High strength paper from high yield pulps by means of hot-pressing

Tove Joelsson

Main supervisors:
Prof. Per Engstrand, Mid Sweden University

Co-supervisors:
Dr. Gunilla Pettersson, Mid Sweden University, Dr. Anna Svedberg,
MoRe Research Örnsköldsvik

Faculty of Technology, Science and Media
Thesis for Licentiate degree in Chemical Technology
Mid Sweden University
Sundsvall, 2020-02-20
Akademisk avhandling som med tillstånd av Mittuniversitetet i Sundsvall framläggs till offentlig granskning för avläggande av filosofie/teknologie licentiatexamen torsdagen den, 20 februari 2020, kl. 10.15, sal O102, SCA-salen, Mittuniversitetet Sundsvall. Seminariet kommer att hållas på svenska/engelska.

High strength paper from high yield pulps by means of hot-pressing

© Tove Joelsson, 2020-01-20
Printed by Mid Sweden University, Sundsvall
ISSN: 1652-8948

Faculty of Science of Technology and Media
Mid Sweden University, SE-851 70 Sundsvall, Sweden
Phone: +46 (0)10 142 80 00
Mid Sweden University Licentiate Thesis 167
Acknowledgement

I would like to thank supervisors, Prof. Per Engstrand, Dr. Gunilla Pettersson, Dr. Anna Svedberg, Dr. Sven Norgren and Emeritus Prof. Hans Höglund for their support and encouragement throughout the work. I am deeply grateful for having had the opportunity to be a part of this professional, open-minded group. I also want to thank my mentor Prof. Magnus Norgren for his scientific and academic help in my doctoral planning and his genuine engagement in my research.

This work would have been less successful without the endless and heartfelt dedication shown by all my colleagues at MoRe Research in Örnsköldsvik, and especially the department of paper laboratory, the research group, and our amazing Dr. Anna Svedberg for her professionalism and endless encouragement. The daily work has been so enjoyable because of the enthusiasm of all colleagues throughout the Whole House, i.e. Hela Huset. A special thanks to Dr. Hans Grundberg for sharing his knowledge and for kind support. I also thank the staff at FSCN/Miun for their helpfulness and great support.

This work has been performed in close cooperation with several industrial partners within the program Eco-mat: IPCO, Holmen, SCA, Storaenso, Valmet, and MoRe Research. I thank them all for the invaluable expertise they have provided throughout the work.

The participation and the colleagues in the graduate school FORIC have given me valuable experience of learning and training for my research in general.

I gratefully acknowledge financial support from the Knowledge Foundation (KKS) with FORIC (Forest as Resource Industrial Research College, a part of Treesearch), EU/Tillväxtverket, the Kempe Foundation, IPCO AB, MoRe Research Örnsköldsvik AB, and Mid Sweden University.

Finally, I would like to thank my family; my beloved sons Johan and Gustaf and my beloved daughter Rebecka for constantly reminding me of what’s most important in life. I am also grateful to all my wonderful friends for their support and encouragement.
# Table of contents

Abstract ........................................................................................................................... vii  
Sammanfattning ............................................................................................................ ix  
List of papers ................................................................................................................ xi  
Contributing to the reports ........................................................................................ xii 
Related material ............................................................................................................ xii 
1 Objectives .................................................................................................................... 1  
1.1 Research question and objectives of this work ..................................................... 1  
1.2 General remarks ....................................................................................................... 1  
2 Background .................................................................................................................. 2  
2.1 Hot-pressing since the 1920s ................................................................................. 2  
2.2 Wood components .................................................................................................. 4  
  2.2.1 Cellulose and hemicellulose ............................................................................ 6  
  2.2.2 Lignin .............................................................................................................. 7  
  2.2.3 Extractives ....................................................................................................... 9  
  2.2.4 Water .............................................................................................................. 9  
2.3 Strength development in HYP ............................................................................... 12  
2.4 High yield pulp used in this work ....................................................................... 13  
  2.4.1 Thermomechanical (TMP) ............................................................................ 13  
  2.4.2 Chemithermomechanical (CTMP) ................................................................. 14  
  2.4.3 High Temperature Chemithermomechanical (HT-CTMP) ......................... 14  
  2.4.4 Neutral Sulphite Semi-chemical (NSSC) pulp ............................................. 14  
  2.4.5 Semi-chemical pulp with alkali impregnation (SCP_al) ............................. 15  
3 Experimental ............................................................................................................. 15  
3.1 Materials and Methods ......................................................................................... 15  
  3.1.1 Sheet preparation ............................................................................................ 19  
  3.1.2 Hot-pressing .................................................................................................. 20  
  3.1.3 Spectroscopic methods ................................................................................ 25  
  3.1.4 Strength properties (ISO 1924-3 and ISO 9895:2009) ............................... 26  
  3.1.5 Wet stability (ISO 3781 and T558) ................................................................. 26  
4 Results and discussion ............................................................................................. 27  
4.1 Morphology by microscopy analysis ................................................................. 27  
4.2 The effect of pressing load and temperature on paper properties ...................... 29  
4.3 Development of wet strength ............................................................................... 37  
4.4 Contact angle change due to temperature and lignin ......................................... 42  
4.5 The stability of native lignin in paper sheets over time ....................................... 47  
5 Conclusion ................................................................................................................... 48  
6 References ................................................................................................................... 49
Abstract

High Yield Pulp (HYP), i.e. TMP, SGW or CTMP, is normally used in printing papers (News, SC and LWC) or in a middle layer on cardboard i.e. in products that either have high demands on printability and runnability in fast printing presses or contribute to high bulk in cardboards in order to minimize pulp consumption at a certain sheet stiffness. Tensile strength as a function of density is significantly higher for HYP compared to chemical pulps such as sulphate and sulphite pulps. However, chemical pulp is mainly used in packaging materials that require very high tensile strength, while at the same time allowing the density of the paper to be high. By utilizing the softening properties of high-yielding lignin-rich fibres by hot-pressing technology, it is possible to significantly increase sheet density and thereby strength closer to the level of chemical pulps. Furthermore, due to the presence of high levels of lignin, it was shown that considerably higher wet strength can be achieved compared to chemical pulp without the addition of strengthening agents. The study focuses on the softening of stiff and lignin-rich fibres in papers based on HYP with sufficiently high moisture contents, when hot-pressing at temperature levels significantly above the softening temperature (Tg) of lignin. Hot-pressing increases the density of the sheet which increases the contact surface between the fibres in the paper structure. The high pressing temperature can be said to induce a viscous flow of lignin, which also increases the potential for fibre-fibre bonding. It is conceivable that covalent bonds are obtained via condensation reactions and partly that interdiffusion between the lignin in the fibre walls can be obtained as they come close enough to each other during the hot-pressing. The research also shows that hot-pressing greatly improves properties in the form of dry and wet strength as well as hydrophobicity for HYP and for lignin-rich kraft paper. The first part of the study shows the effect of hot-pressing on strength properties of paper sheets based on CTMP, HT-CTMP, TMP, NSSC, SCP and NBSK. The second part includes a study on how and to what extent different amounts of residual lignin in the pulp contribute to the dry and wet strength of the sheets of paper during hot-pressing as a function of increasing temperature. To demonstrate this, pilot scale cooking of unbleached pulp to various lignin levels was carried out. In all experiments in parts one and two, laboratory sheets with a surface weight of 150 g/m² and a dry content of 50% were made with a Rapid Köthen (RK) sheet former, after which the sheets were hot-pressed in a cylinder press at temperatures up to 200°C, constant high pressure of about 7 MPa, nip
pressure dwell time of 1.5 sec and production speed 1 m/min. The third part includes a study on the optimization of variables in a new design of a dynamic cylinder press for hot-pressing technology. This design is based on previous research at Mid Sweden University combined with key knowledge of steel band technology within IPCO AB. The new pilot machine is based on heating of a steel belt with infrared heat (IR) up to 300°C, a maximum line load of 15 kN/m in two press nips and a dwell time of 23-240 ms in the nip depending on the production speed which is up to 5 m/min. The experiments in part three were based on RK paper sheets with 100 g/m² and approximately 63% dry content made by HT-CTMP. The results confirm that hot-pressed HYP-based paper sheets enable permanent densification by softening lignin, which provides a very high dry tensile strength and a remarkable improvement in wet tensile strength compared to bleached kraft pulp without the need for wet strength agents. A tensile index of 75 kNm/kg, compression strength index (SCT) of 45 kNm/kg and wet tensile strength index of 16 kNm/kg were obtained, which can be compared with the corresponding values for bleached kraft pulp based paper sheets of 85 kNm/kg, 35 kNm/kg and 5 kNm/kg respectively, all with the same density after hot-pressing at 200°C. The NSSC reached the highest tensile strength index of 92 kNm/kg. The study with the unbleached kraft pulps showed that the lignin content had a significant effect on both the dry and wet tensile strength indices. The pulps showed a linear relationship between wet strength and lignin content. The increase in lignin content from 0% to 12% improved the dry tensile index by 20% and SCT by 35% and gave a very significant increase in the wet strength index from 3 to 23 kNm/kg after hot-pressing. All lignin-rich paper samples exhibit good wet stability for at least 24 hours and an improved surface hydrophobicity by increasing the pressing temperature and lignin content.

Optimization of the new steel belt based press machine showed that high nip pressure and two press nips had a great effect on density and strength. Whereas high temperature, well above Tg of lignin, and long pressing time were more important to achieve high wet strength. The highest wet strength index value, 27 kNm/kg, was reached when the pressing temperature was 290°C, the nip pressure about 8 MPa, the pressing time in the press nip 40 ms and the dwell time in contact with the steel belt 23.5 sec. It was also noted that no delamination occurred in these tests.

In order to obtain both high dry and wet strength, it is important to have high lignin content, high temperature, high nip pressure and sufficiently long pressing time.
Sammanfattning

Högutbytesmassa (HYP), d.v.s. SGW, TMP eller CTMP, används normalt i tryckpapper (News, SC och LWC) eller i mittskikt i kartong dvs i produkter som har höga krav på tryckbarhet och körbarhet i snabba tryckpressar eller för att bidra till hög bulk i kartong så att man därmed kan minimera förbrukningen av massa för att nå en viss arkstyvhet. Dragstyrka som funktion av densitet är väsentligt högre för HYP jämfört med kemiska massor som sulfat- och sulfitmassor. Däremot används främst kemiska massor i förpackningsmaterial som kräver mycket hög dragstryka, där man samtidigt tillåter att papperets densitet får vara hög. Genom att utnyttja mjukningsegenskaperna hos högutbytesmassors ligninrika fiber genom varm pressningsteknik kan man väsentligt öka arkdensitet och därigenom styrka till i nivå med kemiska massors. Vidare visas att man t tack vara närvaro av höga halter lignin kan nå väsentligt högre våtstyrka jämfört med kemisk massa utan tillsats av styrkehöjande kemikalier. Studien fokuserar på mjukgörning av styva och ligninrika fiber vid varm pressning vid temperaturnivåer väsentligt över mjukningstemperaturen (Tg) för lignin av HYP-baserat papper med tillräckligt hög fukthalt. Varm pressning ökar arkens densitet, vilket ökar kontaktytan mellan fibererna i pappersstrukturken. Den höga pressnings-temperaturen kan sågas inducera ett visköst flöde av lignin, vilket då ökar möjligheten att få starkare för fiber-fiber-bindning. Man kan dels tänka sig att kovalenta bindningar erhålls via kondensationsreaktioner och dels att man kan erhålla interdiffusion mellan ligninet i fiberväggarna då de kommer tillräckligt nära varandra vid varm pressningen. Forskningen visar också att varm pressning högst väsentligt förbättrar egenskaper i form av torr- och våtstyrka samt hydrofobicitet för både HYP-baserat och ligninrikt kraftpapper. Den första delen av studien visar effekten av varm pressning på styrke-egenskaper hos pappersark baserade på CTMP, HT-CTMP, TMP, NSSC, SCPal och NBSK. Den andra delen inkluderar en studie om hur och i vilken utsträckning olika mängder av kvarvarande lignin i massa bidrar till pappersarbens torrstyrka och våtstyrka vid varm pressning som funktion av ökande temperatur. För att demonstrera detta tillverkades oblekt kraftmassa till olika ligninhalter i pilotskala. I alla experiment i del ett och två i avhandlingen tillverkades laboratoreark med ytviiten 150 g/m² och torrhalten 50% i en Rapid Köthen (RK) arkformare varefter arken varmpressades i en cylinderpress vid temperaturer upp till 200°C och konstant högt tryck på cirka 7 MPa i ett pressnyp med uppehållstiden 1,5 s i pressnypet vid maskinhastigheten 1
m/min. Den tredje delen i avhandlingen inkluderar en studie om optimering av variabler i en ny design av en dynamisk cylinderpress för varmpressteknik. Den nya designen baseras på tidigare forskning vid Mittuniversitetet kombinerat med nyckelkunskap om stålbandsmaskiner inom IPCO AB. Den nya pilotmaskinen är baserad på att ett stålbälte uppvärms med infraröd värme (IR) upp till 300°C, en linjelast upp till 15 kN/m i två pressnyp vardera, med variabel presstid 23-240 ms i pressnypet beroende av maskinhastigheter upp till 5 m/min. Experimenten i del tre i avhandlingen baserades på RK-pappersark tillverkade av HT-CTMP med ytvikten 100 g/m² och torrhalten ca 63%. Resultaten bekräftar att varmpressande HYP-baserade pappersark möjliggör permanent densifiering genom mjukning av lignin, vilket ger en mycket hög torr dragstyrka och en anmärkningsvärd förbättring av våt dragstyrka jämfört med blekt kraftmassa utan att våtstyrkemedel behöver användas. Ett dragindex på 75 kNm/kg, kompressionsstyrkeindex (SCT) på 45 kNm/kg och våtstyrkeindex på 16 kNm/kg erhölls vilket kan jämföras med motsvarande vården för pappersarken från blekt kraftmassa på 85 kNm/kg, 35 kNm/kg respektive 5 kNm/kg, alla med samma densitet efter varmpressning vid 200°C. Lövvedsbaserad NSSC nådde det högsta dragstyrkeindexet på hela 92 kNm/kg. Studien med de oblekta kraftmassorna visade att lignininnehållet hade en signifikant effekt på både torr- och våtstyrkeindex. Kraftmassorna uppvisade ett linjärt samband mellan våtstyrka och lignininnehåll. Ökningen i lignininhalten från 0% till 12% förbättrade dragindexet med 20% och SCT med 35% och gav en mycket signifikant ökning i våtstyrkeindex från 3 till 23 kNm/kg efter varmpressningen. Alla ligninrika pappersprover uppriser god våtstyrkestabilitet under minst 24 timmar och en förbättrad yhydrofobicitet genom ökning av presstrycktemperaturen och lignininnehållet.

Optimering av den nya stålbandsbaserade cylinderpressen visade att högt pressnyttryck och två pressnyp hade stor effekt på densitet och styrka. Emedan hög temperatur, långt över Tg för lignin, och lång presstid var viktigare för att nå hög våtstyrka. Det högsta värdet på våtstyrkeindex, 27 kNm/kg, uppnåddes när presstemperaturen var 290°C, pressnyttrycket cirka 8 MPa, presstiden i pressnypet 40 ms och tiden i kontakt med stålbältet 23,5 sek. Det noterades också att ingen delaminering inträffade i dessa tester. För att erhålla både hög torr- och våtstyrka är det viktigt med högt lignininnehåll, hög temperatur, högt nyptryck och tillräckligt lång presstid.
List of papers

Paper I. **High strength paper from high yield pulps by means of hot-pressing**

Paper II. **Improved paper wet-strength by increasing lignin content and hot-pressing temperature**

Paper III. **Unique steel belt technology for hot-pressing of wood-containing papers**
Tove Joelsson, Gunilla Pettersson, Sven Norgren, Anna Svedberg, Hans Höglund and Per Engstrand, “To be submitted.”

Contributing to the reports

Paper I. Carried out most of the experimental work (preparation of pulp furnish and paper sheets, hot-pressing and some paper analysis) and most of the writing. Pulp characterization and microscopy analysis was done by the personnel at MoRe Research AB.

Paper II. Pilot plant cooking of the kraft pulps was done by the personnel at MoRe. The author carried out the preparation of pulp and paper sheets, hot-pressing and 50% of paper analysis, and most of the writing. Pulp characterization and microscopy analysis was done by the personnel at MoRe Research AB.

Paper III. Did most of the experimental work (preparation of pulp and paper sheets, testing and trials on the new hot-pressing equipment) and most of the writing.
Related material

1. Starka förpackningsmaterial från högutbytesmassa
   PechaKucha-presentation, Tove Joelsson

2. Development of strong and water resistant packaging materials from high yield pulps – fundamental aspects
   Tove Joelsson, Gunilla Pettersson, Sven Norgren, Anna Svedberg, Hans Höglund, Per Engstrand
   International Mechanical Pulping Conference (IMPC), Trondheim, Norway, May 2018.

3. Strong Packaging Materials from High Yield Pulps – fundamental aspects
   Tove Joelsson, Gunilla Pettersson, Sven Norgren, Anna Svedberg, Hans Höglund, Per Engstrand
   ZellCheming-Cellulose Symposium, Frankfurt, Germany, June 2018.

4. Development of strong and water resistance packaging material from high yield pulp
   Tove Joelsson, Gunilla Pettersson, Sven Norgren, Anna Svedberg, Hans Höglund, Per Engstrand
   Conference Science & Innovation Day (SID), Sundsvall, Sweden, October 2018.

5. Unique steel belt press technology for development of high strength wood-containing papers
   Tove Joelsson, Gunilla Pettersson, Sven Norgren, Anna Svedberg, Hans Höglund, Per Engstrand
   11th Fundamental Mechanical Pulp Research Seminar (FMPRS), Norrköping, Sweden, April, 2019.

6. Improving Paper Wet-strength by Means of Hot-Pressing and Increased Lignin Content in Pulp Fibers
   Tove Joelsson, Gunilla Pettersson, Sven Norgren, Anna Svedberg, Hans Höglund, Per Engstrand

7. Upgrading the strength properties of sheets from hardwood high yield pulps
   Pettersson, G., Höglund, H., Norgren, S., Engstrand, P., Peng, F., Granfeldt, T., Bergström, J. and Joelsson, T.
1 Objectives

1.1 Research question and objectives of this work

The research question is: how can we further develop dry and wet strength properties in paper material based on high yield pulp (HYP) by means of hot-pressing? In order to answer this question we have tested different kinds of lignin-rich pulps and performed hot-pressing at different temperatures, nip pressures and nip residence times. To evaluate the experiments, several analyses of paper physical properties have been done regarding dry and wet strength, hydrophobicity and morphology.

The objective of this work is to contribute to the knowledge of development of strong and water resistant HYP-based packaging materials by means of the hot-pressing technique. The scope is to investigate how the lignin-rich paper behaves during hot-pressing at different temperatures and pressures by measuring morphological and physical properties and varying the lignin content in the hot-pressed paper samples. This knowledge is needed when optimizing the processing variables.

In the first part (Paper I) the purpose was to investigate how hot-pressing of HYP-based paper sheets at different temperatures affects the rheological and physical properties. The pressing temperature was varied up to 200°C, well above softening temperature of lignin, whereas the sheet moisture content, nip pressure and dwell time were held constant. Pulp properties and pressing temperature were discussed in accordance with the results of hot-pressing.

In the second part (Paper II), the purpose was to investigate the effect of lignin content in kraft pulps on the paper properties, when hot-pressing at different temperatures. The pressing variables were the same as in the first part. The lignin level in kraft pulp was varied from 0 to 12%.

In the third part (Paper III), the purpose was to optimize the hot-pressing variables and maximizing both the dry and wet strength paper properties at pressing at temperature above 200°C.

1.2 General remarks

The pollution of plastic debris is a serious problem as it is poisoning our seas, depleting nutrition for animals and harming our ecosystems for many hundreds to thousands of years ahead. As paper materials are bio-
degradable in much shorter time perspectives, and wood fibre resources are renewable, there is no doubt that these products are very interesting as substitutes for plastics. High yield pulps (HYP) are traditionally mainly used in printing papers and in paperboard products. Conventional papermaking processes yield too low tensile strength for HYP to be able to compete with kraft pulps in products with high strength demands, such as liner and sack paper products. Since the market for printing papers is declining due to digitalization and the demand for bio-based packaging solutions is increasing, research on methodologies to produce strong paper materials from HYP is of great interest. In order to meet these demands for packaging paper material the dry as well as wet strength of HYP must be improved. The strength in paper is due to bonds in the fibre structure and increasing fibre-fibre contact, which improves as the paper density increases and water is removed. Thus, paper strength increases with increasing solid content when press-drying moist paper sheets. In paper production an effective press-drying before drying section is also favourable because water removal by drying is more expensive than mechanical drainage. Moreover, high temperature and high lignin content in press-drying contribute to enhanced strength and particularly wet strength (Byrd 1979 and Pakarinen et. al. 2010). Naturally occurring lignin has the ability to enhance stability and wet strength to wood as well as in lignin rich paper material when heated (Back 1984; Cristescu et al. 2015; Fratzl 2018). Lignin-rich pulp is an interesting eco-friendly alternative to commercial fossil-based wet strength chemical systems, which often cause problems with runnability and involve serious environmental aspects related to emissions and health issues.

2 Background

2.1 Hot-pressing since the 1920s

The development of wet pressing at high temperatures started with Mason’s 1925 invention: manufacturing of hardboard in a process where coarse high yield fibres were pressed between hot plates. William Mason described in his patent in the 1930s how to utilize the potential of lignin in HYP for increasing wet strength when exposed to heat, moisture and pressure (Mason 1931, 1937, 1938). Arne Asplund improved the Masonite process in 1931 by means of introducing a new way to produce high yield pulp fibres of higher quality (Asplund 1935). The warm-pressing development
continued with Harper in the 1950s and later by Wahren in the late 1970s, i.e. with the Impulse drying technique and developments in press-drying technology by Back in the 1980s (Back 1984; Wahren 1982). Further investigations about the impact of pressing and warm-pressing on HYP and chemical pulp have sparingly been done during recent years (Klinga et al. 2007b; Lucisano 2002; Norgren et al. 2018; Pettersson et al. 2017).

Pressing techniques are primarily used in paper-making to reduce the water content after the wet-end and before the drying section in order to get a more energy efficient drying process. Moving from these conventional drying processes to press-drying techniques, in his 1979 review, Setterholm refers to how wet stiff fibres under compressive forces induce interfibre bonding, greater conformability and more restraint during drying (Setterholm 1979). This makes the HYP containing stiff fibres most suitable for press-drying. Press-drying of HYP at high temperature has been further studied by Pettersson et al. and Norgren et al. in 2017 and 2018, and they confirm the development of strength properties due to densification and increased bonded area in the paper structure (Norgren et al. 2018; Pettersson et al. 2017). However, in the 1980s (Back, Andersson 1979; Back 1984; Back, Olsson 1989; Swensson 1987) investigated heat treatment and dry pressing of unbleached chemical kraft paper products, particularly linerboard with the aim to improve both dry and wet strength properties. The vital role of lignin as a moist resistant and compressive strength improving additive in containerboard was studied later (Saidan 2013, 2015).

The temperature and moisture content at which softening of lignin and hemicellulose occurs is crucial for press-drying in order to create compression, crosslinking and enhance bonding. Water acts as a plasticizer and lowers the temperature for softening of lignin. At the moment of hot-pressing the stiff lignin-rich fibres will collapse, i.e. get a flatter shape, which will increase the density of the material. Fibres from different types of wood have different tendencies for collapsing; their chemical compositions will effect binding, crosslinking, and moreover affect chemical and physical paper properties.

Already in 1963, Goring showed that isolated lignins could bond to paper when heated to a sufficiently high temperature, which produced softening of lignin. He also showed the plasticizing effect of water. The role of water on the viscoelastic properties of the in situ lignin of wood was also investigated in the 1980s by Salmén (Salmén 1984). According to research by Salmén 1982, he softening of several dry paper as composites of cellulose, hemicellulose and lignin occurs at about 230°C attributed to the glass
transition of cellulose (Salmèn 1982). The viscosity and location of water in the fibre structure is of great importance for the softening and displacement at pressing at high temperature (Heikkilä, Paltakari 2010). The adhesion effect of lignin has later been seen in press-drying of a moist web at temperatures above Tg of lignin and resulting in enhanced wet strength, wet stiffness and swelling restrictions (Back 1984). To achieve this effect when press-drying, the temperature needs to be well above the Tg, i.e. about 170°C (Atack 1972). The nip pressure and residence time under pressure are important in order to avoid a spring back effect of fibres if temperature and pressure is released before the fibre structure is bone dry (Klinga et al. 2007b).

2.2 Wood components

Wood is a porous and fibrous composite material constituting cellulose fibres embedded in a matrix of hemicellulose and lignin. The constituents in tracheid (softwood) or libriform (hardwood) fibres will be described in short here (Fig 1 and Fig 2) (Lönneberg 2009a).

The middle lamella, ML, is heavily lignified and stiff and it is shared with adjacent fibres. The lignin makes the middle lamella hard and acts as a hydrophobic sheathing around the fibres. The primary layer, P, is outermost formed on the cambial cell division, and contains cellulose fibrils embedded in amorphous pectic hemicelluloses and much lignin, therefore it has little swelling capacity.

The outer secondary wall, S1, is formed during the maturation of the fibre. It consists of two counter-rotating helices of cellulose microfibrils, and contains also lignin and hemicellulose. The main secondary wall, S2, forms the bulk of the fibre and varies with species; high content of cellulose is present in microfibrils in a helical arrangement. The microfibrillar framework of cellulose is encrusted with amorphous hemicellulose and lignin. This makes the structure dense. The inner secondary wall, S3, consists of a single lamella towards the lumen and the cellulose fibrils are arranged in a Z helix. It is remarkably resistant to chemicals, which may be a result of its dense morphological structure. W is the warty layer or lumen for transportation of water.
Fig 1. A schematic drawing of the various layers of a fibre wall. ML middle lamella, P primary wall, S1 transition lamella, S2 main layer of secondary wall, S3 tertiary wall, or tertiary lamella of secondary wall, Meier, (Brändström, 2002)

Fig 2. An approximate distribution of cellulose, hemicellulose and lignin in the cell wall of soft wood fibre (Panshin and DeZeeuw 1970)
Fig 3. Schematic illustration of typical fibre dimensions and degree of possible fibre shape collapse of various types of wood. Thickness/Width describes the fibre wall thickness and fibre width respectively. Length is the length of the fibres (Vesterlind, E.-L., Höglund, H. SPCI international conference, Stockholm, 2005).

The early wood spruce and aspen collapse more easily than spruce late wood and birch. Fig 3 shows the collapsing resistance $C_r$ (Vesterlind and Höglund 2005), the area moment of inertia, $I$, which represent the estimated bending stiffness, for different species. The $C_r$ is proportional to the compression load needed to collapse fibres. It increases with increasing fiber wall thickness. The $I_{sc}$ is the term for semi-collapsed fibres and describes how the compression forces affect the different fibres.

### 2.2.1 Cellulose and hemicellulose

The cellulose, about 40% of dry wood, is entirely linear and possesses a certain stiffness and forms a framework of linear and partly crystalline aggregates whereas the hemicellulose, about 25–30% of dry wood, is branched and therefore amorphous. The cellulose aggregates are of indefinite length and varying width. Cellulose is virtually absent in the middle lamella. The cellulose content increases towards lumen, whereas the hemicelluloses penetrate the entire fibre wall but is predominantly found in the outer regions of the main secondary wall. The hemicellulose consists mainly of the carbohydrates xylose (in hardwood) and mannose (in softwood), and the cellulose consists of glucose. The softening temperature for wet hemicellulose is about 50–60°C and is lower than for lignin (90-100°C). The corresponding values in the dry state are given as 200°C and
240-250°C respectively. Hemicellulose absorbs more water than lignin whereas water do not soften cellulose fibrils (Goring 1963). The structure of cellulose and hemicellulose is given in *Fig 4*

![Cellulose and Hemicellulose Structures](image)

*Fig. 4. The structure of cellulose (glucose) and hemicellulose (galacto glucomannan).*

### 2.2.2 Lignin

The lignin content of wood is somewhat less than 30% of dry softwoods and about 20% of dry hardwoods (some eucalyptus species up to 28%). The lignin appears in concentrated, compact form in the middle lamella, and in more scattered and porous form in the cell wall. The concentration of lignin in spruce was found to be 10–20% in the cell wall and near lumen, and 60–90% in the middle lamella. The primary wall is heavily lignified but the secondary wall contains very small amounts of lignin. Lignin is a three-dimensional polymer, *Fig 5*, with a molecular weight of about 20 000 u and shows viscoelastic behaviour as amorphous polymers. Compared to hemicellulose it is hydrophobic but still absorbs some water. The main chemical constituents of lignin are p-hydroxyphenyl-, guaiacyl- and syringyl units, *Fig 6*. Softwood contains mostly guaiacyl-lignins with one methoxy group and hardwood mostly syringyl-lignins with two metoxyl-groups. The amount of methoxy groups varies in lignin depending on from which species it originates.

The importance of lignin and its properties in mechanical pulping is quite well known and much effort has been made to increase the knowledge of its behaviour in the pulping process (Byrd 1979; Höglund et al. 1997; Salmén 1984). The softening of lignin is crucial for facilitating defibration in the lignin-rich middle lamella and thereby reducing energy costs, and to obtain
smooth and undestroyed fibres. Softening temperature or Tg has therefore been investigated by many researchers. Due to the kinetic transition of the lignin, the Tg may shift depending on the shear rate in refining or the frequency used in the laboratory testing methods. This means that a high load rate increases the softening temperature of lignin, which is the case in a high frequency dynamic load refiner where high shear rates apply. This is true for polymers in general, viscoelastic behaviour depends on the time scale of measurement loading procedures as well as the temperature (Irvine 1984, 1985). Below Tg, the lignin coated fibres are rigid and glassy, have low flexibility, require more energy to defibrate, and have poorer fibre-fibre bonding ability. Tg is lowered by water, which works as a plasticizer, and the more lignin is sulphonated the more hydrophilic it will become (Irvine 1985; Kelley et al. 1987; Salmén 1982) i.e. even sulphonation reduces the Tg. Lignin is a complex cross-linked structure with phenylpropane as its main component and it contains free phenolic groups, methoxyl groups and carbonyl groups. In 1997 Olsson and Salmén found that an increase of methoxyl groups in the lignin, was correlated to a decrease in softening temperature of wet wood (Olsson 1997).

![Lignin](image)

Fig 5. A schematic drawing of a probable structure of lignin.
Fig 6. The chemical building blocks of lignin. The p-hydroxyphenyl has no methoxy-group and occurs only sparingly in wood; Guaiacyl has one methoxy-group that occurs 90–95% in softwood and 25–50% in hardwood; Syringyl has two methoxy-groups and occurs 0–1% in softwood and 50–75% in hardwood (Grundberg 2009).

2.2.3 Extractives

The extractives or resins can be either water-soluble or organo-soluble and are concentrated in the medullary rays and other parenchymatic cells as well as in the resin ducts. Their functions are to reserve the wood and to protect substances in the parts of the xylem that become exposed to the atmosphere. The organo-soluble extractives consist of fatty, resin acids and esters, as well as phenolic compounds and neutral components such as fatty alcohols, terpenes and sterols. These are all hydrophobic and as a consequence lead to problems in the pulping process.

2.2.4 Water

The water in wood and in the paper structure plays an important role as hygroplasticizer in softening the carbohydrates and lignin. In wood and chips the water softens the lignin and the hemicellulose prior to mechanical separation of the fibres HYP processes (Lönnberg 2009b; Persson 2003). This is a requirement to get more of undamaged long fibres and less shives and fines. The mean water content in green wood is about 40-70% and differs between species and parts of the tree. In papermaking, the water content after the press section is about 50% and in the final paper less than 10%. Water in the fibre material is classified as free water in the macropores, bound freezing water and bound non-freezing water in the micropores (Fig 7) (Heikkilä, Paltakari 2010). Micropores are voids inside the fibre walls, while macropores are mostly found between fibres (Fig 8.). The bound water as well as the bound non-freezing water is thought to be absorbed into the
amorphous regions of the fibre wall. In a paper sheet with a dry content of about 40–50%, most of the water is inside the fibre walls.

---

Fig 7. Water fractions and their removal from paper (Heikkilä, Paltakari 2010).

Fig 8. Different water location in the sheet (Heikkilä, Paltakari 2010).
The water inside the spruce wood fibre cell walls can be described using the fibre saturation point (FSP), this is normally reckoned to be 25% as dry content, i.e. 0.33 g/g (Barkas 1935). The amount of water held by a high yield pulp is however much higher even at the g-force of 3000 used as standard method when measuring water retention value (WRV). A for this work relevant study was performed the high yield pulp HT-CTMP where WRV was studied as function of temperature, charge, counter ion and pH (Fjellström et al. 2013) see figure 9.

![Figure 9](image_url)

Fig 9. Swelling measured as water retention value WRV, g/g as function of temperature in the range 25-95°C for peroxide bleached HT-CTMP with total charge 233 mmol/kg. Pulps used in this study; Ref, Na, H, Mg, Ca and Al forms (Fjellström et al. 2013).

From this work it was concluded that the reference pulp and the pulp in sodium form had highest WRV which was unchanged when increasing temperature. The WRV of pulps in Mg, Ca, Al and non-dissociated form was decreasing with increasing temperature. In theory the swelling potential should increase with increasing temperature when lignin is softened due to that the fibre structure becomes more flexible. As the compressibility is also improved with softening, the swelling effect is compensated for. When using 2+ or 3+ valence metal ions the swelling potential is reduced and the net result is increased compression with increasing temperature.
Moreover, the cell wall of a mechanical pulp fibres contain less water than a cell wall in a chemical pulp fibres, 0.9 and 2 g/g dry solid respectively (Heikkilä, Paltakari 2010). The effect of water on the viscoelasticity has been studied by Salmén, among others and it’s well established that the moisture content is important in order to soften the stiff, lignin-rich fibres in mechanical pulping and papermaking (Salmén 1984).

2.3 Strength development in HYP

Strength in paper web develops mainly during the drying process when water is removed from the fibre mat by pressing and drying, creating bonding between fibres. According to Page’s theory, the tensile strength of paper depends on the fibre strength as well as the bond strength between individual fibres (Page 1969). The fibres take up the applied load and provide strength and stiffness, whereas the paper matrix holds the fibres in position relative to each other. In more recent studies, the bonding energy for mechanical interlocking, interdiffusion, capillary bridges, hydrogen bonding, Van der Waals forces, and Coulomb forces have been calculated by atomic force microscopy. It was found in these experiments that primarily Van der Waals forces, but also capillary bridges contributed to the bonding strength in paper forming (Hirn, Schennach 2015).

HYPs are historically considered to possess lower sheet strength properties than chemical pulps, which could depend on the mechanical treatment in the pulping process, smaller contact areas between fibres due to fibre stiffness (Klinga et al. 2007a) and extractives that hinder strong bonding between cellulose surfaces (Kokkonen et al. 2007; Rundlöf et al. 2002). Stone and Clayton have shown, by measuring with zero span, that lignin in fibre might possess little tensile strength of its own. They removed lignin by treatment with sodium chlorite at pH 4.5, which decreased the strength per individual fibre, but increased the strength per unite weight (Stone, Clayton 1960).

Research at FSCN has confirmed that improved strength of HYP based paper is largely controlled by the density, which, in turn, is related to the fibre stiffness that determines how much each fibre collapses. A higher amount of fully collapsed long fibres means higher strength (Höglund 1997). The strength is developed mostly due to the inter-fibre bonds, which are more easily created as the contact areas increase due to densification. Moisture and heat will affect the development of inter-fibre bonding. Water
as an incompressible medium will hinder and resist the consolidation if the dry content is less than about 50%. By raising the temperature, the viscosity of water will reduce fluid surface tension. The high temperature together with moisture will soften the lignin-rich fibres in HYP. This enhances the compressibility and inter-fibre bonds may form and increase the strength of the paper. Differences in tensile index as function of density between high yield pulps and kraft pulp when making standard SCAN handsheets are shown in Fig 10.

![Tensile index, kNm/kg](image)

Fig 10. High yield pulps as Chemimechanical Pulp (CTMP) Thermomechechanical Pulp (TMP) and Groundwood pulp (GWP) can be formed into sheets with higher bulk (lower density) at same tensile as that of kraft pulps, that however has a higher maximum tensile index level (Höglund 1992). High yield pulp used in this work

### 2.3.1 Thermomechanical (TMP)

TMP is mainly produced for use in graphic paper, where high light scattering is needed for good opacity, but also in products such as paperboard and tissue paper to give high bulk. In the TMP process, the chips are preheated with steam in the range of 115–150°C and thereafter refined in a pressurized system. The elevated temperature softens the lignin and makes it easier to separate the fibres more energy efficiently. TMP is usually made from spruce and contains high amounts of lignin, about 28%.
The amount of fines and fine particles are important to get high tensile strength, opacity (light scattering) and a smooth surface in order to achieve good printability.

2.3.2 Chemithermomechanical (CTMP)

CTMP pulp is mainly used in the middle ply in paperboard and in tissue for absorbent products. The process of CTMP is similar to that of TMP, but with a pre-treatment of chips with lignin softening chemicals. Softwood chips are first impregnated with a week solution (about 2%) of sodium sulphite (Na$_2$SO$_3$), whereas hardwood chips usually are impregnated with combinations of Na$_2$SO$_3$/NaOH or alkaline hydrogen peroxide. Thereafter the chips are normally heated to a higher temperature (115–135°C) to soften the lignin and to give a gentle fibre separation. This will result in more of long stiff fibres, less fines and lower shive content, which increases the bulk of sheets from the pulp. CTMP pulp is made from both hardwood (usually birch, aspen and eucalyptus) and softwood (usually spruce). The yield is normally 95% and the lignin content about 26% in spruce CTMP and 20% in birch CTMP.

2.3.3 High Temperature Chemithermomechanical (HT-CTMP)

HT-CTMP is a development of CTMP towards a more energy saving product, which is characterized of a higher long fibre fraction, almost similar to that of chemical softwood pulp. The preheating is performed at higher temperature, about 170°C. This process yields pulp with long, smooth and well-preserved lignin coated fibres. The shive and fines contents are very low. These long, stiff and lignin coated fibres are considered to give poor bonding ability, but are a good raw material for absorption materials. The yield and the lignin content are about the same as for CTMP. The high fibre stiffness, high long fibre content and low shive content makes the HT-CTMP suitable for products for filtration and liquid absorption.

2.3.4 Neutral Sulphite Semi-chemical (NSSC) pulp

The neutral sulphite cooking process is a semi-chemical cooking process mostly used on hardwood, predominately birch and aspen in Scandinavian, because of low lignin content (less than 20%). The wood chips are first chemically cooked with Na$_2$SO$_3$ and NaOH, but only to the extent that the fibres can be separated mechanically without major fibre damage. The product is cheap and therefore the production is compromised in terms of
chemical cooking and mechanical defibration. A high content of hemicellulose and a rather low content of lignin are significant for NSSC pulp. The yield is about 75–85% and the main product is fluting for corrugated boards.

2.3.5 Semi-chemical pulp with alkali impregnation (SCP\textsubscript{al})

SCP\textsubscript{al} is a semi-chemical pulp based on alkali impregnation with Na\textsubscript{2}CO\textsubscript{3} and NaOH and a preheating at 170°C. In the present study, the raw material was Brazilian Eucalyptus. This process targets low hemicellulose and high sulphur-free lignin content. In this case, a eucalyptus mixture was used in a pilot trial at Valmet in Sundsvall. The yield was 80% and lignin content was 24.6%.

3 Experimental

3.1 Materials and Methods

In the first part of my research (Paper I) different HYP pulps were used, CTMP, HT-CTMP, TMP, NSSC, SCP\textsubscript{al} (presented in chapter 2.4) and one northern bleached softwood kraft pulp (NBSK). CTMP and HT-CTMP were both Norway spruce based, peroxide bleached and flash dried, from SCA Östrand, Sundsvall, Sweden. CTMP (CSF 420 ml) has been used as reference pulp in earlier studies at Mid Sweden University. HT-CTMP (CSF 630 ml) is a high temperature but low refining energy pulp with somewhat lower fines and shive content than CTMP. TMP was a low freeness, unbleached, pulp of Norway spruce from Ortviken, Sundsvall Sweden. No softening chemicals were used in the pulping process. In the process many fibres are torn resulting in high content of fines, lignin and extractives. The birch/aspen based NSSC sulphur-rich pulp was refined at MoRe Research laboratory. Eucalyptus based semi-chemical pulp from the sodium carbonate alkali (SCP\textsubscript{al}) process (sulphur-free) was pilot-scale produced by Valmet in Sundsvall, Sweden. Both semi-chemical pulps (NSSC and SCP\textsubscript{al}) had a yield of about 80%. The SCP\textsubscript{al} has less hemicellulose but more lignin (Klason) than NSSC. The northern bleached sulphate kraft (NBSK) is a standard pine-based pulp produced for liner in packaging materials, from Metsä Board, Husum mill, that was refined at MoRe Research. The cellulose content is high, hemicellulose rather intermediate and the lignin content is close to
zero. The chemical process rinses out fines, shives, lignin and extractives and leaves a yield of about 40%, but gives high mean fibre length. In the second part of my research (Paper II), unbleached Northern softwood kraft pulps (NSK) of three different lignin levels were produced in order to investigate the effect of lignin content on paper properties. The pulps were produced at pilot scale at MoRe Research from same sawmill spruce chips according to the chemical sulphate process, batch wise with Na$_2$S and NaOH at a temperature of maximum 163°C. The different lignin levels were achieved by changing the time of cooking and targeting a kappa level of 25, 50 and 80. These pulp qualities were NSK K25 (lignin content of 3%), NSK K50 (lignin content of 7%) and NSK K80 (lignin content of 12%). The standard NSBK (same as in the first part) with 0% lignin content was used as reference and CTMP (same as in the first part) was used as comparison to HYP.

The paper samples in the third part (Paper III) were based on HT-CTMP (the same pulp as in part one) only. The purpose of these experiments was to optimize the variables in a new dynamic hot-pressing machine. Table 1 shows the pulp characterizations and Table 2 summarizes the methods of the analyses used.
# TABLE. 1. PULP CHARACTERIZATION

<table>
<thead>
<tr>
<th>Pulp</th>
<th>CTMP Cellulose, (%)</th>
<th>HT-CTMP Cellulose, (%)</th>
<th>TMP Cellulose, (%)</th>
<th>SCP$_{al}$ Cellulose, (%)</th>
<th>NSSC Cellulose, (%)</th>
<th>NBSK Cellulose, (%)</th>
<th>NSK K25 Cellulose, (%)</th>
<th>NSK K50 Cellulose, (%)</th>
<th>NSK K80 Cellulose, (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose,</td>
<td>47</td>
<td>48</td>
<td>46</td>
<td>63</td>
<td>52</td>
<td>82</td>
<td>80</td>
<td>75</td>
<td>70</td>
</tr>
<tr>
<td>Hemicellulose,</td>
<td>26</td>
<td>24</td>
<td>24</td>
<td>12</td>
<td>25</td>
<td>18</td>
<td>17</td>
<td>17</td>
<td>17</td>
</tr>
<tr>
<td>Lignin Klason, (%)</td>
<td>27</td>
<td>26</td>
<td>28</td>
<td>21</td>
<td>17</td>
<td>0</td>
<td>3</td>
<td>7</td>
<td>12</td>
</tr>
<tr>
<td>Soluble lignin, (%)</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>3.5</td>
<td>6.1</td>
<td>0.4</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Acetone extract, (%)</td>
<td>0.15</td>
<td>0.19</td>
<td>1.27</td>
<td>0.15</td>
<td>0.55</td>
<td>0.04</td>
<td>0.31</td>
<td>0.27</td>
<td>0.48</td>
</tr>
<tr>
<td>Fibre length LW, (mm)</td>
<td>1.46</td>
<td>1.66</td>
<td>0.83</td>
<td>1.11</td>
<td>1.99</td>
<td>2.48</td>
<td>2.51</td>
<td>2.58</td>
<td>2.58</td>
</tr>
<tr>
<td>Fibre width LW, (µm)</td>
<td>31</td>
<td>32</td>
<td>30</td>
<td>27</td>
<td>25</td>
<td>28</td>
<td>29</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>Fines, (%)</td>
<td>34.5</td>
<td>29.0</td>
<td>62.4</td>
<td>13.6</td>
<td>11.2</td>
<td>8.9</td>
<td>10.9</td>
<td>13.2</td>
<td>13.2</td>
</tr>
<tr>
<td>Shive content, (Sum/g)</td>
<td>572</td>
<td>112</td>
<td>4907</td>
<td>2556</td>
<td>28</td>
<td>24</td>
<td>348</td>
<td>3697</td>
<td>3697</td>
</tr>
<tr>
<td>CSF, (ml)/°SR</td>
<td>420</td>
<td>630</td>
<td>55</td>
<td>559</td>
<td>25o</td>
<td>27o</td>
<td>26o</td>
<td>25o</td>
<td>25o</td>
</tr>
<tr>
<td>Dry content, (% d.c.)</td>
<td>92.1</td>
<td>91.8</td>
<td>29.5</td>
<td>29.1</td>
<td>18.7</td>
<td>23.9</td>
<td>26.3</td>
<td>22.5</td>
<td>21.6</td>
</tr>
<tr>
<td>Yield, (%)</td>
<td>95</td>
<td>95</td>
<td>98</td>
<td>80</td>
<td>83</td>
<td>45</td>
<td>44</td>
<td>45</td>
<td>46</td>
</tr>
<tr>
<td>Species</td>
<td>Spruce</td>
<td>Spruce</td>
<td>Spruce</td>
<td>Euk</td>
<td>Birch/aspen</td>
<td>Pine</td>
<td>Spruce</td>
<td>Spruce</td>
<td>Spruce</td>
</tr>
</tbody>
</table>
## TABLE 2. METHODS FOR CHARACTERIZATION

<table>
<thead>
<tr>
<th>Main techniques</th>
<th>Characterization</th>
<th>Standard/method</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pulp characterization</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lignin Klasson</td>
<td>Lignin content, insoluble</td>
<td>T222</td>
</tr>
<tr>
<td>Soluble lignin</td>
<td>Lignin content, soluble</td>
<td>T-UM250</td>
</tr>
<tr>
<td>Acetone extracts</td>
<td>Extractives</td>
<td>ISO 14453</td>
</tr>
<tr>
<td>Carbohydrates</td>
<td>Cellulose, hemi-cellulose content</td>
<td>SCAN-CM 71:09</td>
</tr>
<tr>
<td>Fibre dimensions</td>
<td>Length, width, fines, shives</td>
<td>ISO 16065-2</td>
</tr>
<tr>
<td>CSF (ml)/SR, Dry content (%) d.c.</td>
<td>analysed by PulpEye</td>
<td>ISO 5267-1, -2, ISO 638</td>
</tr>
<tr>
<td><strong>Light microscopy</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KMnO₄ Staining method and</td>
<td>Visualize lignin in pulp and cross section of paper sheets before and after hot-pressing</td>
<td></td>
</tr>
<tr>
<td>fluorescence</td>
<td>Visualize the structural change in paper sheets caused by hot-pressing</td>
<td></td>
</tr>
<tr>
<td><strong>SEM</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Visualize the structural change in surface of paper sheets caused by hot-pressing</td>
<td></td>
</tr>
<tr>
<td><strong>Paper properties</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>Compressibility</td>
<td>ISO 5364</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>Strength</td>
<td>ISO 1924-3</td>
</tr>
<tr>
<td>Tensile stiffness</td>
<td>Resistance to bending</td>
<td>ISO 1924-3</td>
</tr>
<tr>
<td>Elongation</td>
<td>Brittleness</td>
<td>ISO 1924-3</td>
</tr>
<tr>
<td>SCT</td>
<td>Cross directional short span compressive strength</td>
<td>ISO 1924-3</td>
</tr>
<tr>
<td>Wet tensile strength</td>
<td>Wet strength and wet stability</td>
<td>ISO 9895</td>
</tr>
<tr>
<td>Contact angle</td>
<td>Hydrophobicity of paper sheet surface</td>
<td>ISO 3781</td>
</tr>
<tr>
<td></td>
<td>Automatic drop method with DAT 1100-Fibro System AB</td>
<td>T558</td>
</tr>
</tbody>
</table>
The carbohydrates were analysed with ion chromatography according to SCAN-CM 71:09. The calculation of cellulose and hemicellulose for hardwood and softwood is done according to KA 10.314, which is the internal standard at the laboratory, Equation 1, 2 and 3.

For hardwood:

\[
Cellulose (\%) = \text{Glucose (\%) of Carbohydrates} - \frac{\text{Mannose (\%) of Carbohydrates}}{2}
\] (1)

For softwood:

\[
Cellulose (\%) = \text{Glucose (\%) of Carbohydrates} - \frac{\text{Mannose (\%) of Carbohydrates}}{3}
\] (2)

\[
\text{Hemicellulose (\%)} = 100 \% - \text{Cellulose (\%)}
\] (3)

Cellulose, hemicellulose, lignin, acetone extract (the amount of extractives) and acid soluble lignin content in each pulp sample are calculated as percentage of the total weight. The fibre data analysed by PulpEye instrument, in Table 2, is calculated as follows:

\[
l = \frac{\sum (l \times l)}{\sum (l)}, l > 0.2 \text{mm}
\] (3)

\[
b = \frac{\sum (b \times l)}{\sum (l)}, l > 0.5 \text{mm}
\] (4)

\[
\text{Fines (\%)} = \frac{\sum a}{\sum A \times 100(\%)}, l < 0.2 \text{mm}
\] (5)

\(\Sigma a\) is the total area for fibre objects defined as fines, \(\Sigma A\) is the total area for all analysed objects. The shive content is calculated as the Sum of width, \(b = \text{Area / Length}\), when \(b > 75 \mu \text{m}, l > 0.3 \text{ mm per 1 gram of pulp.}\)

### 3.1.1 Sheet preparation

Pulp furnish was prepared in the same way for all samples in part one, two and three, hot disintegrated according to ISO 5263-3, and no chemicals added. Handmade sheets were prepared in the Rapid Köthen (RK) sheet former, Fig 11, according to ISO 5269-2. The fibre suspension was 6.0 g/l and was formed into paper sheets after vigorous aeration. The sheets were then press-dried at a pressure of 100 kPa under restrained conditions at 90°C until they reached the desired dryness content. For the paper sheets in the experiments in part one and two, the chosen grammage was 150 g/m² and the dryness content about 50%. In part three, the grammage was 100 g/m² and the moisture content about 63%. The paper sheets are circular with a
diameter of 20 cm, and have no fibre orientation. After sheet preparation, all handmade sheets were stored in well-sealed plastic bags for about 24 hours before hot-pressing in a cylinder press.

Fig 11. Rapid Köthen sheet former (left) and cylinder press (right).

3.1.2 Hot-pressing

THE CYLINDER PRESS

The experiments in part one and two were performed on a hot cylinder press machine located at MoRe Research Örnsköldsvik AB (Fig 11). The diameters of the cylinder and the press roll were 0.8 m and 0.2 m respectively. The larger cylinder was oil heated, and the fabric was a two-ply felt. The feeding rate was 1 m/min and the press nip was 7 MPa throughout all trial points. The press time of the felt was about 70 sec and the press nip time was about 1.5 sec calculated on a nip length of about 25 mm measured with sensor films from Fuji (Prescale LW 2.5–10 MPa). Fig 12 shows a drawing of the principle of the hot-pressing equipment used. Hot-pressing was performed at four different temperature levels, 20°C, 100°C, 150°C and 200°C. The out-coming sheet dryness was above 93%, which was important for the dimensional stability and to avoid spring-back of the densified fibre structure.
The trials in Paper III were performed on a new rotating press machine, installed at MoRe Research Örnsköldsvik AB 2018, (Fig 13). This press-drying technique is similar to impulse pressing (Lucisano 2002). The main differences are that here there is a hard nip and no extended nip, and the heated steel belt covers the unheated central cylinder. This gives short dwell times in the hard nip but a long dwell time between steel belt and central cylinder.

The press machine is equipped with a central cylinder and two press rolls, which results in two press nips. A moving externally heated steel belt carries the paper material, which is in direct contact with the unheated central cylinder. The steel belt width is 400 mm, thickness 0.8 mm and it covers the central cylinder for 1.173 m. At running the machine at a chosen temperature the central cylinder will be equally heated within one hour. Vertically, underneath the steel belt and the central cylinder there is the first press roll; the second press roll is on a movable distance from the first one. The steel belt is heated with an infrared (IR) heating system, placed at a distance of about 40 cm from the first nip. The maximum temperature in the first nip is 300°C. The heat will transfer through the steel belt into the paper sheet. The water in the moist paper material will be pressed out and evaporate in the nip. The diameter of the cylinder and the press rolls is 0.8 m and 0.2 m respectively. Maximum speed is 5 m/min, line load is up to 15
kN/m. The maximum steel belt pressure can be set between 0.03–0.21 MPa. Dwell time at press nip is about 27 to 240 ms, depending on the chosen speed and depending on the nip length which is in the actual machine design measured, without paper sample, to approximately 2 mm. Dwell time of steel belt it is between 14 and 140 seconds. The total weight of the machine is 2500 kg, length 3.3 m and width 1.6 m.

Fig 13 a. The dynamic press machine with an IR-heated steel belt. A drawing of the machine from IPCO AB.

Fig 13 b. The dynamic press machine with an IR-heated steel belt. A photo showing how the paper sheets are fed on to the steel belt.
Table 3. Trial set-up for experiments in.

<table>
<thead>
<tr>
<th></th>
<th>Ref</th>
<th>Tp1</th>
<th>Tp2</th>
<th>Tp3</th>
<th>Tp4</th>
<th>Tp5</th>
<th>Tp6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Speed m/min</td>
<td></td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>4.3</td>
</tr>
<tr>
<td>Temperature °C</td>
<td>100</td>
<td>200</td>
<td>210</td>
<td>280</td>
<td>290</td>
<td>290</td>
<td>300</td>
</tr>
<tr>
<td>Force press roll (nip 1, 2) kN</td>
<td>0</td>
<td>3</td>
<td>3,3</td>
<td>3</td>
<td>3,3</td>
<td>6</td>
<td>6,6</td>
</tr>
<tr>
<td>Mean pressure (nip 1, 2) MPa</td>
<td>0</td>
<td>4</td>
<td>4,4</td>
<td>4</td>
<td>4,4</td>
<td>8</td>
<td>8,8</td>
</tr>
<tr>
<td>Dwell time (nip) ms</td>
<td>0</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>28</td>
</tr>
<tr>
<td>Press impulse (nip) kPa s</td>
<td>0</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>300</td>
<td>209</td>
<td></td>
</tr>
<tr>
<td>Steel belt pulling force kN</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Steel belt pressure MPa</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>Steel belt dwell time s</td>
<td>23.5</td>
<td>23.5</td>
<td>23.5</td>
<td>23.5</td>
<td>23.5</td>
<td>16.4</td>
<td></td>
</tr>
</tbody>
</table>

The trials were run at 3 and 4.3 m/min and gave a dwell time in press nip of 40 and 28 ms respectively and in steel belt 23.5 and 16.4 seconds. The nip length in the press nip without paper sample was measured with sensor films from Fuji/Prescale and was estimated to be about 2 mm. The actual press nip length is probably different with paper samples because both width and thickness have effect. In this trial we calculated the mean pressure by using the 2 mm nip length and this resulted in 3.75 MPa (rounded to 4 MPa) and 7.5 MPa (rounded to 8 MPa) when the applied force was 3 kN and 6 kN respectively. It was also observed that at increasing temperature above approximately 180°C the pressure became uneven due to uneven heating of central cylinder. The pressure applied from the steel belt was 0.15 MPa.

The temperature was measured with IR-sensor just before the first press nip. The sensor was unfortunately not adjusted according to the correct emission factor and may therefore have proved incorrect. Even so, the level is likely to be quite accurate. The paper samples were fed onto the steel belt with a shovel (Fig 13 b) just before the press nip. To avoid moist paper sample to adsorb or stick to the surfaces, thin porous blotters were set on both sides.

No delamination occurred, probably due to the long residence time of the steel belt giving high enough strength in the z-direction.

**Mean pressure, dwell time, pressing impulse**

The mean pressure on the two press nips can be adjusted by choosing a force between 0 and 6 kN for each. By calculation, according to equation (4), the graph in Fig 14 could be plotted for the steel belt alone as the width, \( b \), is 400 mm and the nip length, \( l \), was estimated to 2 mm, resulting in an area of 0.0008 m².
\[ \text{Mean pressure, } P, [kPa] = \frac{\text{force [kN]}}{\text{press area [m}^2\text{]}} \]  

(4)

Dwell time as a function of speed can be plotted by calculating the equation (5). A speed of 0.5 and 4.5 m / min then gives the dwell time 27 and 240 ms, respectively. Equation (5) and Fig 15

\[ \text{Dwell time, } t, [s] = \frac{\text{nip length [m]}}{\text{speed [m/s]}} \]  

(5)

Fig 14. Mean pressure as function of force on press roll. Press nip length was about 2 mm

Fig 15. Dwell time as function of speed. Press nip length was about 2 mm.

The pressing impulse was calculated from equation (6) and plotted in Fig 16 as a function of speed for different forces on the press roll.

\[ \text{Pressing impulse, } I, [\text{Pa s}] = P \times t \]  

(6)

Fig 16. Press impulse as a function of speed calculated for different press forces (1 kN to 6 kN) in the first nip.

The recommended applied pulling force of steel belt is between 50 and 70 kN. The dwell time induced by the steel belt varies between 14.7 and 140.7
seconds, Fig 19. The arc length is 1.173 m which corresponds to 46.7% of total central cylinder.

Fig 18. This shows the steel belt pressure as a function of steel belt force.

Fig 19. Dwell time of steel belt as a function of speed.

3.1.3 Spectroscopic methods

In the light microscope (LM) instrument, visible light and magnifying lenses are used to examine small objects not visible to the naked eye. LM is an easy method for the visual analysis of wood raw material, pulp and fibre down to the micrometre scale. In this research, cross-sectional pieces of paper sheets were investigated by transmitted light and camera lenses with a magnification of 20x and a resolution of 300x. The samples were stained with potassium permanganate, which oxidizes lignin and turns it into a brown colour. In this way, it is possible to distinguish lignin in the paper structure.

A fluorescence microscope is used to examine structures that bind fluorescing species. It utilizes the phenomenon called “fluorescence” which is a property held by certain atoms and molecules, in which they absorb light of a particular wavelength and then re-emit light at longer wavelengths. This can be used when studying lignin as they contain phenol groups with conjugating double bonds, which are fluorescing wavelengths of UV light, 270 and 280 nm. Here cross-sections of paper sheets were evaluated with fluorescent microscopy, camera lenses 20x (20 μm) and a resolution of 600x.

Scanning electron microscope (SEM) is an electron microscope that creates images of objects by scanning it with an electron beam with a raster pattern. The electrons interact with the atoms on the object, which in turn emits signals about the object’s topography, composition and other properties. In this work, the sheet surface was evaluated using a resolution of 500x.
3.1.4 Strength properties (ISO 1924-3 and ISO 9895:2009)

The testing machine for tensile properties is designed to strain the test piece at a constant rate of 100 mm/min. Both the tensile force and the elongation are recorded. The index values are tensile property divided by grammage. The width of the test piece is 15 mm and the initial length is 100 mm. *Tensile strength* (kNm/kg) is the maximum strength of the material when tension is applied, usually at the moment when the material fails completely. *Tensile stiffness* (MNm/kg) is the maximum slope of the curve obtained when tensile force per unite width is plotted versus strain. *Elongation to failure* (%) is the strain at maximum tensile force and is given as the percentage of the initial test length.

The *SCT* (short-span compression test) (kNm/kg) is a test of compressive strength for paper and board produced for packaging and especially containers and boxes. The compressive strength is the maximum force per unit width that a test piece can withstand until the onset of failure. The test piece is 15 mm wide and clamped between two clamps, spaced 0.7 mm apart, which are forced towards each other until a compressive failure occurs.

3.1.5 Wet stability (ISO 3781 and T558)

The *wet strength* was tested as follows. Paper strips of 200 mm x 15mm are wetted in tap water for 1 min, 1 hour and 24 hours and thereafter measured in the tensile strength equipment described above. Wet strength was also measured on the samples stored for one year, both dry and in room temperature, in order to evaluate the stability of the established wet strength properties.

*Contact angle* measurements were carried out according to an automatic drop method with DAT 1100-Fibro System AB. The measurements are used to study the relative sorptive rates of uncoated paper. A specified drop volume of a liquid is automatically applied to the test piece of paper surface. In this present study, deionized water is used as liquid. Images of the drop in contact with the paper test piece are captured by a video camera. The contact angle between the drop and the substrate at various time intervals are determined by image analysis techniques. The contact angle at specified time, changes in droplet height and the diameter can be analysed. In these studies, the contact angle was measured in order to analyse the gluing characteristics of lignin and/or extractives on the surface as well as the surface change (density) caused by hot-pressing.
4 Results and discussion

The research presented here is based on three parts, describing how the paper properties are developed when hot-pressing paper sheets based on HYP and kraft pulp with different lignin content at different temperatures, pressures and dwell times. Starting with part one, where paper sheets based on 5 different HYP pulps and a bleached kraft pulp were compared. Part two includes hot-pressing paper sheets based on kraft pulps with different lignin contents. Part three was a study on optimization of the hot-pressing variables (temperature, pressure, pressing time, speed and press impulse) using a new steel-belt based technology. Only paper sheets based on HT-CTMP was used.

4.1 Morphology by microscopy analysis

The lignin in pulp fibres can be visualized by light microscopy after staining with potassium permanganate, KMnO₄ for 6 min. It is known to oxidize lignin and other aromatic and unsaturated extractives, giving a brownish colour at room temperature, while having little effect on structural carbohydrates (Van Soest, Wine 1968). The more intense the colour, the more lignin is present. Fig 20 shows pulp fibres of NBSK 0% lignin, NSK K25 3% lignin, NSK K50 7% lignin, NSK K80 12% lignin and CTMP 26% lignin.

Fig 20. The picture shows pulp fibres stained with KMnO₄ analysed by light microscopy, transmitted light, bright field, lens 20x(300x). A is NBSK (0% lignin), B is NSK K25 (3% lignin), C is NSK K50 (7% lignin), D is NSK K80 (12% lignin) and E is CTMP (26% lignin)

The SEM analyses showed the CTMP based paper sheets pressed at 20°C and 200°C. It is visually clear that the sheet surface, when pressed at high nip temperature, was much denser and that the fibre lines almost vanished compared with the paper sheet pressed at 20°C, (Fig 21).
Lignin is sensitive to UV light (Scott et al. 1969) and gives a fluorescence effect that is utilized in fluorescence microscopy analyses to reveal the presence of lignin as in the present study of paper cross-sections of CTMP and TMP samples hot-pressed at 20°C and 200°C (180°C for TMP). Lignin is shown as bright yellowish (marked with arrows) areas, mostly surrounding the fibres, and reveals how the rheology changes the form of fibres under these conditions (Fig 22). The location of lignin seemed to remain after hot-pressing at 200°C and 180°C (Fig 22: B and D).
The compression effect on the fibre structure when hot-pressing was visually studied with light microscopy on a cross-section of paper sheets stained with KMnO₄ (Fig 23). The colour shows the presence of lignin, and thereby the morphological change for lignin-rich compared to lignin-poor pulp based paper sheets. It was clearly seen that hot-pressing at 200°C lignin-rich stiff fibres in CTMP (26% lignin) gives high compression compared to the already collapsed lignin-poor fibres in the NSK samples. The structure for the NSK was almost the same at 20°C and 200°C hot-pressing despite of high lignin content. The colours show clearly different levels of lignin in the pulps, NBSK, NSK K25 and NSK K80: 0, 3%, and 12% lignin respectively.

Fig 23. Paper cross-sections stained with KMnO₄ for 6 min and analysed by light microscopy, transmitted light, bright field, lens 20x. The pictures show samples of NSK K80, NSK K25, NBSK and CTMP hot-pressed at 20°C and 200°C.

4.2 The effect of pressing load and temperature on paper properties

The density (Fig 24 and 25) increases significantly with increasing temperature from 20°C to 200°C when hot-pressing of the paper sheets based on HYP, whereas sheets from NSK were much less affected (Part I and II). CTMP, HT-CTMP, TMP and SCPₐl paper samples have high bulk from the beginning because of the fairly high freeness pulps, compared to the samples based on NSSC and NSK pulps. Above 100°C, the density increases more rapidly, probably because Tg of lignin is reached and consequently the enhancing softening of stiff fibres starts. The highest temperature in these experiments was 200°C, but the development of the density could perhaps increase further if the temperature was raised even more. The NSK pulp
based samples do not increase that much in density compared to HYP due to the already collapsed fibres. In the case of NSSC pulp, which is refined, chemically treated and contains more flexible fibres, the density is already high at low pressing temperature, only a slight increase occurs with increasing temperature.

Interesting is that density for the HYP based samples show almost the same value, only about 10% lower, as for the NSK based samples when pressed at 200°C. This was previously verified by Norgren and Pettersson at FSCN/Mid Sweden University (Norgren et al. 2018; Pettersson et al. 2017). The increase in density was about 100% for HT-CTMP, 50% for CTMP and 75% for TMP. The main reason why the HT-CTMP gains more density than CTMP was the initially higher bulk as a result of the very low refining energy demand to reach a certain low shive content compared to conventional CTMP, Table 1. The SCPs with CSF 559 ml shows an increase of 40% in density. The increase in density by increasing pressing temperature is similar for all the HYP based paper sheets. This is probably connected to the softening of stiff lignin-rich fibre structure that occurs above Tg of lignin. Differences in fibre dimensions, fines and pulp chemistry (such as hemicellulose content and sulphonation) does affect as well, but is not discussed at depth in this thesis.

![Density as a function of temperature in the pressure nip. The figure shows 5 samples of different HYPs and one sample of NBSK. All samples were pressed at 20°C, 100°C, 150°C and 200°C, only TMP at max 180°C.](image)

Fig 24. Density as a function of temperature in the pressure nip. The figure shows 5 samples of different HYPs and one sample of NBSK. All samples were pressed at 20°C, 100°C, 150°C and 200°C, only TMP at max 180°C.
Fig 25. Density as a function of temperature in the pressure nip.; the figure to the right shows 4 different samples of NSK pulp with lignin levels of 3, 7, and 12% and one sample of CTMP. All samples were pressed at 20°C, 100°C, 150°C and 200°C, only TMP at 180°C.

In the third part trials HT-CTMP based paper sheets were run on the new press machine with focus on different settings of temperature, load pressure and speed. Density is shown in Fig 26. Increasing load pressure from about 4 to about 8 MPa increases density by 40% at about the same temperature (280–290°C). Adding a second press nip increased the density by 20–30%. Temperature alone above 200°C did not affect the density more than 10%. The reference was run twice to get a bone dry sheet, which gave a double dwell time of 2*23.5 seconds, with a steel belt pressure of 0.15 MPa, which resulted in rather high density of 581 kg/m³. A higher speed gave a shorter dwell time in the press nip as well as shorter dwell time on the steel belt resulting in reduced density even when run with two press nips. Thus, the dwell time seems to have more impact on density than number of press nips. The importance of residence time was stressed by Horn and Setterholm in their experiments on a continuous press-drying with high yield hardwood pulp (Horn, R. A., Setterholm 1983).
The strength properties increase mostly due to improved joints and more close contacts between the fibres in the network as the density increases, and this occurs when the stiff lignin-rich fibres are softened by hot-pressing the moist paper sheets. It is also possible that new bonds are created, but this is not investigated in this research. However, this is suggested by Back 1984; Byrd 1979; Irvine 1985; and Lindström et al. 2005, among others. Nevertheless, in this work we also see a likely contribution of lignin to increased strength and especially wet strength.

The increase in tensile index (Fig 27) is the greatest for all the HYPs as the density increases, when hot-pressed up to 200°C. The tensile index increases for paper sheets based on CTMP is 100%, HT-CTMP 150%, TMP 80%, NSSC 45% and SCP 100%. The level of tensile index reached for CTMP and HT-CTMP is about 70 kNm/kg, which is close to that for NBSK (85 kNm/kg), but at a density of about 10% lower. It is also interesting that the tensile index of the NSSC increases to a very high level (93 kNm/kg), even higher than for the NBSK.

The paper samples based on NSK with a lignin content 0–7% increases only slightly, whereas the NSK K80 with 12% lignin increases by 20%. The lignin content from 0 to 12% shows a contribution of 20% in tensile index. At the highest temperatures (150°C and 200°C), the results of the NSK pulps demonstrate a linear increase in tensile index at increased lignin content,
whereas below the Tg of lignin, we cannot reveal the same linear relationship (Fig 28).

![Figure 27](image1.png)

Fig 27. Tensile index as a function of density. Error bars indicate 2SD. The increasing values are nearly linear with the increase in temperature in pressure nip, except for NBSK.

![Figure 28](image2.png)

Fig 28. Tensile index as a function of lignin content. Error bars indicate 2SD. Results show a potential to increase the tensile stiffness index and SCT for paper sheets based on kraft pulp by increasing the temperature in
combination with high lignin content. Hot-pressing moist HYP based paper sheets show a similar effect on SCT (Fig 29) and tensile stiffness as on tensile strength. The HYP reach high strength values at lower density than the NBSK, which is an advantage for packaging paper applications. Fig 30 shows the SCT development by means of hot-pressing and increasing lignin content. Increasing in SCT by increasing lignin content is linear as temperature is 150°C or higher. Similar results were obtained for tensile stiffness index.

Fig 29. SCT index as a function of density. Error bars indicate 2SD. The graphs show a significant increasing SCT with increasing nip temperature for HYP.
Fig 30. SCT index as a function of lignin content for paper sheets based on NBSK (0% lignin), NSK K25 (3% lignin), NSK K50 (7% lignin) and NSK K80 (12% lignin) hot-pressed at 20°C, 100°C, 150°C and 200°C, and paper sheets based on CTMP (26% lignin) hot pressed at 200°C. Error bars indicate 2SD.

The elongation to failure is a property that indicates how brittle a material is. For packaging solutions, the brittleness is very important as a measurement for how well it can resist crushing. These results show a significant negative effect on elongation to failure for all the kraft pulp based paper sheets when increasing pressing temperature, whereas the HYP based paper sheets do not change in these tests, possibly because the elongation values are low already at 20°C (Fig 31 and Fig 32).
Fig 31. Elongation to failure as a function of temperature for paper sheets based on different HYPs and NBSK hot-pressed at 20°C, 100°C, 150°C and 200°C. Error bars indicate 2SD.

Fig 32. Elongation to failure as a function of temperature for paper sheets based on NBSK (0% lignin), NSK K25 (3% lignin), NSK K50 (7% lignin), NSK K80 (12% lignin) and CTMP (26% lignin) hot-pressed at 20°C, 100°C, 150°C and 200°C. Error bars indicate 2SD.

The dry tensile (Fig 33) index measured on HT-CTMP paper sheets hot-pressed showed more sensitivity to temperature increase than load pressure increased. Two press nips seems to have a small improvement on tensile
strength and a shorter dwell time has a negative effect when pressing at these temperature ranges (above 200°C).

![Bar chart showing tensile index and mean pressure as a function of temperature.](chart.png)

**Fig 33.** Tensile index and mean pressure as a function of temperature. HT-CTMP based paper sheets.

### 4.3 Development of wet strength

Packaging is used to protect products from bumps, dirt and in many cases from moisture, so it might be important that the material in the packaging is water resistant and retains its strength in wet state. To obtain wet strength and water resistance in paper materials, large quantities of fossil-based chemicals are currently used; these are toxic to nature and cause health problems during handling. It is desirable to find eco-friendly alternatives to such chemical systems.

Improved wet-stability by means of hot-pressing of wood containing fibre boards has long been known as well as that lignin contributed to this property (Mason 1931, 1937). It is suggested that lignin creates new joints and cross-links and also covalent bonds by condensation reactions at high temperatures or inter-locking surfaces by interdiffusion when fibre structures are hot and plasticized (Lindström et al. 2005; Windeisen, Wegener 2008). The results presented here verify that wet strength is developed by pressing and heat treatment of lignin-rich fibre materials.
Fig 34 and 35 show wet tensile strength index measured on paper sheets after hot-pressing at temperature 20°C, 100°C, 150°C and 200°C and drained in distilled water for 1 hour. For all lignin-rich pulp-based paper sheets, wet strength increases slowly at low pressing temperature and rapidly above 150°C which is well above Tg. The highest wet strength was developed at pressing a temperature of 200°C. The NBSK (0% lignin) and NSK K25 (3% lignin) showed no increase in wet strength. NSK K80 with a lignin content of 12% shows the highest wet strength of 23 kNm/kg and the CTMP and HT-CTMP with a lignin content of 26–27% shows a wet strength of 16 kNm/kg. NSSC and SCPal pulp containing less lignin, 17 and 21% respectively, show slightly lower wet strength 10 and 13 kNm/kg. Sulphonation increases the hydrophilicity and lowers the Tg of lignin, but in combination with hot-pressing it seems to improve the development of wet strength. Hardwood based NSSC contains more syringyl-lignin units and is therefore more sulphonated than CTMP and HT-CTMP, which might reduce wet strength. Eucalyptus-based SCPal is treated with alkali, and therefore contains no sulfonated groups, but nevertheless does not reach higher wet strength. Another reason for differences in wet strength might be a greater degree of condensation reactions in softwood than in hardwood (Shimada et al. 1997). The high wet strength of NSK K80 with only 12% lignin compared to CTMP with 26% is interesting and must be further investigated. Improved wet strength for kraft paper and linerboard was studied already in the 1970s and was explained by auto cross-linking initiated by partial oxidation at high temperature (Back 1976, 1984; Swensson 1987).

The study with different lignin levels in the kraft pulp shows that the amount of lignin is positively linear with the wet strength at the same density and with the same chemical composition with respect to cellulose and hemicellulose (Fig 36, Table 1). This is true at all temperature ranges in the current study. The development of wet strength is stronger at 200°C than at lower temperatures for all lignin levels.

The paper sheets hot-pressed at 200°C were also evaluated with respect to different immersion time; 1 minute, 1 hour and 24 hours (Fig 37, 38). The results are shown as wet tensile strength of dry tensile strength, which is a common way to describe the efficiency of wet strength chemicals when producing commercial wet strong papers. 15% wet/dry strength is the general level above which a standard paper being defined as wet strong paper (Dunlop-Jones N. 1991). The NSK samples containing 7% lignin or more reach 15% wet/dry strength. The CTMP shows higher wet/dry strength relation than NSK due to its much lower dry tensile strength (70 and 107
kN/m/kg respectively). In the time interval of 24 hours the wet tensile strength was decreased by a maximum of five unites. Thus, the wet strength obtained by hot pressing of lignin-rich materials remains. Moreover, the linearity between wet strength and lignin content remains independent of the immersion in water for the given time interval.

Fig 34. Tensile index wet after immersed in water 1 hour as a function of temperature. Error bars indicate 2SD. HYPs and NBSK.
Fig 35. Tensile index wet after immersed in water 1 hour as a function of temperature. Error bars indicate 2SD. Fig 35: NBSK, NSK (K25, K50, K80) and CTMP.

![Graph showing tensile index wet after immersed in water 1 hour as a function of temperature](image)

Fig 36. Wet tensile index as a function of lignin content for paper sheets based on NBSK (0% lignin), NSK K25 (3% lignin), NSK K50 (7% lignin) and NSK K80 (12% lignin) and CTMP 27% lignin hot-pressed at 20°C, 100°C, 150°C and 200°C.

![Graph showing wet tensile index as a function of lignin content](image)

Fig 37. Wet/dry tensile index * 100% measured after 1 min, 1 hour and 24
hours immersion in water after hot-pressing at 200°C, TMP pressed at 180°C. The red line shows the general level for wet strong paper, which is 15%.

Fig 38. Wet/dry tensile index for NBSK and NSK (K25, K50, K80) measured after 1 min, 1 hour and 24 hours immersion in water after hot-pressing at 200°C. The red line shows the general level for wet strong paper, which is 15%.

The wet tensile index measurement on HT-CTMP paper sheets hot-pressed on the press machine is shown in Fig 39. The current study shows that the wet strength increases 10.6 kN/m as the temperature increases from 200 to 280°C pressing at same load pressure. Doubling the load pressure increases the wet strength by almost 100%. This would indicate higher sensitivity to increase in temperature than to increase in density. However, it is obvious that the temperature must be high to achieve high wet strength. Moreover long pressing time (dwell time) is important, as shown by the last trial point, where the dwell time is shorter. When hot-pressing at 290°C with one nip at high load pressure (about 8 MPa), wet strength index reaches 27 kNm/kg, which is a level much higher than with the oil heated cylinder press. A second nip seems to have less impact on the wet strength. This can be explained by a probably higher dry content in the second nip since the paper sheet is certainly dried in the first nip. High enough moisture content in paper sheets is a prerequisite to soften the lignin and hemicellulose in the fibre walls and between the fibres (Back, Andersson 1979; Norgren et al. 2018; Pettersson et al. 2017).
4.4 Contact angle change due to temperature and lignin

The interpretation of the contact angle measurements is complex as the results are affected both by surface structure parameters such as: surface roughness, surface structure and micropores as well as by the surface chemistry (Erbil 2014; Huhtamäki et al. 2018). Despite this, the contact angle gives us some important information about how the water behaves on the surface of the paper sheets when comparing similar substrates. A general statement is that a solid surface is defined as hydrophobic if the contact angle of the water droplet is 90° or greater. The contact angle in these experiments was measured on paper sheets hot-pressed at 20–200°C, and all samples were produced in the same sheet former and pressed in the same equipment.

The contact angle (Fig 40) for CTMP, HT-CTMP and NSSC samples hot pressed at 200°C show a surface hydrophobicity as the contact angle is above 90°. In this study, the TMP at a nip temperature of 180°C gives a contact angle above 100°, which is a significant surface hydrophobicity. The SCP shows low hydrophobicity, despite rather high wet strength (Fig 34),
which indicates that there are differences in the paper surfaces, such as roughness, porosity and chemical properties. The NBSK pulp sheets are not considered hydrophobic, since the values do not exceeding 65°. The CTMP and the NSK K80 with a lignin content of 26% and 12% lignin respectively have almost the same contact angle (Fig 41), which is surprising as a higher lignin content was expected to give higher hydrophobicity. This may be explained by chemical differences of the lignin, as the lignin in CTMP is sulphonated giving hydrophilic properties compared to the kraft lignin. Another possible explanation might be the differences in the sheet structure of CTMP and lower density, which results in a more open sheet structure. It is likely that the content of extractives influence as well as the surface energy and consequently the contact angle (Kokkonen et al. 2007). An increase in hydrophobicity can be interpreted as an effect of an increased proportion of lignin (Fig 41).

![Contact angle (°) measured on samples pressed at 200°C](image)

Fig 40. Contact angle for paper sheets pressed at 200°C nip pressure (TMP at 180°C). Error bars indicate 2SD.
Fig 41. Contact angle as a function of lignin content at different setting times; 0.01, 0.1, 2, and 10 sec for NSK pulp based and CTMP pulp based paper sheets pressed at 200°C. The longer the time setting, the more important the lignin content.

The contact angle was measured on paper sheets based on CTMP, HT-CTMP, TMP, NSSC, SCPαl, NSK25, NSK50 and NSK80. The test was performed on samples hot-pressed at 20°C, 100°C, 150°C, and 200°C (Fig 42–50). CTMP and HT-CTMP based samples hot-pressed at 200°C have a contact angle at 90° below 2 seconds and a contact angle at 80° up to 10 seconds. The TMP based samples have a much higher contact angle below 2 seconds already at low temperatures, probably due to the very low freeness value of 55 ml (a dense structure on the surface). Above 2 seconds and up to 10 seconds the contact angle remain very high for the paper sheets hot-pressed at 150 and 180°C. At 180°C, the contact angle is about 110°, which is well above the general level for hydrophobicity at 90°. The paper sheets based on NSSC, hot-pressed at 100, 150 and 200°C show a contact angle of 90° below 2 seconds and still above 80° up to 10 seconds. All the NSSC based samples, including the one pressed at 20°C have high density compared to the other HYP based samples. This could explain the high contact angle. The hydrophobicity of the paper samples based on SCPαl behaves more like the CTMP and HT-CTMP probably due to the similarity in freeness (open structure in the surface), but the level of contact angle is much lower. It has a contact angle at 75° below 2 seconds and 60° at 10 seconds. This could be explained by surface chemistry and surface roughness, which is not
measured in this study. The series of paper samples based on the laboratory produced NSK with different lignin content show a gradual increase in contact angle with increasing lignin content and increasing pressing temperature.

It is most significant for the NSK25 (3% lignin) and NSK50 (7% lignin). The contact angle of samples based on NSK80 (12% lignin) is rather unclear. This might be due to the disturbing effect from the surface roughness or porosity. The contact angle of the NSK80 150°C is above 90° whereas the NSK80 200°C is 80° at 2 seconds and 90° and 75° at 10 seconds respectively.

Fig 42 Contact angle for paper sheets based on CTMP hot-pressed at 20°C, 100°C, 150°C, 200°C

Fig 43 Contact angle for paper sheets based on HT-CTMP hot-pressed at 20°C, 100°C, 150°C, 200°C

Fig 44 Contact angle for paper sheets based on TMP hot-pressed at 20°C, 100°C, 150°C, 180°C

Fig 45 Contact angle for paper sheets based on NSSC hot-pressed at 20°C, 100°C, 150°C, 200°C
Fig 46 Contact angle for paper sheets based on SCP_al hot-pressed at 20°C, 100°C, 150°C, 200°C

Fig 47 Contact angle for paper sheets based on NSK K80 hot-pressed at 20°C, 100°C, 150°C, 200°C

Fig 48 Contact angle for paper sheets based on NSK K50 hot-pressed at 20°C, 100°C, 150°C, 200°C

Fig 49 Contact angle for paper sheets based on NSK K25 hot-pressed at 20°C, 100°C, 150°C, 200°C

Fig 50 Contact angle for paper sheets based on NBSK hot-pressed at 20°C and 200°C
4.5 The stability of native lignin in paper sheets over time

The wet stability was studied over a period of one year for most of the paper grades included in the present work. This was performed on paper sheets hot-pressed at 200°C, by measuring wet tensile strength and contact angle (Fig 51 and 52). The paper samples had been stored dry and dark in room temperature for one year. In 2018, the paper samples were soaked in water for 1 minute and in 2019 the test was repeated and the samples were soaked in water for 1 hour and the same results were obtained. There was no change in wet strength at all. However, the result was the same for all the samples independently of pulp grade or pressing temperature.

The stability of surface hydrophobicity over time was also investigated by measuring contact angle with the automatic drop method. This was performed for TMP, HT-CTMP, CTMP and all the kraft pulps (NSK series) with different lignin content. The results show that no changes affecting the contact angle have taken place after one year.

The study clearly shows that the hot-pressed lignin-rich paper sheets provide permanent wet stability.

![Graph showing tensile index changes](image)

Fig 51. HYP based paper sheets hot-pressed at 4 different temperatures and tested for wet tensile index after being soaked in water for 1 min in 2018 and after being soaked in water for 1 hour in 2019.
Fig 52. The figure contact angle for paper sheets based on HYP and NSK with different lignin content, hot-pressed at 200°C, measured in 2018 and in 2019 after dry storage in room temperature.

5 Conclusion

Our results confirm the potential of using high yield pulps to develop high-density paper with high tensile and SCT index as well as very good wet strength by means of a hot-pressing strategy. HYP could potentially compete with standard chemical kraft pulp in strength when hot-pressed at 200°C or higher, that is, well above the softening temperature of lignin. The pulps used in these trials varied in terms of lignin, hemicellulose, and extractive contents as well as their fines and shives contents. Our general conclusion is that HYPs such as TMP, CTMP, HT-CTMP and NSSC gain enhanced dry and wet strength properties during hot-pressing, while lignin free kraft pulp does not.

It is clearly seen that the wet stability increases remarkably, particularly wet strength, by increasing native lignin content when hot-pressed well above Tg of lignin. A linear relationship between lignin content and wet strength was significant. It was also observed that the wet strength was stable for up to 24 hours. Dry tensile index, SCT index, and tensile stiffness index were significantly improved as well.
We also demonstrated a new steel belt based hot-pressing technique for developing strong and wet stable lignin-rich paper material. Important advantages discovered during these trials were:

- Setting variables was fast and easy: temperature, pressure, one and two press nips, steel belt tension and speed
- Effect of dwell time and press load is also easy to evaluate
- Delamination can be avoided. High temperature and long dwell time of the steel belt pressure is preferable. It is important that the outgoing paper sample is bone dry to avoid spring back effects.
- Highest wet strength was achieved by highest temperature and highest pressure. A second press nip did not further improve the wet strength.

This study concludes that native lignin in pulp has a similar function as natural wet strengthening agent when paper sheets are pressed at high temperature well above the Tg of lignin. Thus, dry and wet strong paper sheets could potentially be produced without adding wet strength chemicals when combining lignin-rich pulp and the hot-pressing technique. The hot-pressing technique is therefore unique for producing environmentally-friendly packaging with demands on wet stability when using renewable and biodegradable lignin-rich raw material without adding strengthening agents.

Continuation of work

It is desirable to further investigate the suggested chemical reactions and new covalent bonds when hot-pressing lignin-rich paper material. Other interesting questions are how do extractives, hemicellulose and fines contribute to the bonding and development of wet stability by means of hot-pressing.

6 References


**Scott, J. A. N., Procter, A. R., Fergus, B. J., Goring, D. A. I.** (1969). The application of


Swensson, R. S. et al. (1987). Kraft liner board by densification and heat treatment. USA.
