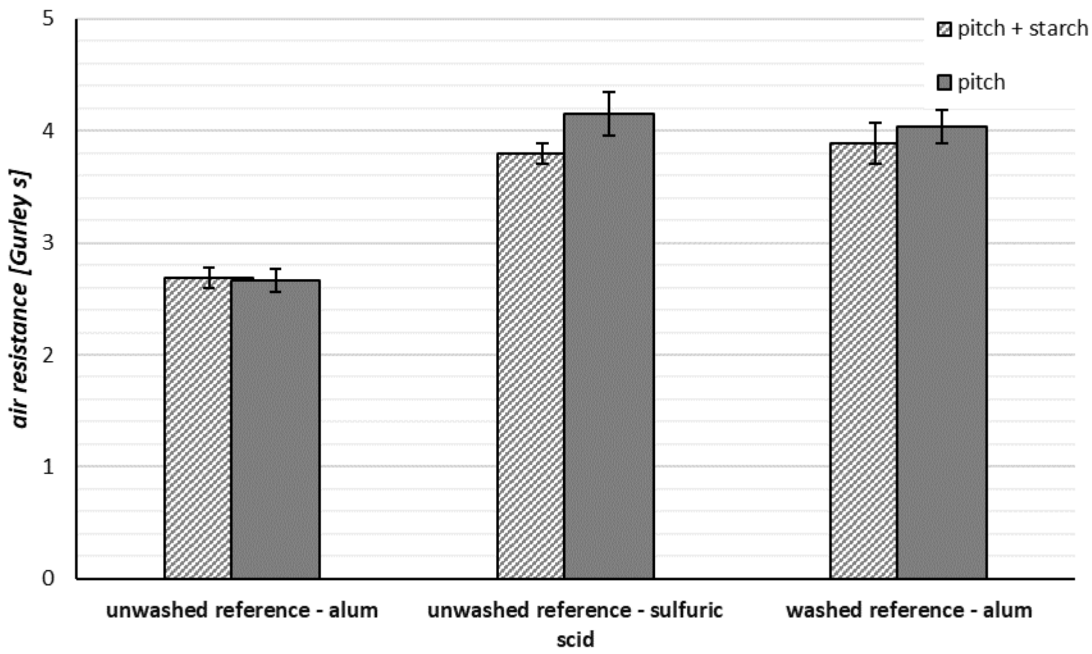

Figure 44: Influence of excessive addition of alum and further purification of the pulp on the air permeance of un-bleached softwood kraft pulp handsheets with and without starch at realistic papermaking pH 6.8

The extracted content of this trial is depicted in Figure 45. Surprisingly the washed reference with alum yielded more extract than the unwashed sample which is shown by the solid bars in the front. Unfortunately, there is no value for the unwashed reference without starch adjusted by sulfuric acid since the petri dish with the substance on it broke.

The striped bars show that there was slightly less extract when comparing the washed and the unwashed sample with alum and starch. The unwashed reference with starch and sulfuric acid had the lowest extracted content.

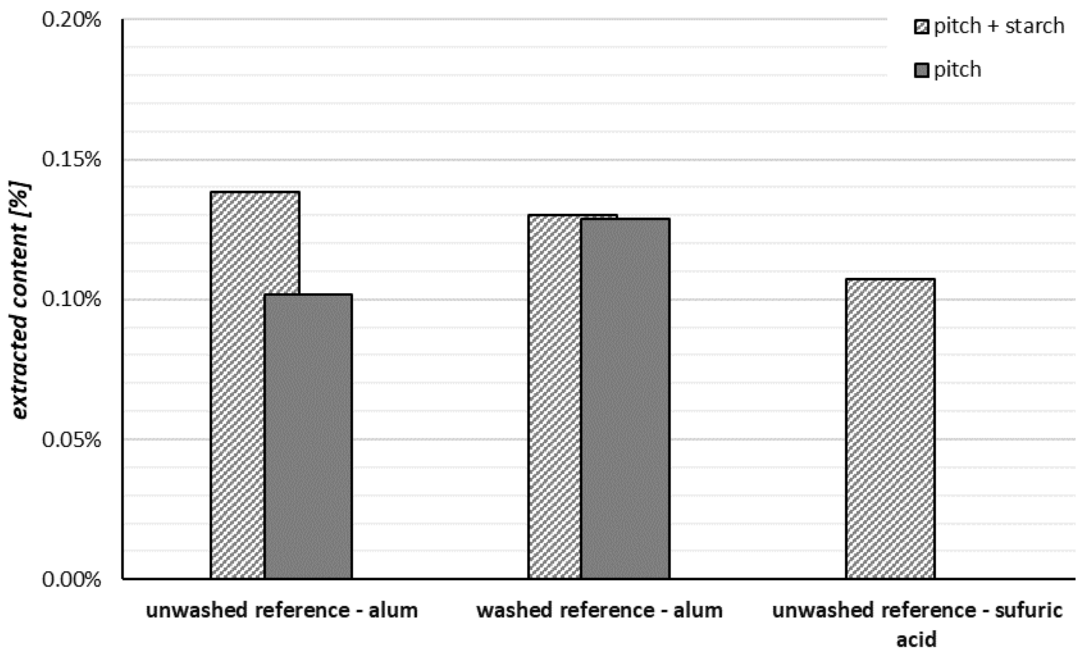

Figure 45: Influence of excessive addition of alum and further purification of the pulp on the extracted content of un-bleached softwood kraft pulp handsheets with and without starch at at realistic papermaking pH 6.8

In this experiment the alum had a strong negative impact on the paper strength of the samples which was quite suspicions. The produced papers with alum felt rigid and crumbled when applying little shear forces by fingers. After a discussion with the industrial partner it was clear that way too much alum was used for pH adjustment. The results therefore represent extremum conditions but were still interesting. Therefore, another trial had to be done with the exact relative amounts of alum used during paper production at the paper mill.

The further purified pulp showed promising results as the tensile strength seemingly raised a little compared to the untreated sample. As a result, the investigation of the influence of further alkaline washing was continued.

3.8 7th trial

Investigation of the influence of alum on paper properties using realistic quantities and impact of pulp purification through alkaline washing

In this experiment a fixed amount of alum (0,015 g alum/ g pulp) was added to the suspension before paper making. The pH was then adjusted with sulfuric acid to process conditions, i.e. 6.8. A sample without alum was adjusted only with sulfuric acid in order to have a comparison.

The purification of pulp was repeated to see if the paper strength increases under certain conditions. Alum was added to the washed pulp and pH adjustment was done with sulfuric acid.

Figure 46 depicts the results of this trial. The solid bars in the front show that the realistic amount of alum didn't have a big impact on tensile strength. There is no statistically significant difference between the tensile index of the unwashed reference with alum and the unwashed reference with sulfuric acid. However, in case of the samples with starch, the tensile strength of the unwashed reference with alum was significantly lower than the unwashed reference with sulfuric acid. Since starch and alum are both cationic compounds, the addition of alum might interact or compete with the starch and hinder its positive effect on paper strength.

When comparing the unwashed to the washed sample with alum, the further purified pulp showed higher tensile strength with and without starch.

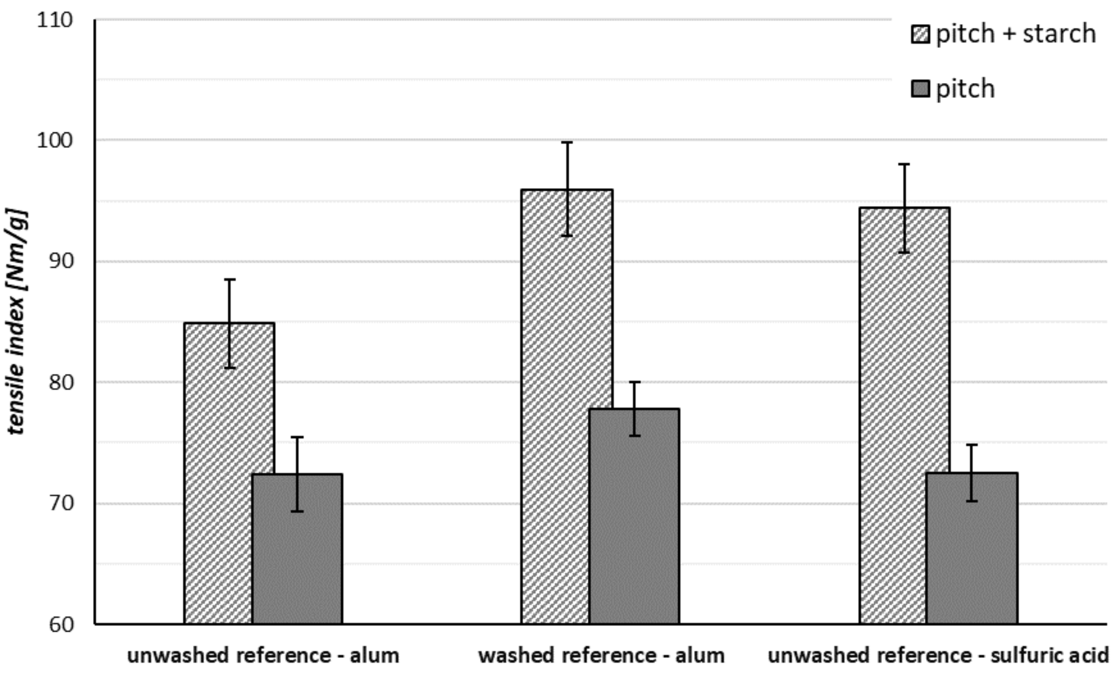

Figure 46: Influence of reasonable addition of alum and further purification of the pulp on the tensile index of un-bleached softwood kraft pulp handsheets with and without starch at at papermaking pH 6.8

The results of the TEA index depicted in Figure 47 are similar to the results of the tensile index.

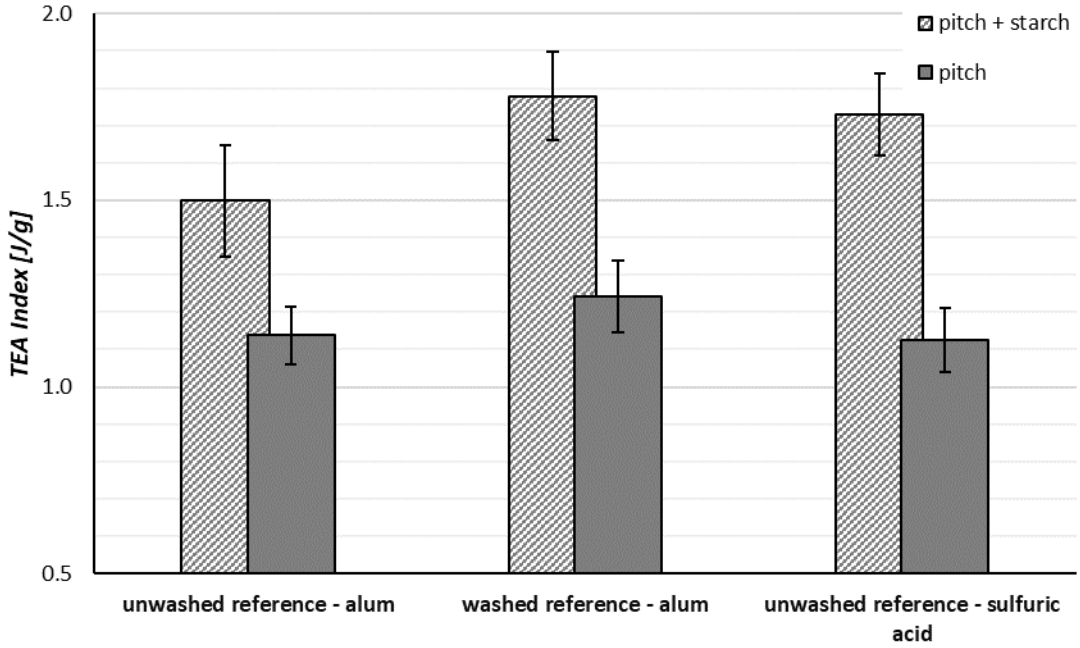

Figure 47: Influence of reasonable addition of alum and further purification of the pulp on the TEA index of un-bleached softwood kraft pulp handsheets with and without starch at at papermaking pH 6.8

The air permeance of the unwashed sample with alum was slightly better than the one of the unwashed sample with sulfuric acid which is shown in Figure 48. The washed sample with alum exhibited a higher Gurley value than the unwashed sample with alum.

The addition of starch had no significant impact on the air permeance of any sample except the sulfuric acid sample.

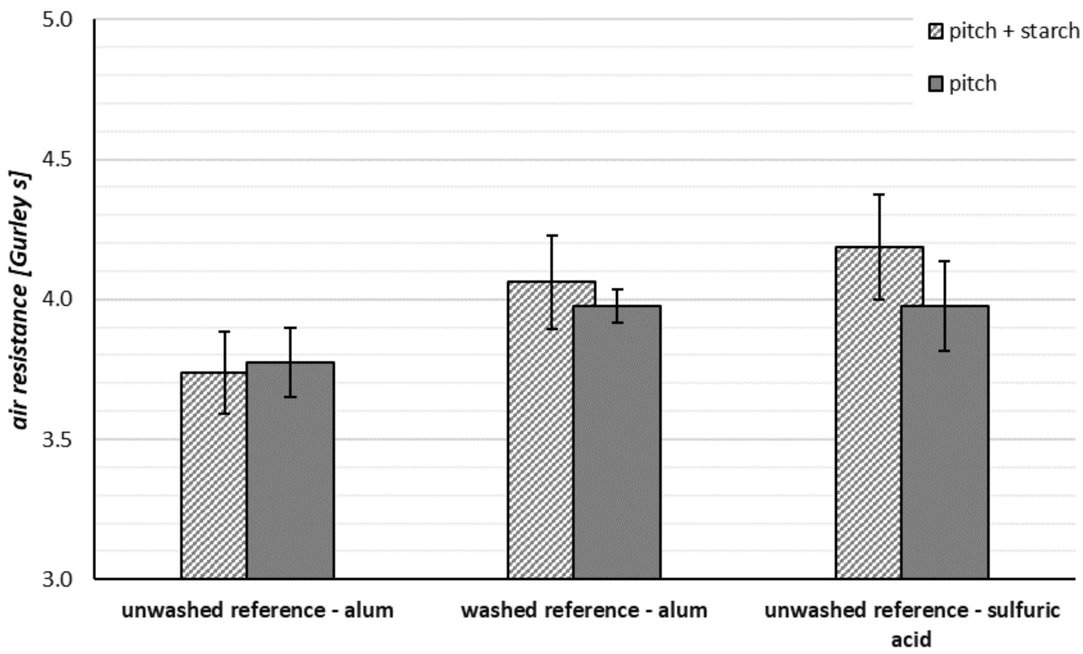

Figure 48: Influence of reasonable addition of alum and further purification of the pulp on the air permeance of un-bleached softwood kraft pulp handsheets with and without starch at at papermaking pH 6.8

The contact angle of the unwashed reference with alum exhibited higher values then both the washed sample and the unwashed reference with sulfuric acid. The addition of starch didn't alter the values significantly as shown in Figure 49.

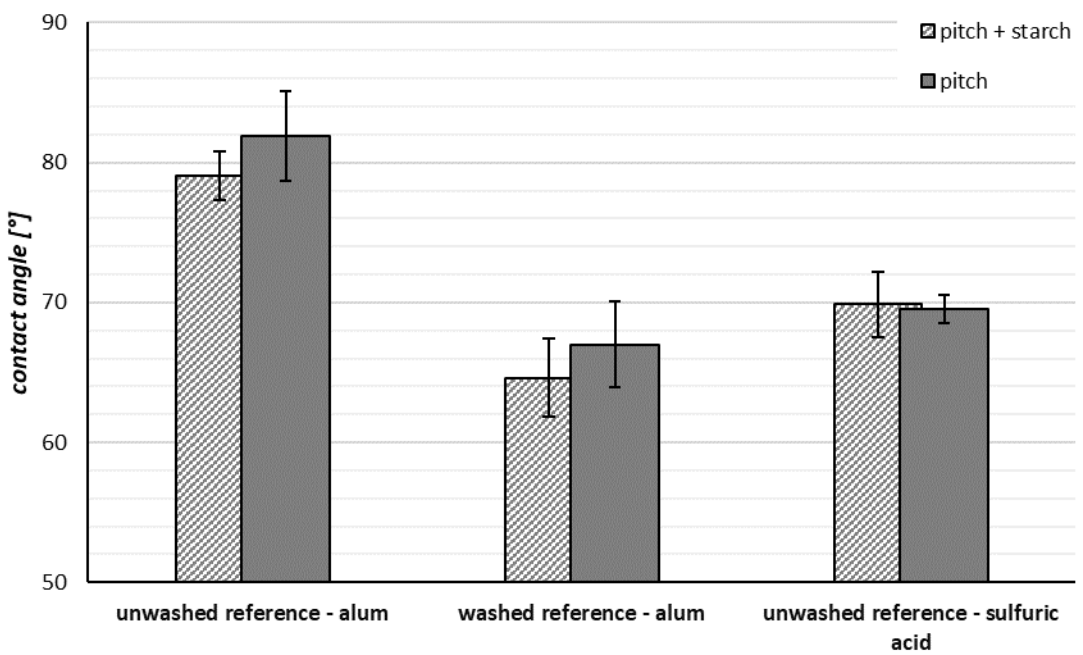

Figure 49: Influence of reasonable addition of alum and further purification of the pulp on the contact angle of un-bleached softwood kraft pulp handsheets with and without starch at at papermaking pH 6.8

As depicted in Figure 50, the extracted content of the unwashed reference with alum was approximately the same as the unwashed reference with sulfuric acid.

The further purified pulp had lower extracted amounts than the unwashed realistic papermaking sample which was expected.

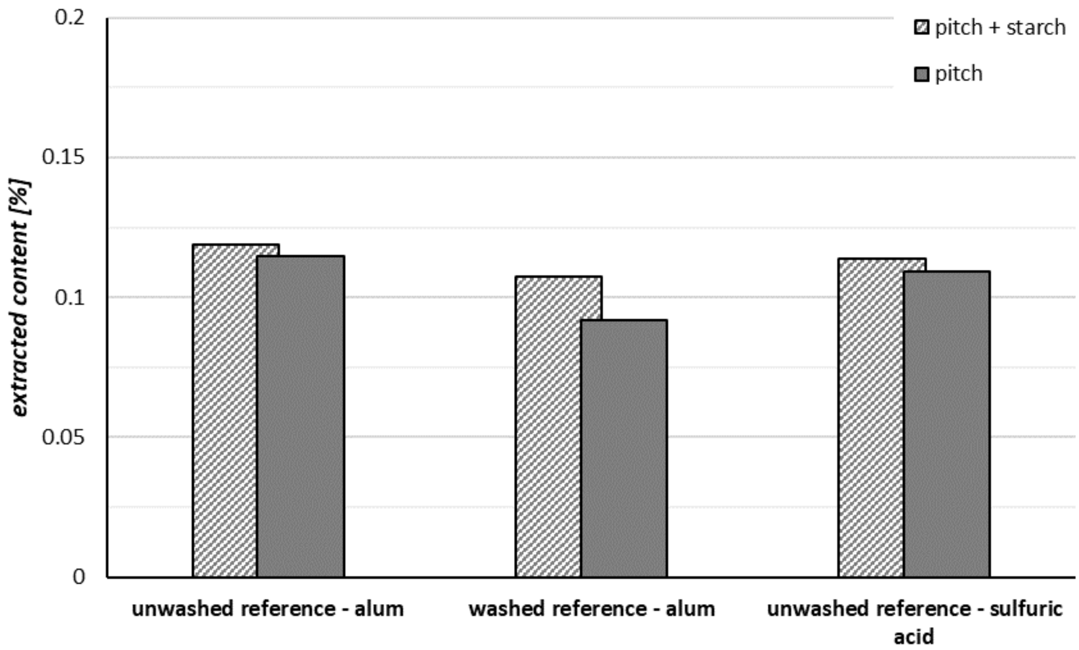

Figure 50: Influence of reasonable addition of alum and further purification of the pulp on the contact angle of un-bleached softwood kraft pulp handsheets with and without starch at papermaking pH 6.8

The lower amounts of added alum yielded better results for the paper strength than the previous trial. While the tensile index of the unwashed samples with alum and sulfuric acid without starch were identical, the positive effect of starch was slightly hindered by the addition of the retention aid.

The further purification of pulp yielded better strength properties for the papers. The alkaline washing seemed to remove some of the harmful pitch compounds. In order to verify these results another related experiment was performed.

3.9 8th trial

Further investigation of the influence of washing and alum on paper properties

In this experiment the used pulp was washed under harsh alkaline conditions. Before the washing process the pH was risen to a value of 13 and maintained at this level by further addition of NaOH solution. Only washed pulp handsheets were produced in this trial, therefore analogies to unwashed samples were drawn to previous experiments.

The tensile index of this experiment is depicted in Figure 51. The solid bars in the front indicate the samples without starch. The strength for the washed reference with sulfuric acid seems to be lower than the washed reference with alum.

In combination with starch, the washed reference with alum exhibited higher tensile strength than the washed reference with sulfuric acid.

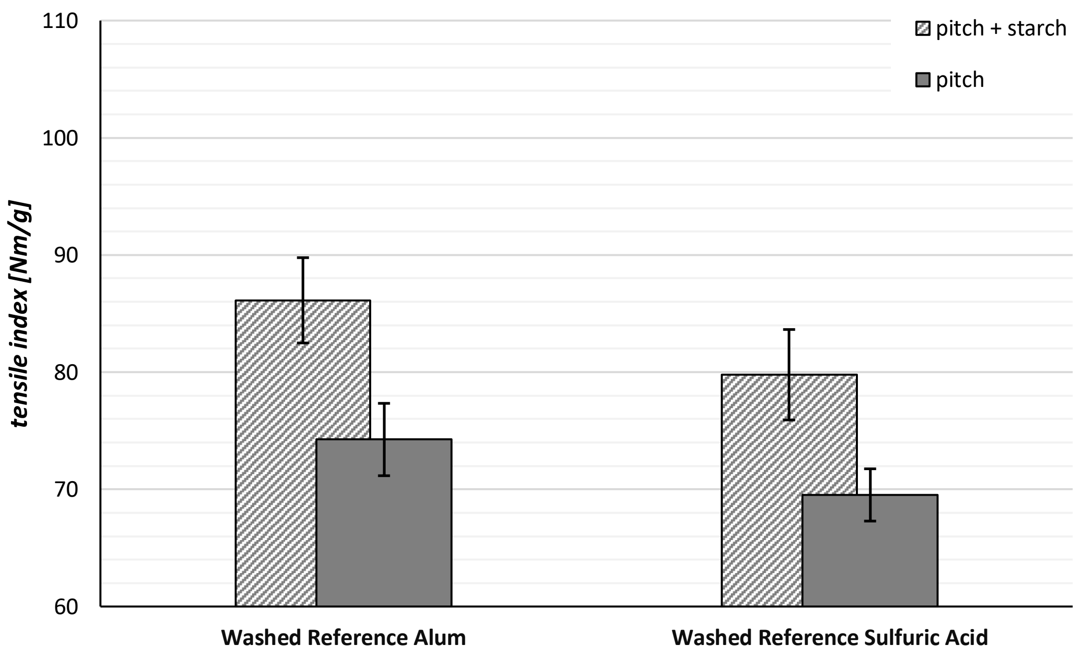

Figure 51: Influence of the addition of alum on the tensile index of further purified (through highly alkaline conditions) kraft pulp handsheets with and without starch at papermaking pH 6.8

The results of the TEA-index for this trial are shown in Figure 52 and mimic the results of the tensile index.

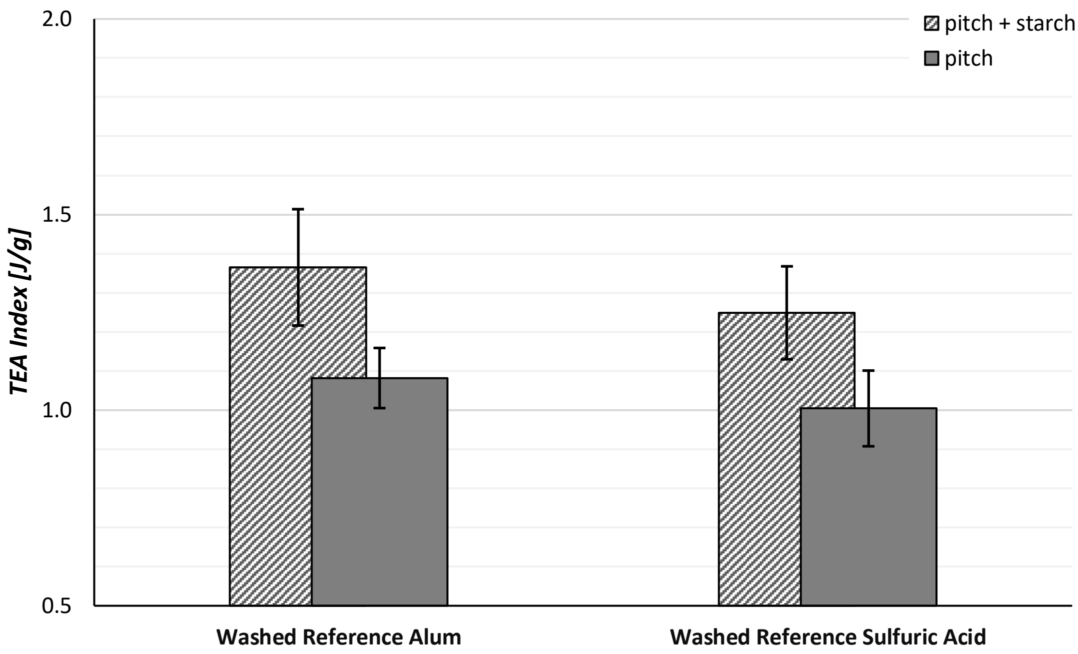

Figure 52: Influence of the addition of alum on the TEA index of further purified (through highly alkaline conditions) kraft pulp handsheets with and without starch at papermaking pH 6.8

Figure 53 shows the results for the air permeance test of this experiment. The addition of starch had no significant impact on either of the samples. However, the washed reference with sulfuric acid exhibited a higher air resistance than the washed reference with alum.

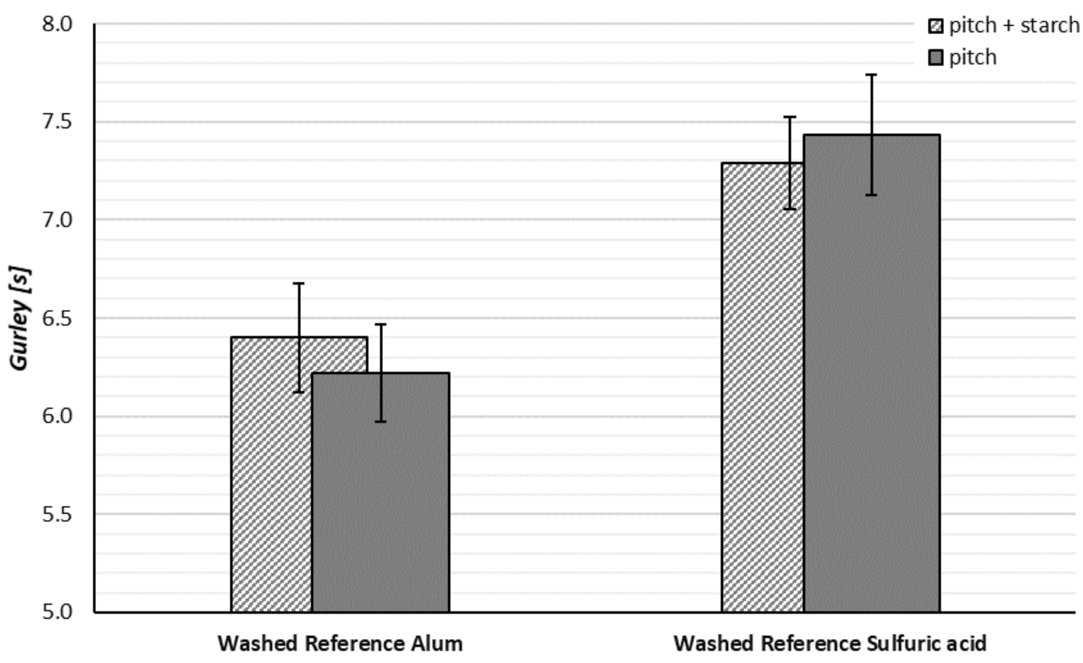

Figure 53: Influence of the addition of alum on the air permeance of further purified (through highly alkaline conditions) kraft pulp handsheets with and without starch at papermaking pH 6.8

The tensile index of the samples from this experiment is significantly lower than the tensile index of the samples from previous trials (e.g. Trial 7). It seems like the extreme pH during the alkaline washing had a negative influence on the fibres and therefore yielded lower strength properties. Most probably the fibers were damaged due to the extreme pH treatment. While further purification has proven to be beneficial for paper strength in previous experiments, using too high pH in this process may yield to worse results. The use of alum in reasonable quantities has no significant negative impact on the tensile strength of paper itself. Nevertheless, the substance might have an adverse impact on the positive effect of starch, but this was not confirmed in this trial. The contact angle and the extracted amount were not measured for this trial.

4. Conclusion

The lipophilic extractives of unbleached softwood kraft pulp, provided by a European kraft pulp mill, were successfully analyzed with GCMS. The majority of substances present in the summer and winter samples were apparently fatty acids, followed by terpenes, sterols and fatty alcohols. The most abundant compounds were oleic acid, linalool, β-sitosterol, docosanol and abietic acid. The papermaking trials performed with those compounds indicate, that the influence on paper strength is not only dependent on the compound itself, but also on the retention. At higher concentrations, oleic acid (fatty acid) and docosanol (fatty alcohol) have proven to be the most harmful components for tensile strength, as shown in the 2^{nd} trial.

In general, the addition of cationic starch was beneficial for the paper strength, especially when pitch compounds were present. However, the magnitude of the positive effect of starch was hindered by certain pitch compounds at high concentrations. In combination with the strength agent, compounds like β-sitosterol, oleic acid and docosanol exhibited lower tensile strength of paper than other pitch components (2^{nd} trial). The retention of those compounds with starch was especially high. At lower concentrations, the negative effect of those pitch substances was significantly lower or vanished.

In case of the 4^{th} trial, the use of alum as a fixing agent reduced the paper strength dramatically for every pitch compound at low concentrations. Papers produced with docosanol (fatty alcohol) and stearic acid (fatty acid) without starch exhibited the lowest values for tensile strength. Nevertheless, every pitch compound proved to be harmful for paper strength in combination with alum. The addition of starch yielded a big increase in paper strength for every compound. Overall, the tensile strengths of all components were approximately the same under these circumstances. Oleic acid exhibited the lowest tensile index value and the lowest increase in tensile strength.

The addition of talc had no significant influence on paper performance under these conditions. The pitch compounds had probably already interacted with the alum and therefore effect of talc was mitigated.

The 6th trial proved, that the usage of excessive amounts of alum has a devastating influence on the paper performance. The produced handsheets with excessive amounts of alum exhibited barely any stress resistance. However, moderate amounts did not affect the tensile strength significantly, in case that no additional pitch compounds or starch were present in the fiber suspension (7th trial). When starch was present, the tensile index of produced hand sheets was slightly lower with alum when compared to the reference sample without alum. The usage of moderate amounts of alum had no significant influence on the tensile index of papers when oleic acid and starch was present, at least in the 5th trial. Nonetheless, this experiment should be repeated with several compounds in order to gain clarification.

Further purification of the pulp, through alkaline washing, seemed to be beneficial for paper strength. On the other hand, the usage of very high pH values (pH 13) during this process has proven to be harmful for paper strength (8th trial). Extreme pH conditions most probably damage the fibers and lead to weaker tensile strength for paper.

In order to enhance the tensile strength of paper, future trials could focus on the reduction of pitch compounds in process streams. Harmful compounds like fatty acids may be susceptible to enzymatic treatment. Further purification of the pulp, through enhanced cooking and washing steps, may prove beneficial for pitch reduction in the process water. There is a risk that alum could reduce paper strength if the added amount is too high, therefore other alternative fixing agents might be more suitable.

Table of figures

Table of tables

Bibliography

Abitz, P. and Luner, P. (2018) 'THE EFFECT OF REFINING ON WET FIBER FLEXIBILITY AND ITS RELATION-', pp. 67–86. doi: 10.15376/frc.1989.1.67.THE.

Alén, R. (ed.) (2000) *Papermaking Chemistry*. 2nd Editio. Finnish Paper Engineers' Association.

Allen, L. H. (1980) 'Mechanisms and Control of Pitch Deposition in Newsprint Mills.', *Tappi*, 63(2), pp. 81–87.

Blazey, M. A., Grimsley, S. A. and Chen, G. C. (2002) 'Indicators for forecasting "pitch season"', *Tappi Journal*.

Brandal, J. and Lindheim, A. (1966) 'The influence of extractives in groundwood pulp on fibre bonding', *Pulp and Paper Magazine of Canada*, 67, pp. 431–435.

Brouwer, P. H. (1997) 'Anionische Massestärke rein - Oberflächenstärke raus?', *Wochenblatt fuer Papierfabrikation*.

Davison, R. W. (1972) 'Weak link in paper dry strength', *Tappi*.

Doshi, M. R. (1994) 'Properties and Control of "Stickies" in Paper Recycling', *MRS Bulletin*. Cambridge University Press, 19(2), pp. 36–40. doi: 10.1557/S0883769400039270.

Ekman, R. and Holmbom, B. (2000) 'The chemistry of wood resin.', in *Pitch control, wood resin and deresination*.

Gill, B. J. (1974) 'Controlling pitch deposits in pulp mills with talc', *Pulp Paper*, 48(8), p. 104.

Gutiérrez, A. *et al.* (1998) 'Analysis of lipophilic extractives from wood and pitch deposits by solid-phase extraction and gas chromatography', *Journal of Chromatography A*, 823(1–2), pp. 449–455. doi: 10.1016/S0021-9673(98)00356-2.

Gutiérrez, A. *et al.* (2006) 'Main lipophilic extractives in different paper pulp types can be removed using the laccase-mediator system’, *Applied Microbiology and Biotechnology*, 72(4), pp. 845–851. doi: 10.1007/s00253-006-0346-1.

Hubbe, M. A. (2007) ‘Water and papermaking 3. Measures to clean up process water’, *Paper Technology*, 48(3), pp. 23–30.

Hubbe, M. A. *et al.* (2012) ‘Dissolved and colloidal substances (dcs) and the charge demand of papermaking process waters and suspensions: A review’, *BioResources*, 7(4), pp. 6109–6193. doi: 10.15376/biores.7.4.6109-6193.

Hubbe, M. A., Rojas, O. J. and Venditti, R. A. (2006) ‘Control of tacky deposits on paper machines - A review’, *Nordic Pulp and Paper Research Journal*, 21(2), pp. 154–171. doi: 10.3183/npprj-2006-21-02-p154-171.

Johansson, C. *et al.* (2012) ‘Renewable fibers and bio-based materials for packaging applications - A review of recent developments’, *BioResources*, 7(2), pp. 2506–2552. doi: 10.15376/biores.7.2.2506-2552.

Kokkonen, P., Fardlm, P. and Holmbom, B. (2004) ‘Surface distribution of extractives on TMP handsheets analyzed by ESCA, ATR-IR, ToF-SIMS and ESEM’, *Nordic Pulp and Paper Research Journal*, 19(3), pp. 318–324. doi: 10.3183/npprj-2004-19-03-p318-324.

Kokkonen, P., Korpela, A. and Sundberg, A. (2002) ‘Effects of different types of lipophilic extractives on paper properties’, *Nordic Pulp and Paper Research Journal*, 17(4), pp. 382–386. doi: 10.3183/npprj-2002-17-04-p382-386.

Lindström, T., Wågberg, L. and Larsson, T. (2005) ‘On the nature of joint strength in paper – a review of dry and wet strength resins used in paper manufacturing’, *13th Fundamental Research Symposium*, 32(May 2005), pp. 457–562. Available at: https://www.researchgate.net/publication/267385974.

Márton, J. and Marton, T. (1976) ‘Wet end starch: adsorption of starch on cellulosic fibers.’, in.

Matijević, E. and Stryker, L. J. (1966) ‘Coagulation and reversal of charge of lyophobic colloids by hydrolyzed metal ions. III. Aluminum Sulfate’, *Journal of*

Colloid And Interface Science. doi: 10.1016/0021-9797(66)90068-3.

Möller, H. W. (1966) 'Cationic starch as a wet-end strength additive.', *Tappi*, 49(5), p. 211.

Page, D. H. (1969) 'A theory for the tensile strength of paper.', *Tappi Journal*, 52, pp. 674–681.

Stack, K. *et al.* (2012) 'Effect of increased levels of dissolved and colloidal substances from pinus radiata on newsprint paper strength', *Appita Annual Conference*, 65(4), pp. 25–31.

van de Steeg, H. G. M. *et al.* (1993) 'Adsorption of cationic potato starch on microcrystalline cellulose', *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. doi: 10.1016/0927-7757(93)80499-5.

Strand, A. (2013) *The pH-dependent phase distribution of wood pitch components in papermaking processes*.

Sundberg, A. *et al.* (2000) 'Weakening of paper strength by wood resin', *Nordic Pulp and Paper Research Journal*, 15(1), pp. 46–53. doi: 10.3183/npprj-2000-15-01-p046-053.

Tenkanen, M. *et al.* (2002) 'Hydrolysis of steryl esters by a lipase (Lip 3) from Candida rugosa', *Applied Microbiology and Biotechnology*, 60(1–2), pp. 120–127. doi: 10.1007/s00253-002-1063-z.

Theliander, H. (2009) 'Recovery of cooking chemicals: The treatment and burning of black liquor', in *Pulping Chemistry and Technology*. doi: 10.1515/9783110213423.297.