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Modifying kraft pulping to produce a softwood pulp requiring less energy in tissue paper production

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ABSTRACT

Modification of softwood kraft pulp by the addition of either polysulfide (PS) or sodium borohydride ($NaBH_4$) has been shown to increase the pulp yield due to a higher retention of glucomannan. The pulps with higher yield gave a paper with higher tensile index than reference pulp, especially at lower degrees of refining. The higher yield pulps also showed a greater porosity of the fibre wall, indicating an increase in the swelling potential of the fibres. This can lead to increased fibre flexibility and increased joint strength between the fibres and to the higher handsheet tensile index. However, the swelling increase associated with the higher hemicellulose content could also make dewatering more challenging because of the higher water retention of the pulp. The results of this study show however that the positive influence of the increase in yield (fewer fibres and a more open sheet structure) dominates over the negative influence of the higher hemicellulose content on the dewatering properties, especially at lower refining energy levels. Studies simulating full-scale tissue machine dewatering conditions showed that pulps with a higher yield and a higher hemicellulose content had a higher tensile index at the same dryness. Moreover, the same dryness level was achieved in a shorter dwell-time. A given tensile index was also achieved with less refining energy.

Increasing the yield and hemicellulose content by the addition of either an oxidizing or a reducing agent in the softwood kraft pulping process thus has a potential for giving high quality fibres for tissue paper production with less refining energy and lower drying energy costs.

SAMMANFATTNING

Modifiering av kraftmassa av barrved genom tillsats av antingen polysulfid (PS) eller natriumborhydrid ($NaBH_4$) visade sig öka massutbytet på grund av högre retention av glukomannan. Massorna med högre hemicellulosautbyte uppnådde högre dragindex, speciellt vid lägre raffinering. Massorna med högre utbyte uppvisade också en ökad fiberväggsporositet vilket indikerar en ökad grad av svällning av fibrerna. Således kan det antas att fibrernas ökade flexibilitet påverkar fibrernas fogstyrka och därmed leder till högre dragindex. Högre hemicellulosainnehåll kan emellertid göra avvattningen svårare på grund av ökad vattenretention i massan. Resultaten visade dock att den positiva effekten av ett ökat massautbyte (färre fibrer och en mer öppen arkstruktur) dominerade över det negativa inflytandet av en ökning av hemicellulosinnehållet på avvattningsegenskaperna, särskilt vid lägre raffineringsenerginivåer. Dessutom observerades att massorna med ett högre utbyte och högre hemicellulosainnehåll även hade ett högre dragindex vid samma avvattningsförmåga. Ett givet dragindex uppnåddes också med en lägre raffineringsenergi. Ett ökat massautbyte och hemicellulosainnehåll kan alltså erhålles genom tillsats av antingen oxidationsmedel eller reduktionsmedel vid sulfatmasseprocessen. Att öka massautbytet genom tillsatts av polusulfid eller natriumborhydrid visar sig också både ge bättre dragstyrka och bättre avvattning och är därför ett intressant alternativ för att producera massa för tissuetillverkning.

ACKNOWLEDGEMENT

The present study has been carried out at the department of chemical Engineering at Mid Sweden University, during the years 2015-2017 under the auspices of the Forest as a Resource Industrial College (FORIC) at Mid Sweden University. The Knowledge Foundation in collaboration with SCA Forest Products and Mid Sweden University supported the study financially.

When I started to write my thesis, I felt that the acknowledgement would be the easiest part to write. But now I am thinking of how many people supported me for this project, so this page will be the most difficult to phrase.

I wish to express my deep gratitude to Almighty God for blessing me with the knowledge he has given me.

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Hafizur Rahman
March, 2018

TABLE OF CONTENTS

LIST OF PAPERS

This thesis is based mainly on the following papers, referred to by their Roman numerals in the text:

Paper I The effect of increased pulp yield using additives in the soft wood kraft cook on the physical properties of low grammage handsheets.
Rahman, H., Lindström, M.E., Sandström, P., Salmén, L. & Engstrand, P.
Nordic Pulp and Paper Research Journal, 2017, 32 (3), 317-323

Paper II Dewatering properties of low grammage handsheets softwood kraft pulps modified to minimize the need for refining.
Rahman, H., Engstrand, P., Sandström, P. & Sjöstrand, B.
Submitted to Nordic Pulp and Paper Research Journal, 4th Jan 2018

The author´s contributions to the papers appended to this thesis are as follows:

Paper I Principal author: performed literature review, all experimental work, and interpreted results and wrote the paper together with other co-authors.

Paper II Principal author: planned and performed all experimental work, literature review, interpreted results and wrote the paper together with other co-authors.

CONFERENCES

Relevant conference papers not included in this thesis:

Cellulose Material Doctoral Students Summer Conference, 26-28 August 2015, Autrans, France- Oral Presentation: Importance of modification of the kraft pulping process to produce more refining- energy- efficient fibres for tissue paper.

European Doctoral Students (EDS) Summer Conference (An International Network on Cellulose Fibre Technology), Aug 30-Sept 01 2016, Stockholm, Sweden- Oral Presentation: Modified pulp to tissue development (based on theme- Product development with new forest- based materials).

PhD Student Conference, 10-11May 2017, Östanskär, Sweden- Oral Presentation: How affect the increased pulp yield by addition of additives in the softwood kraft cooking for physical properties of lower grammage hand sheets.

ABBREVIATION AND ACRONYMS

BDDJ	Britt dynamic drainage jar
BL	Black Liquor
CMC	Carboxymethylcellulose
CSF	Canadian standard freeness
DSC	Differential scanning calorimetry
EA	Effective alkali
FORIC	Forest as a Resource Industrial Research College
GC	Gas chromatography
ISO	International Organization for Standardization
KPVS	Potassium polyvinyl sulphate polymer
ms	millisecond
PS	Polysulfide
RCS	Refrigerated cooling system
SR	Schopper Riegler
WL	White Liquor
WRV	Water retention value

DEFINITIONS

Black Liquor (BL)

The residual liquor (black) from the delignification process consisting of degraded and dissolved wood components such as lignin and unreacted cooking chemicals.

Effective alkali (EA) (%)

A measure of the free hydroxide ion (OH^-) concentration in the white liquor (WL). The charge of effective alkali in the cook is normally expressed as weight percentage on wood.

For example, 20% EA= 200 kg NaOH / ton of wood, meaning that the liquor to wood ratio must be noted to calculate the concentration

H-factor

A function used to estimate delignification; based on relative reaction rate, which is a function of temperature.

Kappa number

A standardised estimate of the lignin content of a pulp, based on the assumption that potassium permanganate ($KMnO_4$) only oxidises lignin and not cellulose or hemicellulose. The testing conditions are specified in SCAN-C 1:77. A rough estimate of the percentage lignin content can be calculated as Kappa number divided by 6.55.

Schopper –Riegler (°SR)

Determination of the drainability of a pulp suspension.

Sulfidity (%)

A measure of the relationship between hydrogen sulphide ion (HS^-) concentration and hydroxide ion (OH^-) concentration in a kraft cooking liquor, often expressed as a percentage:

$$\text{Sulfidity (\%)} = \frac{2[HS^-]}{[OH^-]+[HS^-]} * 100$$

Tensile Index

The quotient of the tensile strength divided by the grammage (weight per unit area)

Total Yield (%)

Defibrated pulp and reject material expressed as weight on wood (%)

White Liquor (WL)

A mixture of cooking liquor containing fresh chemicals of hydroxide (OH^-) and hydrogen sulphide (HS^-) ions before addition to the cooking system; clear solution, slightly yellow because of the presence of Na_2S. The counter-ion is mainly sodium.

Yield

The ratio of the weight of pulp produced to the amount of wood charged.

Zero- span tensile strength

The tensile strength of paper measured with the shortest possible clamping distance. It is normally related to the fibre strength.

1 INTRODUCTION

This thesis focuses on the modification of the kraft pulping process in order to improve fibre properties for the final functional product of tissue paper and also to reduce the energy demand in the process. The thesis consists of two major papers.

In the first paper, a modification of the carbonyl end group of the hemicelluloses in order to reduce their degradation and thus increase the total yield was investigated. Two different additives (an oxidizing or a reducing agent) were added to the laboratory digester. The effect of yield on the physical properties of low-grammage handsheets was then evaluated.

In the second paper, further studies were performed on these modified softwood kraft pulps to explore the vacuum dewatering properties of low-grammage (20 g/m^2) handsheets using a laboratory dewatering device.

1.1 The composition of wood

Hardwood and softwood are the main raw materials for the production of pulp. Wood consists mainly of polysaccharides (primarily cellulose and hemicellulose) which are carbohydrate polymers and lignin which is a complex polymer. There are also small amounts of extractives in wood, which are low molecular compounds of various species. They can be extracted from the wood with water or organic solvents. The relative amounts of cellulose, hemicellulose, lignin and extractives are different in different wood species. In extractive-free dry wood, the average values are about 43% cellulose, 28% hemicelluloses and 29% lignin for softwood and hardwood about 43% cellulose, 35% hemicelluloses and 22% lignin (Rydholm 1965c).

Cellulose is a homopolysaccharide composed of β-D-glucopyranose units linked together by (1⇾4)-glycosidic bonds *(Fig 1).* Hemicelluloses are heteropolysaccharides. For example, galactogluco-mannans are the principal hemicellulose in softwood (about 20%) and their backbone is a linear and slightly branched chain built up of (1->4)-linked β-D-glucopyranose and β-D-mannopyranose units (*Fig 2*). Hemicelluloses are relatively easily hydrolysed by acid to their major monomeric components such as D-glucose, D-mannose, D-xylose, L-arabinose and L-rhamnose (small amount).

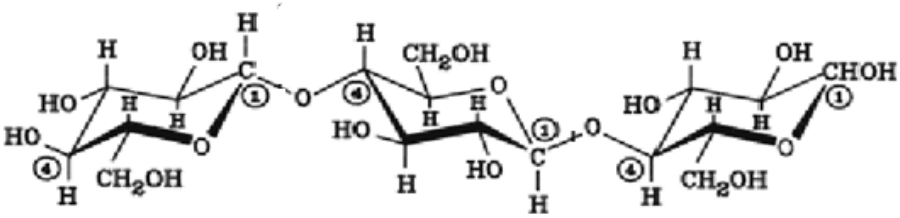

Fig 1- The structure of cellulose (adapted from Sjöström 1981)

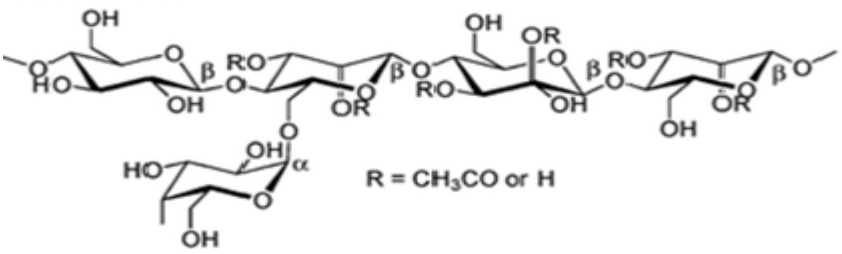

Fig 2- The structure of galactoglucomannan (adapted from Sjöström 1981)

1.2 Production of kraft pulp

Kraft or sulfate pulping is the dominating process for the production of chemical pulp worldwide due to the valuable properties of the pulp produced. In the paper industry, kraft pulp fibres are the most important raw material for the production of paper, board and many other applications. Kraft pulps are produced from hardwood, softwood and annual plants. The properties of the pulps depend not only on the raw material but also on the pulping process, the extent of delignification and the bleaching sequences.

The word "kraft" means "strength" in both Swedish and German. In 1884, C.F. Dahl from Germany was the inventor of the kraft pulping technique when he added sodium sulphide (Na_2S) to the cooking liquor in the soda process (Twede, Selke 2005). The "Kraft pulping process" is also called the "Sulfate pulping process" as sodium sulfate (Na_2SO_4) is used for make up in the chemical recovery cycle. Kraft pulping is generally more efficient than soda (NaOH) pulping due to the presence of both hydroxide ions (OH^-) and hydrogen sulphide ions (HS^-) as active chemicals, whereas in the soda process, hydroxide ions (OH^-) are the only active chemical. The cooking liquor is called white liquor in kraft pulping and consists of sodium

hydroxide (NaOH) and sodium sulphide (Na_2S). The active ions are dissolved in water and the equilibrium, *Eq 1*

$$S^{2-} + H_2O \leftrightarrow OH^- + HS^- \quad [1]$$

is displaced to the right. The overall chemical cooking reactions in kraft pulping depend on the concentrations of active chemicals, time and temperature which have been modelled by Vroom (1975) as the "H-factor model". The H- factor model, *Eq 2* was designed as an integration over time of the Arrhenius equation, *Eq 3*

$$H = \int_{t_0}^{t} e^{\left(43.2 - \frac{16113}{T}\right)} \, dt \quad [2]$$

where it assumes the activation energy, E_A=134 kJ/mol for the whole delignification process and a defined relative rate of 1 at 373 K .

$$k = Ae^{\frac{-E_A}{RT}} \quad [3]$$

1.3 The carbohydrate yield in kraft pulping

During kraft pulping, lignin is degraded and released from the wood fibre through reactions with OH^- and HS^-. The delignification occurs in three phases, the initial, bulk and residual phase. 20-25% lignin is removed during the initial phase (Pekkala 1982) but most of the lignin is removed in the bulk phase. Only 10-15% of the native lignin is removed in the residual phase (Mao 1995).

In kraft cooking, two types of carbohydrate reaction occur: a peeling reaction and an alkaline hydrolysis. The peeling reaction starts early in the cook and results in lower pulp yield because of a degradation of the polysaccharide chains. The peeling reaction basically degrades the polysaccharide by removing terminal sugars one at a time. The reaction takes place at the reducing end of the molecule (aldehyde). The acids formed by the peeling reaction are responsible for most of the alkali consumption. The peeling process stops when an end group is formed which will not peel. In the alkaline hydrolysis reaction, the polysaccharide chain is cleaved within the chain instead of at the end as in the peeling reaction. This generates a new reducing end group which increases the rate of peeling.

It was earlier reported (Janson, Teder 1986; Gustavsson, Al-dajani 2000) that, depending on the pulping conditions, minor amounts of cellulose are dissolved during kraft pulping and that the yield with respect to cellulose can vary between 80% and 90%. Alkaline hydrolysis can also occur at high temperatures, and is then responsible for reducing the degree of polymerization. The alkaline hydrolysis can decrease the degree of polymerisation of cellulose extensively, from at least 9000-10000 in wood to 4000-8000 in pulps (Molin 2002).

The hemicelluloses of softwood kraft pulps differ from those in native wood. For example, the arabinose groups are removed from the arabinosglucoronoxylan and the acetyl groups are removed from the galactoglucomannan (Fengel, Wegener 1984). Glucomannan is readily dissolved during the initial phase of softwood kraft cooking due to the peeling of its rather short chains, and the yield after the cook can vary between 20% and 30% (Aurell, Hartler 1965a; Gustavsson, Al-dajani 2000).

The peeling reaction is less efficient in xylan due to the arabinose and 4-O-methylglucuronic acid units, but large parts of the xylan are dissolved depending on the hydroxide ion (OH^-) concentration during both softwood and hardwood kraft pulping and the yield can vary between 20% and 70% (Aurell, Hartler 1965a; Gustavsson, Al-dajani 2000). Delignification is normally limited to a certain degree within the kappa number 30-35 for the conventional kraft process in order to ensure a good fibre quality and high yield. The glucomannan yield can be substantially increased by using sodium borohydride or polysulfide in the first part of kraft pulping (Rydholm 1965a; Gullichsen, Fogelholm 1999). Lignin is degraded into small soluble fragments during chemical pulping and the lignin content after kraft pulping, in pulps to be bleached, is usually 5% and10% (Molin 2002).

In the kraft pulping process, at high temperature, some cellulose and hemicelluloses are degraded and dissolved by hydroxide (OH^-) ions. But this degradation of carbohydrates at a given lignin content (kappa number) can be reduced by using a lower temperature, an evened-out alkali profile, a low ionic strength, and a low concentration of dissolved lignin or a high concentration of hydrogen sulphide ions (Sjöblom et al. 1983; Johansson et al. 1984; Molin 2002). The degradation of lignin, cellulose and hemicellulose depends on the chemical conditions in the kraft cook, and the overall pulp yield can be increased by using different additives in the kraft cook (Aurell, Hartler 1965a; Paavilainen et al. 1989).

1.4 Modification of kraft pulp

During kraft pulping, lignin is released from the fibre through a delignification reaction with hydrogen sulphide (HS^-) and hydroxide (OH^-) ions. The most challenging aspect of a kraft cook is to remove the lignin while minimizing the losses of cellulose and hemicellulose. It was earlier observed that, up to a certain level, the yield increases in proportion to the concentration of the reducing or oxidizing chemicals, which also stabilise the glucomannan (Rydholm 1965a). A reducing additive is sodium borohydride ($NaBH_4$), which yields stable alcohol (-OH) groups (Rydholm 1965a; Gulsoy, Eroglu 2011) and sodium borate according to the reaction (Rydholm 1965a), Eq *4*:

$$4RCHO+NaBH_4+2NaOH+H_2O \rightarrow 4RCH_2OH+Na_3BO_3 \quad [4]$$

An oxidizing chemical additive is polysulfide, which can be produced by adding elemental sulfur to white liquor (Rydholm 1965; Lindgren, Lindström 1995), in which the following reaction takes place already at 70°C, *Eq 5*:

$$nS(s)+HS^-+OH^- \rightarrow S_nS^{2-}+H_2O \quad [5]$$

Polysulfides in the cooking liquor stabilise hemicellulose at lower temperatures (100°C-120°C) by oxidizing the reducing end groups of the polysaccharides into alkali-stable aldonic acids, and this reduces the carbohydrate degradation in kraft cooking (Hägglund 1946). The oxidation of the end-groups in carbohydrate chains makes them stable against end-wise peeling by hydroxide (OH^-) ions. Polysulfide addition has also been found to have a slightly positive effect on delignification when cooking to low kappa numbers (Lindström, Teder 1995).

It has been reported that a higher content especially of glucomannan can be achieved by increasing the hydroxide ion (OH^-) concentration, but this reduces the amount of xylan retained (Aurell, Hartler 1965b; Brännvall, Lindström 2007).

1.5 Characterization of fibre properties of kraft pulp

1.5.1 Fibre strength

The chemical composition of the kraft pulp greatly affects the fibre strength. An increase in either cellulose (Gurnagul et al. 1992) or hemicellulose (Spiegelberg 1966) content has been reported to lead to an increase in fibre strength, but the relation between fibre strength and hemicellulose content is not linear (Molin, Teder 2002). A positive correlation between fibre strength and cellulose content may be found up to 70-80% cellulose content (Page et al. 1985), since the cellulose is the backbone of the fibre wall and the main contributor to fibre strength. Softwood kraft pulps usually have a cellulose content higher than 75% (Molin, Teder 2002). Up to a certain level, an increase in cellulose content is thus expected to increase the overall strength of the fibre material (Salmén 1993). The Wet Zero-span test is a fast method that can be used to determine single fibre strength properties (Mohlin, Alfredsson 1990; Clark 1994; Cowan 1994).

1.5.2 Tensile strength

Tensile index is the most important parameter for low grammage sheets, where the tensile strength of a paper depends primarily on the degree of bonding between fibres. The tensile strength increases with increasing fibre length, increasing fibre strength and increasing fibre joint strength. Fibre length is very dependent on the raw material, where hardwoods have shorter fibres than softwoods.

1.5.3 Fibre/ fibre joint strength

Hemicellulose is required for sufficient softening of the fibre wall and it also plays a role in bonding . An increase in the bonded area between fibres and an increase in the strength of the bond can increase the fibre joint strength (Laine, Stenius 1997). The Z-direction strength is the best method for measuring bonding strength (Kauba, Koran 1995). An increase in fibre-to-fibre bonding leads to an increase in Z- strength (Singh 2007).

1.5.4 Surface charge

The fibre-fibre joint strength increases with increasing surface charge of the fibres due to an increase in surface swelling (Torgnysdotter 2006). Pulps with a higher surface charge have been shown to give stronger fibre joints

and surface softness is of primary importance for the utilisation of the joint strength (Forsström, Torgnysdotter 2005), and it has earlier been suggested (Andreasson et al. 2003) that surface charge determination can provide a measure of the ability of the fibres to form strong joints.

1.5.5 Fibre swelling

Water retention within the cell wall is an important pulp property which influences most phases of paper production. A commonly used empirical method to characterise fibre swelling (capacity to hold water) is the water retention value (WRV). Increasing the hemicellulose content results in a greater swelling of the kraft pulp, and an increase in swelling generally increasesthe fibre bond area and also affects the pore volume of the fibre wall (Stone et.al. 1969). The pore voulme in the cell wall can be determined by differential scanning calorimetry (DSC) (Maloney, Paulapuro 2001).

1.6 Effect of refining

Refining makes the fibres more flexible and increases the available bonding sites of the fibres (Annegren, Hagen 2007). Refining increases the swelling ability of the fibres and increases the conformability of the fibres during the consolidation of the fibre web, so that the fibres come into closer contact and thus create better adhesion which leads to greater strength in the paper (Wang 2006; Annergren, Hagen 2007). Secondary fines are also produced during refining creating a greater fibril character than the primary fines present after the pulping process (Kullander 2012). Fines are considered to increase the tensile strength and Z-strength due to their large surface area (Paavilainen 1990; Retulainen et al. 2002; Sirviö, Nurminen 2004; Pruden 2005).

1.7 Suction box dewatering

In the production of tissue paper, the fibre suspension is to a large extent dewatered by removal of the water in the vacuum suction boxes. It is important to maximize the amount of water removed in order to reduce the cost of the final dewatering and the energy consumption in the final drying of the sheet (Räisänen 2000; Granevald et al.2003; Kullander et al. 2012).

The dewatering in the suction boxes involves three mechanisms: compression dewatering, displacement dewatering and rewetting (Åslund, Vomhoff 2008) in *Fig 3.*

When the web passes over the suction box, the vacuum in the box creates a pressure/compression from the air above. Displacement dewatering occurs when air is sucked through the web, but undesirable rewetting occurs when water flows back into the sheet (Rantanen, Maloney 2013; Sjöstrand et al. 2015).

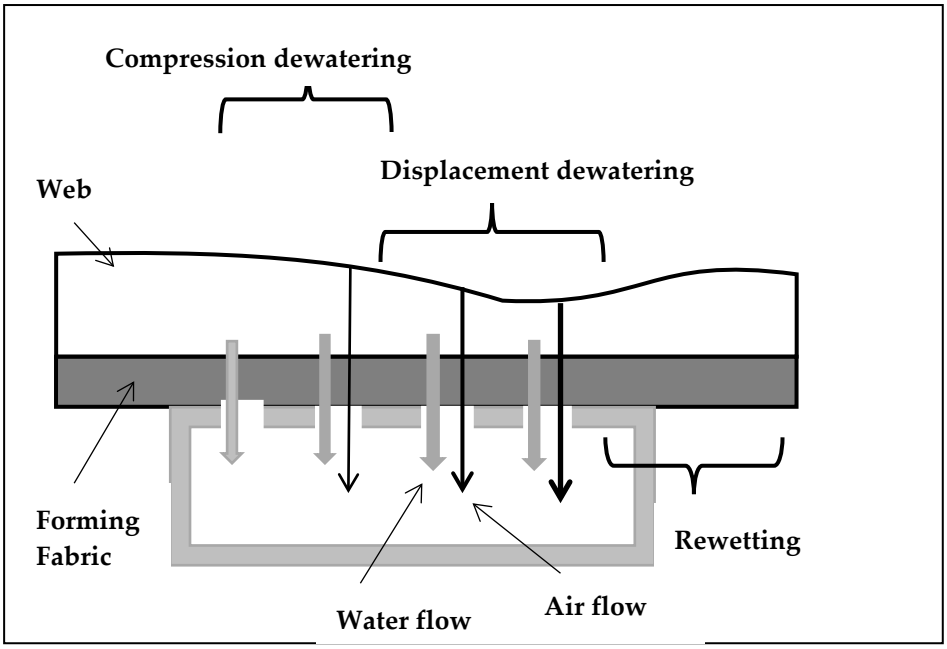

Fig 3- The mechanism of suction box dewatering (Redrawn from Åslund and Vomhoff 2008)

The magnitude of dewatering that can be reached depends on the pressure drop (vacuum level), the dwell time in the vacuum and the dewatering resistance of the pulp (Attwood 1962; Neun 1994), which depends on the type of fibres, the degree of refining of the pulp and the fines content. It has also been seen that the conventional measurement of degree of refining, the °SR number or the CSF value does not always predict the actual dewatering on the paper machine (Rydholm 1965b).

2 RESEARCH OBJECTIVES

This thesis focuses on softwood kraft pulp for high quality tissue papers. The approach has been to show how a kraft pulping process can be modified to improve the fibre properties important for tissue products. Kraft pulp fibres have to be treated/ beaten in refiners to achieve the appropriate bonding / adhesion properties. Refining increases the fibre surface area by fibrillation and releases fines (fine particles) from the fibre surfaces. In tissue production, the aim is to minimize the amount of free fines at the same time as the fibre-fibre-bonding/adhesion is increased. Different approaches to increase the strength of the fibre -fibre joint have been tested in this work:

- Firstly, ways of increasing the proportion of hemicelluloses in the pulp fibres have been studied by modifying the kraft cooking process through the addition of new chemicals (oxidative and reducing agents).

- Secondly, the strength of pulps produced by adding new chemicals and refining the pulps has been evaluated and the strength for different beating levels has been determined.

- Thirdly, the pulps produced with the addition of new chemicals were tested with regard to their vacuum-dewatering properties under conditions simulating a paper machine.

3 EXPERIMENTAL

3.1 Materials (I) (II)

Industrial chips as a mixture of Spruce (*Picea abies*), 70%, and Pine (*Pinus sylvestris*), 30%, were obtained from SCA Östrand mill, Sundsvall, Sweden. The chips were screened, knots & bark were removed and the fraction with a thickness of 2-8 mm was retained. The chips were dried at room temperature and the dry solids content was determined (~ 91%, when dried at 105°C).

White liquor (WL) and black liquor (BL) were taken directly from the Östrand mill. The cooking conditions were effective alkali (EA) 20% (as NaOH), sulfidity 35%. Two different additives: polysulfide (PS) 2% or sodium borohydride ($NaBH_4$) 1% calculated on wood dry chips were charged.

3.1 Methods

3.1.1 Preparation of pulps (I) (II)

A laboratory digester (1L) with a capacity of 100g of dry chips was used. The liquor/wood (L/W) ratio was adjusted to 4:1. The chips were impregnated with cooking liquor by increasing the temperature from 70°C to 160°C at a rate of 1°C/min. The duration of the treatment at the maximum temperature was varied depending on the target kappa number, i.e. 35 (±2 units) and 40. The temperature was kept at 160°C for the remainder of the cooking time until the H-factor for the target kappa number was reached. The pulps were then screened in cold water on a sieve plate with 0.15 mm slot width, with backwater reversal. To determine the yield, the dry solids content of the wet screened pulps and the amount of dry shieves/reject were measured using a halogen moisture analyser after drying at 105°C overnight. The kappa number (ISO 302:2014) was measured on three replicates of each pulp according to the standard SCAN-C 1:77 method. Bleaching was carried out in a single chlorinedioxide (ClO_2) stage for all the pulps followed by drying of the pulps. The bleaching conditions were: pulp consistency 10%, temperature 25°C, and time 18 hours. The charge was calculated as kappa number*4(acl/ton of pulp). Although the ISO brightness was only about 80%, most of the lignin was removed. The purpose was to eliminate most of the effect of lignin and extractives. This is important as almost all softwood kraft pulps for tissue applications are bleached. The pulp was washed with

de-ionised water after bleaching. Finally, the bleached pulps with starting kappa 35±2 were selected for the preparation of laboratory handsheets after different degree of refining. *Fig 4* shows images from chips to bleaching stage.

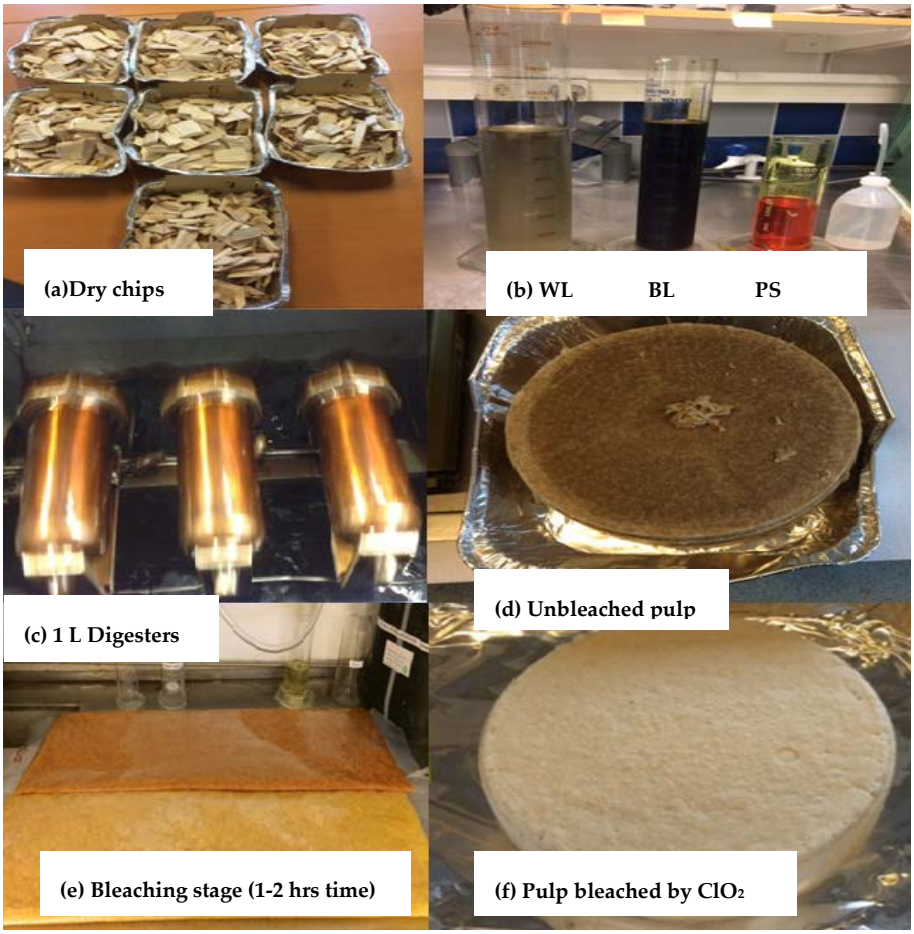

Fig 4- Some images of kraft pulp (from chips to bleached condition) taken, at the SCA R&D centre.

3.1.2 Sheet preparation (I) (II)

Bleached kraft pulps (Ref, PS and $NaBH_4$-kraft pulp) were refined in a PFI mill at refining levels of 0, 500, 1000 and 2000 revolutions according to ISO 5264-2:2011. 20 g/m^2 and 60 g/m^2 handsheets were prepared according to the

ISO 5269-2:2004 standard with tap water using a conventional sheet former of surface area 0.021m^2.

3.1.3 Physical Testing (I) (II)

The density, tensile strength (ISO 1924-3), Z- strength (ISO 1.4 MPa) and wet Zero- span tensile strength (ISO 15361) of the handsheets were determined. The sheet grammage and thickness were determined according to ISO 5270. The physical properties were determined at 23 ± 1°C and 50 ± 2% relative humidity. The percentage increases in tensile index and Z strength were calculated from interpolated curves for each condition. 7 or 8 samples were measured for each physical test and the mean value was calculated.

Dewatering resistance was determined as Schopper-Riegler (°SR) value according to the ISO 5267-1999 standard.

To determine the Water Retention Value (WRV) according to the ISO 14487 standard (*Fig 5)*, the test pad was centrifuged under a defined centrifugal force for a specific time, weighed, dried and weighed again. The WRV was calculated from the wet mass of the centrifuged test pad and the dry mass of the test pad.

Fig 5- The equipment used for the determination of the Water retention value (WRV) at the SCA R&D Centre.

3.1.4 Charge Analysis (I)

Conductometric titration was used to determine the total charge of the fibre material i.e. the amount of carboxyl and sulfonic acid groups on the cellulose fibres (Wågberg et al. 1985). The acid groups are first charged to their proton form by reducing the pH and the suspension is then titrated with a NaOH (0.01M) solution. To minimize the effect of Donnan-equilibrium, i.e. the differences in pH between bulk solution and fibre wall, NaCl (0.01M) was added. Nitrogen gas (N_2) was bubbled through the test solution during titration to remove any disturbing O_2 and CO_2.

Polyelectrolyte titration (*Fig 6)* was carried out to determine the surface charge according to the method described by Wågberg et al. (1989). The excess of polymer in the solution was titrated with an anionic potassium polyvinyl sulphate polymer (KPVS) which, together with a cationic indicator, toluidine blue, gave a colour shift from blue to pink at the end point of the titration.

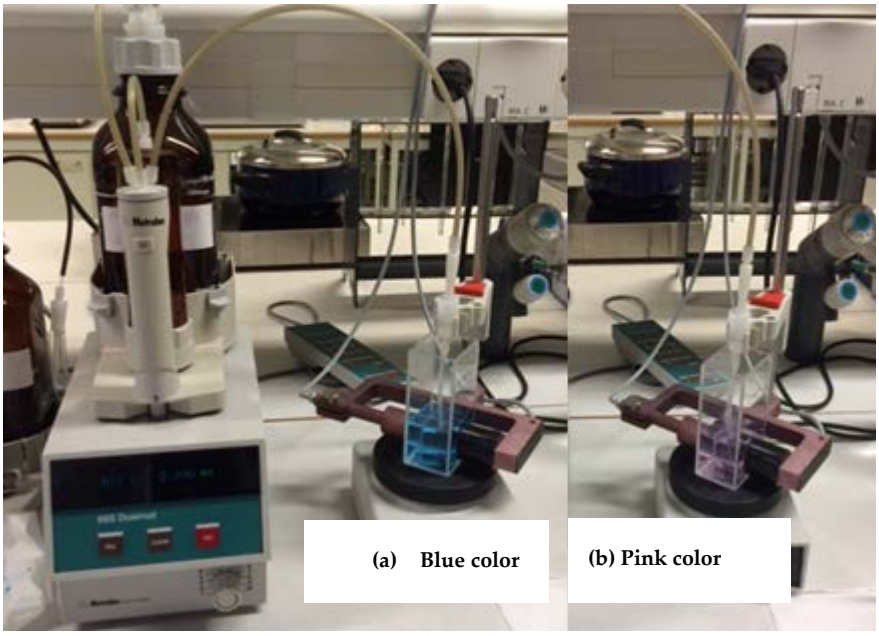

Fig 6- The determination of surface charge used in this study, at the SCA R&D Centre.

3.2 Instruments

3.2.1 Gas Chromatography (GC) (I)

Gas Chromatography was used for the analysis of dried unrefined kraft pulps (Theander, Westerlund 1986). Neutral monosaccharides arabinose, galactose, glucose, xylose and mannose were determined according to SCAN-CM 71:09 using a Gas Chromatography-Flame Ionization Detector (GC-FID). The analyses were carried out on a HP (Hewlett Packard) 6890 with a BPX 70 column (12 m, 0.32 μm I.D. and 0.25 μm film thickness). The samples were first hydrolyzed with 72% sulfuric acid (H_2SO_4) using a two-step technique and the hydrolyzed samples were then reduced and acetylated. The resulting alditol acetates of the monosaccharides were determined by GC, the alditol acetate content of each mono-carbohydrate being recalculated to polysaccharide assuming that the ratio of glucose to mannan in softwood glucomannan is 1.0:3.5 and that the other polysaccharides present were cellulose and xylan (Antonsson et al. 2009).

3.2.2 Differential Scanning Calorimetry (DSC) (I)

To determine the pore size distribution of the pulp fibres, differential scanning calorimetry (DSC) (*Fig 7)* was used (Maloney, Paulapuro 2001). Measurements were made using a TA Q1000 DSC instrument equipped with a refrigerated cooling system (RCS). To integrate the areas under the melting peaks, analysis 2000 version 4.0 C software was used. Nitrogen (N_2) was used as carrier gas at a rate of 50 ml min^{-1}. The technique is based on the fact that water retained within small pores shows a depressed melting temperature due to the increased pressure of water in cavities with a curved interface. The pore diameter (D) is calculated from the Gibbs-Thomson equation, *Eq 6*:

$$D = \frac{-4V_m\sigma_{ls}}{\Delta H_m ln\frac{T_m}{T_0}} = -\frac{k}{T_m} \quad [6]$$

where V_m is the molar volume of ice, σ_{ls} is the surface energy at the ice-water interface, T_0 is the melting point of water at normal pressure, T_m is the melting temperature and ΔH_m is the latent heat of melting.

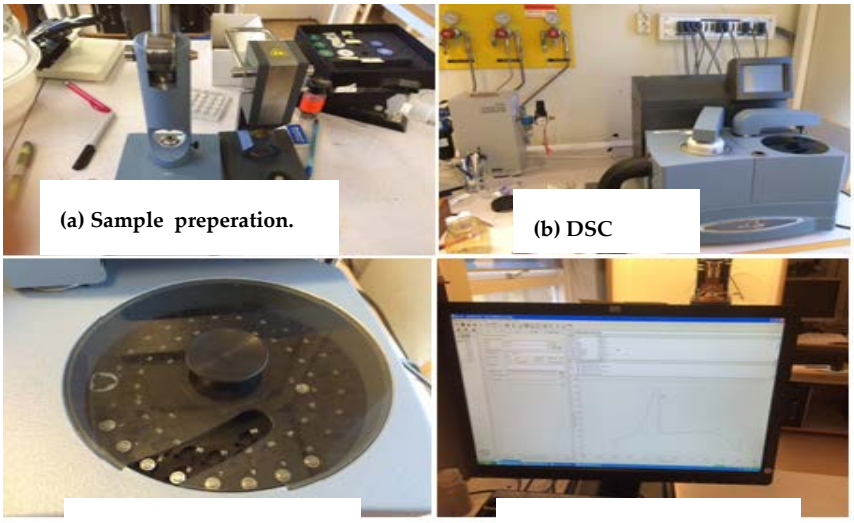

Fig 7- Analysis of pore volume by DSC at different stages (images a- d) at RISE Bioeconomy.

The melting temperatures between -33 and -0.1°C correspond to pore diameters between 1.3 and 431 nm studied in accordance with earlier studies (Fahlén, Salmén 2005). Samples of unrefined kraft pulp were analysed at a moisture content of 3-10 g g^{-1} using a sample size of 0.5-3 mg. All measurements were made in triplicate and the average pore volume (ml g^{-1}) was calculated.

3.2.3 PulpEye Analysis (II)

The fibres of the unrefined and refined kraft pulps were characterized with a PulpEye analysing system (*Fig 8)* to give the population of fibres (n/g), the fibre length (mm) and the fibre width (μm).

Fig 8- The PulpEye instrument used to determine fibre characteristics at the SCA R&D Centre.

3.2.4 Britt Dynamic Drainage Jar (BDDJ) (II)

The primary and secondary fines contents of the pulps were determined according to SCAN-CM 66:05 using the BDDJ method (*Fig 9)*.

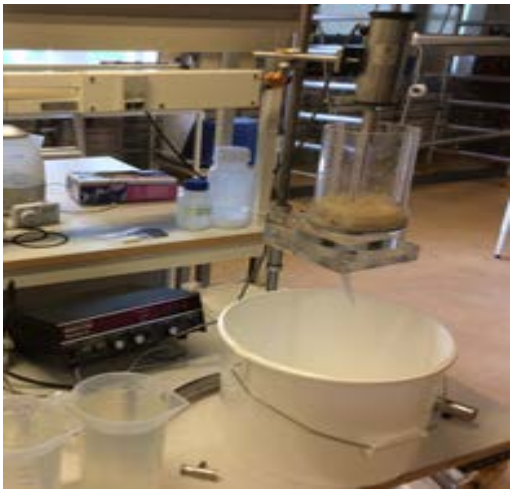
Fig 9- Specially- designed Britt Dynamic Drainage Jar (BDDJ) used at the SCA R&D Centre.

3.2.5 Dewatering (laboratory scale) (II)

Bench-scale laboratory equipment was used for the vacuum dewatering trials, where the sample passes on a frame over a plate with a 5 mm opening, a vacuum tank, pressure sensor and operation panel (*Fig 10)*. Handsheets (20 g/m^2) with a solids content of 6-7% were formed in a standard handsheet former on a fabric. The fabric with the handsheet was then transferred to the sample frame for vacuum dewatering (*Fig 11)*. Three pulps (Ref, PS and $NaBH_4$-kraft pulp) were tested with four different degrees of refining (0, 500, 1000 and 2000 PFI revolution) and with three replicates of six different dwells times (0, 1.0, 2.5, 5.0, 10.0 and 20.0 ms). Different dwell times were obtained by adjusting the speed of the plate while the vacuum level was kept constant at 27 kPa during the trial. A suction pulse was created while the slot passed between the sheet and vacuum tank. The inner region of the sheet with a diameter of approximately 80 mm was collected, and the solids content was determined according to the ISO 638 standard. The contact time between sheet and fabric after dewatering was at least 1 min. To compensate for the air that leaked into the vacuum tank without passing through the sample sheet, a fabric with a plastic cover was placed in the sample holder. It was repeated for each dwell time and subtracted from all the measurements.

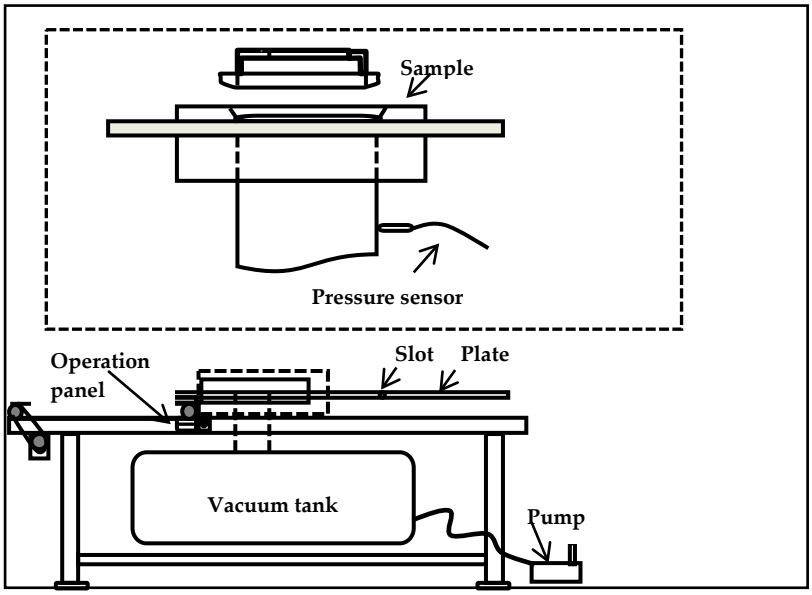

Fig 10- The vacuum dewatering apparatus (redrawn from Granevald et al. 2003).

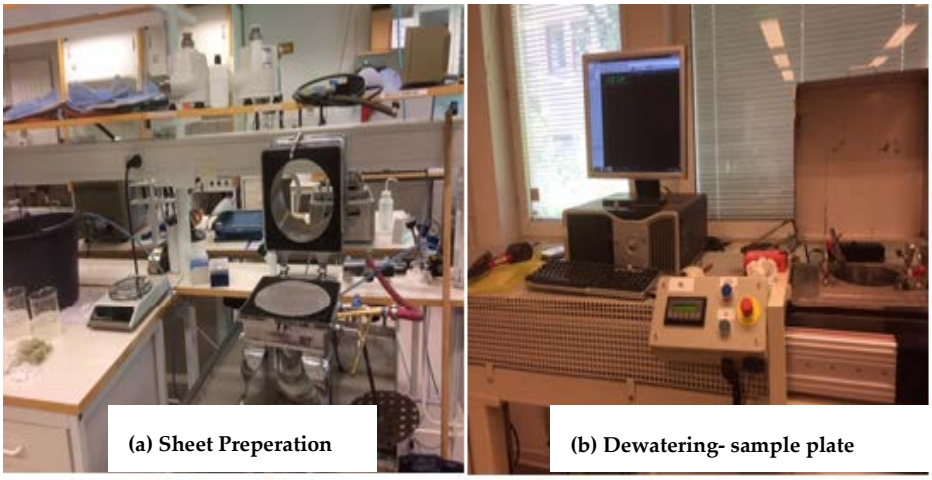

Fig 11- Dewatering instruments used at Karlstad University.

The amount of air that passed through the sample and fabric was calculated from the pressure drop corrected for leakage, atmospheric pressure and volume of vacuum tank according to the equation, *Eq 7* (Nilsson 2014):

$$Air\ volume\ (dm^3) = \frac{Tank\ volume\ (dm^3)}{101325\ (Pa)} * \Delta P\ (Pa) \qquad [7]$$

where ΔP is the pressure increase during the pulse calculated as

$\Delta P_{real} = (\Delta P_{measured} - \Delta P_{blank})$.

The volume of the tank was 300 dm^3.

4 RESULTS AND DISCUSSION

4.1 The yield of different kraft pulps (I) (II)

The effect on the pulp yield of adding sodium borohydride ($NaBH_4$) or polysulfide (PS) during the first part of the softwood kraft cook was studied. *Fig 12* shows that at a kappa number of 35±2, the total yield of the PS - kraft pulp and the $NaBH_4$- kraft pulp increased from 48.1% to 50.2% and from 48.1% to 52.6% respectively.

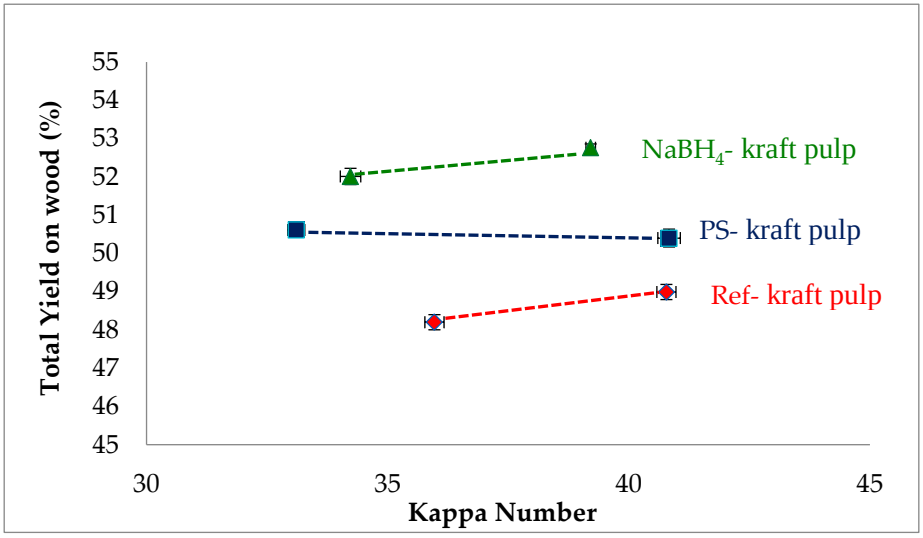

Fig 12- Total yield on wood (%) vs. kappa number after kraft cooking with two different alkali charges, where polysulfide (PS) 2% or sodium borohydride ($NaBH_4$) 1% was added based on dry wood chips.

In both cases, the yield increase was related to an increase in hemicellulose content. *Table 1* shows that PS and $NaBH_4$ enhanced the retention of glucomannan content from 9.0% to 10.8% and 14.8% respectively. Sodium borohydride ($NaBH_4$) reduces the aldehyde end group of hemicellulose to stable alcohol end groups while polysulfide (PS) oxidises the aldehyde end groups to carbonyl end groups (Wang et al.2005). As the aldehyde group in cellulose is also oxidized or reduced, the yield increase of the PS and $NaBH_4$-kraft pulps is due to both an increase in cellulose, 1.5% to 2%, and in glucomannan, 1%- to 3%, contents based yield on wood.

Table 1-The relative carbohydrate composition and yield of the respective pulps

Kraft Pulp	Estimated Relative composition (%)					Yield on wood (%)				
	Cellulose	Gluco-mannan	Galactan+ Arabinose	Xylan	Total Hemi cellulose	Cellulose	Gluco-mannan	Galactan+ Arabinose	Xylan	Total Hemi cellulose
Ref	80.4	9.0	1.5	9.1	19.6	34.1	3.8	0.6	3.9	8.3
PS *(2% on dry wood chips)*	78.5	10.8	1.5	9.2	21.6	35.5	4.9	0.7	4.2	9.8
$NaBH_4$ *(1% on dry wood chips)*	77.2	14.8	1.2	6.9	22.8	36.1	6.9	0.5	3.2	10.6

4.2 Effect of yield on physical properties (I)

The physical properties, especially the tensile index, were evaluated on 20 g/m² and 60 g/m² handsheets at the lower degree of refining, 0-2000 PFI revolutions. *Fig 13* and *Fig 14* show the effect of pulp yield on the tensile index for these handsheets.

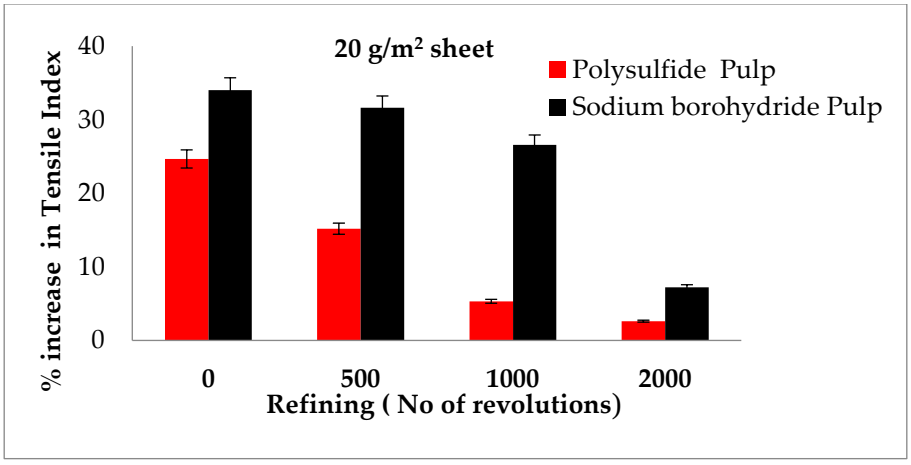

Fig 13- Percentage increase in tensile index compared to reference pulp at different PFI-refining levels for 20 g/m² sheets plotted from the experimental data of interpolated curves as described under experimental.

In both *Fig 13* and *Fig 14*, the tensile index increase of the $NaBH_4$- kraft pulp compared to reference kraft pulp was greater than that of the PS kraft pulp, but the percentage increase in tensile index decreased with increasing refining, although the percentage increase in tensile index for the 60 g/m² handsheet was much less than for the 20 g/m² handsheet (*Fig 13).*

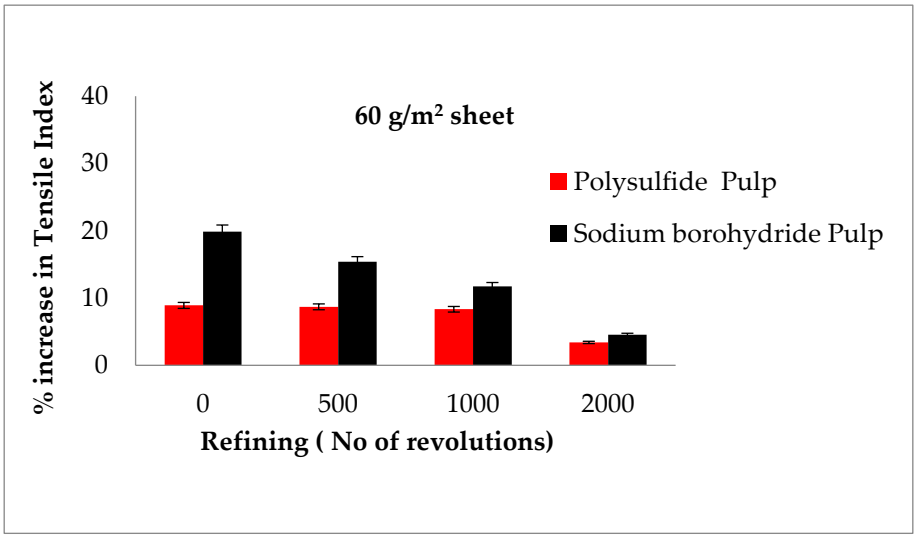

Fig 14- Percentage increase in tensile index compared to reference pulp at different PFI-refining levels for 60 g/m² sheets plotted from the experimental data of interpolated curves as described in experimental.

The addition of $NaBH_4$ or PS to the first part of the softwood kraft cook influenced the tensile index more for 20 g/m² handsheets, probably because there are fewer fibres in the network than in the 60 g/m² sheet. The joint strength between the fibres is therefore more important in the 20 g/m² than in the 60 g/m² sheet.

Fig 15 shows that the addition of $NaBH_4$ or PS lowered the wet Zero-span strength for 60 g/m² sheets at a given degree of refining and that $NaBH_4$ had a greater effect the PS. For the $NaBH_4$- kraft pulp there was an 8% difference from the reference. One explanation of the lower wet Zero-span, may be that these sheets contain fewer fibres per gram of paper since the pulp contains more hemicellulose, and that the Zero-span value may be related to the effective cellulose content (cellulose yield/g of pulp), as given in *Table 2*.

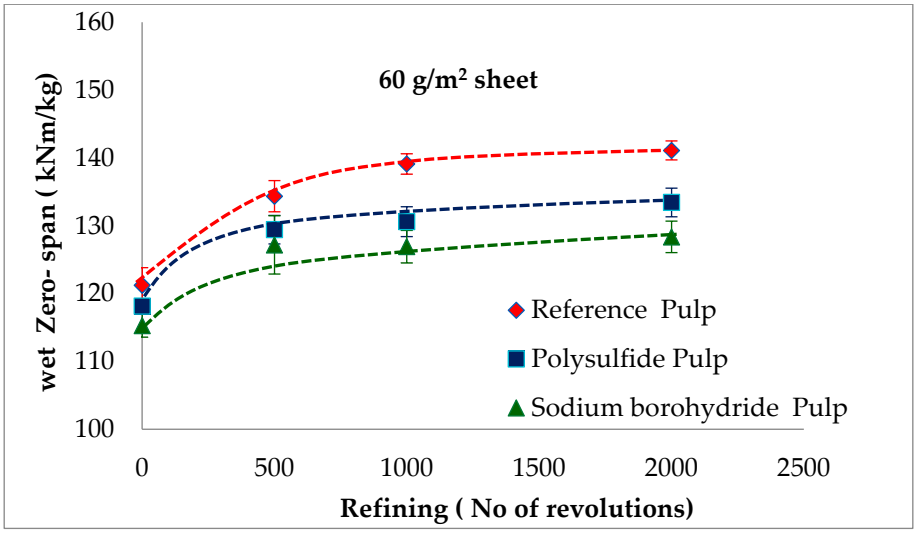

Fig 15- wet Zero-span versus degree of refining for 60 g/m² sheet of three different kraft pulps.

Table 2- The estimated Zero-span strength at 1000 PFI revolution

Pulp	**Total Yield (%)** (Cellulose +Hemicellulose)	**Cellulose Yield** (%)	**Zero-span** (kNm/kg)	**Zero-span of Cellulose**
Ref- pulp	42.4	34.1	139.1	173.0
PS-pulp	45.3	35.5	130.6	166.5
$NaBH_4$-pulp	46.8	36.1	126.9	164.3

After compensation for the pulp yield, the reference pulp seemed to have the strongest fibres, and the increase in tensile index on addition of $NaBH_4$ or PS cannot be explained by an increase in fibre strength.

A higher hemicellulose content increases the fibre joint strength and the bonding ability of fibres in paper is usually described by the bonded area and the bonding strength between fibres (Laine, Stenius 1997). *Fig 16* shows that the z-strength in the 60 g/m² sheets for both $NaBH_4$- kraft pulp and PS-kraft pulp was greater than that of the reference kraft pulp at all refining (0-2000 PFI rev) levels. Thus there seems to be a correlation between the

increase in z-strength and the increase in tensile index for $NaBH_4$- kraft pulp and PS- kraft pulp, that could be due to an increase in fibre joint strength.

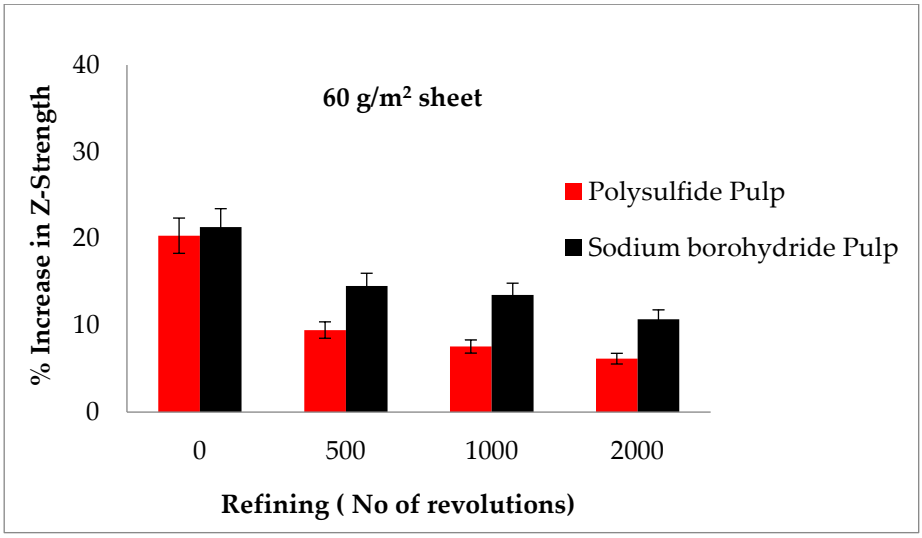

Fig 16- Percentage increase in Z-Strength at four different refining levels for $NaBH_4$ and PS-pulps from interpolated curves described in the experimental.

4.3 Hemicellulose yield and dewatering properties (II)

An increase in hemicellulose content in a kraft pulp is generally considered to increase the swelling of the fibre (Saukkonen 2014) and to promote refining efficiency. An increase in swelling improves the adhesion between fibres (Molin, Teder 2002; Danielsson, Lindström 2005) because hemicellulose can soften the fibre wall, increasing the flexibility and fibre joint strength (Laine, Stenius 1997). Kraft pulp with higher a hemicellulose content was therefore interesting for the study of tissue paper dewatering properties, since on increase in pulp yield can reduce the dewatering ability due to the increase in hemicellulose content and the ability of hemicellulose to hold water.

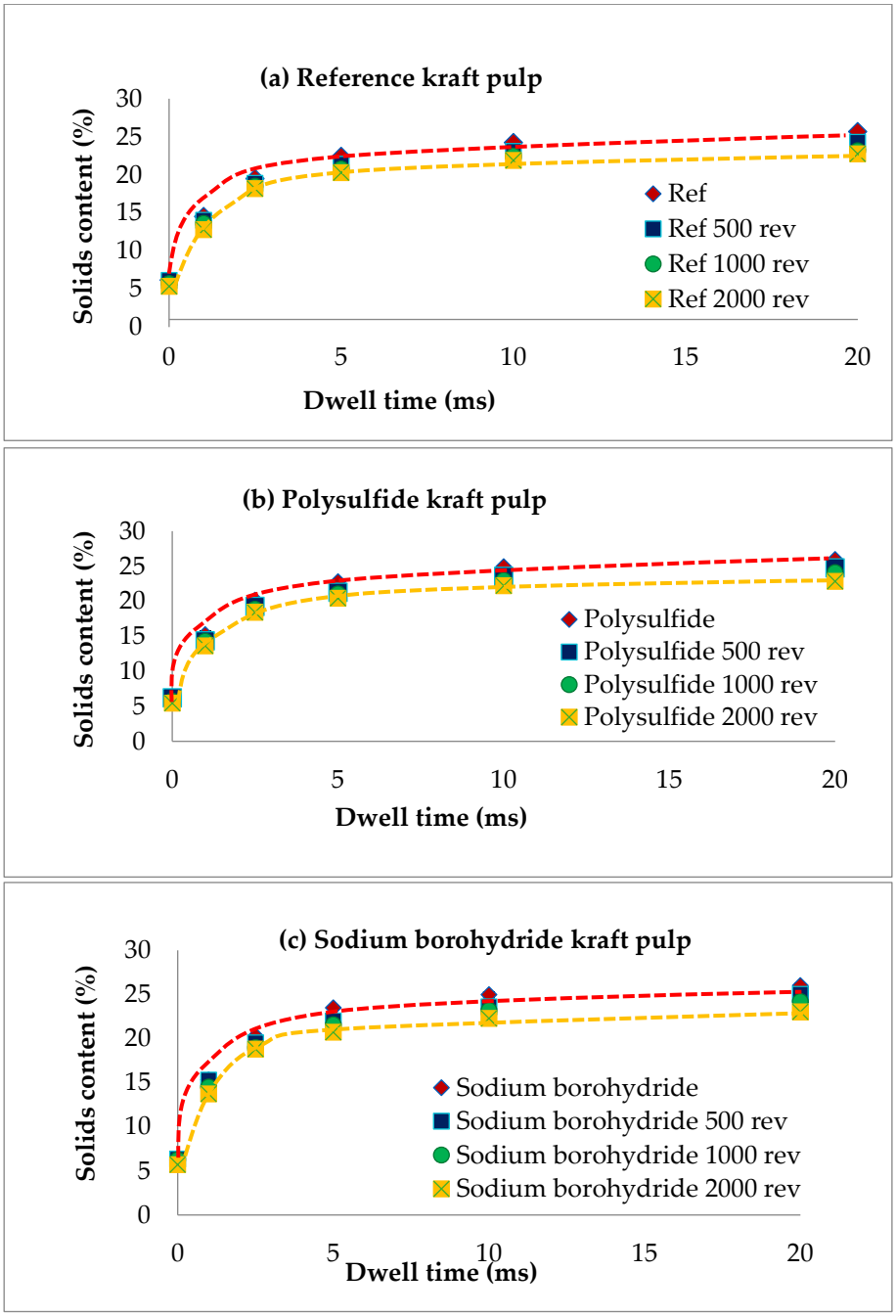

Fig 17- Solids content of the pulps (a) Ref-kraft, (b) PS-kraft and (c) $NaBH_4$-kraft as a function of dewatering dwell time for different degrees of refining.

Fig 17 shows that at different dwell times ((0, 1.0, 2.5, 5.0, 10.0 and 20.0 ms) the solids content of 20 g/m² handsheets of all three kraft pulps increased by from 5.4 to 6.4% after sheet forming by gravity with increasing dwell time to an average of 15 to 25%. In all cases, the solids content decreased with increasing degree of refining, so the final solids content level was dependent on the pulping process and on the degree of refining. The difference in solids content between refined and unrefined pulps is more pronounced. *Fig 18* shows that sheets made from refined pulps (2000 PFI rev) had a solids content 2-4% lower at a given dewatering dwell time than the unrefined kraft pulps.

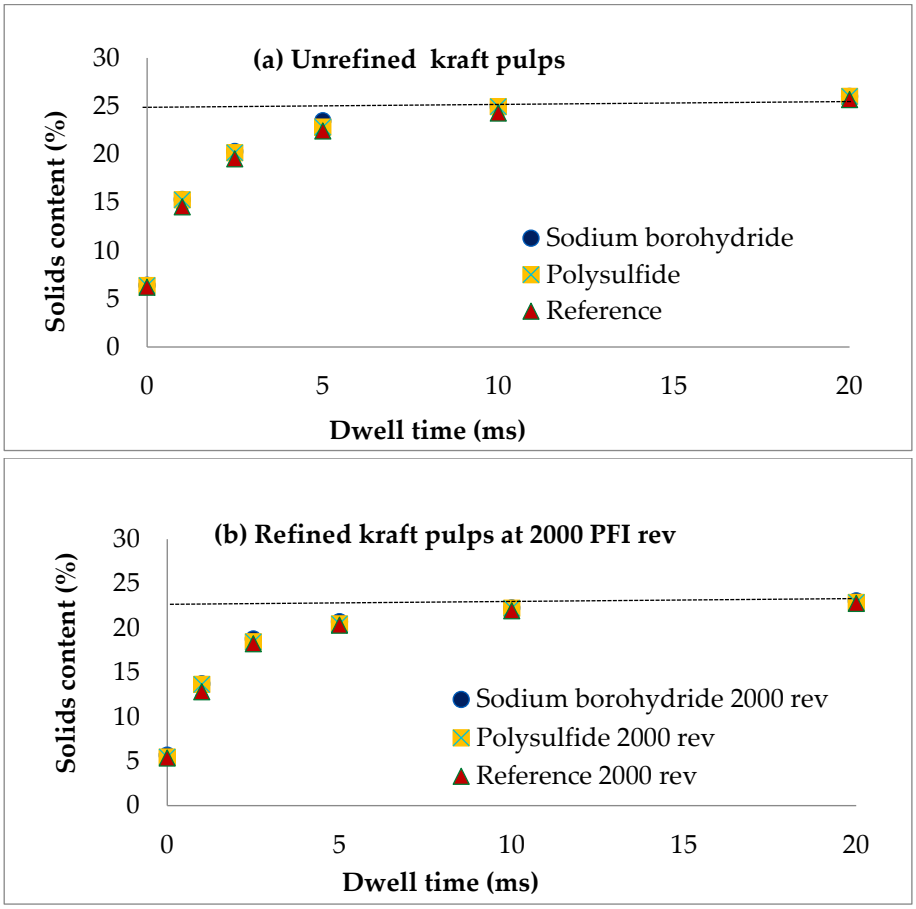

Fig 18- Solids contents of three different pulps as a function of dewatering dwell time under (a) unrefined and (b) refined (2000 PFI rev) conditions.

The solids content in *Fig 18* decreased in the order; $NaBH_4$ > PS > Ref-kraft pulp. The error bars in the graphs (0.02-0.3%) are based on three dryness measurements at each dwell time.

4.4 Hemicellulose yield and fibre characteristics (I) (II)

An increase in hemicellulose content in a kraft pulp is generally considered to increase the swelling of the fibre, and thus increase the fibre surface flexibility and the bonding potential (Rydholm 1967; Schönberg et al.2001; Hannuksela et al. 2004). Earlier studies have reported a correlation between the fibre joint strength and the fibre surface charge (Forsström, Torgnysdotter 2005).

In the present study, no increase in surface charge was observed, as shown in *Table 3.* These was however an increase in the total charge in the case of the $NaBH_4$- pulp and PS pulp, and this may lead to a greater swelling of the fibre, and a greater degree of sheet consolidation.

Table 3- Charge analysis of unbeaten pulps

Kraft Pulp	**Total Charge[1]**		**Surface Charge[2]**	
	Mean value (μekv/g)	Standard Deviation (±)	Mean value (μekv/g)	Standard Deviation (±)
Ref	79.0	0.91	15.0	0.10
PS	108.0	0.35	1.84	0.07
$NaBH_4$	95.0	1.84	15.0	0.33

[1] Determined by polyelectrolyte adsorption (Polybrene, Mw≈$8x10^3$) around pH 7.5

[2] Determined by polyelectrolyte adsorption (Poly-DMDAAC, Mw>$3x10^3$) around pH 7.5

Increasing the amount of hemicellulose in the fibre wall counteracts the aggregation of cellulose during the drying of the fibre (Salmén, Olsson 1998; Larsson, Salmén 2014). A less aggregated fibre wall has a greater flexibility and can lead to an increase in the fibre joint strength, resulting in a higher tensile index.

It has been reported (Laivins, Scallan 1996) that both external and internal fibrillation induced by refining increase the surface area and increase the swelling of the pulps, making dewatering more difficult. The chemical conditions in the pulping process affect the proportions of cellulose and hemicellulose within the fibre wall. A larger content of hemicellulose resulting in a higher overall yield makes each fibre somewhat heavier and a paper sheet of a given grammage made from such a pulp will thus contain fewer fibres than the reference. Compared to the reference, the $NaBH_4$ pulp sheets had about 10% fewer fibres when the yield increased from 48% to 53% (Rahman et al.2017). The PulpEye analysis system indicated however that the difference in number of fibres could be almost 20%, see *Table 4.*

Table 4- Fibre characterization of the three kraft pulps at different degrees of refining

Kraft pulp	**Total Yield**	**Population**	**Mean fibre length**	**Mean fibre width**	**Fines content**
	(%)	(10^6/g)	(mm)	(μm)	(%)
Ref -unrefined	48.1	2.33	2.11	29.9	2.19
Ref 500 rev			2.19	29.5	2.31
Ref 1000 rev			2.19	29.8	2.45
Ref 2000 rev			2.22	29.7	2.61
PS-unrefined	50.2	2.27	2.11	30.2	2.34
PS 500 rev			2.19	30.4	2.48
PS 1000 rev			2.19	30.5	2.81
PS 2000 rev			2.24	30.5	2.85
$NaBH_4$ -unrefined	52.6	1.91	2.17	29.8	2.77
$NaBH_4$ 500 rev			2.24	30.1	2.89
$NaBH_4$ 1000 rev			2.24	29.7	3.24
$NaBH_4$ 2000 rev			2.25	30.1	3.60

The retention of hemicelluloses in the pulp, results in a greater swelling, and an increase in swelling generally improves the fibre bonding area .The swelling ability is strongly related to the porosity of the fibre wall (Berthold,

Salmén 1997). *Fig 19* shows that the pore volume of both the $NaBH_4$ and the PS-kraft pulps was somewhat higher than that of the reference kraft pulp.

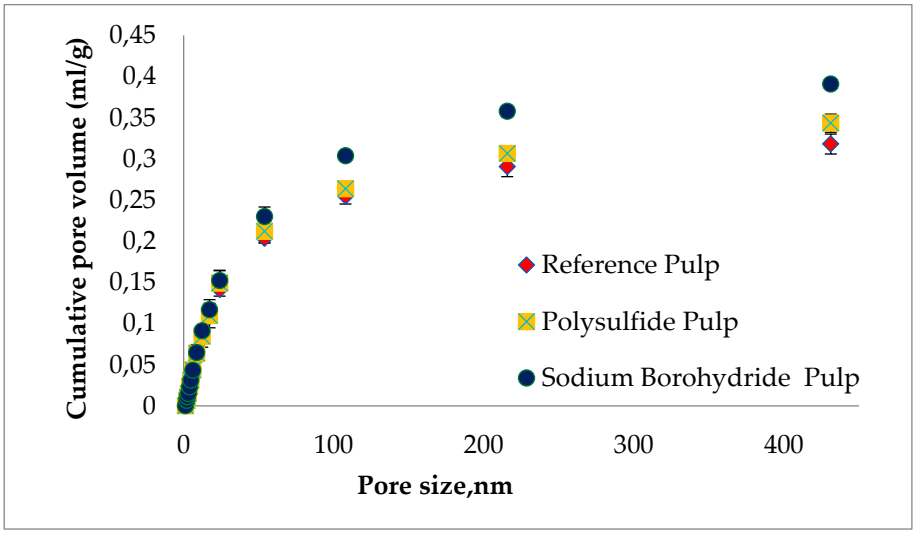

Fig 19- Cumulative pore volume as a function of pore diameter from thermoporosimetry measurements on unrefined kraft pulps.

This supports the hypothesis that these high-yield pulps may have a higher fibre flexibility that may result in stronger bonds and a higher tensile index of handsheets made for the pulps.

Fig 20 shows that the solids content and water retention value (WRV) at a given dewatering dwell times were higher for the pulps with a higher yield and higher hemicellulose content. This can be related both to the ability of hemicellulose to hold water and to the more open fibre network of the $NaBH_4$ and the PS-kraft pulps.

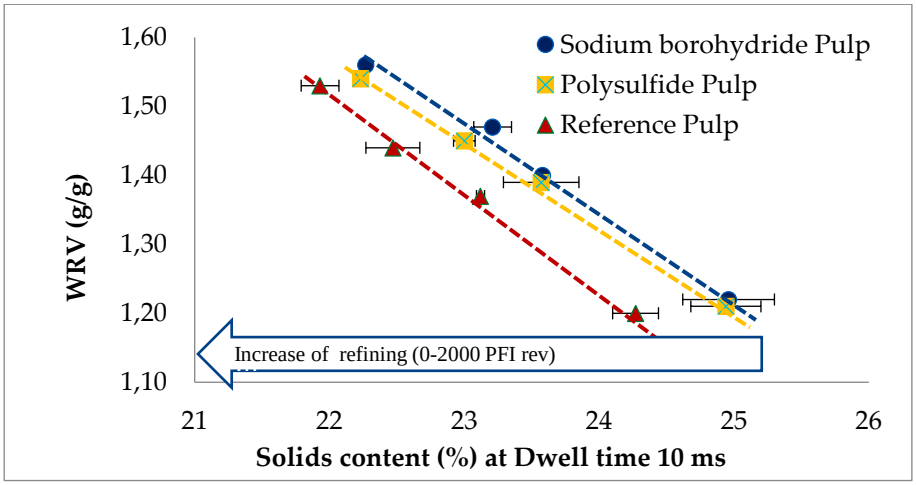

Fig 20- Solids content at a dewatering dwell time of 10 ms as a function of WRV for three different kraft pulps at 0-2000 PFI rev.

Fig 21 shows that at low degree of refining, for example, 500 PFI- revolutions, the $NaBH_4$ and PS-kraft pulps had a tensile index of 45.5 and 52 kNm/kg respectively which corresponds to a 15%-32% higher value than that of the reference kraft pulp, 39.5 kNm/kg, when the solids content was about 23% at 500 PFI-rev for all three kraft pulps, *Fig 22*.

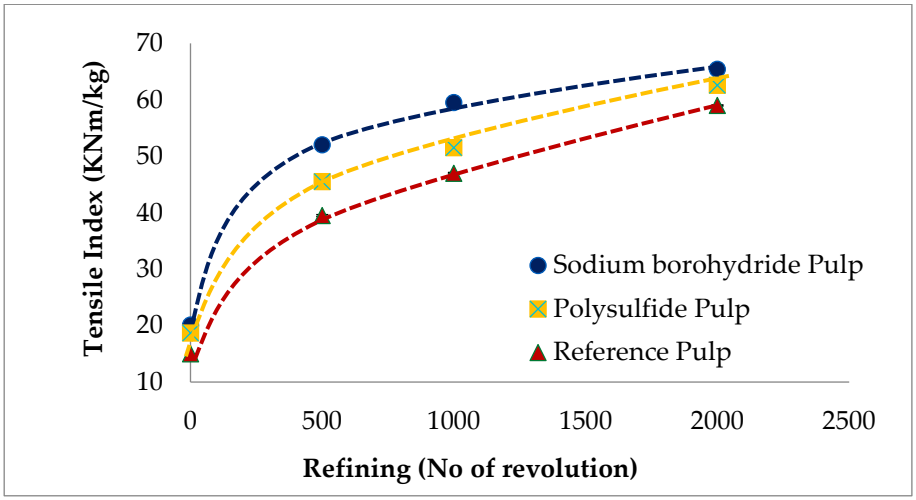

Fig 21- Tensile index versus number of refining revolutions for 20 g/m^2 sheets of three different kraft pulps.

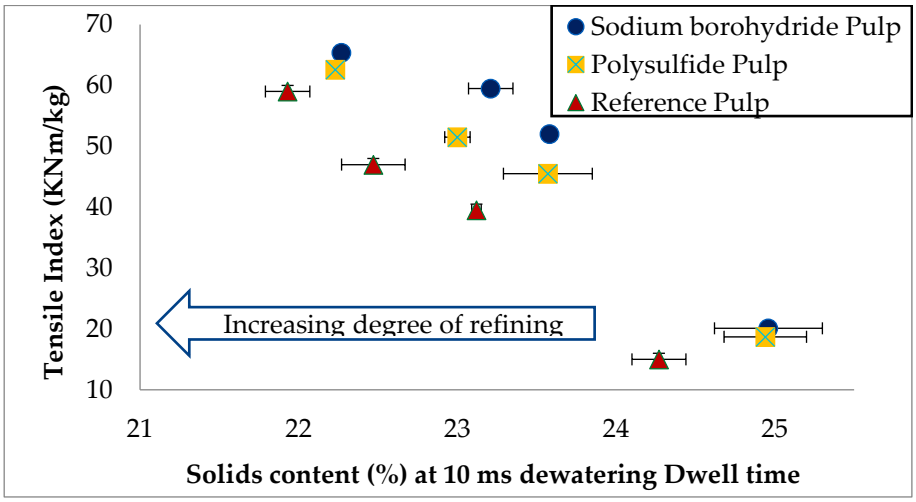

Fig 22- Tensile index after a dewatering dwell time of 10 ms as a function of solids content for three different kraft pulps refined at 0-2000 PFI rev.

The hemicellulose rich pulps, the $NaBH_4$-kraft pulp followed by the PS- kraft pulp, clearly exhibit better dewatering i.e. a higher dryness at a given tensile strength. Kraft pulps produced using either $NaBH_4$ or polysulfide addition can thus give either a higher strength for a given amount of refining or the same strength with less refining energy.

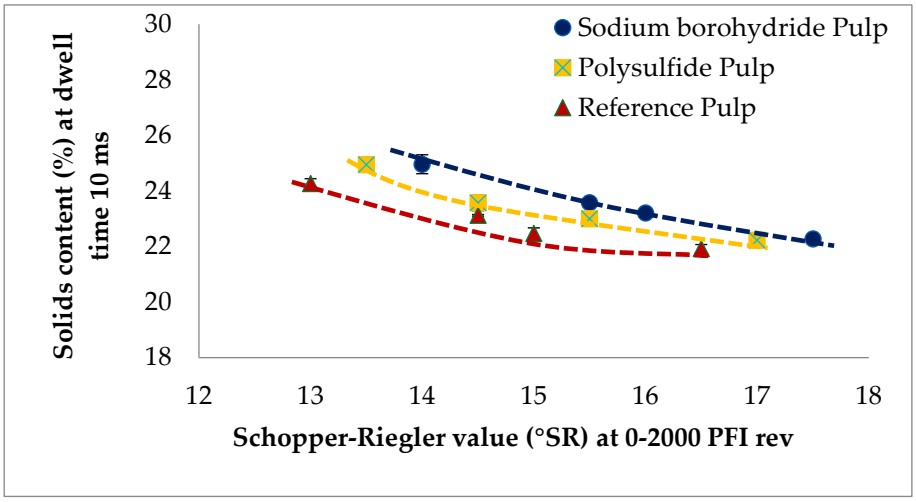

Fig 23- Solids content after a dewatering dwell time of 10 ms as a function of dewatering resistance of the three kraft pulps at 0-2000 PFI rev.

There is a good correlation between solids content and dewatering resistance of the pulps as shown in *Fig 23* i.e. the solids content decreases as the dewatering resistance increases. In the figure, the solids content after a dewatering dwell time of 10 ms is plotted against the Schopper-Riegler (°SR) value as dewatering resistance at different refining levels (0 – 2000 rev) for the three pulps. The solids content at a given Schopper-Riegler (°SR) value decreases in the order: $NaBH_4$>PS> Ref-kraft pulp, indicating that the pulps with a higher yield, $NaBH_4$ and PS kraft pulps can hold more water under the dewatering conditions used in the Schopper Riegler test.

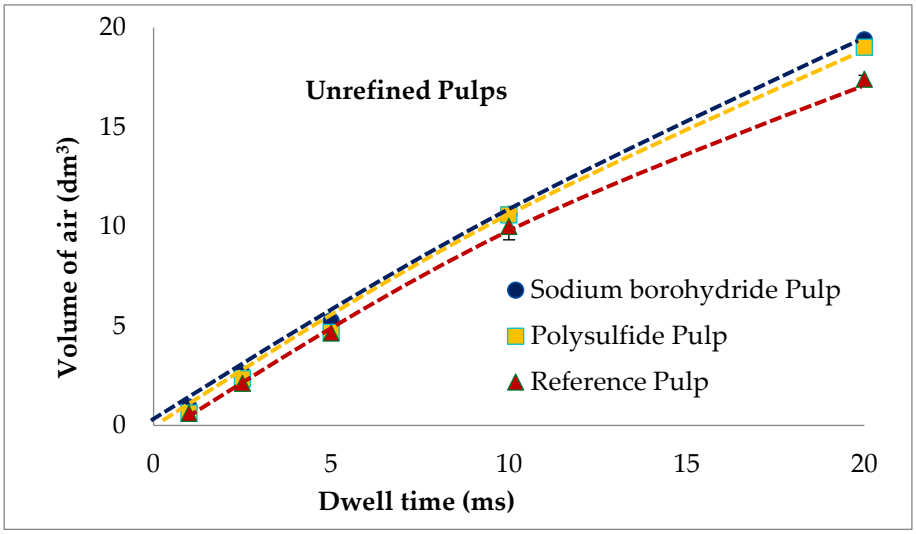

Fig 24- Volume of air passing through the sheet as a function of dewatering dwell time for the three unrefined kraft pulps.

The more open network of the sheets made from pulps with a high yield leads to a higher porosity and air can pass more rapidly through the sheet, as shown in *Fig 24*. The order of air passing through the sheet is the same as the order of dewatering: $NaBH_4$>PS> Ref- kraft pulp, so the more open network of the $NaBH_4$ and PS- kraft pulps promotes faster dewatering than the reference kraft pulp.

5 CONCLUSION

This thesis has the following conclusion:

- Modifying the kraft pulping process by the addition of an oxidizing agent (polysulfide) or a reducing agent (sodium borohydride) increased the pulp yield, by increasing the retention of glucomannan.

- The pulps with increased glucomannan yield had a higher tensile index. This effect was most pronounced at low degree of beating and low grammage.

- The higher yield resulted in an increase in the pore volume, which indicates a greater degree of swelling of the fibre and thus an increase in flexibility that probably leads to an increase in the bond strength, resulting in the higher tensile index. The greater swelling was also seen in the higher WRV values.

- When the pulp yield increased from 48% to 53%, the paper sheets had 10% fewer fibres at given dryness level for the $NaBH_4$ kraft pulp than for reference kraft pulp. This leads to a more open sheet structure which explains the faster dewatering speed.

- For the pulps studied here, the effect of the more open sheet structure dominates over the effect of increased swelling regarding dewatering under conditions mimicking full-scale dewatering. This means that pulps with a higher yield have a faster vacuum dewatering when refined to a given tensile strength.

6 SUGGESTIONS OF FURTHER WORK

- In the production of tissue paper, the dewatering in the pressing section is also of great importance, so to fully understand the behaviour of the modified kraft pulps it is also necessary to further study dewatering during wet pressing.

- The creep behaviour of tissue is of utmost importance and it is important to study possible differences between the modified kraft pulps in relation to this.

- Kraft pulp modification can also be performed by changing the chemical profiling in the digester and by adding new chemicals (different carbohydrate compound for example, xyloglucan, CMC etc).

- Consider the importance of different retention times for liquor and chips in continuous industrial digesters.

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