LAPPEENRANNAN-LAHDEN TEKNILLINEN YLIOPISTO LUT
LUT School of Engineering Science
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UNDERSTANDING THE FINES IN BCTMP PROCESS

Examiners: Professor Antti Häkkinen
Associate Professor Ritva Tuunila

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ABSTRACT

Lappeenrannan Lahden teknillinen yliopisto LUT
LUT School of Engineering Science
Master's Programme in Chemical and Process Engineering

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Understanding the fines in BCTMP process

Master's thesis

2020

90 pages, 82 figures, 16 tables and 7 appendixes

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Key words: BCTMP fines, BCTMP process, fines

The target of this thesis was to understand the generation, properties and effects of fines generated in refining in the BTCMP (chemi-thermomechanical pulp) process. This thesis includes a theoretical part and an experimental part. In theoretical part the focus was in raw material properties, BCTMP manufacturing process, fines generation, fine types and effect on the BCTMP process and product qualities. In experimental part Metsä Board Joutseno BCTMP mill was studied. Samples were collected around the process from specified pulp and filtrate streams and were analyzed in Metsä Board Joutseno, Äänekoski TC (Technology Center) and KCL (Keskus-Central Laboratorium).

The generation and properties of fines in Joutseno BCTMP mill were analyzed. Obtained results indicate that the fines content stays relatively constant through the BCTMP process; no major difference can be found between unit operations. Results also revealed an interesting factor about fines and bleaching; bleaching chemicals do not affect the fines content at all. One could assume that bleaching chemicals would alternate the fines surface and morphological properties, but this is not the case.

Experimental refining with different refiner blade type considering the fines generation was executed. No difference in fines generation and fractions was seen when comparing original refiner blades and experimental blades. The SEC (specified energy consumption) however was affected significantly.

TIIVISTELMÄ

Lappeenrannan Lahden teknillinen yliopisto LUT
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BCTMP prosessissa esiintyvän hienoaineen ymmärtäminen

Diplomityö

2020

90 sivua, 82 kuvaa, 16 taulukkoa and 7 liitettä

Tarkastajat: Professori Antti Häkkinen
Tutkijaopettaja Ritva Tuunila

Avainsanat: BCTMP fines, BCTMP process, fines, hienoaine

Tämän diplomityön tarkoituksena oli lisätä ymmärrystä BCTMP (kemihierre) -prosessissa esiintyvän hienoaineen synnystä, ominaisuuksista ja vaikutuksista valmistetun massan laatuun. Työ sisältää teoreettisen osuuden sekä kokeellisen osuuden. Teoreettisessa osuudessa keskityttiin raaka-aineiden ominaisuuksiin, BCTMP -prosessiin, hienoaineen muodostumiseen, hienoainetyyppeihin sekä niiden vaikutuksiin valmistetun kemihierteen laatuun. Kokeellisessa osuudessa tarkastelun kohteena oli Metsä Board Joutsenon tehdas. Näytteitä kerättiin ympäri BCTMP -prosessia ja massa sekä suodosnäytteet analysoitiin Metsä Board Joutsenossa, Äänekosken Technology Centerissä sekä KCL:n (Keskus-Centrum laboratorium) toimesta.

Hienoaineen syntyä ja ominaisuuksia Joutsenon BCTMP -tehtaalla tarkasteltiin. Saaduista tuloksista huomattiin, että hienoainepitoisuudet pysyvät suhteellisen samalla tasolla koko prosessin ajan; huomattavia eroja yksikköoperaatioiden välillä ei ollut. Yllättävä tulos saatiin myös valkaisusta ja hienoaineesta; valkaisukemikaalit eivät vaikuta syntyneen hienoaineen määrään. On oletettu, että valkaisukemikaalit muuttaisivat hienoaineen pintaominaisuuksia ja morfologiaa, mutta tulosten mukaan näin ei ole.

Hienoaineen syntyä vaihtoehtoisilla energiaa säästävillä jauhinterillä myös tarkasteltiin. Eroa syntyneissä hienoainefraktioissa ei ollut. Jauhimien ominaisenergiankulutus tosin tippui runsaasti.

ALKUSANAT

Tämä diplomityö on tehty Metsä Board Oyj:n tutkimuskeskuksen (Äänekoski Technology Centre) toimeksiantona 2019 aikana. Haluan kiittää kuitukehityspäällikkö Pirkko Syrjälää erittäin mielenkiintoisesta diplomityöaiheesta. Haluan myös erityisesti kiittää Pirkko Syrjälää siitä, miten hän oli mukana työn valvomisessa ja käytännön toteutuksissa. Pitkiä päiviä tehtiin tehtaalla näytteitä analysoitaessa. Lisäksi iso kiitos koko Metsä Board Joutsenon väelle, jotka autoitte toteuttamaan tämän työn ja tsemppasitte.

Haluan kiittää ohjaajiani professori Antti Häkkistä ja tutkijaopettaja Ritva Tuunilaa hyvästä työn ohjaamisesta.

Eipä muinoin kun 2014 aloitin kemiantekniikalla Lappeenrannassa tullut ajateltua, että joskus minustakin tulee diplomi-insinööri. Kaikki silloin kaukaisilta tuntuneet asiat ovatkin viimeaikoina konkretisoituneet ja ei tässä voi kuin ihmetellä sitä kuinka nopeasti aika rientääkään. Paljon on opiskeluaikana koettu ja olen äärettömän kiitollinen niistä kaikista ikuisista ystävyyssuhteista mitä täällä on tullut solmittua. Iso kiitos teille ystävät!

Lopuksi haluaisin välittää mitä suurimmat kiitokset perheelleni ja läheisilleni. Olette olleet koko opiskeluajan tukena ja teidän tuella tämäkin diplomityö on saatu valmiiksi. Nyt kohti uusia seikkailuja!

Lappeenrannassa 8.4.2020

Mikko Lamminen

List of symbols

R_∞	brightness
k	light-absorption coefficient
s	light-scattering coefficient
Δp	pressure drop
L	total bed height
v_S	superficial velocity
μ	fluid viscosity
ϵ	porosity of the bed
$\emptyset_s$	sphericity of the particles in the bed
Dp	the diameter of the volume equivalent spherical particle

ABBREVIATIONS

BCTMP	Bleached Chemi-thermomechanical Pulp
CMP	Chemimechanical Pulp
CSF	Canadian Standard Freeness
CTMP	Chemi-thermomechanical Pulp
DDJ	Dynamic Drainage Jar
FAS	Formamidine Sulphinic Acid
HC	High consistency
ISO	International Organization for Standardization
LC	Low consistency
M	Middle Lamella
MC	Medium consistency
P	Primary Wall
PGW	Pressure Groundwood
PGW-S	Super Pressure Groundwood
PRMP	Pressure Refiner Mechanical Pulp
RMP	Refiner Mechanical Pulp
S1-S3	Secondary Wall Layers
SEC	Specific Energy Consumption
SEL	Specific Edge Load
SGW	Stone Groundwood
TMP	Thermomechanical Pulp
W	Warty layer

Contents

1 Introduction

The consumption of packaging materials is growing every year. Replacement of traditional plastic packages for shipping with bio-based alternatives is relevant in present markets. The environmental benefit is not only depending from the design of the packaging, but the consumers will to buy products which are supporting sustainable and renewable packaging as the information for different products is coming more globally available (Steenis et al., 2018). There are many packaging materials available on markets, but especially paperboard is a popular choice due to its light and strong structural characteristics. As paperboard being a good thermal insulator, it can be used for protecting certain products, such as beer or other consumable products (Paternoster et al., 2017). Paperboard's and FBB's (Folded Box Board) main composition is BCTMP (bleached chemi-thermomechanical pulp), as the intermediate of the cardboard is wanted to be as light and as strong as possible (Lönnberg, 2009).

BCTMP processes have relatively good yield, as it uses the lignin that bonds the wood fibers together. Good yield can be achieved by combination of mechanical and chemical pulping. Chemi-thermomechanical pulps can be defined to have yield above 90 %. Table I presents common yields for most common pulping processes.

Table I Yields found for common mechanical pulping processes. (Lönnberg, 2009).

Label	Description	Yield, %
SGW	Stone Groundwood	98,5
PGW	Pressure Groundwood	98,5
PGW-S	Super Pressure Groundwood	98
TGW	Thermo Groundwood	98,5
RMP	Refiner Mechanical Pulp	97,5
PRMP	Pressure Refiner Mechanical Pulp	97,5
TMP	Thermomechanical Pulp	97,5
CMP	Chemimechanical Pulp	80-95
CTMP	Chemi-thermomechanical Pulp	>90

Because lignin as a substance is not transparent, the BCTMP process includes a bleaching unit or units to gain wanted product brightness. Different wood species can be applied to this process, but in this thesis the wood species which are relevant are spruce, birch and aspen.

The aim of this thesis is to investigate fines generated in BCTMP process. In the literature part of this thesis the BCTMP process, BCTMP properties, fines generation routes and fines effect on the final product are described. The experimental part of this thesis inspects the fines fraction generation and distribution through the Joutseno mill BCTMP process. The possible utilization of fines is also discussed. The discussion about fines starts from chapter 6.

2 Wood species

The used wood species and the ratio of these species have a significant effect on the mechanical pulping and pulp quality. Generally wood species can be sorted in poplar (hardwood) and pinophyte (softwood) species. For example, birch belongs to poplar species and spruce to pinophyte species. The morphological difference between species within wood species is not that severe; the usage depends greatly on the growing location of wood. In tables II and III characteristics of various softwood and hardwood species are presented.

Table II Fibre properties and chemical composition of various softwood species. (Barbe et al., 1993)

Species	**Black spruce** Picea mariana	**White spruce** Picea glauca	**Balsam fir** Abies balsamea	**Jack Pine** Pinus banksiana	**Lodgepole pine** Pinus contorta	**Pendero sa Pine** Pinus ponderosa	**Loblolly pine** Pinus taeda	**Slash pine** Pinus elliottii	**Radiata pine** Pinus radiata	**Caribbean pine** Pinus caribaea
Fibre length, mm	3,5	3,3	3,5	3,5	3,1	3,6	3,6	4,2	4,0	2,6-3,9
Fibre width, µm	25-30	25-30	30-40	28-40	35-45	35-45	35-45	-	35-45	40-50
Cell wall thickness, µm	2,2	2,4	2,5	2,5-2,9	3,0	2,4	3,3	4,2	3,0	6,0-7,1
Coarseness, µg/m	160-290	-	250	270-400	230	260-460	300-560	290-670	-	-
Lignin, %	27,6	29,4	29,4	28,3	27,7	25,6	28,6	26,8	28,9	26,2-31,2
Extractives,	2,2	2,0	2,5	4,0-4,2	3,5	4,4-5,0	3,2-5,4	3,4-6,0	5,4	4,2

Table III Wood and fibre characteristics of various poplar species. (Lehto, 1995)

Scientific name	P. tremula x tremula	P. tremula x tremuloides	P. tremuloides	P. balsamifera	P. grandidentata	P. deltoides x nigra	P. trichocarpa	P. maximowiczii x trichocarpa
Species	Aspen hybrid	Aspen hybrid	American aspen	Balsam poplar	White poplar	Poplar hybrid	California poplar	Poplar hybrid
Fibre length, mm	0,90	0,96	1,02	0,88	1,08	1,00	0,95	0,99
Coarseness, µg/m	121	132	132	112	136	135	111	138
Lumen diameter, µm	16,3	15,8	14,0	16,4	18,4	19,1	17,1	16,0
Cell wall thickness, µm	6,1	7,1	7,0	6,2	5,7	6,8	4,8	6,1
Vessel cells, %	27,6	24,8	26,9	29,3	29,2	29,6	20,8	26,0
Lignin, %	20,4	19,9	21,2	24,1	20,9	26	24,5	21,5

Hardwoods have more complex morphological fibre structure than softwoods. Softwoods contain in general only one type of fibre cells (tracheids), while hardwoods contain labriform fibres, vessel elements with relatively large diameter and a larger amount of parenchyma cells compared to softwoods. Hardwoods' advantages are that they tend to have great luminous-shattering characteristics and sheet surface properties. However, the sheet surface strength properties are quite poor. When applying hardwood chips in mechanical pulping, a chemical pretreatment is required to gain needed strength for equal ratio between sheet strength and other properties such as brightness. There are considerable amount of factors even in single species that cause variation in wood quality. The variations are caused by the abnormality of the genetic origin, tree age, environmental factors and tree grown pattern.

The structure in cell level is not quite the same, as the pinophyte species have simpler structure and morphology. The chemical composition of these species also differs from each other, which has a straight effect for instance on the brightness of the product. In mechanical pulping processes small amounts of hardwood chips are often blended with softwood chips to gain optimal properties for the product sheet (Lönnberg, 2009). Also consistency in chip size and wood properties leads to steady product quality and efficiency (Wood, 1996).

2.1 Spruce

Spruce belongs to softwood species, having a wood density of 430 kg/m^3. Average fibre length for spruce is determined to be 3,2 mm (Ilvessalo-Pfäffli, 1977). This fibre length value is an average value of all spruce species, while table II represents only few species with their individual fibre lengths. It has been recognized that wood species from the spruce family, especially Norway spruce (Picea abies), are the most favourable raw material for mechanical pulping (Lönnberg, 2009). Apprehension for this recognition can be seen from the morphology: spruces have been observed to have favourable fibre properties, such as fibre length, wall thickness, microfibril structure, low amount of extractives and high initial brightness of the wood. Great strength and optical properties can also be found from spruces when considering for example different kind of paperboard grades. A chemical pre-treatment, usually done by impregnation with Sodium sulfite (Na_2SO_3) or sodium bisulfite ($NaHSO_3$) is needed for softwood species as only few softwood species are suitable without any chemical treatment. Spruce species used in mechanical pulping include Norway spruce (Picea abies), Black spruce (Picea mariana), White spruce (Picea glauca), Red spruce (Picea

rubens), Sitka spruce (Picea sitchensis) and Engelmann spruce (Picea Engelmanni) (Richardson et al., 1992; Härkönen et al., 1989; Lönnberg, 2009).

2.2 Birch

Birch belongs to hardwood species, having wood density of 472 kg/m^3. Average fibre length for ungrinded birch was determined to be 1,1 mm, diameter 21,6 µm, coarseness 0,296 mg/m and cell wall thickness 2,44 µm (Law and Valade, 1999; Ilvessalo-Pfäffli, 1977). Hardwoods in general are applied based on their density, fibre cell wall thickness and the average fibre length. These characteristics are important when considering the woods' ability to defibrate in the grinding process (Lönnberg, 2009). Chemical and morphological composition in different hardwood species varies much more than in softwood species. Alkaline peroxide treatment is usually applied for hardwood species. Only few hardwood species, such as aspen or poplar, are not suitable for mechanical pulping without any chemical pretreatment.

2.3 Aspen

Aspen also belongs to hardwood species, having wood density of 350 kg/m^3. The pulp made from aspen is known to have good light-scattering coefficient and brightness, but poor fibrillar bonding properties (Lönnberg, 2009). This leads to poorer sheet strength properties for example compared to spruce. A suitable compromise between sheet strengths and optical properties can be achieved via chemical pretreatment of the chips. Aspen has the lowest density when compared to birch and spruce (350 kg/m^3). This means that aspen requires less energy when refined to gain the wanted freeness (pulps water filterability) level. Mixtures of low density wood species and high density wood species will correlate with reduced energy needed for the refining process. Average fibre length for aspen was determined to be 0,96 mm, diameter 20,8 µm, coarseness 0,241 mg/m and cell wall thickness 1,93 µm (Law and Valade, 1999). These values are average values for all examined aspen species, while table III represents only few aspen species and their properties.

3 Wood properties

As the product quality and properties depend on the raw material used in the process, blending different wood species with high and low densities should be considered. Fiber length is important when considering the strength of the product. Longer fibres tend to

produce fewer weak bonds in the product sheet when comparing to short fibres. When inspecting the properties of paperboard or folded box board, the forces between fibre layers (z-forces) also play key role in the product quality. The wood fibres are constructed from six layers; middle lamella (M), primary wall (P), secondary wall (S1, S2 and S3) and warty layer (W). A schematic of a fibre wall layering can be seen in Figure 1.

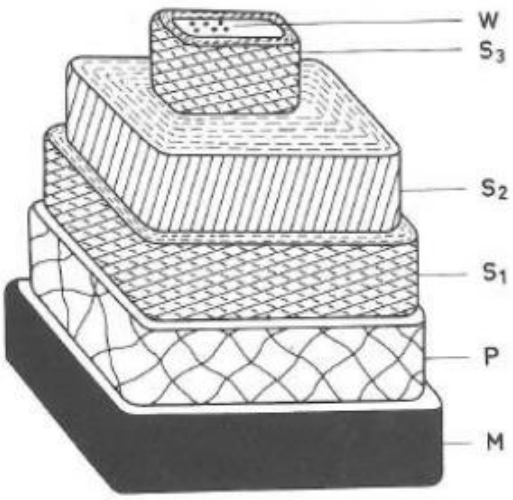


Figure 1 A schematic of fibre wall layering (Ilvessalo-Pfäffli, 1977)

The chemical compositions vary between fibre wall layers. Graphical illustration of the principal chemical constituents within S1, S2 and S3 layers can be seen in Figure 2 and the chemical composition distribution between these layers can be seen in tables IV and V.

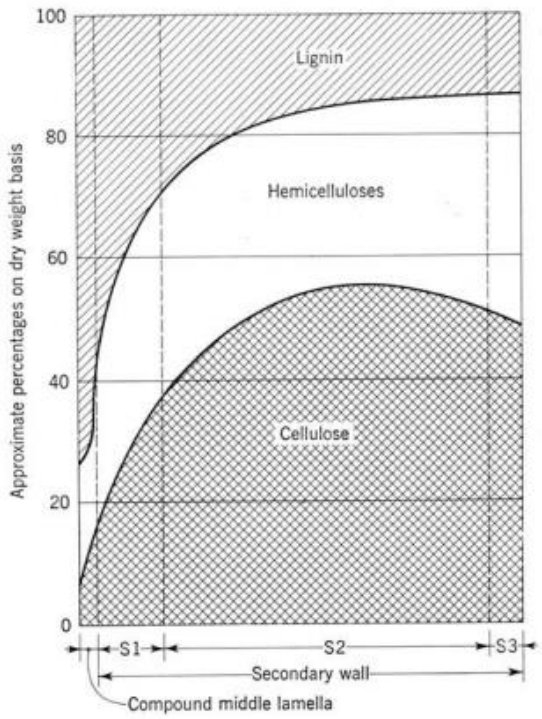


Figure 2 Main chemical constitutes within the secondary wall layers. (Panshin and De Zeeuw, 1964)

Table IV The relative mass proportions of the main constituents in the softwood tracheids (% of the total dry matter of each layer). (Stenius, 2000)

Constituent	Morphological region	
	M + P	S1 + S2 + S3
Lignin	65	25
Polysaccharides	35	75
Cellulose	12	45
Glucomannan	3	20
Xylan	5	10
Others (mainly pectic substances)	15	< 1

Table V The distribution of the main constituents in the softwood tracheids (% of the total amount of each constituent). (Stenius, 2000)

Constituent	Morphological region	
	M + P	S1 + S2 + S3
Lignin	21	79
Polysaccharides	5	95
Cellulose	3	97
Glucomannan	2	98
Xylan	5	95
Others (mainly pectic substances)	75	25

As seen in table IV, the lignin content in middle lamella and primary layer (M + P) is high, but because this layer is thin, only a small fraction of total lignin is located in this layer. The fractions vary between softwood and hardwood species for every constituent. For example, in softwoods the lignin content in middle lamella is around 70 % of the total material. For hardwoods lignin content in middle lamella is lower. It has been noted that the lignin content can be very high in the middle lamella cell corners (10-30 % higher), where the fibres and vessels are associated.

The overall chemical component distribution and their difference between softwood (Scots pine, *Pinus sylvestris*) and hardwood (silver birch, *Betula pendula*) can be seen in Figure 3. Typical chemical composition for woody feedstocks used for pulping can be seen in Table VI.

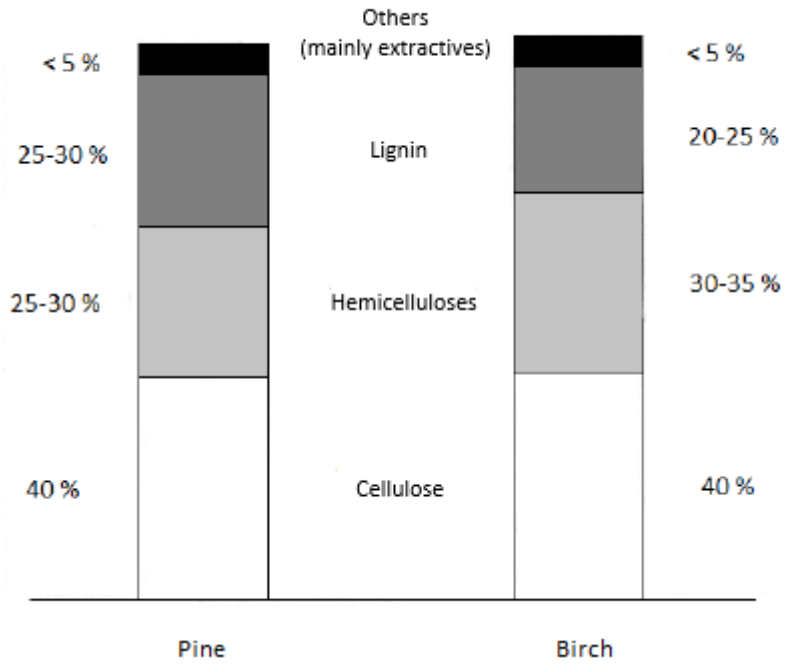


Figure 3 The chemical compositions of pine and birch (Stenius, 2000)

Table VI Typical chemical composition of woody feedstocks used for pulping (Stenius, 2000)

Component	Woody feedstock (% of the feedstock dry solids)
Carbohydrates	65-80
Cellulose	40-45
Hemicellulose	25-35
Lignin	20-30
Extractives	2-5
Proteins	< 0,5
Inorganics	0,1-1
SiO_2	< 0,1

3.1 Cellulose

Cellulose is a dominant structural compound in plant cells. It provides mechanical strength and chemical stability within the wood matrix. Cellulose is a polysaccharide with a linear chain of thousands of D-glucose units, bonded by β-1,4 glycosidic bonds. It is a natural polymer with a six-carbon ring, also called as pyranose. Each pyranose ring includes three hydroxyl groups that can interact with each other, forming intermolecular hydrogen bonds which give the cellulose its crystalline structure, strength and chemical stability. Crystalline and non-crystalline regions can be found within the cellulose. A structure of a cellulose polysaccharide can be seen in Figure 4.

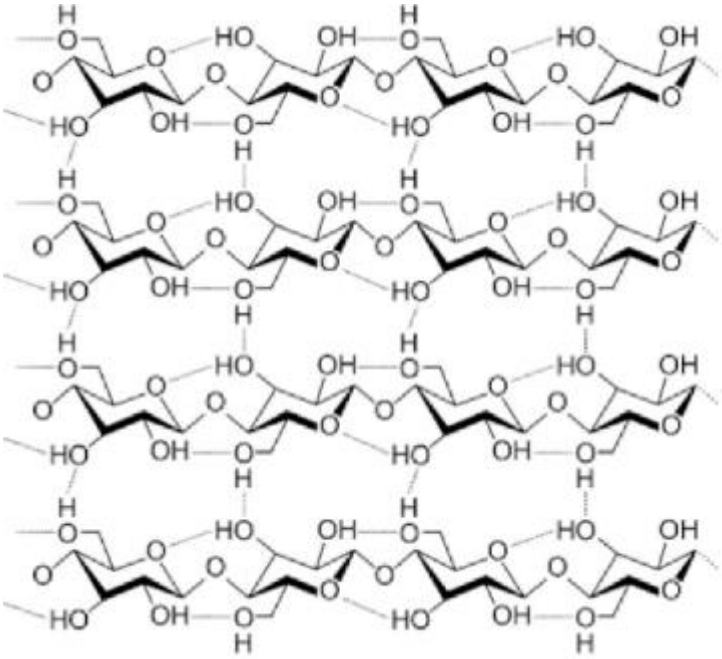


Figure 4 An illustration of a cellulose complex. (Dhyani and Bhaskar, 2018)

3.2 Lignin

Lignin is an aromatic three dimensional phenolic polymer which is constructed of random formation of differently bonded methoxyl and hydroxyl substituted phenylpropane units. These phenylpropane monomers can be characterized as syringyl, guaiacyl and p-hydroxylphenyl units (Carrier et al., 2011). Lignin is mainly found in the outer layer of the fibers and it is responsible for the structural stiffness. Also it holds the fibrous polysaccharides together. Lignin percentage varies when inspecting different wood species; the amount of lignin that can be found from softwood species varies from 23 to 33 % and 16 – 25 % in hardwoods. Cellulose fibrils are covered with hemicellulose molecules and their empty spaces are filled with lignin (Lee, Hamid and Zain, 2014). An example of a lignin complex can be seen in Figure 5.

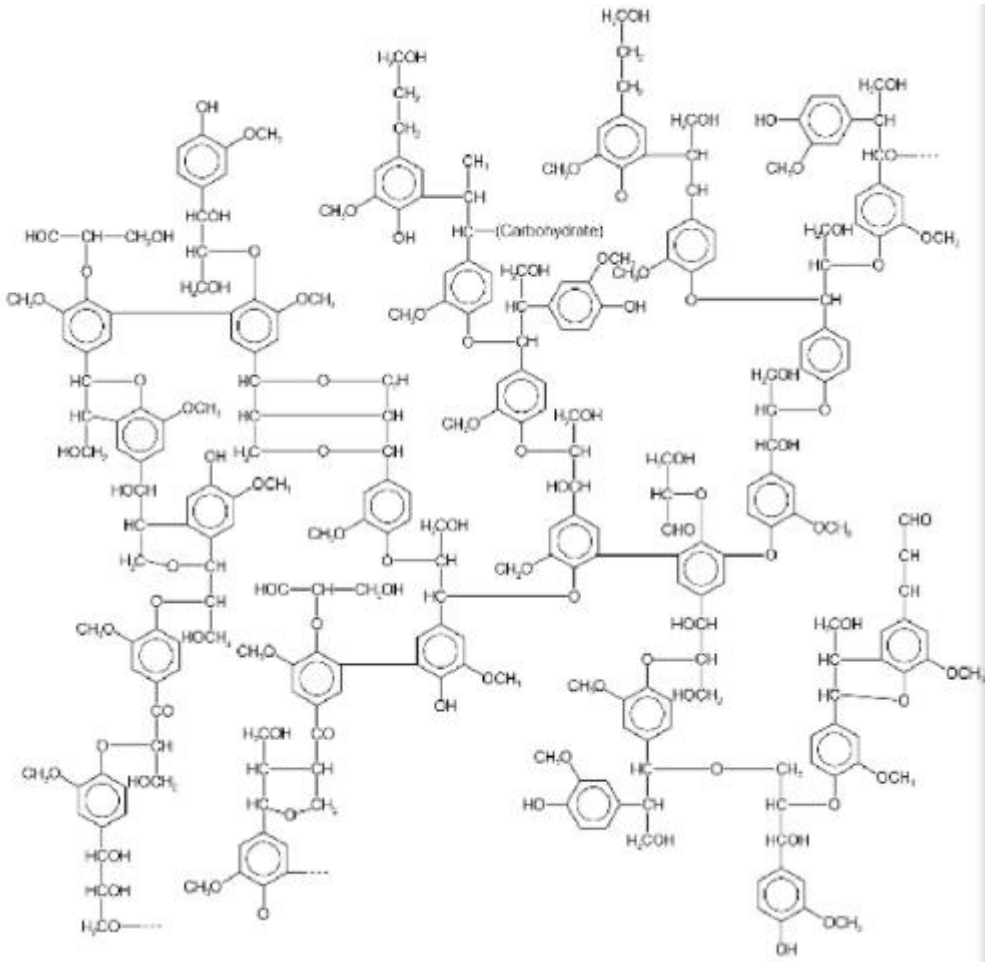


Figure 5 An illustration of lignin complex. (Dhyani and Bhaskar, 2018)

The structure of lignin varies within the wood species. Hardwood and softwood species have divergent lignin structures. The dominant lignin structure found in softwoods, guaiacyl, is a polymer with higher fractions of coniferyl phenylpropane units. Guaiacyl-syringyl structure of lignin, that is dominant in hardwood species, is a copolymer of both coniferyl and sinapyl phenylpropane units (Pandey, 1999).

3.3 Hemicellulose

Hemicellulose surrounds the cellulose fibres and works as a link between cellulose and lignin. Hemicellulose is a heterogeneous group of branched polysaccharides, containing different monomers, such as glucose, galactose, mannose, xylose, arabinose and glucuronic acid. As the hemicellulose chains differ from cellulose, hemicellulose does not polymerize as much as cellulose, thus it is amorphous with only a small amount of physical strength (Li,

2014). Structures of polysaccharides found in hemicellulose complex can be seen in Figure 6.

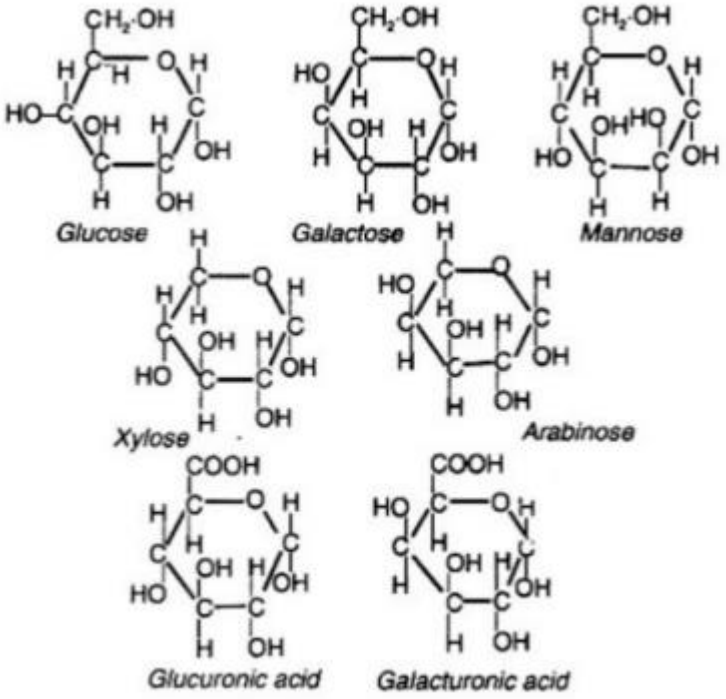
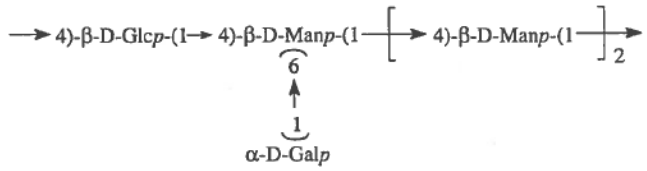


Figure 6 An illustration of polysaccharides found in hemicellulose. (Dhyani and Bhaskar, 2018)

Because hemicellulose is not hydrolysis-resistant, it can be diluted by certain acids, bases or hemicellulose enzymes.

In softwoods, the primary hemicellulose components are galactoglucomannans (glucomannan) and arabinoglucuronoxylan (xylan). Glucomannans (15 – 20 % of the total dry wood mass) are mainly located in the back of (1 → 4)-linked β-D-glucopyranose and β-D-mannopyranose units. Galactoglucomannans can be distributed into two fractions based on their galactose contents (poor and rich). In the galactose-poor fraction (2/3 of the total glucomannan), the ratio of galactose:glucose:mannose is 0,1-0,2:1:3-4, when in the rich fraction (1/3 of the total glucomannan) the ratio is 1:1:3. The acetyl group content in both of these cases is around 6 % of the total glucomannan, corresponding to one acetyl group per 3-4 hexose units. Xylan (5 – 10 % of the total dry wood mass) however is constructed of linearly structured (1 → 4)-linked β-D-xylopyranose curonic acid (4-O-Me-α-D-GlcpU) and (1→3)-linked α-L-arabinofuranose (α-L-Araf). A typical ratio for arabinose:glucuronic

acid:xylose is 1:2:8. A chemical structure for glucomannan and xylan found in softwoods can be seen in Figure 7.



Galactoglucomannan

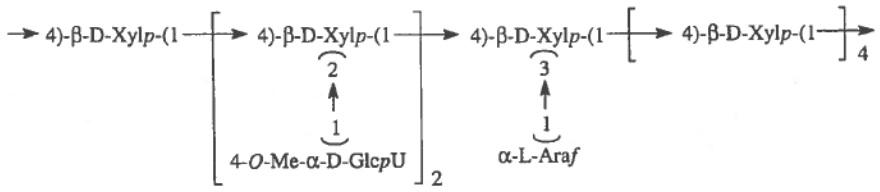


Figure 7 A partial chemical structure of glucomannan and xylan in softwoods (Stenius, 2000)

In hardwoods the primary hemicellulose components are glucomannan and glucuronoxylan (xylan). The glucomannan found in hardwoods has the same chemical framework as the glucomannan found in softwoods, except that it is unsubstituted, it is not acetylated and it has higher glucose to mannose ratio (1:1-2). While the glucuronoxylan (20 – 30 % of the total dry wood mass) has the same framework as the arabinoglucuronoxylan found in softwoods, it has less uronic acid substituents (2-3 substituents per one xylan molecule). The uronic acid substituents are not evenly distributed in the xylan chain. Xylan also contains small amounts of L-rhaminose (α-L-Rhap) and galacturonic acid (α-D-GalpU). A chemical structure for glucomannan and xylan found in hardwoods can be seen in Figure 8.

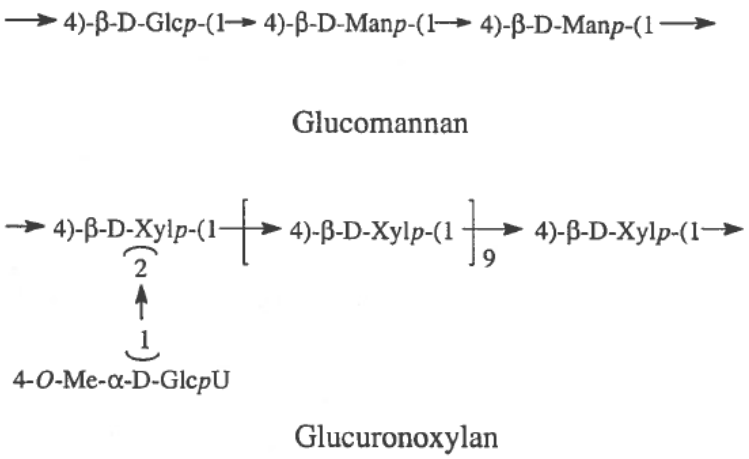


Figure 8 A chemical structure for glucomannan and xylan found in hardwoods. (Stenius, 2000)

3.4 Extractives and inorganics

In addition to previously described components, wood species also contain different extractives and inorganic components. Extractives include alkaloids, essential oils, fats, glycosides, gums, mucilages, pectins, phenolics, proteins, resins, saponins, sugars, starches, terpenes and waxes. These can be extracted from the wood using either polar, such as alcohol, methylene-chlorine or non-polar solvents, such as hexane and toluene.

The role of extractives is to work as intermediates in metabolism, working as energy reserves and plants defense against microbial attacks. (Mohan, Pittman, and Steele, 2006) Also some inorganic elements can be found within different wood species and variations between tree growing locations has been found. The amount of inorganics is small (0,1 – 0,5 % of the total dry solids in temperate zones). However, in subtropical regions, the amount of inorganics can rise up to 5 %. Table VII represents the classification of the extractives found in wood while table VIII displays the amounts of inorganics found in woods.

Table VII The classification of organic extractives in wood (Stenius, 2000)

Aliphatic and alicyclic comopunds	Phenolic compounds	Other compounds
Terpenes and terpenoids (including resin acids and steroids)	Simple phenols	Sugars
	Stilbenes	Cyclitols
	Lignans	Tropolones
Esters of fatty acids (fats and waxes)	Isoflavones	Amino acids
	Condensed tannins	Alkaloids
Fatty acids and alcohols	Flavonoids	Coumarins
Alkanes	Hydrolyzable tannins	Quinones

Table VIII The amount of inorganics found in the woods (Stenius, 2000)

Range, ppm	Element									
400-1000	K	Ca								
100-400	Mg	P								
10-100	F	Na	Si	S	Mn	Fe	Zn	Ba		
1-10	B	Al	Ti	Cu	Ge	Se	Rb	Sr	Y	Nb
-	Ru	Pd	Cd	Te	Pt					
0,1-1	Cr	Ni	Br	Rh	Ag	Sn	Cs	Ta	Os	
< 0,1	Li	Sc	V	Co	Ga	As	Zr	Mo	In	Sb
-	I	Hf	W	Re	Ir	Au	Hg	Pb	Bi	

4 BCTMP process

Raw material for BCTMP (bleached chemi-thermomechanical pulp) process can be acquired via purchase or production at the mill site. If raw material is made at the mill site, an additional debarking, chipping and chip screening is needed. A general BCTMP process includes chip washing unit, impregnation unit, primary refining or grinding unit with heat recovery unit, primary screening unit, reject refining or grinding unit, reject screening unit, bleaching unit(s) and a storage unit for further distribution. Different process stages are discussed later. A general concept of a BCTMP process can be seen in Figure 9.

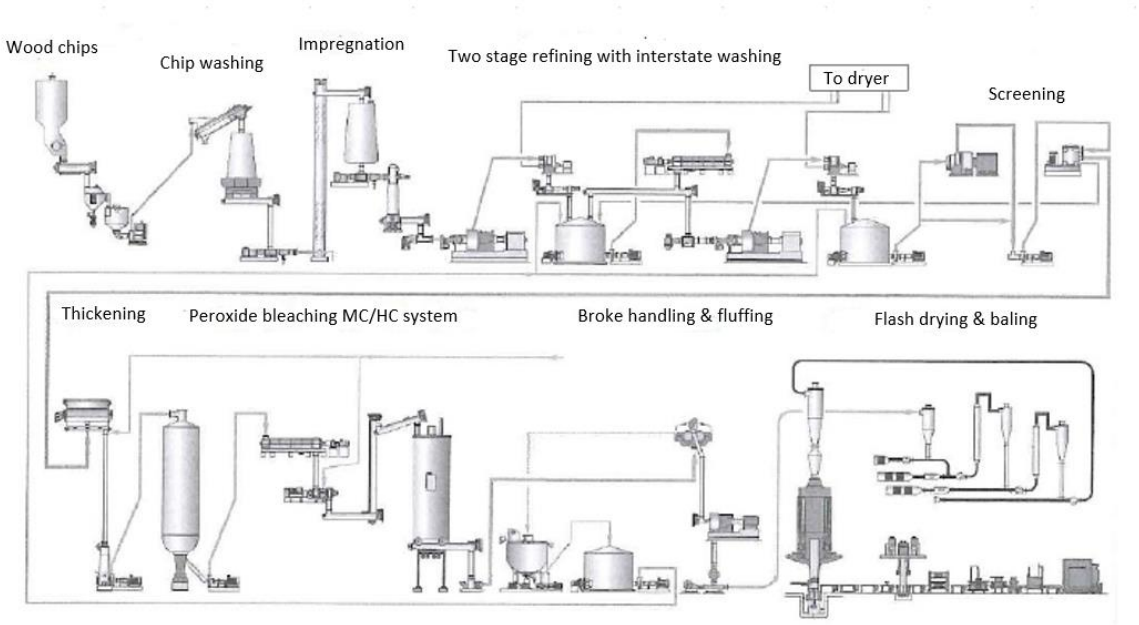


Figure 9 An illustration of BCTMP process (Lönnberg, 2009)

4.1 Chip washing

Before the chips can be used in the refining stage, the chips have to be washed from any impurities that are conveyed along with the chips, such as saw dust, sand, rocks, and heavier metallic compounds. Any impurities left in the chips could harm the refining instruments and weaken the product quality. Process water that circulates around the process is used in the chip washing stage, so any excessive water supply for this stage is not needed. Water and the chips are being mixed rapidly, which allows the impurities detach efficiently from the chips (Sundholm, 1999). An illustration of a chip washer can be seen in Figure 10.

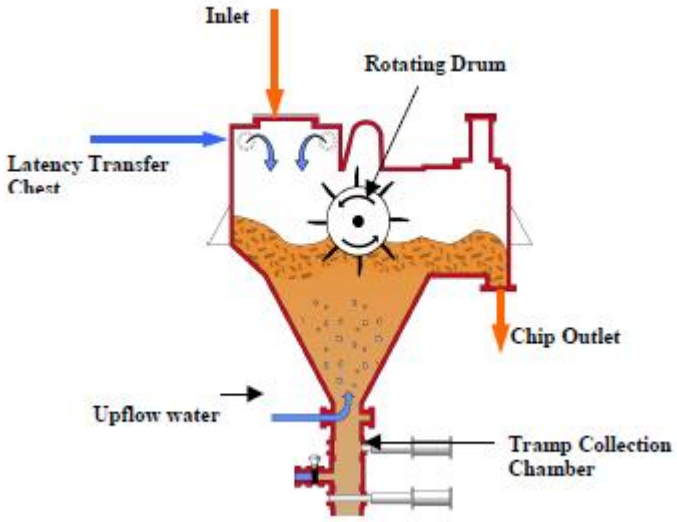


Figure 10 A chip washing unit (Courtesy of Andritz, 2001).

4.2 Impregnation

In impregnation phase the wood chips are impregnated with chemicals. Usually the impregnation is set to occur after the chip washing stage and before the refining stage. The impregnation includes chemical absorption when in contact with the chips or with the pulp. Chemicals can be added in several stages during the process (El-Sakhawy, 2005). The chemicals that are commonly used in BCTMP process for softwoods are sodium bisulfite ($NaHSO_3$) and for hardwoods sodium hydroxide and/or sodium bisulfite. Other chemicals, such as oxidized green liquor and oxidized white liquor with different mixtures with sodium hydroxide and sodium bisulfite can also be used (Lönnberg, 2009). It has been noted that adding chemicals during the pulping process enhances the product properties, thus reducing the total process energy consumption. Whether the impregnation is occurring in any of the chemical treatment stage, a successful impregnation is important because of low diffusion time between the chemicals and chips/pulp. Incomplete impregnation can result into

increased shive content, even if the average sulfonate content is high (Lönnberg, 2009; Kurra et al., 1985).

Various methods that can be used for impregnation: Steaming the wood chips and soaking them in a cold sulfite solution, using mechanical compressor to compress the chips and expanding them with a sulfite solution, spraying the chemicals on the chips or adding chemicals into the refining process (Ferritius and Moldenius, 1985). In Figure 11 an example of an impregnation unit can be seen.

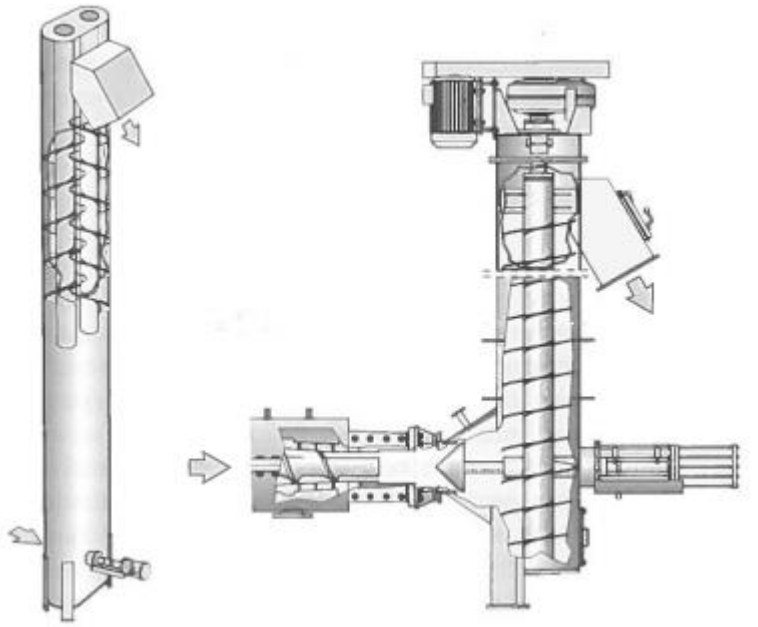


Figure 11 An example of a impregnation unit. (Lönnberg, 2009)

When producing pulp from softwood and hardwood species, the used chemical type and amount as well as conditions in the impregnation unit can have some variations. However when producing BCTMP from softwood, the following conditions have been relatively standardized: Sodium sulfate charge 2 – 4 % on the wood chips, pH 9-10, temperature 120 – 135 °C and retention time 2 – 15 min (Jackson & Åkerlund, 1984). All specified values for these parameters are chosen independently for the used process, because mills producing BCTMP have variation in process conditions compared to each other. Variation can be found in raw material and process equipment.

4.2.1 Chemical treatment

Mechanical pulping processes, especially BCTMP processes often include several chemical treatment units, such as pretreatment or interstage units with various treatment integrates or

post-treatment. Chemicals that are used in the pulping process have several effects on the raw material. The woods fibrillar matrix can be altered chemically in various ways that have a direct effect on the wood behavior in refining, giving a possibility to modify the fibre properties. Some chemicals can be used for example in pretreatment stage to soften lignin (sodium bisulfite), other chemicals have enhancing effect on sheet product properties, like strength or brightness.

There are a large amount of chemicals used in different pulping processes, however, a dominating chemical for softwood is determined to be sodium sulfide, sodium hydroxide or sodium sulfide for hardwood. Oxidized green liquor or oxidized white liquor have also expressed to be successful chemicals when considering pretreatment on chemi-thermomechanical pulping (Lönnberg, 2009). Chemical treatment generally tend to reduce the needed refining energy without affecting the wanted characteristics for the pulp. For example, alkaline peroxide treatment may reduce the energy needed in refining by 20 % (Bian et al., 2008).

Different pulping processes have different effects on the fibre rupture mechanisms. Because in BCTMP process the lignin is softened via chemicals, less wood material is broken, resulting in a lower amounts of fines. Typical rupture mechanisms for mechanical pulping processes (table I) can be seen in Figure 12.

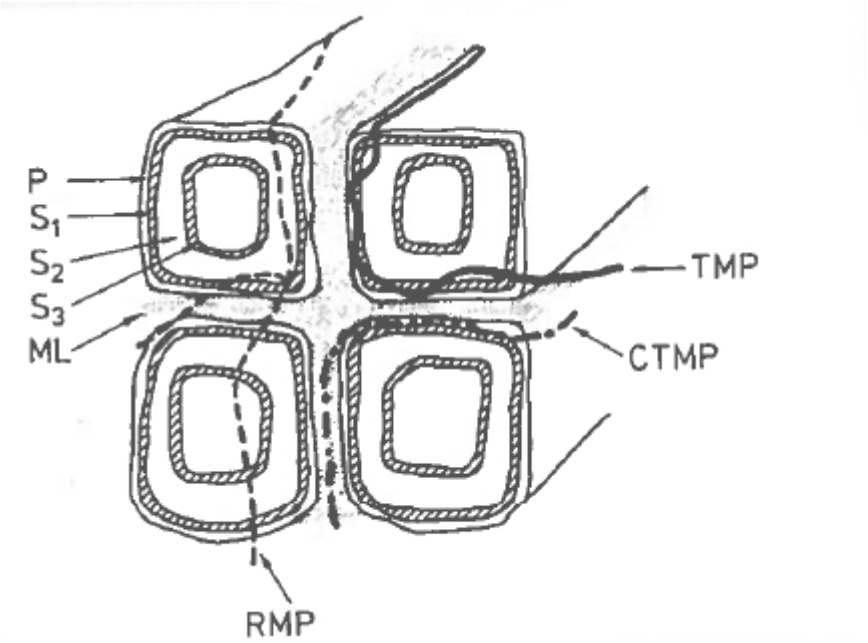


Figure 12 Typical fibre rupture mechanisms in different pulping processes. (Franzén, 1986)

In chemi-thermomechanical pulping the different fibre properties compared to other pulping processes results in a low shive content in high freeness levels. Shive content as a function of pulp freeness for TMP and CTMP processes can be seen in Figure 13.

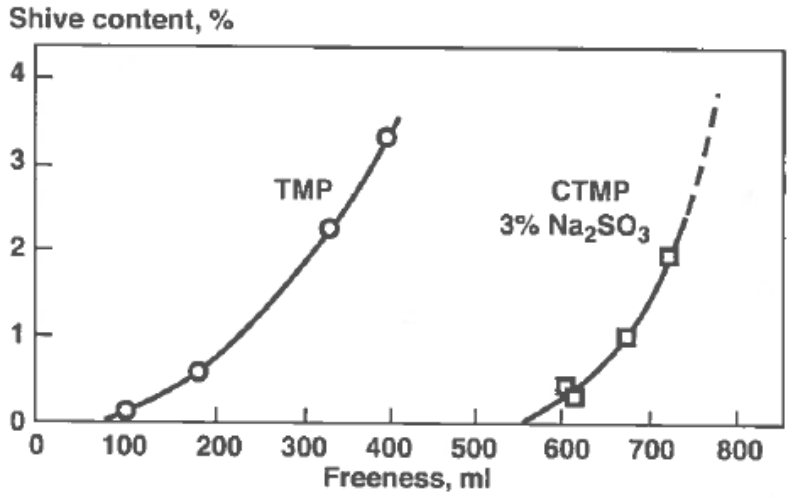


Figure 13 Shive content as a function of freeness level for TMP and CTMP processes. (Jackson and Åkerlund, 1984)

As it can be seen from Figure 13, the CTMP can be used with high freeness level, having the same amount of shives compared to TMP. The chemical treatment stages, such as pre-

treatment, interstage treatments (treatments after refining) and post-treatments play a key role in CTMP mass properties. These treatments are shortly discussed within the next chapters.

4.2.1.1 Pretreatment

The principle of pretreating stage is to enhance the pulping performance. Pretreating the chips offer great potential for modifying pulp properties because of its direct impact on the fundamental fiberizing stage. When pretreating softwood species, dominant chemical used is alkaline sulfite. Hardwood treatment usually includes alkali, with or without sulfite or peroxide. Hardwood species that need some kind of pretreatment, such as birch, can be treated with a integration of modified alkaline stage (removal of carbohydrates) and sulfate stage (softening of lignin). There are some variations how the species even inside one species react with this pretreatment method. However, the variations are results of the abnormality of the species growing environment, not from the pretreatment itself. Especially in BCTMP production alkaline peroxide pretreatment combined with high consistency peroxide bleaching is often applied.

4.2.1.2 Alkali treatment

The purpose of alkali treatment is to treat the carbohydrates found in wood tracheids. White liquor is a dominant alkali source in mechanical pulp mills (Hutterer et al., 2017). A synthetic white liquor that is used in industrial mechanical pulp mills is consisted of sodium sulfide, sodium hydroxide and sodium carbonate. Xylan is one of the hemicellulose groups that is found in hardwood and softwood species. It is an alkaline soluble compound that can be removed from the pulp with caustic treatments. Getting rid of almost all of the hemicellulose is desirable. As the hemicellulose is dissolved, it has some decreasing effects on the conversion in alkaline processes. Hardwood species generally contain more xylan than softwood species.

4.2.1.3 Enzyme treatment

Enzymes are biological catalysts that reduce the activation energy of the process to start and accelerate the chemical reactions. In mechanical pulping enzyme treatment can be applied for example as a prior treatment of wood chips to enhance the separation of xylose into a more liquefied form. Enzymes are quite sensitive for operation condition variations. To gain

maximum benefit from enzymatic treatment, steady process conditions are necessary. It should also be noticed that there is no universal enzyme that comprehends the same way with different wood species and operating conditions, so a specific enzyme have to be developed for the pulping process.

4.2.1.4 Interstage treatment

Chemi-thermomechanical pulps can be produced via various combinations of mechanical operations and chemical treatments. Interstage treatments take place inside the process. In chemical interstage treatments the chips or pulp can be impregnated and conveyed at the same time, or the absorption can occur in a specified interstage vessel. If so, the vessel have a certain retention time and the mass will be hold in the vessel before pumping it further to the process. Interstage treatment can be used to prepare chips/pulp for a certain unit operation or to remove some impurities that are still attached to the chips/pulp. For example, EDTA (ethylenediaminetetraacetic acid) is used to get rid of metallic compounds that can be found in the mass.

4.2.1.5 Post-treatment

Post-treatment can be combined with all types of mechanical pulping processes, no matter whether they include refining or grinding. Post-treatment does not have any effect on releasing fibres from the wood and therefore the modifications for the fibre and pulp properties are limited. For wood species that tend to have low bonding properties, for example peroxide can be added for enhancing the bonding properties while bleaching the pulp. While mechanical pulping post-treatments are mainly based on the application of enzymatic hydrolysis, caustic extraction and ionic liquid extraction, a possible upgrade for the post-treatment process could also be made by focusing on the removal of hemicellulose fractions. (Gehmayr, et al., 2010; Ibarra et al., 2009; Janzon et al., 2006; Froschauer et al., 2013 ; Roselli et al., 2014)

4.3 Refining

Probably the most important aspect when considering chemi-thermomechanical processes is related to the changed behavior of the wood fibres in the mechanical refining stage (Lönnberg, 2009). The main principle in refining, as it works as a mechanical defibration process, is to get the wooden raw material into a vacillated cyclic motion and stress, where

the wooden raw material absorbs the mechanical energy formed in the process, breaking down the fibrous framework. The fibres are separated from the wood and from each other.

The most important parameters in the refining stage are SEC (Specific Energy Consumption) and freeness. The freeness (pulps water filterability) of the chemi-thermomechanical pulp is highly dependent on the SEC value. Refining stage is often modeled by plotting freeness as a function of SEC. Processes that apply chemical treatments with yields above 85 % when operating with softwood will have higher SEC for achieving the needed freeness value. However, strong interstage treatments can reduce the SEC value for the second refining stage. For achieving suitable pulp quality, the SEC can be adjusted in both refiner stages (if operated with two stage refiner process). This can mainly be done by altering the freeness level of the pulp.

Because the refining efficiency is highly dependent on the equipment used in the refining stage, several improvements have been made for example considering refiner blade patterns in the past years. A common refiner unit is a disc refiner, which grinds the chips to a certain fibre fractions. The fraction margin and the fibrillation degree can be altered by modifying the discs physically or changing the operation parameters, such as disc rotation speed and gap between discs. The refiner disc unit consists of two discs that have a certain physical pattern that is designed to optimize the fibrillation when refining the pulp. An illustration of a disc refiner can be seen in Figure 14.

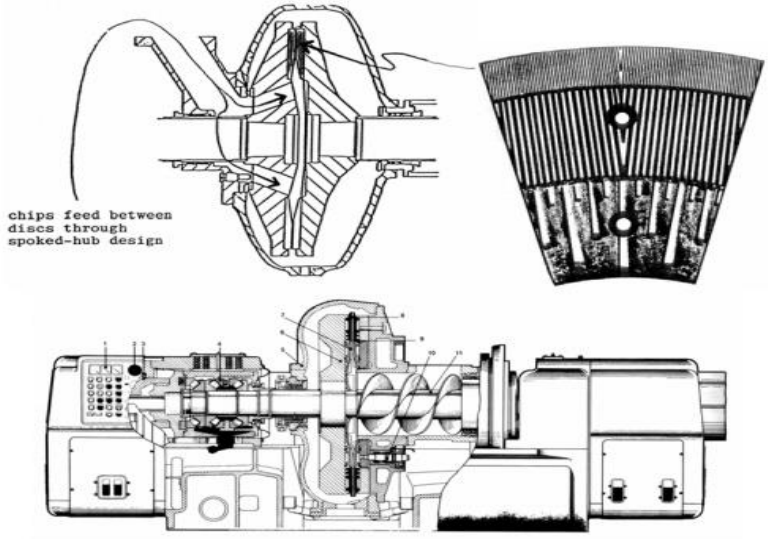


Figure 14 A double disc pulp refining unit. (Lumiainen, 1998)

The characteristics of the grindstones in the grinder unit have severe effect on the grinders' production rate, SEC and naturally the product quality. These features have been under a development for many years, and they still are. Features such as the overall grinding process, grinder type thus wood species selection and consistency should be taken into account. The right grindstone selection and optimizing the grinding conditions however are the most critical factors. (Lönnberg, 2009)

4.4 Latency removal

A phenomenon occurring in any thermomechanical pulping process is the latency generation, which generates twisted and curled fibres. Latency removal is therefore critical in chemi-thermomechanical pulping. The removal efficiency of latency is a major factor when considering the quality of the final product. The basic principle in latency removal is to separate and straighten the fibres, making the pulp accessible for the following unit operations in the pulping process and improve the flexibility and strength of the fibres. If no latency removal is executed, poor product quality, low strength level and high freeness levels cannot be avoided (Beath et al., 1966).

The formation of latency is a result of a change in fibre morphology because of the extreme conditions the fibres go through in the mechanical pulping process. The goal of latency removal is therefore to restore the fibres to their original isolated state after the refining stage via deflocculation and fibre straightening. The formation of fibres are dependent on the nature and the intensity of the mechanical pulping process. The changes in fibres can occur in three ways (Page, 1989; Seth et al., 1992, Page et al., 1985):

- Change in fibre surface – new external surfaces are developed as going through the fibrillation or new internal surfaces can be developed via fibre wall stratification;
- Change in fibre length – an increase in the overall length of fibre via swelling or decreasing in length due to cutting or fibre break;
- Change in fibre morphology – development of deformations, such as curls, dislocations, kinks and crimps.

The latency removal unit is usually a large CSTR (Continuous Stirred Tank Reactor), where the pulp is mixed with water in low consistency (2 – 4 %), temperature (70 – 80 °C) and in some cases also with chemicals for impurities removal. Latency removal can occur in one or more vessels.

Wood fibres are consisted mainly of cellulose, hemicellulose and lignin (see tables I-III and figures 1-2). The outer cell wall can be described as a crystalline shaped, rigorous microfibril cluster that is surrounded by a matrix of amorphous lignin and hemicellulose (Page, 1976; Salmén and Olsson, 1998). A display of organization of cell wall components can be seen in Figure 15.

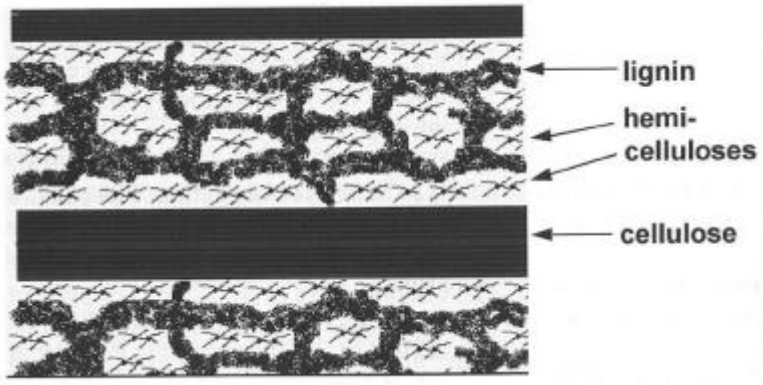


Figure 15 The organization of cell wall components (Salmén and Olsson, 1998)

When inspecting cell walls, cellulose plays a dominant role as a compound. A tight cellulosic crystalline shaped form makes it to be unpenetrable to water, making it insoluble in water. However, the non-crystalline sections and amorphous parts in the cellulose matrix allows water to penetrate, which will result into a breakdown of hydrogen bonds, causing a swelling phenomenon in the cellulose matrix (Müller et al., 2000).

One major factor in fibre deformation is the lignin stiffening in the wood matrix (Beath et al., 1996; Jones, 1996). The high temperatures in refining is softening the lignin in the fibres, making them to curl. When the fibres are cooled, the temperature change will cause the lignin in the fibres to stiff, resulting a fibre deformation and the curling is permanent. Even though the crystalline-shaped cellulosic fibrils tend to have resisting properties for the deformation phenomenon, the overall restoring stress in the cellulose is harmonized by the hemicellulose-lignin complex. As it comes to the fibre straightening, the fibre flocs that restrict the isolated

fibres have a critical effect in preventing of fibre straightening (Kerekes, 2006). Fibres before and after latency removal can be seen in Figure 16.

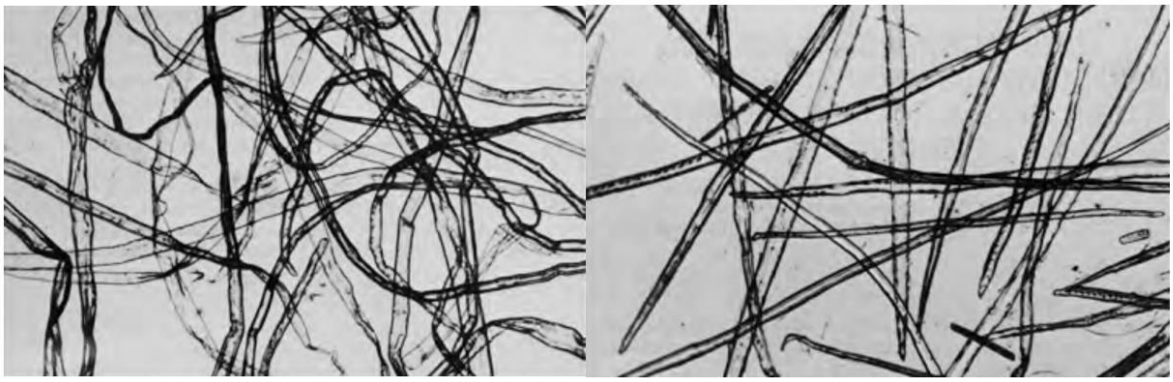


Figure 16 The effect of latency removal on fibres (Page et al., 1985)

Because the curling effect is a result of a stress force in the fibres, the basic mechanical idea in latency removal is to relieve the internal stress and tension between the lignin-hemicellulose matrix and cellulose. Softening processes for lignin will result to lignin and hemicellulose flow, which will ease the internal stresses located inside the fibres. When the lignin is not restricting the straightening and the temperature is rised in the latency removal vessel, the fibres are elastic enough to gain their straightened state. (Goring, 1963; Beath et al., 1966; Jones, 1966; Htun et al., 1988; Seth, 2006).

4.5 Screening

In screening stage, the pulp is sorted to certain fractions. After the refining/grinding stage, the pulp contains many impurities, most of them being shives and fibre clusters, but also some sand, bark and metal particles may still be attached to the fibres. Having multiple washing and screening stages within the process is recommended, because the impurities within the pulp tend to cause reduced quality in the final product, may cause instrument damage and cause runnability problems in the process. The fractions that are accepted will depend from the screening properties, such as mesh size. The smaller the shives are, more difficult they are to remove. There are also some variations from the origins of the shives; most of the large shives are generated when processing early wood and groundwood pulp shives when processing latewood (Gregersen, 1998; Gregensen et al., 2000; Svensson et al., 1994; Reme and Helle, 2000).

Shives and fibre clusters are usually separated from the mechanical pulp with pressure screening units (Lönnberg, 2009). Screening can be done via barrier screening or probability screening. The pressurized screening unit is designed so that it generates a mechanical barrier that divides the fibres into two or more flows, depending on the fibre size and flexibility. Larger particles will remain on the screening surface, while the smaller particles will go through the mesh, generating the accept flow. In Figure 17 an illustration of modern pressurized screening unit can be seen.

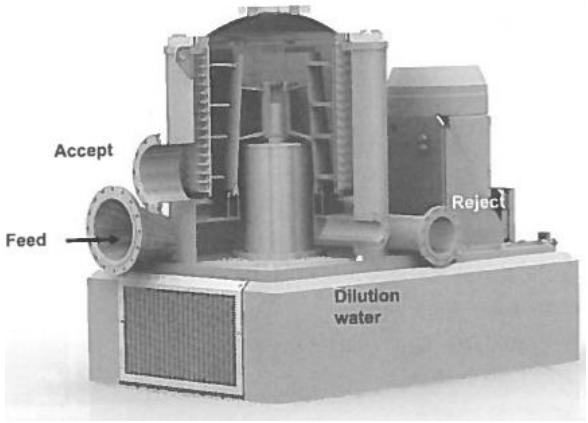


Figure 17 A pressurized screening unit (Lönnberg, 2009).

The feed is divided into a accept flow fractions, where the amount of impurities is low and to reject flow, where the amount of impurities is high. The pulp fraction in accept flow is ready for further process, but the pulp fraction in reject flow is directed to a further processing to gain the same fibre characteristics as the accept fraction flow. If the process does not contain reject processing, there would be severe effects on the process efficiency and yield. The lack of reject processing would mean that high volumes of treatable mass would be removed from the process (decreasing process efficiency and influencing the overall process capacity).

Reject fraction contains fibres that are underdeveloped when considering the wanted characteristics of the pulp. The reject flow is directed to reject refineries, where the pulp is grinded the second time to improve the fibre qualities. Screening can contain several meshes that fractionalizes the flow. The traditional way to fractionalize mass flow is via Bauer-McNett fraction method, which usually includes R16 mesh (nominal size of 1,190 mm), R30 mesh (nominal size of 0,595 mm), the short-fibre fraction R200 mesh (nominal size of 0,074 mm) and the fines fraction P200 (particles that have passed the R200 mesh)

(Techlabsystems.com, 2019). Generally however particles that are below 0,2 mm length (passes through the R50 mesh) can be called as fines (Luukko, 1998). The Bauer-McNett method is based on the length of the fibres.

4.6 Reject handling

After screening, the reject pulp is treated and refined again so, that the fibre characteristics fulfill the accept pulp characteristics. After the reject refining stage, a separate screening for reject pulp is executed. In BCTMP processes, there is no need for holed plates because of the defibrillation stage, so slotted plates for fine treatment can be used. This however demands that the reject refining is well controlled and efficient. When screening the reject pulp, a one or multistage screening process can be used. With multiple screening units the quality of the accept pulp stream is naturally better and therefore the final product quality will be higher.

The pulp is thickened when the water is removed. Pulp dewatering is often executed in multiple stages (via screw press and screen press). A pre-thickening unit can be applied to increase the pulp consistency to 3 – 5 % before the final thickening stage, where the consistency will be 30 % or higher. The screw press is the most commonly used because of its low cost of investment. In Figure 18 an industrial screw press can be seen.

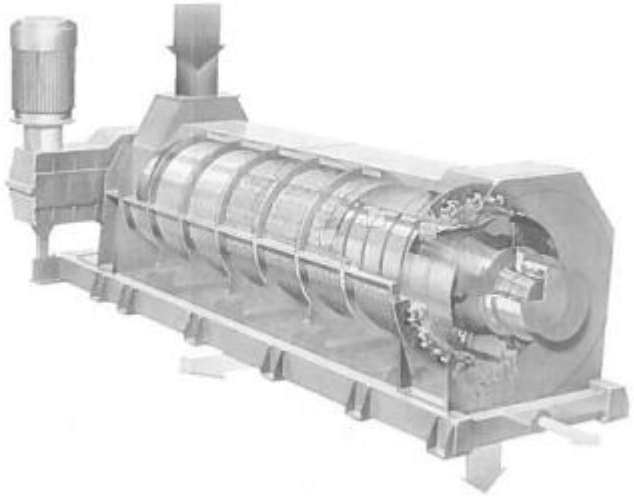


Figure 18 A screw press (Lönnberg, 2009)

The principle of a screw press is quite simple and one of the advantages are both maintenance and operational supervision reduction. However, because certain parts of the screw press are

operated under high pressure and torque, the interiors in these parts will be influenced by wearing. Wearing may be enhanced if the pulp contains any unwanted solid particles.

4.7 Pulp bleaching and washing

The objective of bleaching in different pulping methods is the same; to increase the brightness of the pulp. In BCTMP the bleaching methods are based on treating of residual lignin found in the fibres. This can be done in MC (Medium Consistency) and HC (High Consistency) bleaching units, where the bleaching chemicals are added to the pulp mass. High brightness levels (85 - 87 % ISO) can be achieved in BCTMP process. Even though high brightness levels could be achieved, it would require optimum and steady process conditions through the pulping process. Therefore, the final ISO (International Organization for Standardization) brightness levels are usually set a bit under the maximum achievable level and the product properties are always discussed with the customer. A graphical concept of bleaching stages can be seen in Figure 19.

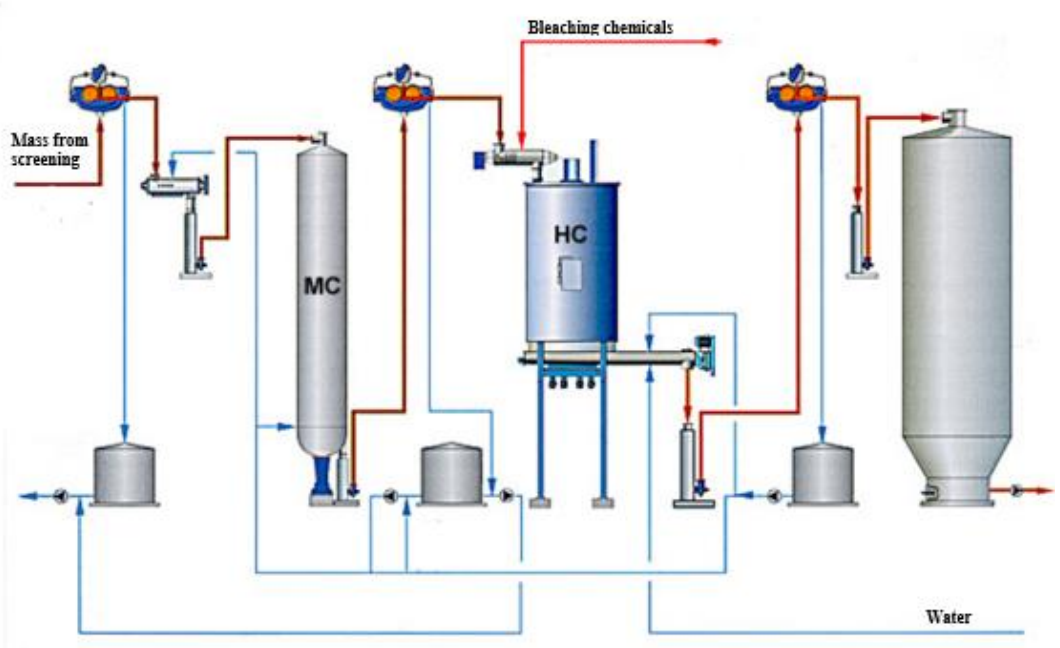


Figure 19 An example from MC/HC bleaching stage. (Knowpulp.com, 2019)

In general pulp brightness can be determined using pulp sheets' the light-absorption capacity and light-scattering ability. When analyzing the optical properties of pulp, a theory founded by Kubelka-Munk can be applied (Kubelka and Munk, 1931). It concludes the relation between pulp optical properties. The relation can be seen in equation 2.

$$R_\infty = 1 - \frac{k}{s} - \sqrt{(\frac{k}{s})^2 + 2(\frac{k}{s})} \quad (2)$$

where R_∞ is the brightness
k the light-absorption coefficient
s the light-scattering coefficient

The light-absorption coefficient is a measure of the quantity of colored substances in the pulp, while the light-scattering coefficient depends on the pulping method. As the brightness level of the pulp increases, light-scattering coefficient increases, thus the light-absorption coefficient decreases. This can be seen in Figure 20, where the relationships between light-absorption and light-scattering coefficients were determined for various brightness levels for various wood species.

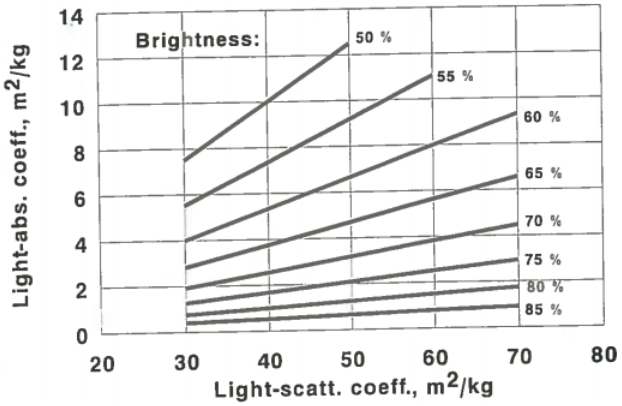


Figure 20 The relationship between light-absorption and light-scattering coefficients at various pulp brightness levels. (Lönnberg, 2009)

Cellulose and hemicelluloses, which belong to the main components of wood, are relatively colour-free. Lignin on the other hand is the main source of colour in wood species. The colourness is not homogenic in lignin, but it contains certain functional groups called chromophores that absorb light, making the wood look like coloured. The main functional groups in chomophores are coniferylaldehyde groups, α-carbonyl groups and different variations of quinone structures. The occurance of these functional groups in lignin can be seen in Figure 21.

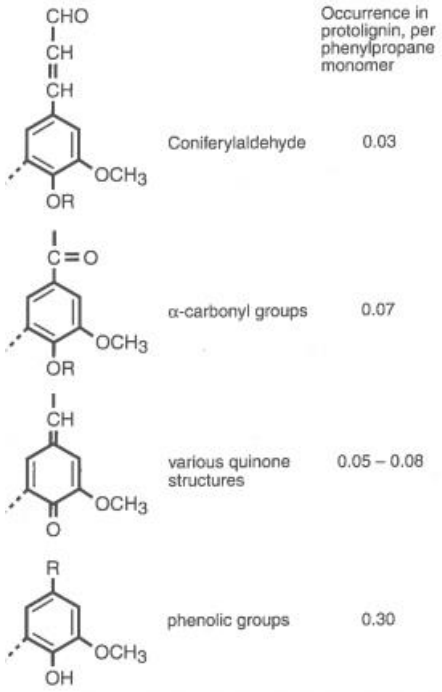


Figure 21 The occurance of chomophores in lignin. (Rydholm, 1965)

Phenolic groups found in lignin are not necessarily coloured. The appearance varies in different temperatures. When temperature rises in certain stages in the pulping process, the coloured structures may be emerged. The total value of light-absorption coefficient in wood species varies as the composition and amount of chomophores vary. The amount of extractives for example varies between species, and they contribute in the brightness difference. However, generally the total amount of extractives found in wood is relatively small when compared to chomophores found in lignin. Impact to the light-absorption coefficient by the main components of wood can be seen in Table IX.

Table IX The contributions to the light-absorption coefficient by the main wood components (Norway spruce) (Lönnberg, 2009).

	Relative amount	**Light-absorption coefficient, m^2/kg**	**Contribution to the light-absorption coefficient of the pulp, m^2/kg**
Carbohydrates	0,70	0,35	0,25
Lignin	0,28	20	5,6
Extractives	0,02	7,5	0,15
Whole pulp	1,00	-	6,0

As seen in table IX, the amounts of carbohydrates and extractives compared to lignin are relatively small and over 90 % of the coloured substance comes from lignin and its functional groups.

As the main goal of pulp bleaching is to increase the overall brightness of the pulp, it can also have other functions, such as reduction of extractives or/and increasing the fibre bonding properties and therefore the overall strength of the pulp sheet. When applying the bleaching on chemi-thermomechanical pulp, removal of all lignin would need several chemical treatment steps, resulting to a low pulp yield. Therefore the bleaching of chemi-thermomechanical pulp is focused on the neutralization of the specified lignin functional groups that cause the colourness. Pulp should be properly washed before the bleaching stage, because of the possible amounts of carry-over sulfite that may significantly diminish the bleaching efficiency by consuming the peroxide.

4.7.1 Peroxide bleaching

Hydrogen peroxide (H_2O_2) is a colourless liquid that dissolves in water completely. In peroxide bleaching there are two reactions that compete between each other in the presence of alkali. Hydrogen peroxide and sodium silicate are the main sources of alkali in bleaching. Other reactions will increase the brightness and other one reduces the brightness due the alkali that is present in the reaction. Therefore it is important to optimize the reaction conditions so, that the reactions which increase the brightness will be maximized and the reaction that effects on the decomposition of brightness will be minimized. The main mechanism for the elimination of the chomophores is executed via perhydroxyl anion (OOH^-). The formation of perhydroxyl anion can be seen in reaction 3:

$$H_2O_2 + OH^- \rightarrow OOH^- + H_2O \qquad (3)$$

Enhancement for the perhydroxyl anion can be made either by increasing the pH or by increasing the temperature. Hydrogen peroxide decomposes rapidly under the bleaching conditions according to the reaction 4:

$$2H_2O_2 \rightarrow O_2 + 2H_2O \qquad (4)$$

A stabiliser agent, sodium silicate or magnesium salts, is usually added to the bleaching stage (Le Févre et al., 2001). These salts tend to improve the hydrogen peroxide bleaching by deactivating the transition metal ions, reducing the catalytic activity towards the hydrogen peroxide decomposition. However, when using sodium silicate, some scaling problems may occur in the process equipment and piping system (Seccombe and Crowe, 2007). Transition metals, such as iron, manganese and copper which can enter to the bleaching process within the raw material or/and within the process water have a catalytic effect on the peroxide decomposition via radical mechanisms shown in the reactions 5, 6, 7 and 8 (Colodette et al., 1988; Asgari and Argyropoulos, 1998):

$$H_2O_2 + M^{n+} \rightarrow M^{(n+1)+} + HO^- + HO\cdot \quad (5)$$

$$OOH^- + M^{(n+1)+} + HO^- \rightarrow M^{n+} + H_2O + O_2^{-}\cdot \quad (6)$$

$$M^{(n+1)+} + O_2^{-}\cdot \rightarrow O_2 + M^{n+} \quad (7)$$

$$O_2^{-}\cdot + HO\cdot \rightarrow O_2 + HO^- \quad (8)$$

Where M is the transition metal, $O_2^{-}\cdot$ is a superoxide radical and $HO\cdot$ is a hydroxyl radical.

A possibility for metals entering the bleaching process is a dissolvement from the process equipment themselves. Reason for the hydrogen peroxide consumption by the transition metals is that they promote the decomposition of perhydroxyl anion and formation of radicals (Abbot and Hobbs, 1992; Bambrick, 1985). Because of this scenario, the amount of metal compounds in the pulp must be reduced with a chemical treatment stage before the pulp reaches the bleaching stage, for example with chelating agents or acid, such as EDTA (ethylene diamine tetra-acetic acid).

However, removal of metal compounds from the fibres can be successful only if the bond generated between the chelating agent and metal ion is greater than the bond between the fibre and metal ion. The dose of the hydrogen peroxide added to the bleaching process has a significant impact on the brightness of the pulp. Even a small dose of peroxide added to the pulp will have an increase of 6 – 8 % ISO on the brightness. Pulp brightness can be increased up to 15 – 20 % ISO when adding peroxide correctly and when operated in optimum conditions (Lönnberg, 2009). The bleaching response for different pulp types were analyzed by Kouk et al., 1989. Results can be seen in table X.

Table X The ISO brightness increase when bleached with hydrogen peroxide (2,5 %) for themomechanical pulp (TMP), chemi-thermomechanical pulp (CTMP) and chemimechanical pulp (CMP). (Kouk et al., 1989).

Pulp type	Sulfonate content, % on pulp	Peroxide consumption, % on pulp	Brightness increase %, ISO
TMP	-	2,2	12,3
CTMP	-	1,7	15,0
CMP 1	1,3	1,0	11,7
CMP 2	1,6	1,2	11,4

When pulp is bleached with hydrogen peroxide, some of the substances will be removed from the fibres, which results in an increased strength of the fibres. The higher alkaline concentration also seem to favour the strength development and better yield. This occurs because high alkalinity concentration increases dissolution of pulp and increases the formation of carboxylic acid groups, which improves the fibre bonding properties, the swelling characteristics and fiber wall flexibility. Softening lignin and removing extractives will make the fibres more hydrophilic, which will also improve the overall fibre bonding properties (Korpela, 2002; Pan, 2004; He et al., 2005; Tchepel et al., 2006).

4.7.2 Sodium hydroxide and pulp pH

The pH level is an important parameter when considering pulp bleaching. Too high pH levels will have a negative effect on the perhydroxyl anion formation and the decomposition reactions will be enhanced. The optimum pH will depend on the wood and pulp type, reaction temperature and retention time, dose of the added peroxide and pulp consistency and the wanted fibre properties, such as strength and bulk. The silicate added to stabilize the process will generate a buffer to the pH, so in this case the pH is not a good control parameter, even though the formation of bleaching compound of peroxide is dependent on the available free alkali. When the peroxide reacts in stabile conditions, the optimum pH is quite high (10,5 – 11.5). Optimal conditions in this case includes the low concentration of transition metals. For this stage, a suitable control parameter instead of pH, would be the ratio of total alkali to peroxide fed to the system.

4.7.3 Sodium bisulfite

Sodium bisulfite ($NaHSO_3$) can be used as a bleaching agent for pulp, as it tends to react with the conjugated carbonyl groups, generating sulfonic acids. With 1 % addition of sodium bisulfite, an increase of 3 – 4 % (ISO) on brightness can be achieved (Lönnberg, 2009). It is possible to achieve even 6 – 7 % (ISO) increase on brightness by increasing the sodium bisulfite dose, but economically it is not often worth it. Sodium bisulfite can also be applied to pretreatment stage. When adding bisulfite in the early stage of the process, some chromophores can already be destroyed in the early stage of the process. This leads to the reduction of the light-absorption coefficient, resulting in an increasing effect on pulp brightness.

4.7.4 Pulp washing

Pulp washing is probably the most common unit operation in the mechanical pulping process. The purpose of this stage is to separate any undissolved impurities from the pulp. Pulping process can include several washing stages both before and after bleaching. The after bleaching washing stage is used to separate dissolved substances from pulp after the bleaching reactions have taken place.

Washing of pulp usually is consisted of two factors: first the pulp mass is squeezed with a screw or plug press to remove impurities within the filtrate and then the mass is blended with water again. This procedure can be done multiple times and it usually is. However, it is often difficult to determine the exact number of required washing stages; at what point the benefit of washing is not any more profitable considering the pulp purity.

4.8 Drying

Before the pulp is distributed to the clients, it is dried and suggested to be squeezed to bales of 600 – 800 kg/m^3 to reduce storage and transportation volume (Gullichen and Fogelholm, 2000). Evaporation is executed either by heating the pulp with steam heated cylinders or by blowing hot air into the pulp. This so called flash drying includes pulp thickening (35- 45 %), following with a fluffer and a hot air mixer. The hot air is gained from oil or gas burner or preheated air unit.

5 BCTMP end product properties

BCTMP is mostly used for manufacturing paperboard and folded boxboards, where it is used as the middle layer in the multilayer paperboard product. These board types usually include three structural layers (outer layer, middle layer and inner layer). Normal square mass for FBB is ranging between 200 – 400 g/m^2. While the final PB (Paper Board) or FBB (Folded Box Board) product is required to have certain stiffness, which is lastly obtained by optimizing the layering structure, it is also required to have certain surface properties. Because the final product will often be used to deliver certain products to consumers, which can include edible materials, the BCTMP mass cannot include any substances that would have influence to either smell nor taste characteristics. Most important features considering BCTMP mass are strength in every dimension, neutrality (hygienic aspect) and bulk.

5.1 Bulk

The final mass density is reported as bulk. Bulk is presented to be a complement of density and it can be calculated with the equation 9 (Levlin, 1999):

$$Bulk = \frac{1}{\rho} = \frac{1}{cm^3/g} = \frac{cm^3}{g} = \frac{g/m^2}{\mu m} \quad (9)$$

Bulk can be calculated by dividing the measured pulp mass per square meter with the average thickness of a measured pulp sheets. Bulk is wanted to be as high as possible. When comparing different bulk levels, higher bulk level means that the same weight of the mass is obtaining more volumetric area, as seen in Figure 22.

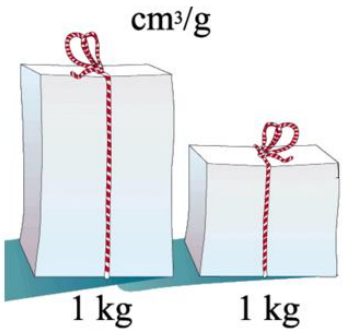


Figure 22 The comparison between higher and lower levels of bulk. (KnowPap.com, 2019)

As the BCTMP is working as a middle layer in the paperboard, the bulk value of pulp directly relates to the stiffness of the paperboard or FBB. The middle layer is wanted to be as thick as possible, resulting in a stiff, thin and reliable product without rising the total material needed to make the final paperboard or FBB product. Higher fibre stiffness contributes with a lower density pulp sheet structures. Bulk value however does not correlate with the product quality alone. Even though high bulk value is wanted, it would be gained by having high amounts of long fibres and low amounts of shives. High amounts of long fibres tend to generate problems when making the final paperboard product.

5.2 Tear strength

The tear strength implies the needed force to cause a certain tear in the product sheet. Two factors can be considered to affect in the tear strength: the force needed to pull out fibres that remain intact and the force needed to break the fibres. Factors affecting to the pullout force for the intact fibres are the friction resisting the pulling, force needed to break the fibre bonds. In latter case fibre bonding force is greater than the pulling force, and resulting into broken fibres. The overall force is consisted of each fibre strength. The mechanism for determining tear strength can be seen in Figure 23.

Figure 23 An illustration of a tear strength test for a paper or paperboard. (KnowPap.com, 2019)

When wood chips are refined, at first the tear strength will increase. As the refining process proceeds, tear strength will decrease while the tensile strength increases. This is because less refined fibres bonding abilities are poorer compared to further refined fibres; refining increases the overall surface area of fibres, increases the bonding surface area and therefore fibres are harder to pull away from each other. Because the fibres are more and more branched as they are further refined, they suspend more fines and other particles which has a direct effect on pulp freeness. Some tear index values in certain freeness levels for various pulp types can be seen in Figure 24.

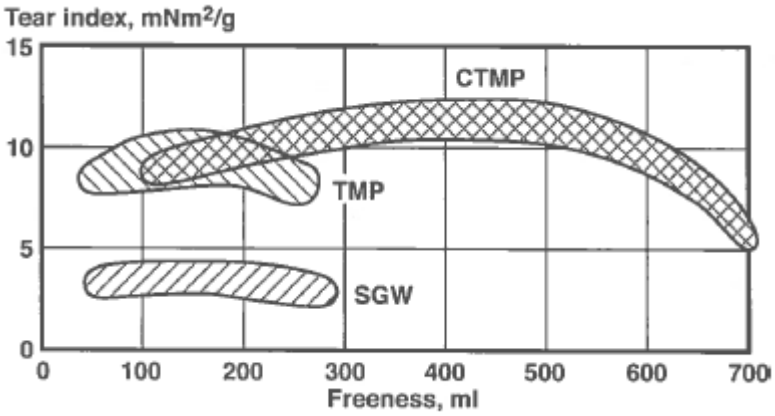


Figure 24 Tear index values for various pulp types in different freeness levels (Åkerlund & Jackson, 1984)

As seen in Figure 24, the benefit of chemi-thermomechanical pulp is that it can be produced in high freeness levels compared to other pulp types before losing tear index value (up to ~ 550 ml).

5.3 Tensile strength

Tensile strength (or pulling strength) describes the highest on plane orientated stress force the product sheet can handle before it ruptures. Certain tensile strength characteristics are required when considering the final paperboard products. These characteristics can be expressed with the tensile strength values. The principle of tensile strength test can be seen in Figure 25.

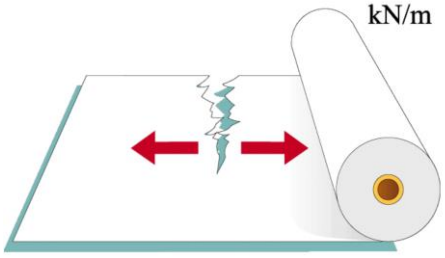


Figure 25 The principle of tensile resistance test. (KnowPap.com, 2019)

The stress force is applied in the direction of the product sheet plane and it is measured as kilo Newtons per meter (kN/m). In addition to the measured stress force, the length change (stretch) in the product sheet is also measured (the length change before a rupture occurs).

Because the square mass of different pulp and product types varies, a tensile index is calculated for better comparing purposes. The tensile index is calculated by dividing the measured tensile strength with the samples square mass and multiplied by a thousand. The tensile index is usually expressed as Nm/g. Typical tensile index values for various pulp types as a function of freeness can be seen in Figure 26 and in Figure 28 tensile index is presented as a function of pulp density.

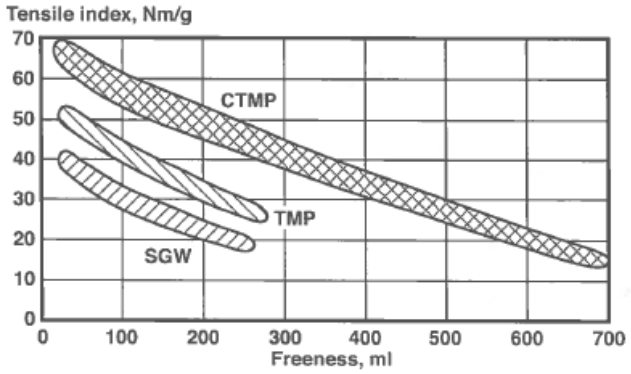


Figure 26 Typical tensile index values for various pulp types. (Åkerlund and Jackson, 1984)

The tear and tensile indexes are important parameters considering the product quality. Figure 27 presents tear index values as a function of tensile index values for various pulp types.

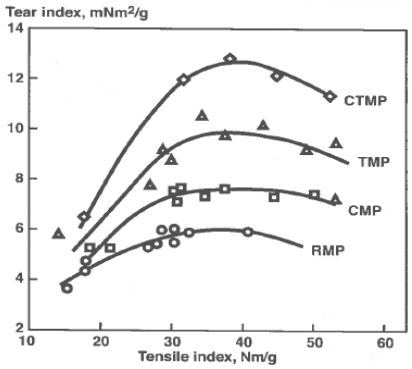


Figure 27 Tear index as a function of tensile index for various pulp types. (Atack et al., 1978)

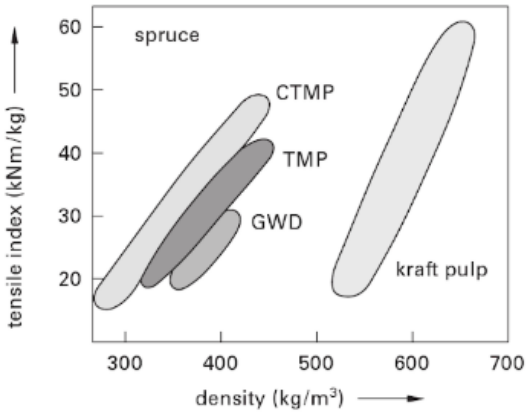


Figure 28 The relationship between strength and density for pulp sheets made from spruce (Ek, 2009)

Tensile index is one way to analyze the pulp strength. In table XI different aspects for pulp strength determination are presented.

Table XI The strength aspects considering pulp qualities. (Muchorski, 2006)

Tensile strength	Is the maximum tensile force developed in a test sample before a rupture occurs, usually presented as the force per unit width of test sample.
Stretch	Is the maximum tensile strain developed in a test sample before a rupture occurs, usually expressed as a percentage. Shows the ratio of the increase in length of the sample compared to the original state.
Tensile energy absoprtion	Is the work required when a sample is stressed to rupture in tension, measured by integral of the tensile strength over the range of tensile strain from zero to maximum strain. Expressed as energy per unit area of the sample.
Tensile stiffness	Is the ratio of tensile force per unit width to tensile strain within the elastic area of the tensile-strain bond.
Breaking length	Is the calculated limiting length of a strip of uniform width, when the strip would break by its own weight as this strip was hold from one end.
Tensile index	Represents the tensile strength in N/m divided by grammage.

5.4 Bursting strength

The bursting strength is determined by applying hydraulic pressure to the sheet. The maximum hydraulic pressure that the sample can take without breaking determines the bursting strength. Pressure is focused to the sheet through a resilient membrane while the sheet is attached on the membrane. The principle of bursting strength determination can be seen in Figure 29.

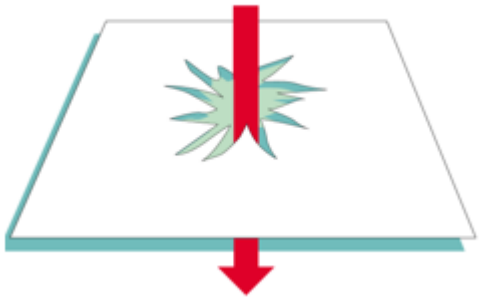


Figure 29 The principle of piercing through paperboard. (KnowPap.com, 2019)

The piercing resistance is usually expressed as kPa. It can also be expressed using a piercing index, which is the measured piercing resistance divided by square mass. The measurement can be executed for example with a Mullen-instrument or L&W bursting strength tester. The L&W tester can be seen in Figure 30.

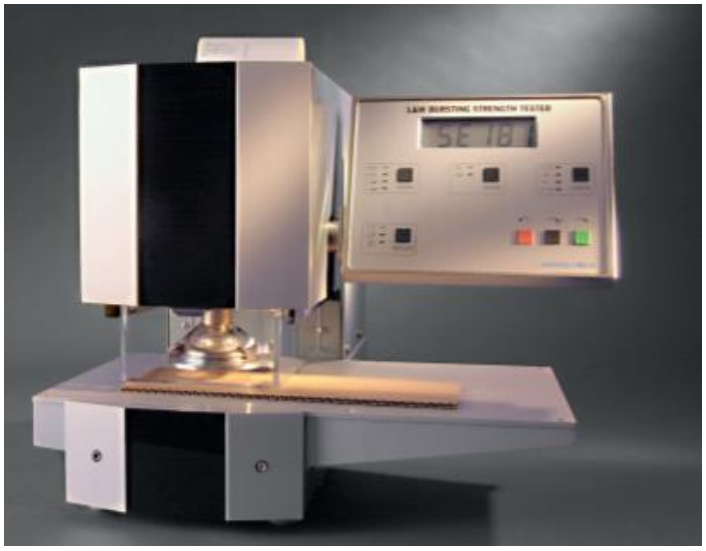


Figure 30 A L&W bursting strength tester. (ABB.com, 2019)

When testing FBB for example, the pendulums piercing head bursts through the sample. Pendulum used to burst the sample has a certain kinetic energy when getting in contact with the sample. As the pendulums head starts to pierce through the sample, the pendulum is losing a certain amount of its kinetic energy, which equals to the bursting strength of the sample.

5.5 Layering strength

Layering strength implies how strong fibres are adhering to each other in the direction of z-axis. Layering strength (or z-axis bonding strength) depends on the bonded area and the specific bonding strength between fibres. The bonded area is influenced by fibre flexibility and the amount of fines, whereas the specific bond strength is more dependent on surface characteristics of the fibres (Ek et al., 2009). Z-strength can be measured by applying tensile forces on both sides of the sheet so, that the tensile forces are orientated in opposite directions (angle between pulling forces 180-degrees). Bonding strength can also be measured with a Scott-bond method. Figure 31 and Figure 32 illustrates the principles of z-strength and bonding strength measurement.

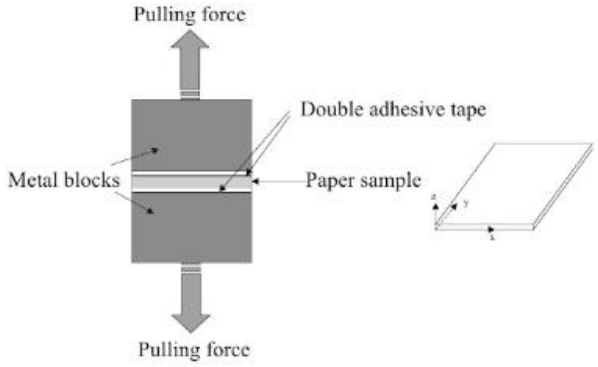


Figure 31 The principle for z-strength determination (Ek et al., 2009)

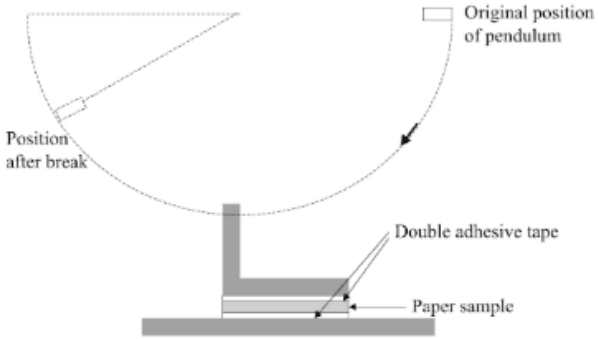


Figure 32 The principle for bonding strength determination using a Scott-Bond tester. (Ek et al., 2009)

The bonded area can be estimated using the sheet's density and light-scattering ability. The higher contact area there is between fibres, the more dense the sheet is due to more tightly packed fibres. While density rises, the light-scattering ability decreases. High density and low light-scattering ability correlates with higher bonded area.

The bonding strength can be determined as the strength in z-direction when applying tensile forces at a 90-degree angle to the plane of the sheet. There are various methods available for bonding strength testing, which of two can be seen in figures above. The principle of both methods is to measure the strength needed to tear the blocks apart (z-strength tester) and tear the metal gauge off the sheet.

5.6 Folding strength

Folding strength (or folding resistance) of paperboard is measured with an amount of back and forth folds (folding number) that the sample can take before a rupture occurs under a certain tensile loading. Folding strength can be expressed as ten times logarithm of the folding number. Folding strength describes the durability of paperboard when influenced by tensile forces that may occur during shipping or retailing. Figure 33 displays the differences between good and bad folding properties.

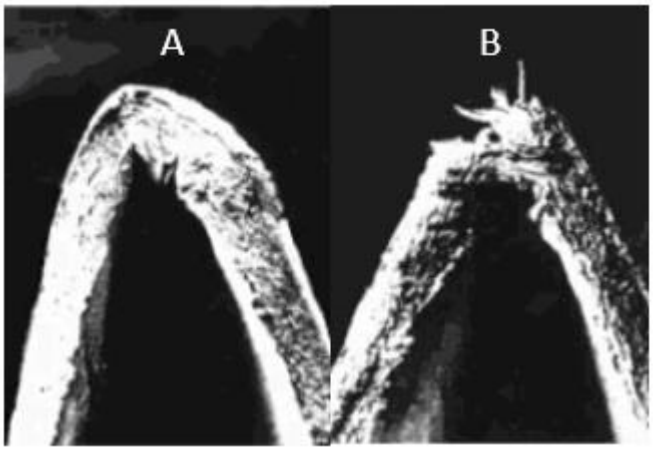


Figure 33 Illustration of paperboard folding strength. A) represents good folding strength properties and B) bad folding strength properties. (KnowPap.com, 2019)

Several factors are influencing on the folding strength properties. Dominant factors are tensile strength and elastic properties. Folding strength is measured using a constant tensile loading and the measurement is not dependent on the square mass of the paperboard sample. Folding strength increases as the square mass increases to a certain point, after this points the folding strength value starts to decrease. Products that have high square mass value, high pulling and compressing forces are found on the surface layer. Therefore there is an optimum point for folding strength and square mass ratio.

6 BCTMP fines

Fibre fractions generated in the BCTMP process, which have cell size below 0,2 mm, can be called fines as mentioned in section 4.5. These fines are assumed to be generated when the wood chips are refined. These fines have several effects on both, chemical and physical characteristics (Law and Valade, 1999). Fines are influencing for example the fibre surface properties and bonding abilities. Although pulp fines are not contaminants, they may

function as pitch and nucleation sources as high level of fines can result into dramatic drop on the freeness level of the product (Gullichsen and Paulapuro, 2000).

As mentioned in section 4.5, the traditional way to analyze the fibre sizes is using the Bauer-McNett fraction method. Typical Bauer-McNett fractions for various pulp types can be seen in Figure 34 and Figure 35.

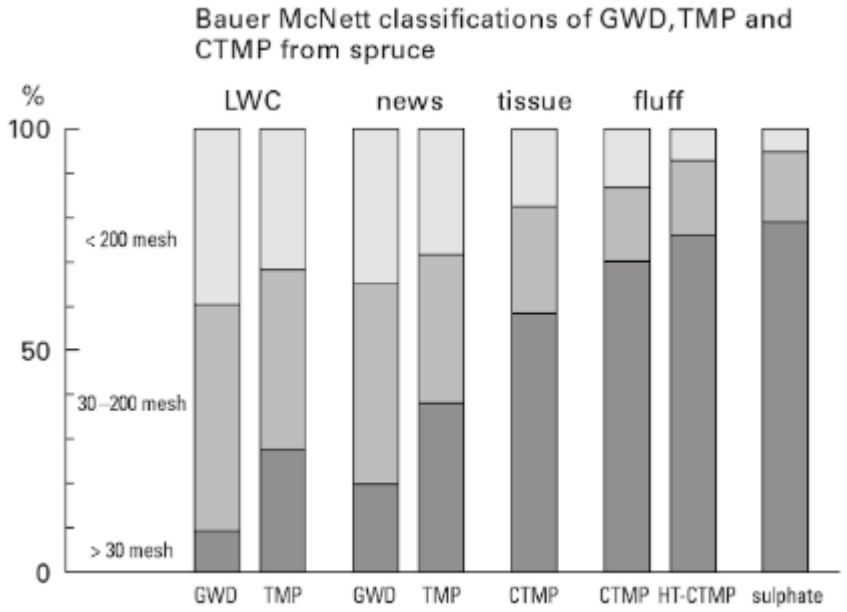


Figure 34 The Bauer-McNett fractions for GWD, TMP and CTMP. (Ek et al., 2009)

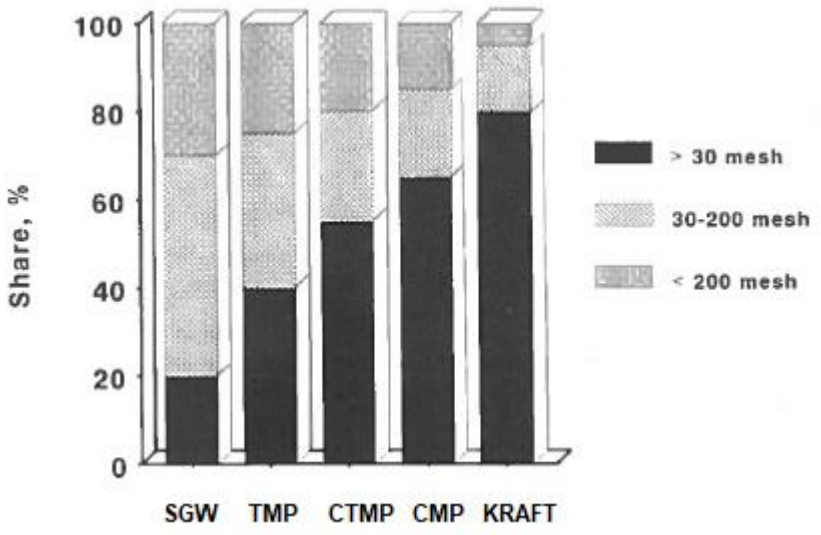


Figure 35 The Bauer-McNett fractions of various pulp types. (Lönnberg, 2009)

While these fraction values are not obtained from a BCTMP process, they can be used to estimate the fraction distribution that could be found using the BCTMP process. The

bleaching stage may influence the fines properties, but the fibre fraction could be estimated to follow same distribution values as the bleaching (B) stage comes in the very end of the process. The bleaching stage is assumed to influence the total amount of extractives. The fibre size analysis are executed in laboratory using a certain freeness level.

6.1 Generation of fines and fine types

Thermomechanical pulping processes include rough conditions that generates different types of fines. As the fibres are isolated from the wood matrix and processed into the final product, fines are also generated. The overall fine generation and path during the pulping process can be seen in Figure 36.

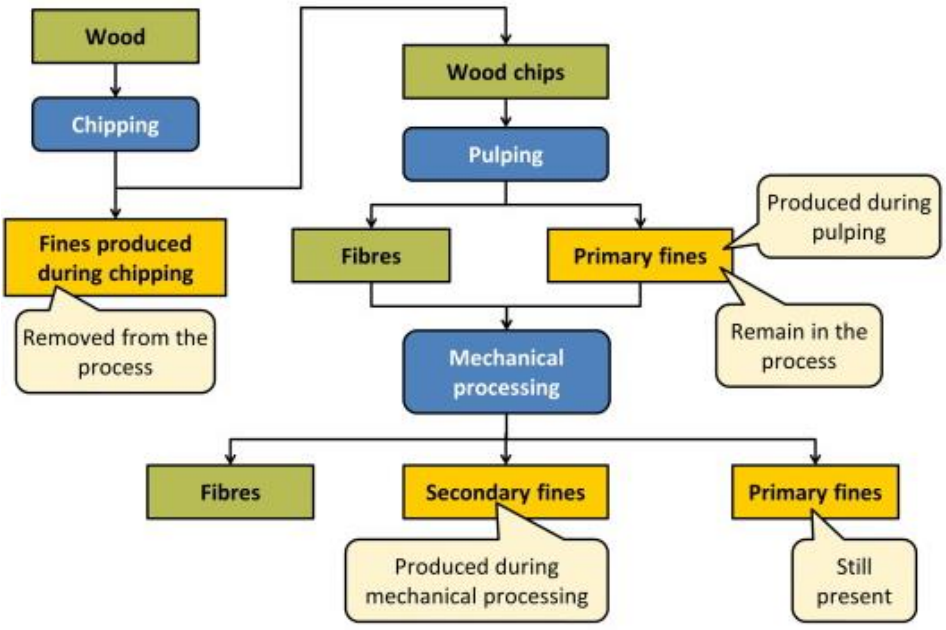


Figure 36 The origin and fines pathways during a pulping process. (Modified, originally introduced by Odabas et al., 2016)

The overall fines generation pathway is pretty much the same within different pulping processes; the pulping section in Figure 36 can be seen as the impregnation stage for CTMP process. Primary fines and secondary fines are used to describe smaller particle fractions of the chemi-thermomechanical pulp. Primary fines contain fines that are generated during the wood debarking and impregnation process and secondary fines represent the fines generated from the further fibre development, such as mechanical processing (Mark, 1984; Luukko,

1998). Mechanical processing in this case illustrates refining. A schematic pathway schematic for chemi-thermomechanical pulp secondary fines can be seen in Figure 37.

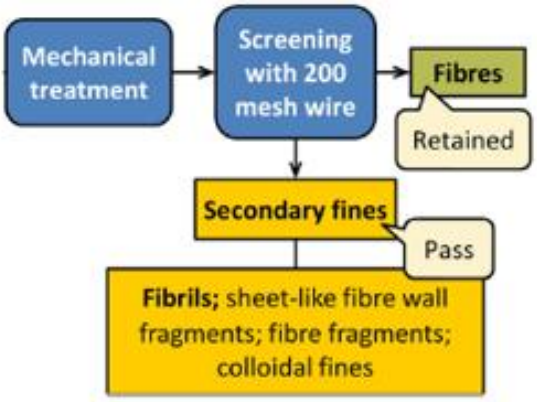


Figure 37 A schematic pathway schematic for chemimechanical pulp secondary fines generation. (Modified, originally introduced by Odabas et al., 2016)

All fine types tend to contain higher amounts of lignin, pectins and hemicelluloses and less cellulose than long fibres (Kleen et al., 2003; Sundberg et al., 2003). Fines are heterogenous and are generally divided to lignin-rich flake-like particles that are formed from the middle lamella and primary cell wall and fibrillar particles formed from the cellulose-rich secondary wall of the fibres (Luukko, 1998; Honkasalo et al., 1983). An illustration of fine formation from different cell layers can be seen in Figure 38.

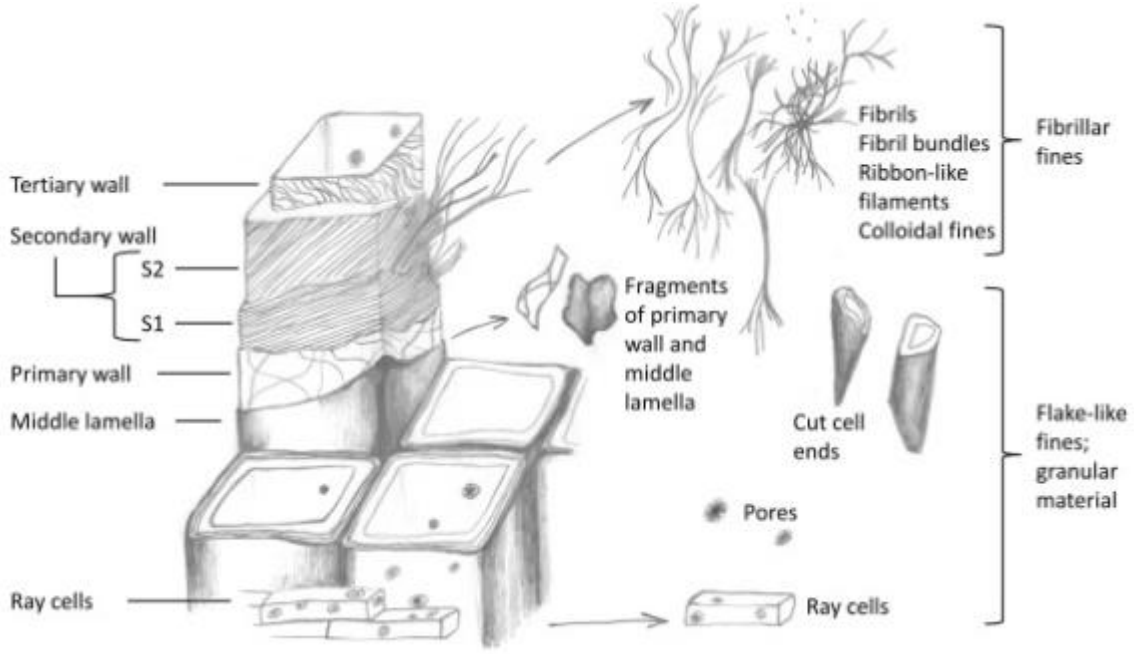


Figure 38 The wood cell layer structures and their relations with fines formation (Odabas et al., 2016)

The proportion of fines include various fine types, such as cell wall fragments, broken fibres, middle lamella fragments, fibrils, ribbons, fibril clusters, boarded pits and ray cells (Kleen et al., 2003). Cellulose-rich fibrillar fines, which are generated from the secondary wall of the fibres tend to give good bonding properties (Marton, 1964; Kallmes, 1960). Ray cells (flake-like cells), which are generated from the middle lamella and primary wall of the fibre, have been found to have decreasing effect on the bonding properties. However, they improve other characteristics of the pulp, such as light-scattering and therefore optical properties (Luukko and Paulapuro, 1999).

Both primary and secondary fines contain fibrillar and flake-like particles. Ray cells are isolated during the pulping process and they are the main component of primary fines. Fibrillar fines are the main component of secondary fines.

The primary fines of chemi-thermomechanical pulp (as well as other types of pulp) contains mostly rectangular ray cells (Capretti and Westermark, 1988). Secondary fines contain sheet-like fibre wall fragments and fibrous structures that are generated during the refining stage. Some granular fragments from softwood species may also be generated, originated from the

thick-walled fibres, due to refining (Paavilainen, 1990). A microscope images of different fines types produced in chemimechanical pulping can be seen in Figure 39.

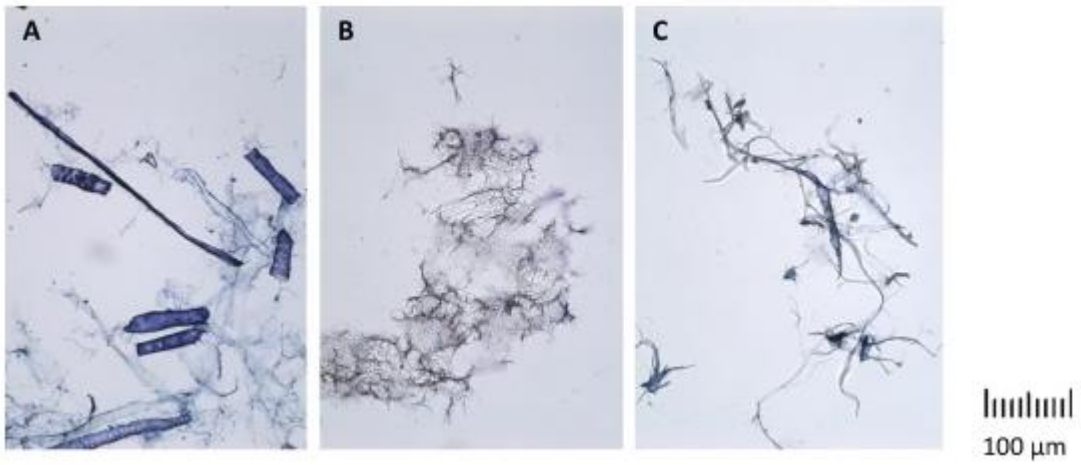


Figure 39 Microscope images representing fine types found in chemimechanical and groundwood pulp. (A) represents the primary fines of chemimechanical pulp; dark ‘’rectangle-shaped’’ structures are ray cells, the rest consists of flake-like fines. (B) represents the secondary fines of chemimechanical pulp; mainly fibrillar material and (C) represents fines from GWP; fibrillar and flake-like structures (Odabas et al., 2016).

The mechanical force needed to isolate fibres in BCTMP process compared to other pulping processes is lower because of the chemical treatment stage, as the fibres are separated from the weakest point of wood. The separation mechanism is dependent on temperature, moisture, stress frequency and chemical pre-treatment (Gustafsson et al., 2003). This results into a high amounts of intact isolated cells, which will have quite equal distribution that can be found from untreated wood, resulting in a smaller amount of fines compared to other mechanical pulping processes (Marton, 1964).

Hardwoods generate more primary fines than softwoods, because of their more complex morphology (Fagerholm et al., 2002). Fines generated from softwood pulping also tend to have higher fibril content compared to hardwood pulping. This was determined by Krogerus and Tiikkaja (2002); fibril contents for kraft pulp fines from pine and birch was found to be 41 % and 25 %, respectively. Laboratory-refined pulps had similar trends, both the specific sedimentation volume of the fines and its fibril content were higher for pine when operated with the same refining level.

A considerable amount of fines are either way generated. The fine fraction that passes the 200 mesh wire is noticed to be the smallest in CTMP processes, having a fine suspension 20 % or less. TMP and GWP generate higher amounts of fines (up to 40 %) (Ek et al., 2009; Lindholm, 1980).

Fines fractions in thermomechanical pulps can be characterized by their fibrillar fine contents, which correlates to their bonding abilities. The mass of a single fine can be calculated using the method represented by Luukko et al., (1997) giving the opportunity to determine the weight fraction of fines. Results using this method have shown that the fibrillar fines are very light; only a 1/4 of fibrillar fines by weight may still comprise 4/5 of the total amount of fines. New methods, such as using a fluorescence microscopy allows to compare fines perimeter to area ratios, providing data of the lignin content for each fine particle (Fernando et al., 2014).

A study executed by Holmbom and Sundberg (2004) analyzed the fine types in different pulping processes. The gained fine type and their content distribution for various pulping processes can be seen in Figure 40.

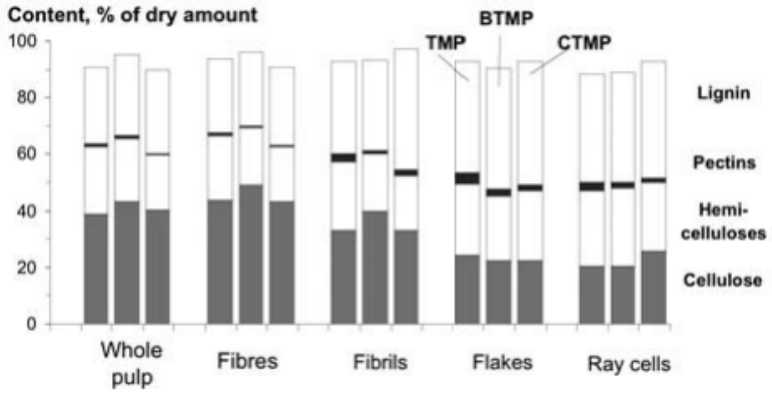


Figure 40 The fines type and content distribution in different pulping processes (Holmblom & Sundberg, 2004).

6.2 Fine properties

Fines differ from each other both with physical and chemical properties. The fine ray cells are lignin-richer than the fibrous ones (Hardell et al., 1980). The fines generated from middle lamella have found to contain higher amounts of lignin, rhamnose, arabinose, xylose and galactose, but less mannose and glucose than the fines generated from the secondary wall of

the fibre (Boutelje and Eriksson, 1984; Sorvari et al., 1986). The sugar unit contents for different fine types in different pulping processes were measured by Holmblom and Sundberg. Results can be seen in Figure 41.

mg/g	Ara	Xyl	Gal	Glc	Man	Rha	GlcA	meGlcA	GalA	Total
Whole pulp										
TMP	13	55	26	46	106	2	5	12	13	278
BTMP	11	57	21	44	94	2	1	14	11	255
CTMP	10	42	19	38	94	2	3	9	8	225
Fibres										
TMP	12	54	22	45	105	2	5	13	10	268
BTMP	9	52	17	42	89	2	1	12	7	230
CTMP	8	42	18	40	95	1	3	9	6	222
Fibrils										
TMP	16	45	45	49	95	4	6	10	27	297
BTMP	12	42	35	46	81	3	1	9	12	241
CTMP	19	35	38	40	69	5	4	7	19	236
Flakes										
TMP	27	71	49	36	71	7	2	16	42	321
BTMP	25	70	43	34	59	7	1	16	27	282
CTMP	30	92	40	21	65	5	4	20	20	297
Ray cells										
TMP	28	84	42	30	81	6	1	26	36	334
BTMP	29	105	39	29	70	6	2	27	23	330
CTMP	25	82	35	26	75	5	4	18	16	286

Figure 41 The sugar unit content in each fine type for various pulp types. (Holmblom and Sundberg, 2004)

The surface properties of fines also vary between fine types. Different fine surfaces have different chemical composition and absorb chemicals differently. The field of surface chemicals is not homogeneous; the chemical density per area can have variations when inspecting different fine and fibre surfaces. An example of lignin and extractive distribution on fibre surfaces can be seen in Figure 42.

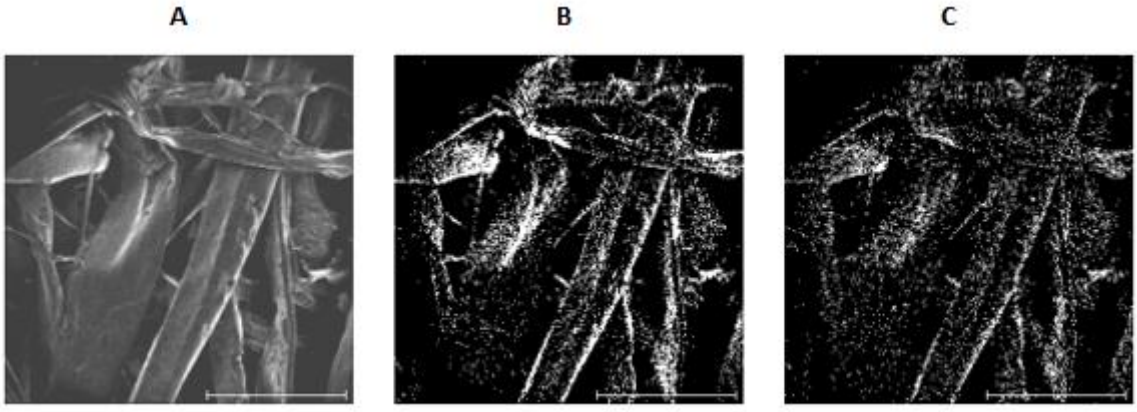


Figure 42 Positive total ion image (A), distribution of lignin on the fibre surface (B) and extractives (C) (Kangas, 2004).

Fines have large surface area compared to fibres when inspecting in the same volumetric area. High amounts of lignin and extractives can be found in fines surface and in the bulk. While the extractive coverage on the surface of fines were found to be high, the surface extractives in carboxylic groups were determined to be low. This indicates that more surface area is prevailed by sterols and/or triterpenes. The amount of polysaccharides on the surface of fines is low (~23 %). It should be noted that the polysaccharides are rich in carboxylic groups because of pectins and methylglucuronic acid groups in xylan (Kleen et al., 2003).

Mechanical pulp fines also tend to have a decreasing effect on the hydrogen peroxide bleaching efficiency. Also transition metals, such as iron, manganese and copper were found to be accumulated in the fractions of fines (Leduc and Daneault, 2007; Roick et al., 1991). Transition metals can form complexes with lignin and extractives that are strongly coloured, which will enhance the darkening reactions in BCTMP process (Yoon et al., 1999; Ni et al., 1999). Fines (ray, flake-like cells) that pass through the 200-mesh (nominal size 76 µm) screen tend to have similar performance structurally and physically as short fibres (De Silveira et al., 1996). As the chemical structure of lignin varies due to its morphological origin in wood, the properties and behavior of fines may vary for example when the pulp is bleached. A higher bleachability for flake-like particles has been observed (Haugan and Gregersen, 2006). The overall brightness response in bleaching depends on the initial pulp brightness; the brighter the initial brightness of the pulp is, the better the brightness response is (Kouk et al., 1989).

6.2.1 Mechanical properties

The fibre to fines ratio is one of the essential factors for the final product properties. Different types of fines generally have an impact on the mechanical properties of the pulp. However, the influence of certain fines when found in lower amounts is not that severe.

The pulp sheet density varies when the fibre to fines ratio varies; higher amounts of fines compared to fibres will increase the overall pulp sheet density. The wet web strength of the pulp sheet varies when the fibre to fines ratio is changed; an equal mixture of fibres and fines give an optimized web strength and tensile index. Too high fibre to fines ratio and vice versa tend to have a decreasing effect on the web strength and tensile index. The relationship between mechanical strength of mechanical pulp and fines content can be seen in Figure 43.

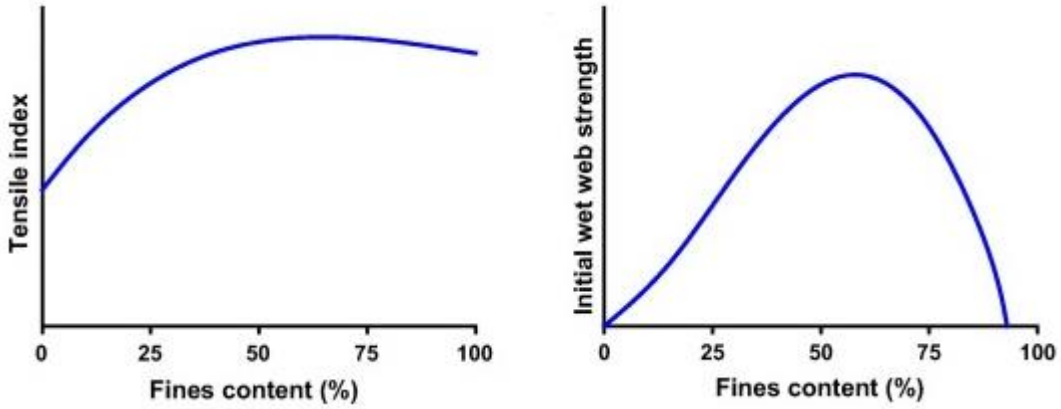


Figure 43 The relationship between mechanical strength of mechanical pulp and fines content (Odabas et al., 2016).

The maximum value for wet web strength and tensile index is obtained at the point where all the empty spaces between fibres are filled with fines. Depending on the nature of fibres and fines, there is a theoretical, optimized maximal value for wet strength and tensile index which is obtained via an optimum fibre to fines ratio. In this maximal value point, both dynamic and statistic strength properties are optimized (Amiri et al., 1996; Lindholm, 1978; Paulapuro and Vainio, 2007).

As said before, one of the fundamental effects of fines considering the mechanical properties of pulp is the densifying phenomena of the fibre network (Luukko, 1998). The inter-fibre bonds are the main factor for pulp sheet strength (both in horizontal axis and z-axis) beside the individual fibres. Higher amount of inter-fibre bonds correlates with shorter segments between bonds and fewer free loops is generated (Retulainen et al., 1993). Fines generated during chemi-thermomechanical pulping process have been obtained to have a ‘’pulling’’ effect on the pulp sheet, shortening the distances between fibres and therefore generating thinner and less porous pulp sheet. This phenomenon has an increasing effect on the fibril content in the fines fraction (Nurminen and Sirviö, 2004).

6.2.2 Optical properties

The final pulp product is wanted to be bright and opaque. A widely used model is the Kubelka-Munk theory (Kubelka and Munk, 1931), where the brightness and opacity are mathematically dependent on a light absorption coefficient and a light-scattering coefficient

(see section 4.7). Light-scattering coefficient correlates with the fibre surface area which is accessible to light. The incident light is only scattered at phase boundaries (Ek et al., 2009). The light-scattering coefficient is directly correlated with the amount of long fibres in the fine fraction. Flake-like fines, specifically the smaller ones increase the light-scattering coefficient.

As the fines in general contains higher amounts of metal ions, lignin and extractives, they consume more bleaching chemicals compared to the long fibre fraction (Karlsson and Agnemo, 2010; Petit-Conil and Laurent, 2003). Bleaching the pulp after removing the primary fines has shown to give more effective bleaching results (Panula-Ontto et al., 2002).

6.2.3 Influence of water on pulp and fines

Different phenomena occurs when fines get in contact with water. Fundamentals of water influence on fines can be examined via physical and chemical means. Occurrence of fines in pulp affect for example pulp swelling, rewetting and fines adsorption properties.

6.2.3.1 Fines and pulp swelling

Swelling of fines and fibres contributes to the structural flexibility, producing certain strength properties for the pulp. The structure and composition of fibres and fines can be altered and improved in the refining stage, where the internal and external fibrillations are optimized. Internal and external fibrillation determine the surface area that is accessible for water. Large surface area of fines means more water can interact with the fines, giving them great swelling abilities. Swelling is determined to be one of the beneficial properties of fines as it allows the material to fit into the structural fibrous network, resulting into an evenly distributed stress inside the fibrous structure (Htun and De Ruvo, 1978).

The general swelling of a pulp contributes with the water retention value. Water retention value determines the amount of water that is left in the fibrous material after centrifugation. When measuring the swelling of fines fraction, a solution exclusion should be applied. Fines swell roughly two times as much as the original pulp (Laivins and Scallan, 1996). Swelling of chemi-thermomechanical pulp fines can be tied to the surface charge and to the amount of cellulose. Surface charge and water retention time vary within the fines; secondary fines

having higher values for both surface charge and water retention time compared to primary fines (Htun et al., 2008).

6.2.3.2 Fines and pulp rewetting

When the chemi-thermomechanical pulp is dried, some of the swelling capability of fines and fibres is lost due to the physical change that occurs when fibres are dried. Hornification, which represents this phenomenon, is a result of increased crosslinking between microfibrils and an internal fibre volume shrinkage. If the fibres are resuspended with water, the original swollen state before drying will not be achieved. This may be possible because of the additional hydrogen bonds that can be found in the cross-linking of microfibrils that are formed during drying and are not broken when rewetting. Hornification phenomenon is restrained by lignin and hemicellulose compounds surrounding the microfibrils, and the swelling for long fibres and fines are roughly the same for never-dried and rewetted pulp (Luukko and Maloney, 1999). Swollen fibres before drying (left) and after drying (right) can be seen in Figure 44.

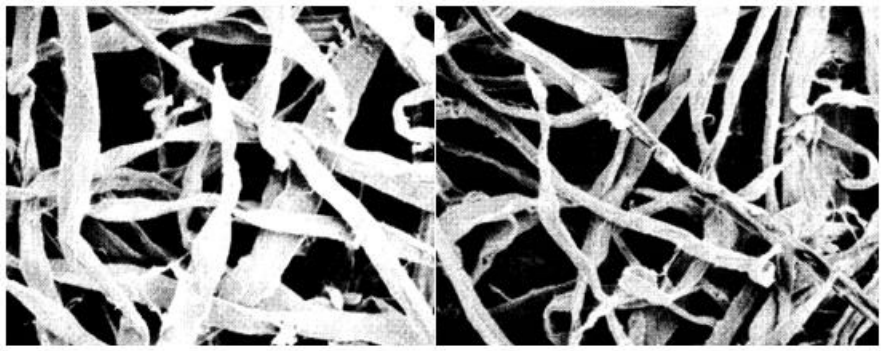


Figure 44 Swollen fibres before and after drying (Minor, 1994)

As can be seen from the left picture in figure 44, fibres suspended in to the water before drying appear much thicker than the dried ones. Swelling of fibres can be restored by refining, where new fines with great swelling capacity is produced. However, fines that goes through extra refining appear to be losing their beneficial effects on fibre bonding (Laivins et al., 1993). The bonding effects on fines can be enhanced by applying alkali in the early stage of pulping process and sodium hydroxide after refining.

6.2.3.3 Fines and pulp dewatering

The small size and high surface area are having negative influence in dewatering speed of the final product, as fines from any pulp type increase the dewatering resistance (Chen et al.,

2009). The smaller the size of the fines are, more resistance in dewatering can be noticed. The pulp sheet drainage and dewatering can be modeled in a simplified way using the Kozeny-Carman equation (Carman, 1937). In this equation, the permeability of a bed (in this case the pulp sheet) is proportional to the square of specific surface area per volume of its particles; when increasing the particle surface, overall flow through the surface will decrease. The identical shapes of particles (as in this case fines) will enhance the dewatering resistance. The Kozeny-Carman equation is presented below (Carman, 1937):

$$\frac{\Delta p}{L} = -\frac{180\mu}{\emptyset_S^2 D_P^2}\frac{(1-\epsilon)^2}{\epsilon^3} v_S \qquad (10)$$

where

Δp	is the pressure drop
L	the total bed height
v_S	superficial velocity
μ	fluid viscosity
ϵ	porosity of the bed
$\emptyset_s$	sphericity of the particles in the bed
Dp	the diameter of the volume equivalent spherical particle

Different fine types may have different influence on dewatering; granular fines may prevent direct interactions with fibres, meanwhile more laminar fines may take part in the interfibre bonding. The Kozeny-Carman model is based on an assumption that fluid flows through capillaries which are orientated at 45 degrees to the inflow direction, meanwhile the contacts between the internal surface of these capillaries and fluid is assumed to inhibit the flow (Wakeman & Tarleton, 1999).

However, a general problem with any filtration model applied in pulp filtration is that the chemical interactions, which illustrate the aggregation of fibres and other particles (like fines and mineral fillers) are very difficult to determine by a simple parameter, such as in this case the specific surface area. Some empiric research have to be made to obtain the influence of particle interactions on overall permeability and mechanisms considering filtration characteristics and therefore fibre suspension.

The Kozeny-Carman model on its own does not consider the different shapes of fines. The Kozeny-Carman equation relies on homogenous particle shape (round). When different fine shapes are also inspected, a choke point model can be applied. This model assumes that fines are conveyed with the flow through the fibrous network until they get stuck in a small space (pores) between fibres, generating a blocking effect (Hubbe, 2002). An experiment was made by Cole et al., (2008). They observed that the dewatering time of a pulp in a given solid content increases as a nonlinear function of the fines content when adding both primary and secondary fines. For secondary fines, the function follows an exponential model. Graphical illustration of primary and secondary fines effect on pulp dewatering can be seen in Figure 45.

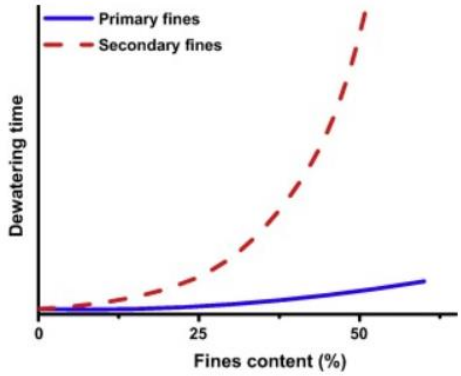


Figure 45 Effect of primary and secondary fines on pulp dewatering (Cole et al., 2008).

Primary fines in chemi-thermomechanical pulps hinder the dewatering of pulp suspensions, but they have relatively small effect compared to secondary fines. Secondary fines are the main source of decreased dewatering properties (Chen et al., 2009). The primary fines do not have major effect on the pulp drainage, unless they exceed over 20 %, which will never be the case in chemi-thermomechanical pulps. However, major changes in dewatering efficiency can be observed when the secondary fines make up only 5 %. Chemi-thermomechanical pulps tend to have larger amounts of very small particles than other pulp types, which reflects to the poorer pulp drainage compared to other types of pulp (Taipale et al., 2011).

As mentioned, the filterability of fibrous network depends on the fibre properties and bonding mechanisms. Wildfong et al., (2000) has presented a mechanism that is based on the effect of fibre flexibility on porosity of the fibrous network: conformable fibres have a

tendency to compress together under applied pressure, which results to the sealing of the fluid passageways and therefore decreasing filtration properties. A schematic of this sealing phenomenon can be seen in Figure 46.

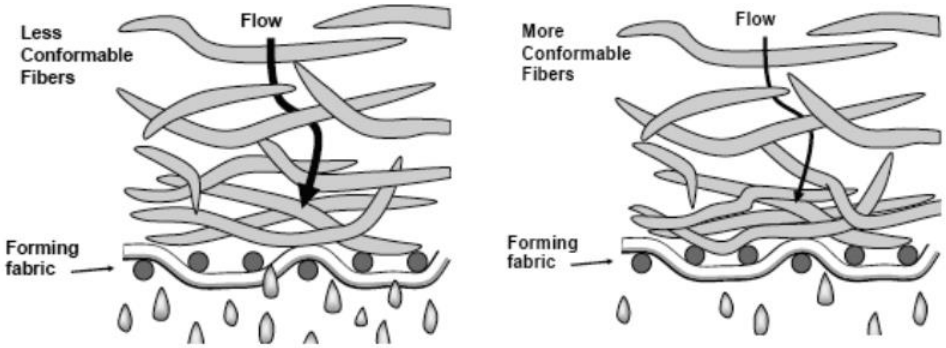


Figure 46 A schematic of fibre sealing. (Hubbe & Heitmann, 2007).

Dewaterability of fibre suspension decreases as fibre flexibility increases (Paavilainen, 1993). More flexible fibres have higher collapsing ratio, resulting in a tighter fibrous matrix that hinders the overall fluid flow through the matrix. Fibre flexibility is only one aspect when considering dewaterability. The friction occurring in interfibre bonds also has been shown to have effect in fluid flow through the fibrous matrix. This is because the actual orientation and structure of fibrous matrix correlates with the interfibre friction value. Higher interfibre friction hinders the sliding of fibres and thus prevents dense structural stacking, resulting to the formation of porous fibrous structures (Sampson & Kropholler, 1995).

Mechanical retaining on the fibrous sheet plays relatively minor role considering smaller particles, such as fines and mineral fillers (like calcium carbonate or kaolin clay). This is because of their dimension characteristics; only a certain amount of smaller solid particles can be retained to the porous fibrillar matrix. Smaller particles are mainly retained via chemical interactions (Liimatainen et al., 2008; 2009). Adsorption properties of fines provides low retention value, which is not desirable. Some retention aids (such as cationic polyacrylamide) that interact with the surfaces of solid particles can be added to improve flocculation and aggregation, leading to reduced total hydrodynamic surface per weight. This results into improved dewatering properties (Hubbe, 2002).

6.2.3.4 Freeness

Freeness of pulp represents the measure of the rate where a dilute suspension of pulp (3 g of pulp in 1 L of water) may be drained. CSF (Canadian Standard Freeness) values are widely used in pulping industry. Many pulp qualities correlate with the CSF-values; the freeness value decreases as the pulp is further refined (Kappel, 1999; Lönnberg, 2009). This is because the further pulp is refined, the more fibres and smaller particles are suspended from the pulp, increasing the initial fibre/particle surface area. Freeness of pulp can be expressed as one of the draining parameters. Freeness (or the rate of draining) is related to the surface conditions and swelling properties of fibres and fines. Freeness is used to follow the changes in drainage rate during refining. When operating at higher freeness levels, longer and more stiff fibre structures can be obtained. This correlates with lower square mass value and increased bulk value, which is desirable. However, tensile strength values tend to decrease in higher freeness levels.

6.2.4 Fines and adsorption

The large specific surface area of fines allows abundant interaction with other solid components such as other types of fines, fibres and filler particles or dissolved colloidal substances (like wood resin) that may be found in the pulping process. The pulp structure is formed as fibres and other solid particles are retained on the forming fabric sheet. Most of the liquid phase drains through the fibrous mesh along with dissolved colloidal substances and any solid material that have not been retained on the generated fibrous sheet. The solids in this filtrate are not suspended because of a closed stream system in modern pulping processes. Fines are capable to adsorb high amounts of expensive chemicals. If a certain fraction of them is not retained on the forming fibrous sheet, they are difficult to recover later in the process and therefore influencing the overall process and cost efficiency (Hemmes, 2013).

6.2.5 Fines and fillers

Fillers are usually mineral particles (for example calcium carbonate) that have similar structural properties as fibres, but are cheaper to produce and use than actual fibres. They can be used in low amounts without affecting the pulp quality. As said before, an important factor when characterizing the fibre suspension filtration is small particle retention. Retention illustrates the total amount of small particles retained within the fibrous matrix

(Eklund & Lindström, 1991). Because the mechanical suspension for smaller and colloidal-sized particles is difficult due to their smaller size, interactions which enhance particle removal for different pulp fractions have great impact in particle retention. Influence of fines fractions on filler particle retention is relatively high because of fines contribution to the particle deposition. As fines have high surface area, they are retained better compared to individual filler particles.

Filler particles that have a cationic charge is found to induce deposition of fillers on fibre surfaces, which has an increasing effect on the dewaterability of a fibre suspension because of a lower total suspension surface area. The anionic surface charge on the other hand promotes cationic filler deposition and therefore caused better dewaterability.

6.3 Utilization of fines

If fines are not expressly removed, they will be circulating within the process or found from the final pulping product, influencing the paperboard properties. As fines tend to consume high amounts of chemicals and other substances due to their large surface area, some taste and smell issues may occur in the final product. This has to be taken into account especially when using BCTMP to manufacture provision packages. No smell nor taste cannot transfer to the edible content. Fines generated in the BCTMP process have both positive and negative features on the final product. To a certain point fines increase some properties (like structural strength) but at the same time they decrease other properties (like dewatering capacity). An overview of fines effect on the pulp properties can be seen in Table XII.

Table XII. The effect of fines on the pulp properties (Odabas et al., 2016; Retulainen et al., 1993).

Property	**Effect**	**Comments**
Drainage time	++	Higher fines content means higher drainage time, since they block the pores in the pulp sheet.
Sheet density	++	Higher fines content increase the overall density; lowers the bulk.
Air permeability	--	As fines block the pores in pulp sheet, air penetrates into the sheet less efficiently.
Wet web strength	+	Maximum point can be found; beyond certain fines consistency value decreases.
Tensile strength	+	No increase if fibril content is low.
Tear strength	+/-	Maximum point can be found; beyond certain fines consistency value decreases. Maximum value is obtained in very low fines content.
Breaking length	+	No increase if fibril content is low.
Specific bond strength	+	No increase if fibril content is low.
Compression strength	+	Higher fibril consistency generates a structure that is more compressable. Fines tend to increase compression strength.
Folding endurance	+	Maximum point can be found; beyond certain fines consistency value decreases.
Tensile stiffness	+	
Shrinkage	+	Fines drying after swelling increases the hornification effect, which can cause some shrinkage on fibre structure.
Light scattering	+/-	Depends on the flake-to-fibril like fines ratio. More fibril content correlates with lower light-scattering properties and vice versa.
Bleachability	-	As fines have large surface area, they consume bleaching chemicals a great amount.
Linting	-	

+ title value increases
- title value decreases

Fines are obtained to also have reducing effect on the energy consumption in the refining process. However, fines can have a negative influence on pulp strength properties, bulk, brightness and light-scattering coefficient. Fines also seem to have increasing effect on the content of shives, while they decrease the problems considering linting or threading. (Brill, 1985; Eriksen et al., 1981)

7 Experimental part

As the literature part of this thesis stated, the fines fractions generated in the BCTMP process influences the BCTMP properties. The goal of the experimental part was to determine the fines generation balance over the Joutseno BCTMP process. Fines generation analyses were done in laboratories located in Joutseno, Äänekoski TC and KCL (Keskus-Centrallaboratorium). Analyses included the determination of the amount of solid particles (consistency), total amount of fines and fines fraction distribution, pH, COD, turbidity, conductivity and the amount of extractives. Also element proportions were analyzed by Labtium and the amount of extractives both in pulps and filtrates was analyzed in Äänekoski TC. However, only the results for the fines fractions are considered from these results in this thesis.

To calculate fines fraction production rates, measured results and results obtained from Balas was exploited. Balas is a specified simulation program for pulping processes, originally introduced by VTT (Technical Research Centre of Finland). Total flowrates needed to calculate production rates for fines were obtained from Balas.

8 Laboratory experiments

The purpose of laboratory experiments was to determine the fines fraction balance for pulps and filtrates through the Joutseno BCTMP process. Analyses for fines fraction determination was done after every unit operation found in the BCTMP process, starting from refining.

In laboratory experiments the fines fractions were analyzed from Joutseno BCTMP pulp and filtrates used in inner water circulation. The generated proportion of fines and fines fractions (flake-like and lamellar-like) was compared between each sample point and the fines fraction balance over the whole BCTMP process was calculated. Different measurements and methods were applied in the laboratory experiments. Some of the measurements used are standardized and some are corporate's own methods. The total amount of sample points analyzed was 65.

8.1 Materials and methods

Samples were taken in a 10 L container. All samples were collected within a few hours. In the time window when samples were collected, no issues in the BCTMP process occurred.

In sample taking the protocols provided by Metsä Board in sample taking were executed to obtain reliable samples. Low consistency samples were properly mixed and a portion of the sample was transferred into 1 L containers for the FS-5 analysis. Samples with high consistency were transferred into minigrip bags. Conductivity (from samples with low consistency) and pH (pulps and filtrates) was measured at this point. The pH and conductivity results were compared to the results given by the DNA process view. DNA is a process and quality monitoring software, provided by Valmet. The equipment and methods used in laboratory experiments are presented in appendix 1.

COD was analyzed from the filtrates. Pulp and filtrate consistencies were analyzed in Joutseno and KCL. DDJ (Dynamic Drainage Jar) analysis was executed in Joutseno. The fines to fibre ratio (w/w %) was analyzed with the DDJ. DDJ analysis was done only for selected and the most interesting sample points because of its long analysis time. The fines fractions were analyzed by KCL from all sample points, using the Valmet FS-5 fibre image analyzer. Before the fines fraction analysis, samples were hot disintegrated. The FS-5 analysis is based on the image analysis; the amount of fines A (flake-like) is measured in percentage from the projection area of the measured fragments while fines B (lamellar-like) is measured in percentage from the overall fibre length. Fines that have length less than 0,2 mm are included to fines A while fines that have length greater than 0,2 mm and width less than 10 µm are included to fines B. Total amount of fines (%) is gained from the length weighted arithmetic distribution. The fragments include all the solid particles found in the sample (not only particles that fulfill the specifications of fines).

9 Results and discussion

The results for fines fractions obtained from the laboratory experiments are represented in this chapter. The outcomes of the results are also discussed.

9.1 Fines and pulps

Consistencies were measured for each sample. The FS-5 uses the sample consistency for calculating the total amount of particles found in the sample. Measured consistencies for main pulp flow samples can be seen in Figure 47 and consistencies for reject pulp samples in Figure 48. Production rates through the BCTMP process can be seen in Figure 49.

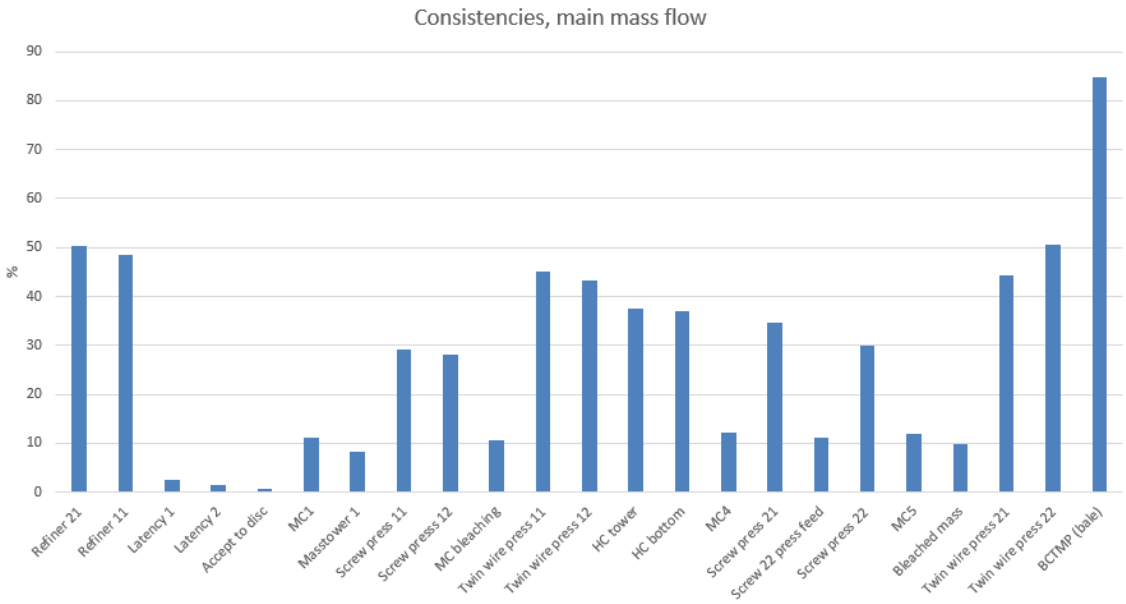


Figure 47 The consistencies for samples obtained from main pulp flow.

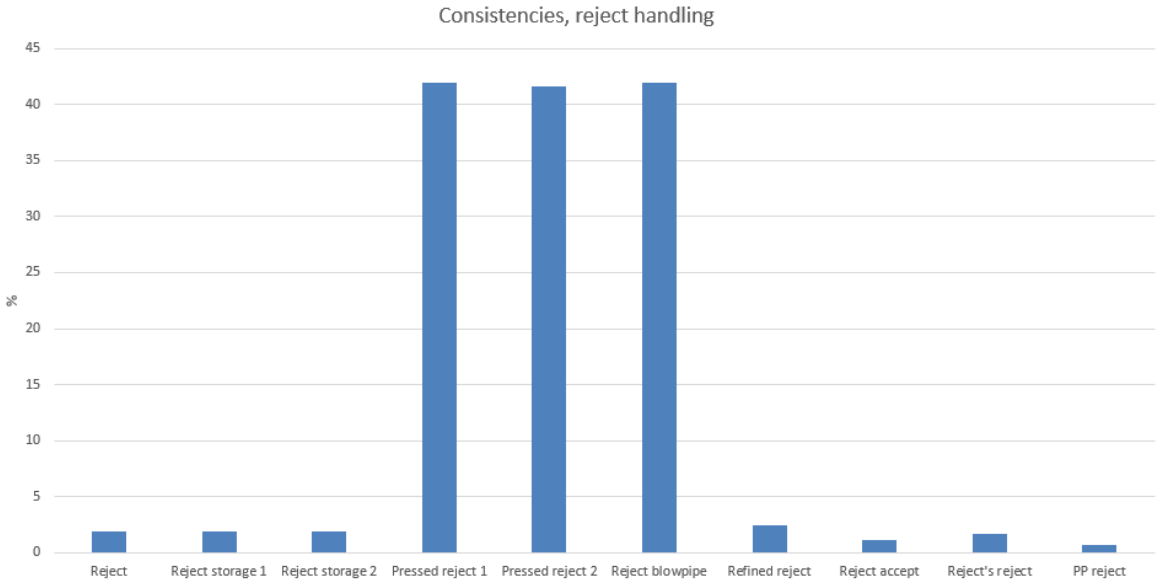


Figure 48 The consistencies for samples obtained from reject handling.

Consistency does not stay constant; it changes through the BCTMP process greatly (as shown in Figure 47 and Figure 48). As different unit operations have different purposes, the conditions in those unit operations vary. Wood chips that are grinded in the refiners have high consistency, as the water inside the wood is evaporating because of the friction and heat generated in the grinding process. After refiners the pulp is transferred into latency tanks, where hot process water within chemicals is mixed with the pulp. Consistency is much lower

at this point. After screening the disc filters' accept flow is diluted even more, which lowers the consistency. Disc filter removes some of the water as filtrate, so the consistency rises in MC1 (pump). Small amounts of water from filtrate tank 2 (SVS2) is pumped to pulp tower 1, so a minor change in consistency is obtained. Washing units (screw presses and twin wire presses) squeeze water from the pulp into filtrates, thus the consistency value rises. The variation of consistency therefore follows the same pattern; when water is removed, consistency rises and vice versa. Knowing sample consistency is crucial, because it influences the FS-5 analysis, as the fines production is calculated based on the total production value, which is influenced by the measured consistency.

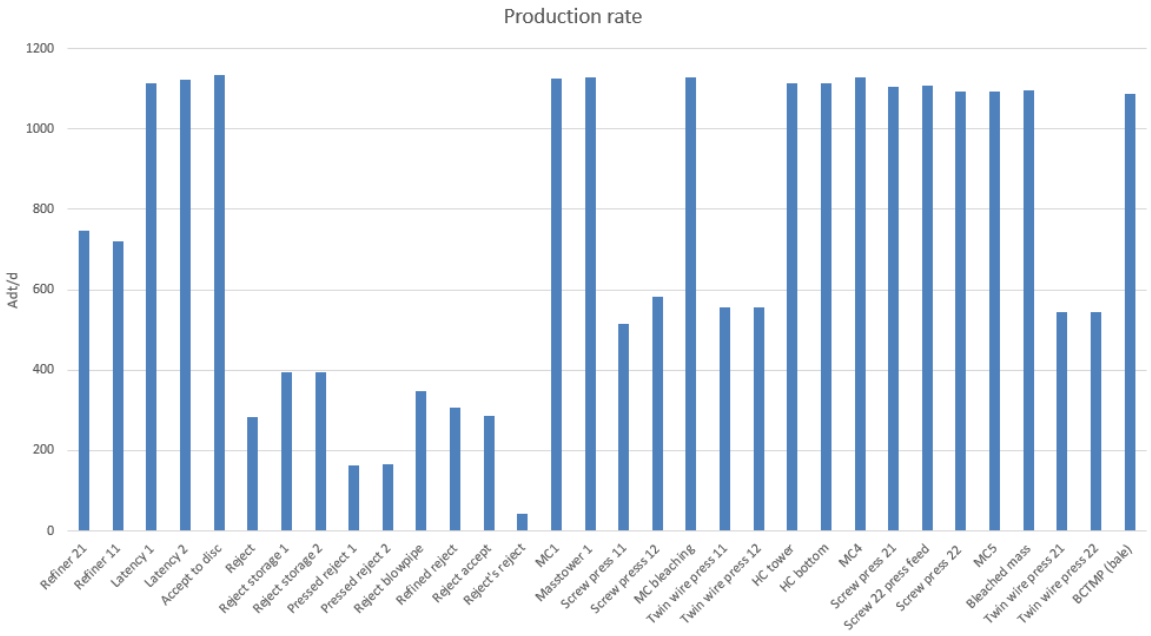


Figure 49 The production rates in Adt/d (Air dried tons/day) through the BCTMP process.

Production rates (Figure 49) are reasonable, except when inspecting refiners production rates and latencies production rates. Its seems that production from refiners outlets in sum is higher than production rate in latencies. This can be explained with either measurement error, poor sample quality or error in simulation. Other unit operations seem to have reasonable results; for example the production rate of ''MC bleaching'' is the sum of the production rates of twin wire presses 11 and 12. As mentioned, fines in these analyses were divided into three fractions; total, flake-like and lamellar-like fines. The fines fraction distribution (%) for all pulp samples can be seen in Figure 50. Blue area in graphs represents the whole bar length (as total fines).

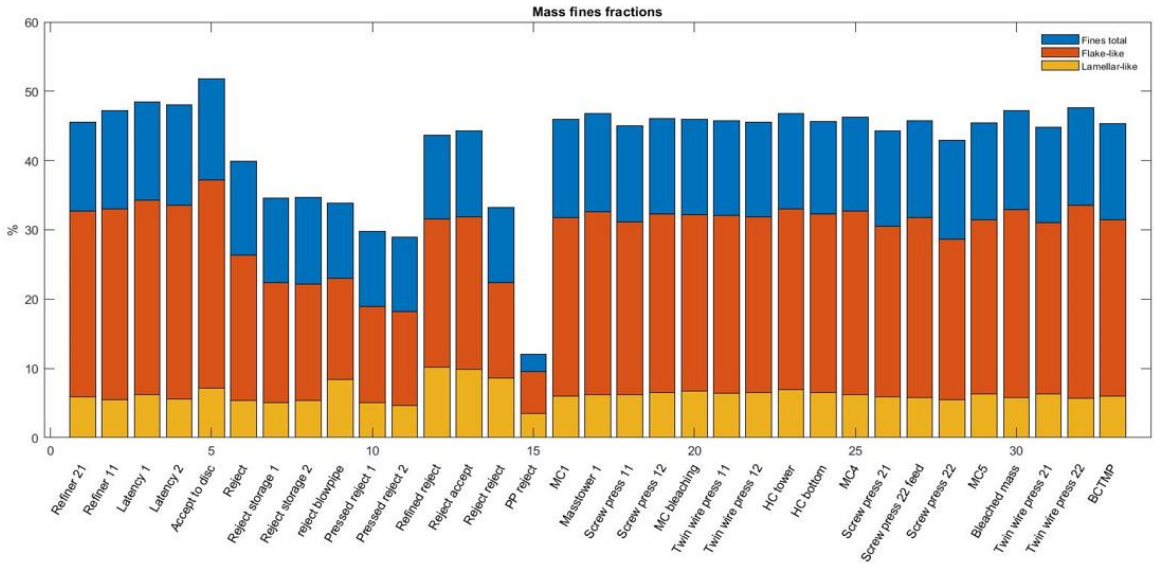


Figure 50 The fines fraction distributions for every pulp sample; total amount of fines (blue), flake-like fractions (red) and lamellar-like fractions (yellow).

The graph in Figure 50 shows that the amount of fines in every fraction stays quite constant after refining. One explanation for this phenomenon could be that fines in the process are not treated at this point in any way and the pulp generated in refining has a certain capacity to retain fines without any retention agents or other retention aiders. Fines that are not retained are suspended into filtrates. Because there has been no fines treatment in BCTMP process, fines will achieve certain equilibrium in the process.

Probably the most interesting result is the effect of bleaching on the fines content. Bleaching (both MC and HC-bleaching) seem to have no influence what so ever in the fines content. Fines content seems to stay quite constant from MC1 all the way to BCTMP (bale). One could assume that bleaching chemicals would have influence on the fines content or at least the overall structure of fines. As seen in Figure 50, the variations in fines fractions (total, flake-like and lamellar-like) practically goes into the error margins. Fines are known to absorb high amounts of bleaching chemicals, but results in this thesis only consider the generation of fines fractions. Figure 51 represents the fines fraction distributions without the reject handling for better visualization considering the main pulp flow.

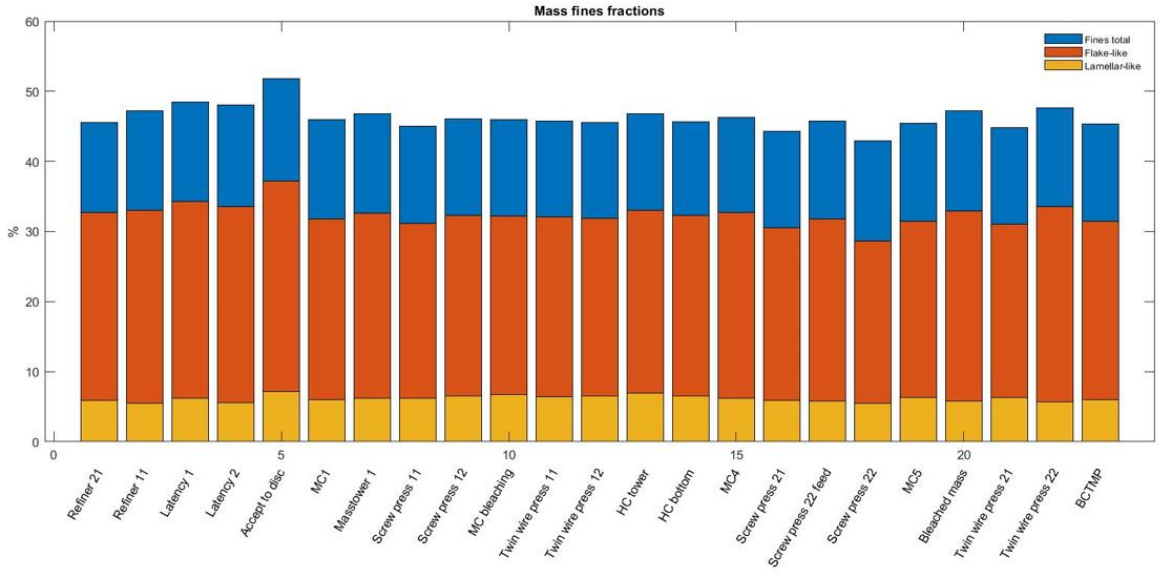


Figure 51 The fines fraction distributions for main pulp flow samples; total amount of fines (blue), flake-like fractions (red) and lamellar-like fractions (yellow).

Figure 52 represents the production rates for fines fractions (kg/s) and Figure 53 the production rates for fines fractions (Adt/d) for the pulp samples. The results of reject handling is not presented in these figures, because accept pulp flow from reject handling merges into the main pulp flow (disc filters accept flow). Reject handling is represented by its own in Figure 54, Figure 55 and Figure 56.

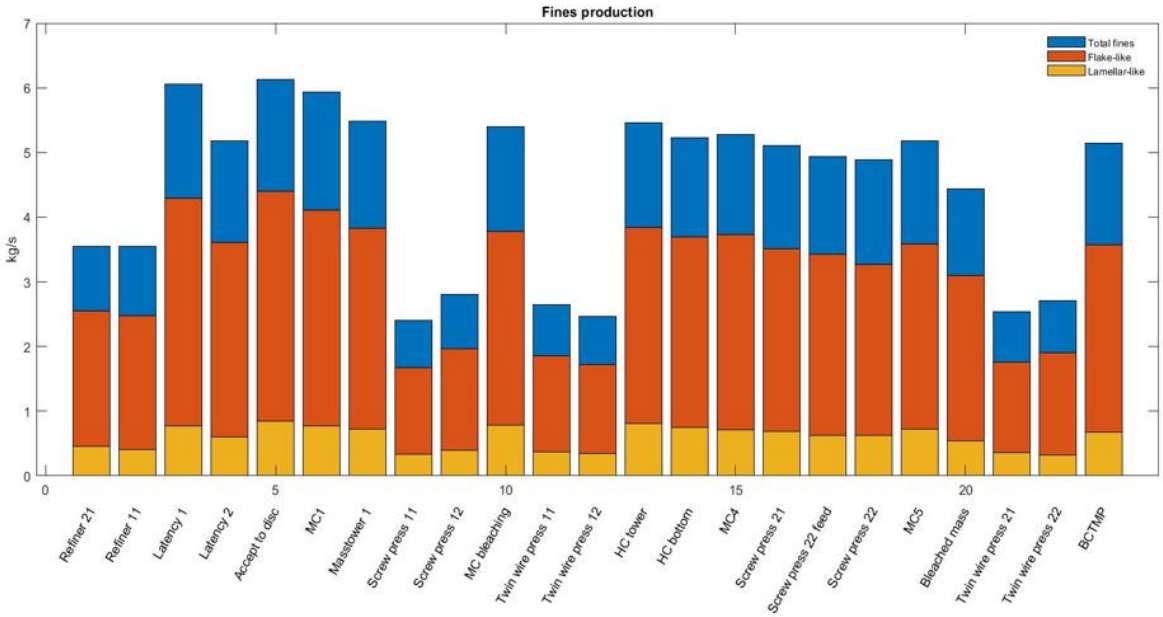


Figure 52 The production rates for fines fractions (kg/s) for pulp samples; total amount of fines (blue), flake-like fractions (red) and lamellar-like fractions (yellow).

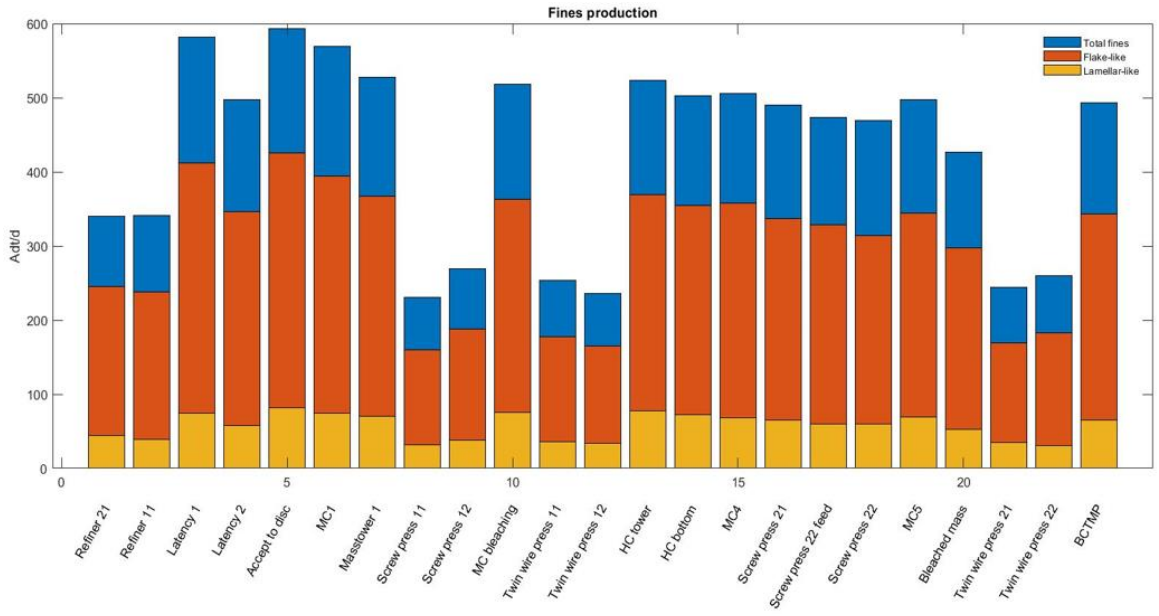


Figure 53 The production rates for fines fractions (Adt/d) for pulp samples; total amount of fines (blue), flake-like fractions (red) and lamellar-like fractions (yellow).

The differences in fines production between unit operations is not unequivocal. The production rates for fines fractions (Figure 52 and 53) is based on the pulp flows (obtained from Balas), measured consistencies fines fractions obtained from FS-5 and the total production value. The fines production difference for example between latency 1 and 2 can be explained with different pulp flow rates. Latency 1 outlet is determined to be 504 kg/s while latency 2 outlet is 718 kg/s. Cloud filtrate from disc filter is merging to both latency 1 and 2 tanks, however with significantly greater volume to latency 2 (10,7 kg/s versus 191 kg/s). Because of the high flow difference, fines production in latency 2 is smaller (as both latency 1 and 2 has the same fines content but different overall volume). Practically every time there is a small drop in fines production, it can be explained with the addition of dilute water. Balance generated with Balas is not presented as it is too large and detailed. Balance over two key operation units are inspected later. All results obtained however can be seen from table XV in appendix 2.

The fines production seems to increase when inspecting the interface of latency 2 and accept to disc filter. Figure 50 states that the fines content in accept flow to disc filter is higher compared to latency 2. This result is reasonable, because the accept flow to disc filtrate has been screened by pressure screener units, suspending longer fibres and clusters into the reject flow. The reject flow is then handled and screened thus the accept flow from reject treatment is merging into the accept to disc flow. The accept flow to disc filter is therefore consisted

of two flows; accepts from main pulp and reject flow. Therefore fines content in proportion to accepted fibres in accept flow increases. When comparing screw presses 11 and 12 with 21 and 22, there is big difference in the production rate. This can be however simply explained with the concept of the presses; screw presses 11 and 12 are installed concurrently while 21 and 22 are in series. Feed to the screw press 22 is the diluted outlet from screw press 21. Fines production is roughly divided by two when inspecting screw presses 11, 12 and twin wire presses; for example the production of ''MC bleaching'' is the sum of twin wire press 11 and 12 fines production.

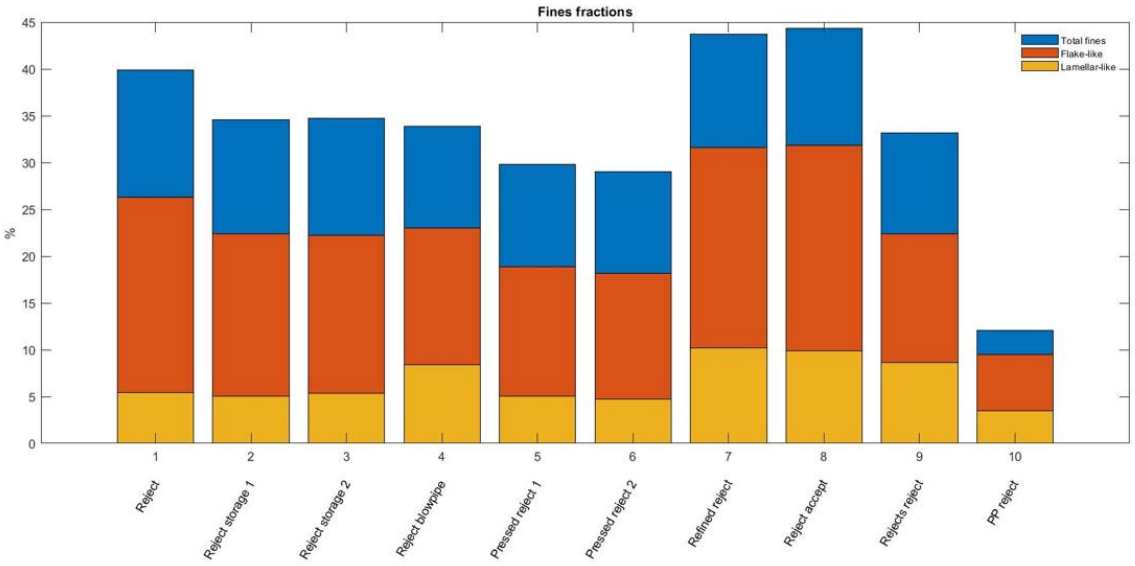


Figure 54 Fines fractions in reject handling. total amount of fines (blue), flake-like fractions (red) and lamellar-like fractions (yellow).

The overall content of fines is smaller in reject treatment compared to the main pulp flow. As mentioned, fines pass through the screening unit to the accept flow, reducing the fines content in reject flow. Fines content drops a bit after the screened reject is transferred into reject storage 1 as there is a water flow (PP-dilute) migrating into the reject storage tank. Increasing overall volume while the amount of pulp is constant, the amount of fines decrease in proportion of overall volume.

No major difference is seen between reject storage 1 and reject blowpipe, as they are only vessels holding and transferring the pulp. Reject's washing units (reject screw presses 1 &

2) seem to have some influence over the fines content. It seems reasonable as a portion of fines is washed away within the filtrates as the pulp is pressed and dried.

As the reject pulp is refined, fines content increases (as it should). According to literature presented by Kappel (1999) and Lönnberg (2009), the further chips and pulp is grinded, the amount of fines increases. Refined reject pulp is screened with the same principle as the main pulp flow; with a pressurized screening unit. The accept flow in reject screening has practically the same fines content as the refined reject flow. Reject's reject flow follows the same pattern as the main flows' reject; the fines content decreases compared to the accept flow. In PP-reject there is a substantial drop in fines content. However, the PP-reject unit has low production rate, which is practically zero. Accept flow from PP-unit was not analyzed. After PP-unit the flow is transferred into the reject storage 1.

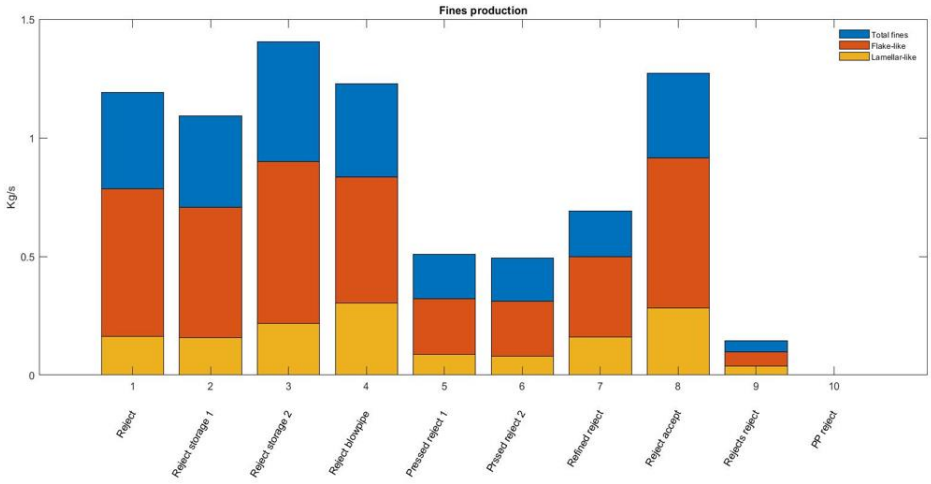


Figure 55 The production rates for fines fractions (kg/s) for pulp samples in reject treatment; total amount of fines (blue), flake-like fractions (red) and lamellar-like fractions (yellow).

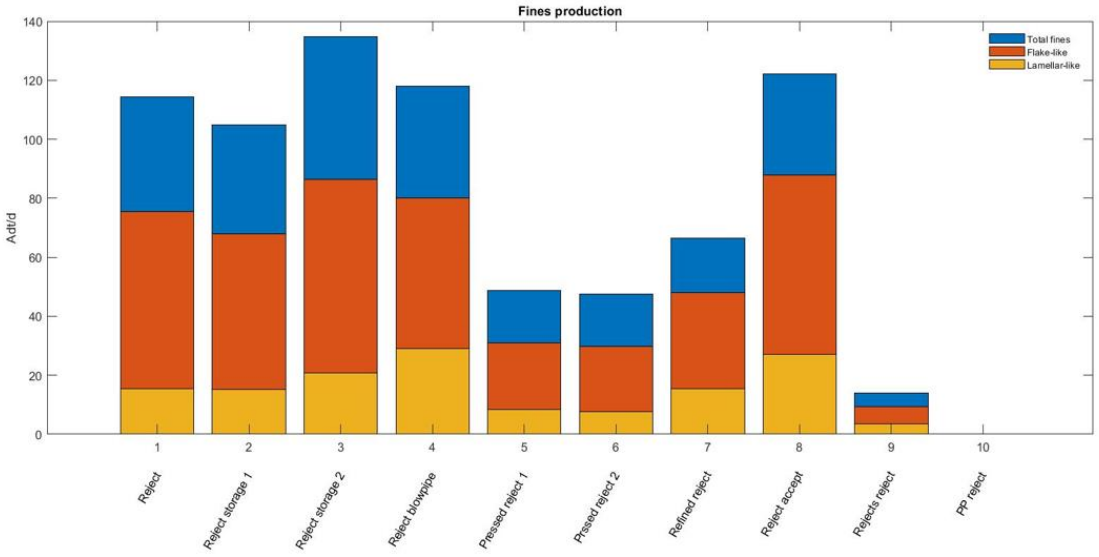


Figure 56 The production rates for fines fractions (Adt/d) for pulp samples in reject treatment; total amount of fines (blue), flake-like fractions (red) and lamellar-like fractions (yellow).

Fines production in reject handling varies, as it does with the main pulp samples. Rejects' accept flow is the key flow considering the overall fines production as it migrates into the disc filters accept flow. Therefore the overall fines content in disc filters accept flow could be affected if rejects' accept flow was treated.

The DDJ analysis was also executed for higher priority pulp samples regarding the BCTMP process. DDJ analysis gives the weight by weight fines-to-fibre ratio (w/w %). Results for selected pulp samples can be seen in Figure 57.

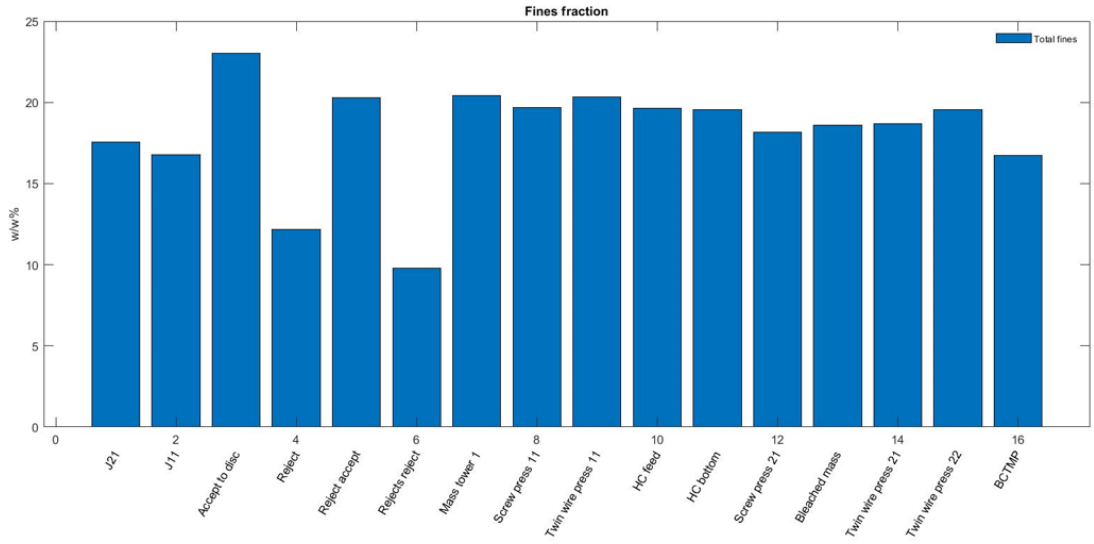


Figure 57 The fines to fibre weight ratio (DDJ).

The results from DDJ analysis also state that the fines content stays within the same level when comparing refiners and BCTMP (bale). Accept and reject flows follow the same pattern as before; accept flow includes more fines in w/w % compared to screening inlets (refiner pulp, reject and rejects' reject). The amount of fines also seems to stay very constant according to the DDJ analyses. Figures 58 and 59 represents the fines production rates (kg/s and Adt/d).

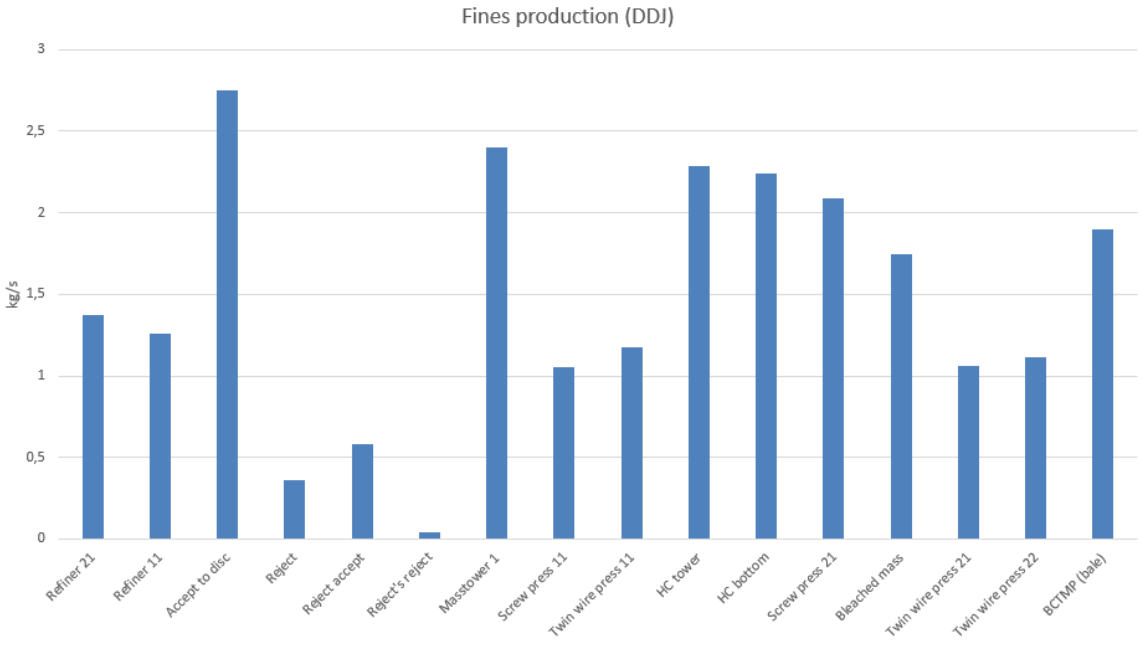


Figure 58 Fines production based on DDJ analysis (kg/s).

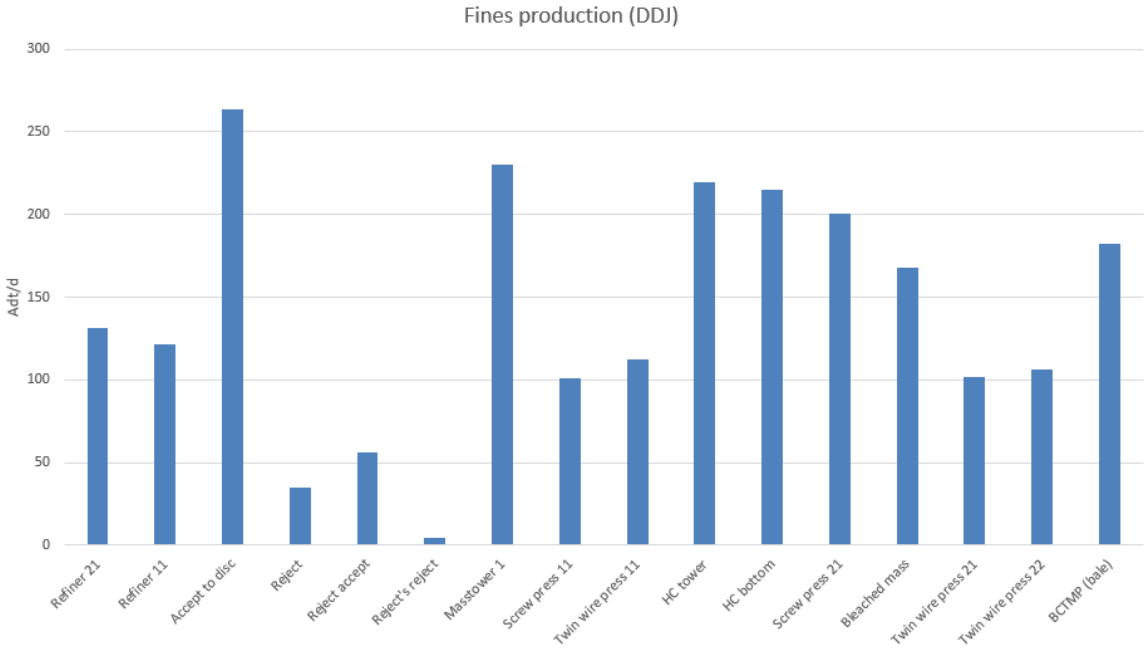


Figure 59 Fines production based on DDJ analysis (Adt/d).

While the DDJ analysis states that the fines content stays quite constant through the BCTMP process, fines production rates have variation in different sections of the process. If one would desire to lower the fines content or even extract fines in whole, the pulp flow that one would want to treat is the pulp flow going to the disc filtrate (accept to disc). This is because the fines content in disc filters accept flow is consisted of firstly screened main flow and ''reject accept'' flow. Reject accept migrates into accept to disc -flow, so treating fines before they enter the disc filter or treating them simultaneously with the disc filter would be reasonable.

One possibility would also be to post treatment fines in MC1 or mass tower 1. More retention agents could be added to MC1 or mass tower 1 to really enhance the fines retention. One could assume that this act would lower the fines content in filtrates in every section further in the process. At this point mass includes freshly generated fines, which will have the best properties considering the product quality. The ground mass has only a certain fines absorbing capacity, so fines proportion that would not stay within the mass could be attached to mass with retention agents or other means. Leftover proportion of fines should be subtracted as they transfer into filtrates; as filtrates are used as inner circulation process water and the high fines content in the process water is not desirable considering product qualities. This way the influence of freshly generated fines on pulp would be maximized along with the product qualities.

As stated, the disc filter is the first operation unit that divides the inlet flow in two outlet flows (pulp flow and filtrate). Figure 60 represents the balance over the disc filter.

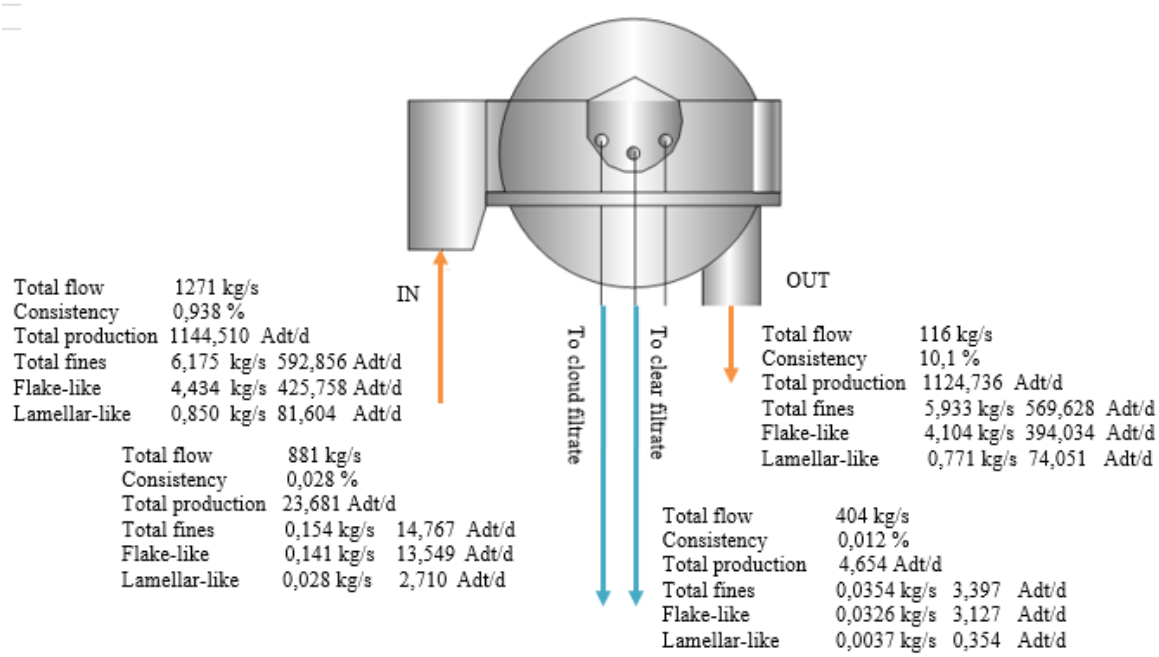


Figure 60 The pulp and fines balance over the disc filter.

The balance over disc filtration includes total flow, consistency, total pulp production and fines production (with fines fraction productions) for all inlets and outlets. There is small error in total pulp production balance, which can be explained with errors occurring in consistency measurements in the laboratory, the quality variation of analyzed sample or approximations in simulation. The error in total pulp production balance is however so small that it practically goes into the error margin. There was however an issue with the ''accept to disc'' pulp sample; the consistency measured from that sample was determined to be 0,7 %, which cannot be right considering the total production rate. That is probably due to some error in sampling; either the sample quality was not good or it was simply taken from a wrong sample point in the field. When calculating the balance over the disc filter, consistency obtained from Balas simulation (0,938 %) was exploited.

The fines production is calculated from the total production value. As the results from FS-5 (Table XV) states, the total fines content in inlet is 51,8 %, flake-like 37,2 % and lamellar-like 7,13 % while total fines content in pulp outlet is 46 %, flake-like 31,8 % and lamellar-like 5,98 %. Corresponding values for filtrate outlets (cloud and clear filtrate) are much higher, but as the total production value is low, the fines production value is also low. When inspecting only the fines production balance over the disc filter, it seems that the production is unbalanced (inlet value does not correspond with the sum of outlet values). This however can be explained with the nature of fines analysis; the FS-5 only measures the total fines content, fine types A (flake) and B (lamellar). Flake and lamellar-like fines are not the only types of fines. The leftover portion includes fines types that the FS-5 does not measure (such as vessels, kinks and ray-cells). If total amount of retented fines is wanted to be higher, some retention aid could be added to the disc filters accept flow, boosting pulp fines retention capabilities. Some of the fines may travel with the pulp flow even though they are not attached to the pulp. Fines that are not retented should be treated before they enter to the first bleaching stage, as fines consume high amounts of bleaching chemicals due their high surface area.

There is also contradiction with the fines production; when inspecting fines production for example in cloud filtrate, total fines production is smaller than flake-like and lamellar-like fines production together. This can be explained with the very principle of FS-5 analyzer; it does not analyze flake-like and lamellar-like fines from the total amount of fines. FS-5 analyses all fractions (total, flake and lamellar) from the total amount of solid particles. This was later verified by the analysis provider (KCL). Regardless of this matter, the vicinity of the results stay the same and the fines production balance can be relied on.

Another key point considering fines circulation within the process is the first washing stage; the screw presses 11 and 12. These presses are squeezing water out of the pulp, dividing the inlet into pulp outlet and filtrate. Removing fines from filtrates or enhancing their retention within the pulp would have considerable effect in the total fines content later in the process. Figure 61 represents the balance (calculated by exploiting measured results and Balas results) over the screw press 12.

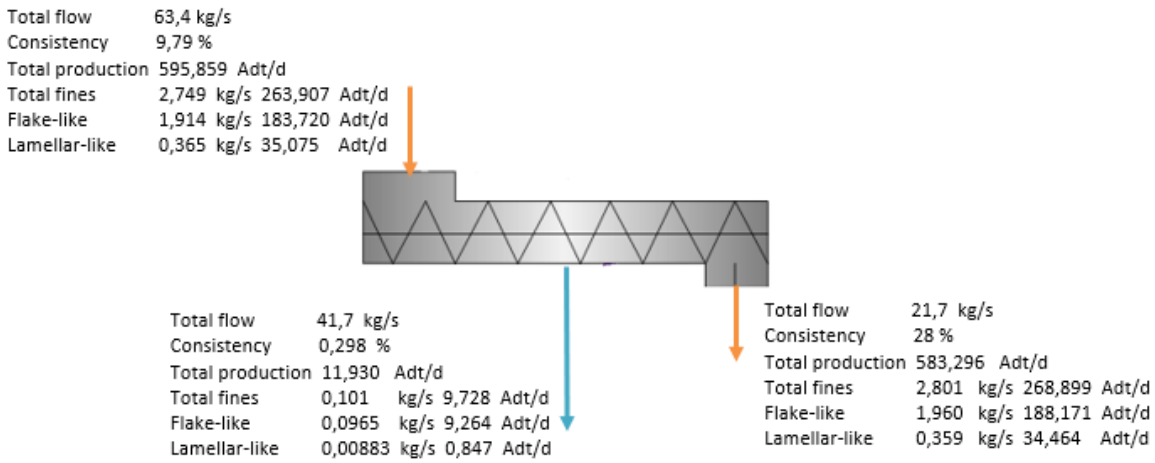


Figure 61 The pulp and fines balance over the screw press 12.

Fines content in inlet and outlets are pretty much in balance. Small differences can be seen, but they are so small that they go to the error margin. Overall production fines production in screw press 12 inlet (pulp tower 1) is roughly divided by two (as the pulp flow from pulp tower 1 is divided into screw press 11 and 12). No major difference can be seen in the content of fines when inspecting screw press 12 inlet and outlet.

After inspecting these two unit operations, overall fines absorption capacity was calculated for refiners, screw presses 12, 21 and 22, reject press 2, twin wire presses and disc filter. Because a certain portion of fines is transferred into filtrates in these unit operations, the maximum fines retention capacity without any retention agents was calculated. The retention capacity determines how large portion of fines is subtracting from the inlet pulp flow to the filtrate. Results can be seen in Figure 62.

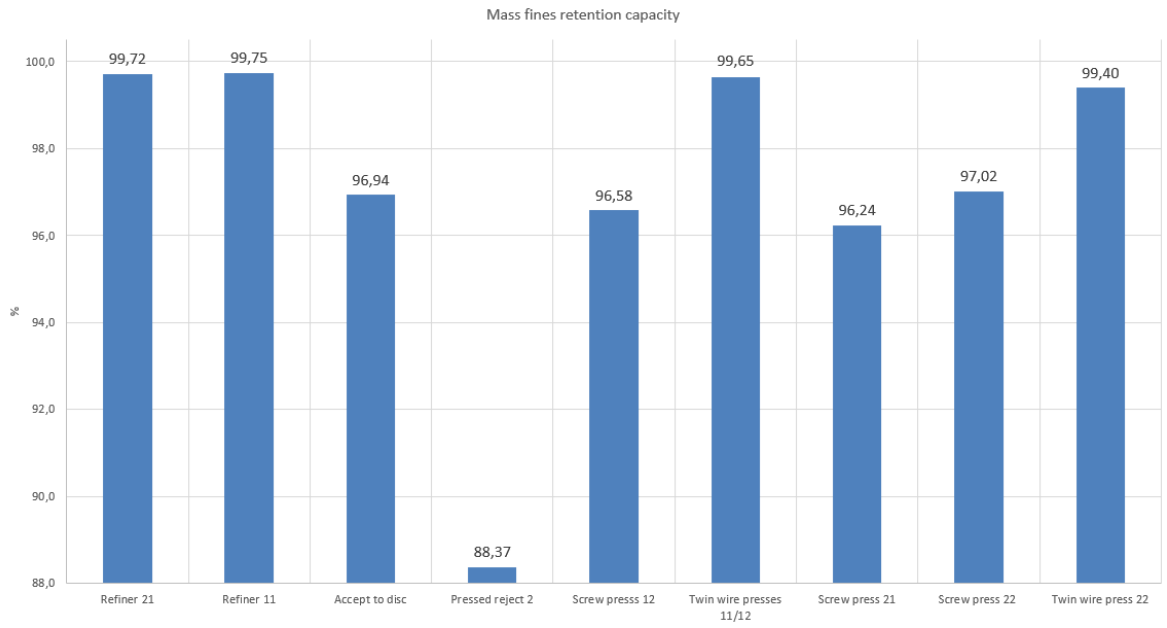


Figure 62 Fines retention capacities for certain unit operations.

As Figure 62 states, pulp has quite high retention capacity for fines without any retention agents. Reject press 2 has a noticeable drop in fines retention capacity. This can be explained with the lower total amount of fines and different fibre texture; reject flow includes bigger fibres in all dimensions, lowering the total retention surface area where the fines can attach to. Average fines retention capacity for these operation units was determined to be 97,07 %.

9.2 Fines and filtrates

The fines proportions in filtrates are much greater compared to pulps in BCTMP process. Only a certain proportion of fines generated in refining stay attached in the fibrous matrix; rest of the fines are extracted from the pulp within the filtrates. The fines fractios for filtrate samples can be seen in Figure 63. The FS-5 results for screw press 11 filtrate are not presented as the results were not reasonable.

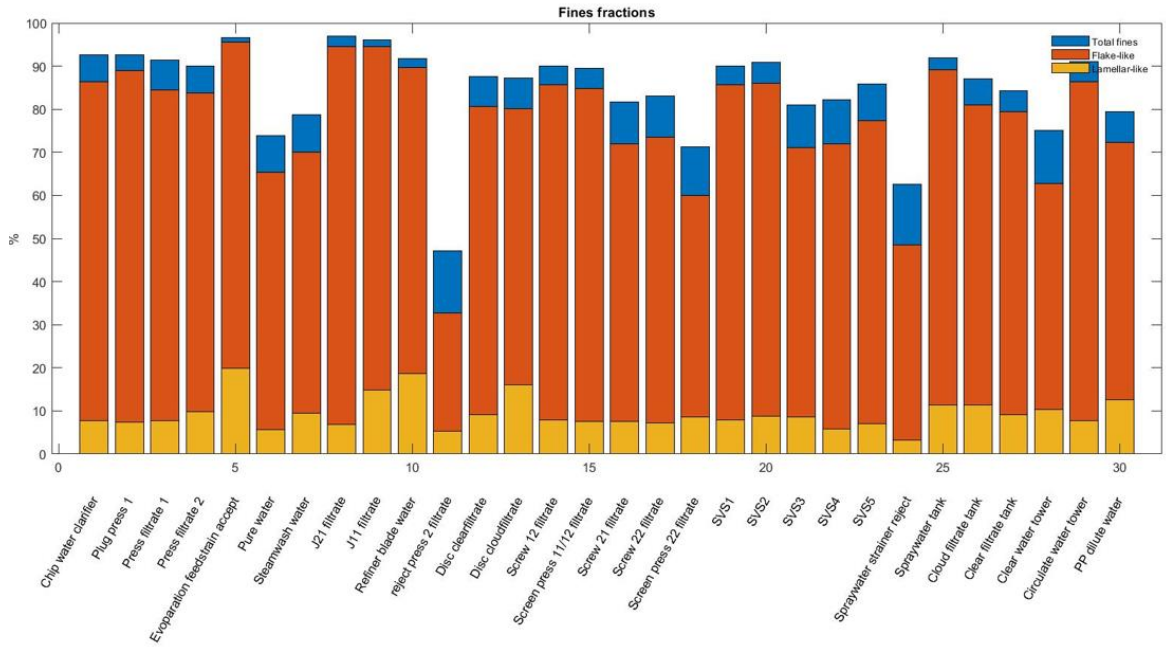


Figure 63 The fines fractions found for filtrate samples; total amount of fines (blue), flake-like fractions (red) and lamellar-like fractions (yellow).

As seen in Figure 63, the amount of fines is very high in the filtrates. Especially content of flake-like fines is higher compared to pulp samples. Flake-like fines bonding abilities with fibres are poorer than lamellar-like fines, so it seems logical that a higher portion of flake-like fines are transferred into the filtrates. Only way at this point the fines can exit the BCTMP process is within the bale or if process water is channeled into a waste canal. Process water is treated as inner water circulation system, so the amount of fines in the filtrates and process water is increasing over time. This explains the high content (in some cases over 95 %) of fines. When inspecting reject filtrates (reject press 2 and spraywater strainer reject), there can be seen a drop in the fines fractions. This is because the reject pulp flow contains higher amounts of long fibres (smaller fibres and fines passes the accept mesh), so when the reject pulp itself contains less ''fines rich'' pulp, the filtrate will also contain less fines. Fines productions (kg/s and Adt/d) for filtrates can be seen in Figure 64 and Figure 65.

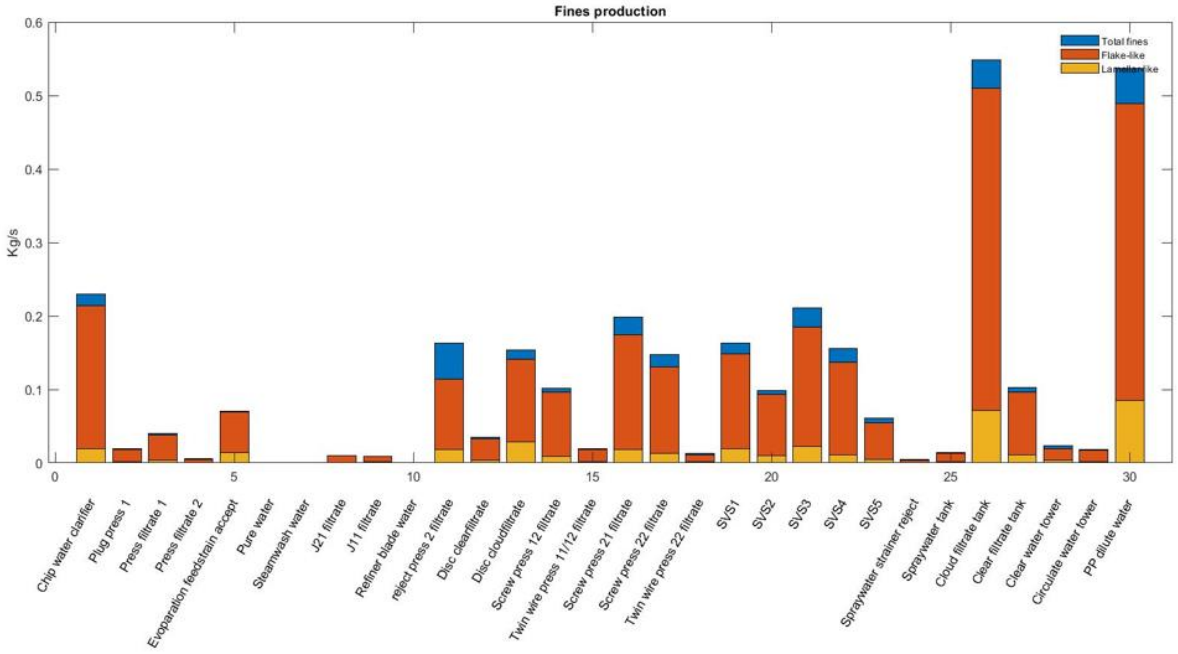


Figure 64 The production rates for fines fractions (kg/s) for filtrates; total amount of fines (blue), flake-like fractions (red) and lamellar-like fractions (yellow).

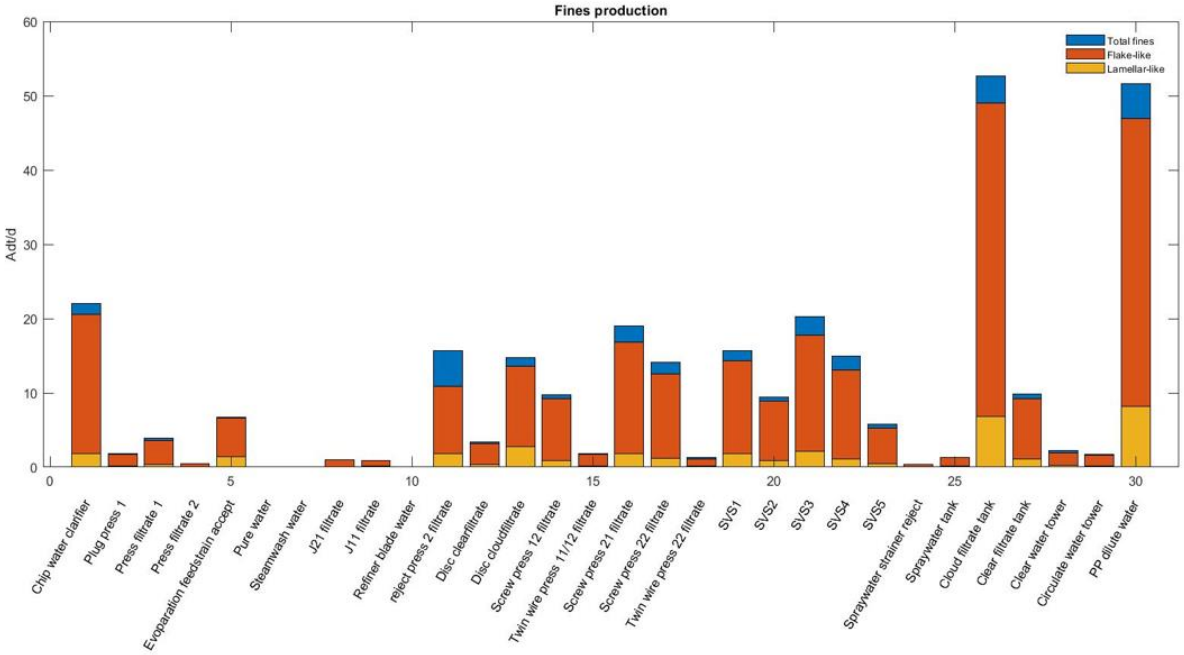


Figure 65 The production rates for fines fractions (Adt/d) for filtrates; total amount of fines (blue), flake-like fractions (red) and lamellar-like fractions (yellow).

Fines production considering filtrates is highest in cloud filtrate and PP dilute tank. This is not really surprising, as the outlet flows from these units are the highest ones in the whole process when inspecting filtrates (process waters). Inlets of the cloud filtrate tank are consisted of twin wire press filtrates (11,12,21 and 22), disc filtration units' filtrate, circulate water towers' water and filtrate water tank 1 (SVS1). The content of SVS1 includes filtrates from all filtrate water tanks (2-5). This means that fines that are suspended within the filtrates from these units are transferred to cloud filtrate tank, which is known to contain ''dirty'' process water. As inlets for PP dilute water tank are consisted of cloud filtrate tank, filtrates from screw press 1 & 2 (reject) and rejects' screening filtrate, the amount of fines is also high in this unit.

Water from cloud filtrate and PP dilute tank is exploited in several process steps (latency, disc filter, reject handling and first screening in main pulp flow) as diluting water, which means that fines that have been circulating from the very beginning in the process are getting in contact with freshly refined pulp. Optimal situation would be that only the fines freshly generated in refining could be adhered into the pulp through the whole process. Fines that suspend from the pulp and circulate through the process within the filtrates and process water lose their abilities to enhance final product properties. There are several ways to achieve this; either with specified retention agents, other suitable chemicals for pulps (like CMC) or suspend the fines from all operation units that generate filtrates (i.e. screw presses and twin wire presses). These methods could also be integrated, as the retention agents would not probably achieve 100 % fines retention. However, if 100 % of fines could be removed from filtrates, pulp would only contain freshly generated fines with the highest capabilities to enhance product qualities.

Lowest fines production (practically zero) can be seen in pure water, steamwash water and refiner blade water. Even though the FS-5 results state (Figure 63) that the fines content for all these units are > 70 %, consistencies in these units are so low that the actual fines production is practically zero.

DDJ analysis was applied only to one filtrate sample due to its long analysis time; screw press 11 filtrate. There was no specific reason why screw press 11 filtrate was chosen (it is known that DDJ takes very long time to finish with filtrate samples, so one sample was

randomly taken). The total amount of fines gained from DDJ analysis was determined to be 83,21 %. This result supports the results obtained from the FS-5 analyses, as the result is close to screw press 12 results. The FS-5 results for screw press 11 filtrate were not reasonable, because they stated that the proportion of lamellar-like fines is 100%, which is not possible. Screw presses 11 and 12 are in concurrent, so the results should be comparable. DDJ result of screw press 11 is presented in Figure 66.

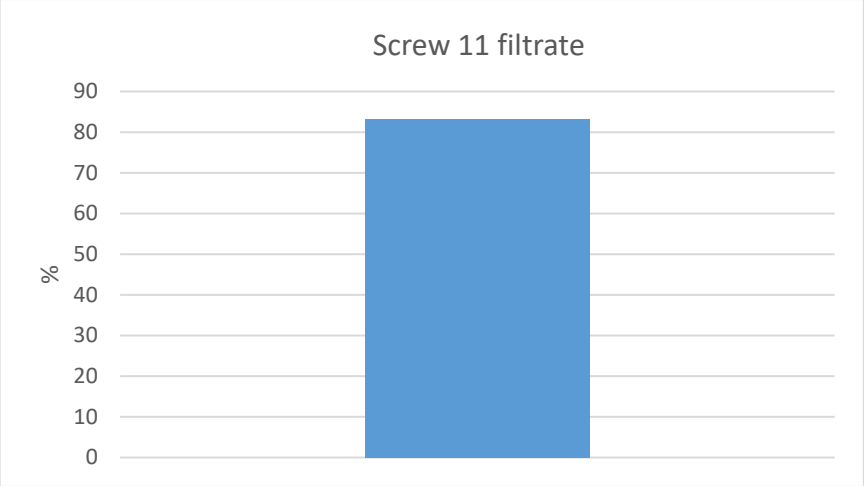


Figure 66 The DDJ analysis for screw press 11 filtrate.

Also the FS-5 results for filtrate tank 1 (SVS1) were not reasonable, as they stated that the proportions for fines fractions were 66,1 % (total), 60,4 % (Flake-like) and 75,7 % (Lamellar-like), which is not possible. Total amount of fines and flake-like fines seems reasonable, but the amount of lamellar-like fines not. SVS1 contains filtrates from screw presses 11 and 12, so one could assume that the fines fractions in SVS1 would comply with the screw presses values. Sample quality or the analysis in this case may be poor or the fibres and fines could be sedimented in different layers inside the filtrate tank. This would correlate with poor sample quality, as the homogeneity of the sample is the base of any analysis.

9.3 Experimental refining

The purpose of the experimental blades testing was to determine how they affect to the amount of fibrillation thus fines generation. The blade pattern varies from the original blade a lot; the pattern is much more straightforward, reducing the amount of edges that tear up the wood chips and cause the fibrillation phenomenon. Because the blade pattern is ''smoother'' considering the resistance factors that cause the fibrillation and also fines generation, less energy should be needed for refining.

Because of the new blade pattern, one could assume that the fines fractions generated in refining may also change. Two resemblance samples within three hour window was taken from both refiners and the samples were analyzed using the Valmet FS-5. Figure 67 represents the comparative fines results for the refiner J11 and J21. Results can be seen from table XVI in appendix 2.

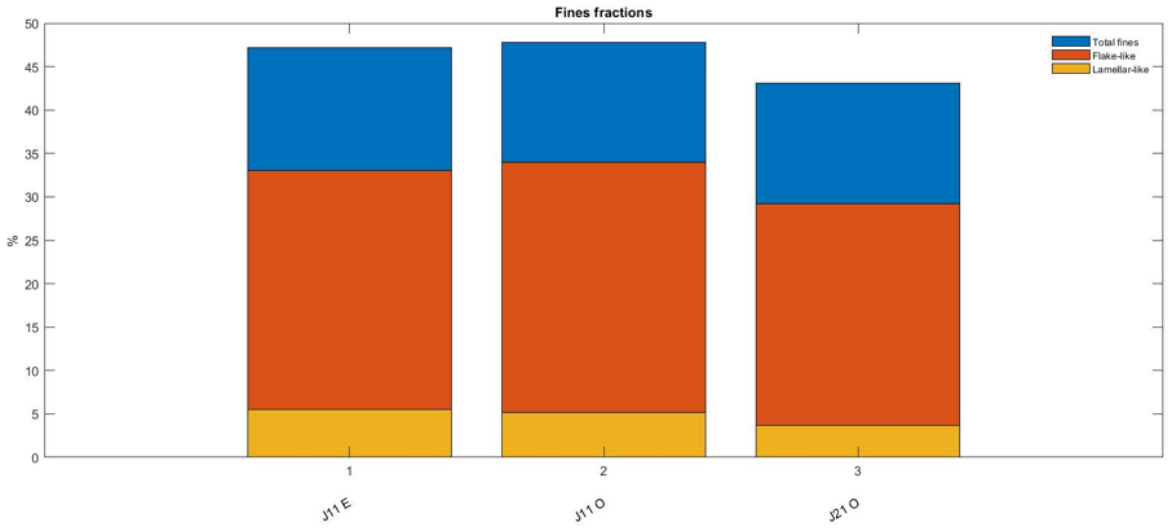


Figure 67 Comparative results for generated fines fractions. J11 E represents the experimental blades for refiner J11, J11 O and J21 O represents the original blades for both refiners.

The amount of fines fractions is a bit higher with the refiner J11 O compared to J21 O. Total amount of fines is higher by 4,70 % as well as the flake-like fines fraction. The amount of lamellar-like fines increased 1,50 %. The experimental blades (J11 E) generates a little bit less fines than the original blade. The difference however is so small that it practically fits into the error margins of measurement.

While surprisingly the fines fractions generated using the experimental refiner blade type did not practically change compared to the original refiner blades, one could assume that other BCTMP qualities (such as bulk and shive values) may change due the different blade pattern and grinding conditions. Noticeable change in specific energy consumption was discovered; specific energy consumption with the experimental refining blades dropped dramatically (~ 0,08 MWh/Adt in average). Graphs for energy consumption can be seen in appendix 2. In Figure 68 bulk values for BCTMP from late march to mid-July is presented. The experimental refining blade was changed between 8 of May and 30 of May (blue line).

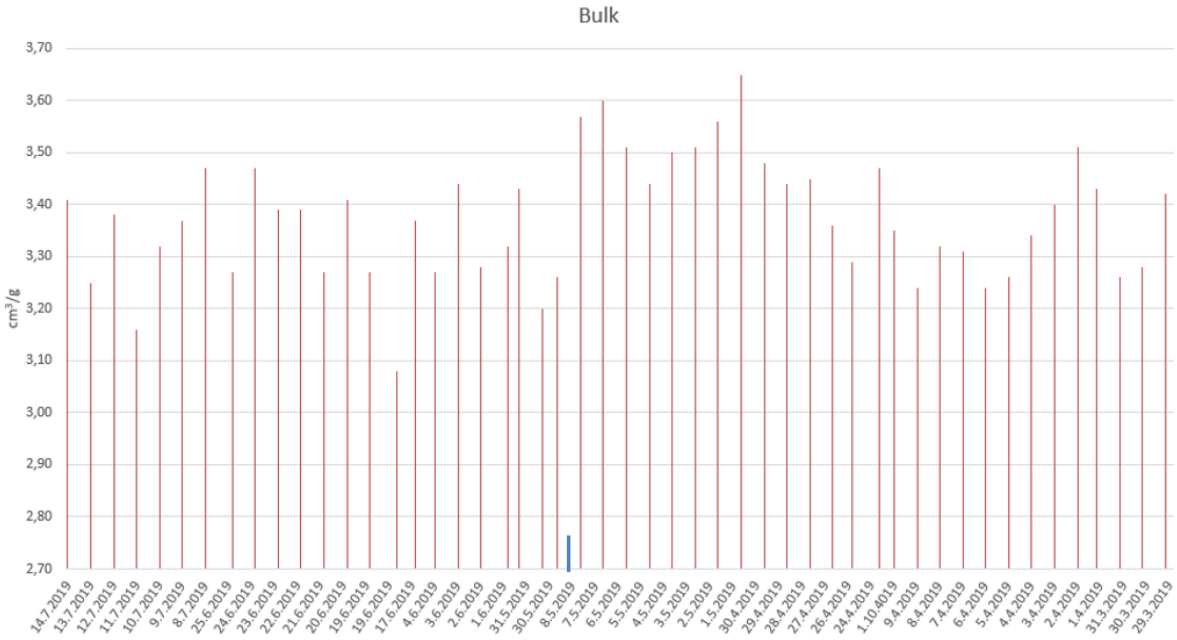


Figure 68 The bulk values for the BCTMP.

The bulk values seemed to drop after the experimental blades were applied. However, when inspecting the bulk values before the blades were changed, the values seem to be gain the same level.

Not only the blade pattern has influence on the amount of energy consumption and bulk, but also on shive and freeness. These values correlate strongly with the pulp quality. Shive content of BCTMP from late May to mid-July can be seen in Figure 69.

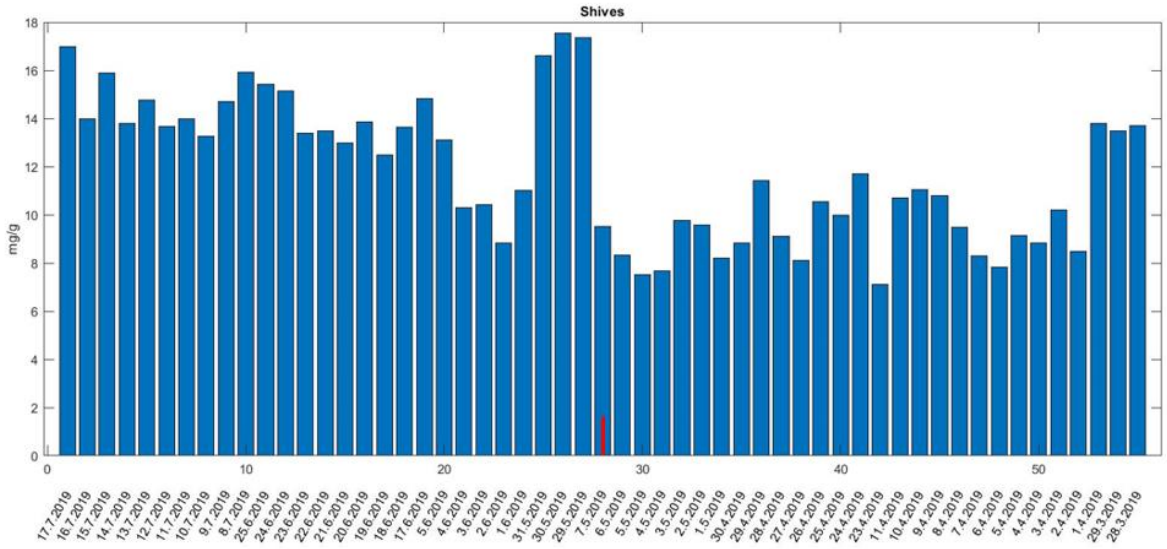


Figure 69 The shives content for BCTMP.

A spike in the shives content can be seen immediately after the experimental blades were applied (red line). The refiner with experimental blades have to be driven with different properties compared to the refiner with original blades, thus optimization of the refiner properties takes some time. However, the shives content in the BCTMP does seem to have increased. The new blade pattern seems to enhance the shives generation. The amount of shives in the BCTMP however is still below the set maximum value. The maximum value for shives is set to be 20 mg/g.

CSF (Canadian Standard Freeness) values were also inspected at the same period of time. As stated in section 6.2.3.4, freeness values illustrates the ''filterability'' of the BCTMP; while the fines content increase, freeness level should decrease. Figure 70 shows that CSF values tend to have high variation. Freeness value can change significantly only within a few hours, so CSF values alone are not suitable to determine fines influence for BCTMP. CSF values were obtained from each day's analyses (~ 8:00). CSF range for BCTMP is set to be 510-570 ml. Red line determines the day when experimental blades were changed.

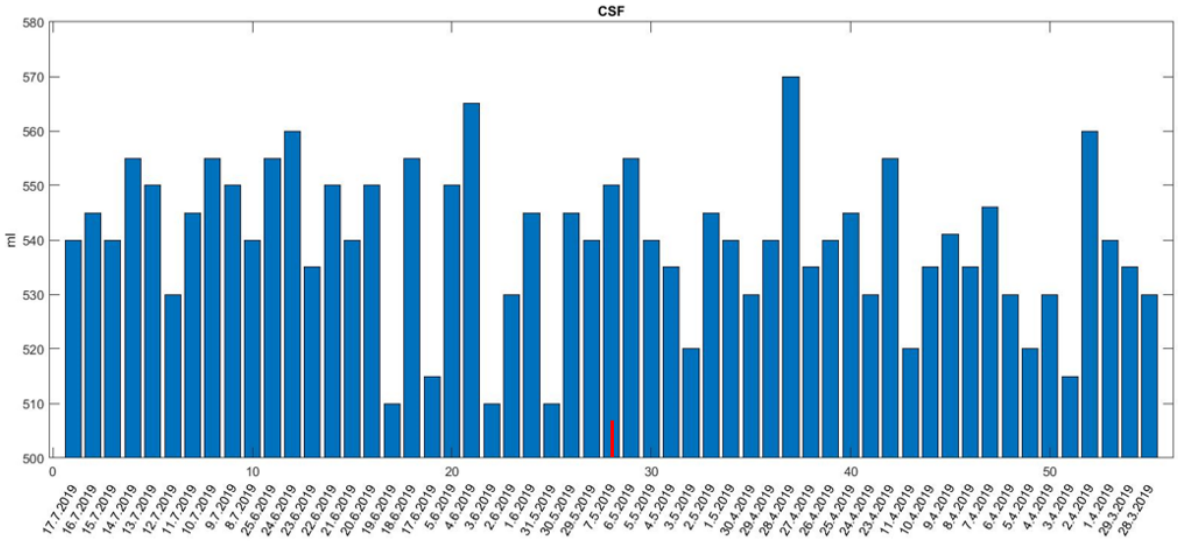


Figure 70 The CSF (Canadian Standard Freeness) values for BCTMP.

As many pulp quality values correlate with freeness values (such as shives content, scott-bond and bulk), it is reasonable to illustrate the CSF values with these values (as there is high variation within the CSF values alone).

Shives are fibre clusters that are generated in refining; they are darker than normal fibres and have effect in pulp strength qualities. High shives content in pulp is not desirable, so optimization between freeness and shives content should be acquired. High shive content correlates with inefficient chip impregnation. Figure 71 illustrates the correlation between CSF values and shive values.

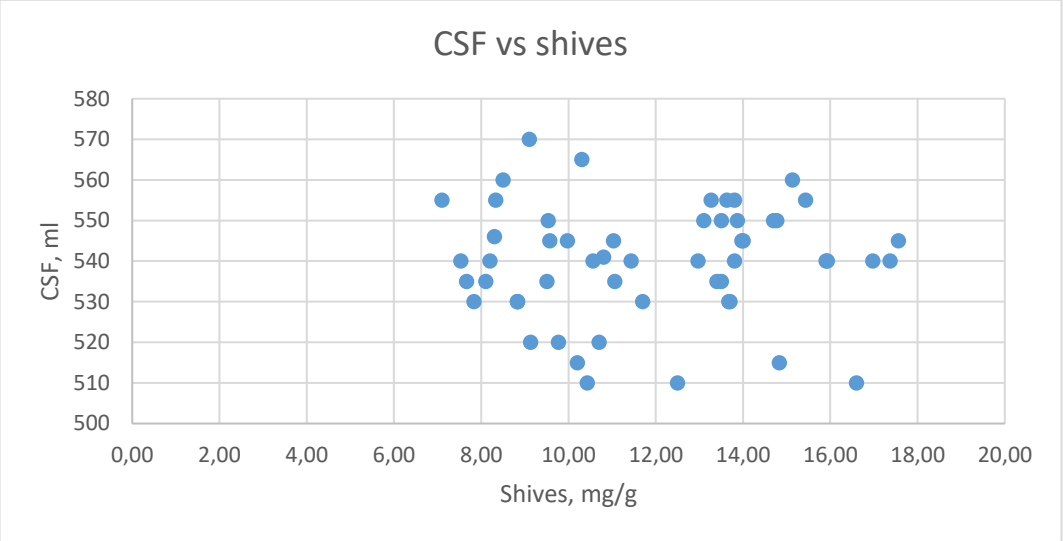


Figure 71 CSF values versus shive values for BCTMP.

Another way to inspect the pulp quality is to illustrate the CSF values with bulk values. In theory the bulk value should increase while the CSF value increase. There is high variation within sample qualities, so in this case any results that supports this theory was not obtained. Higher CSF values should correlate with lower amount of fines; the fibrous matrix is more porous as the amount of fines is not sufficient enough to fill the gaps and pores between fibres. CSF and bulk values are compared in Figure 72.

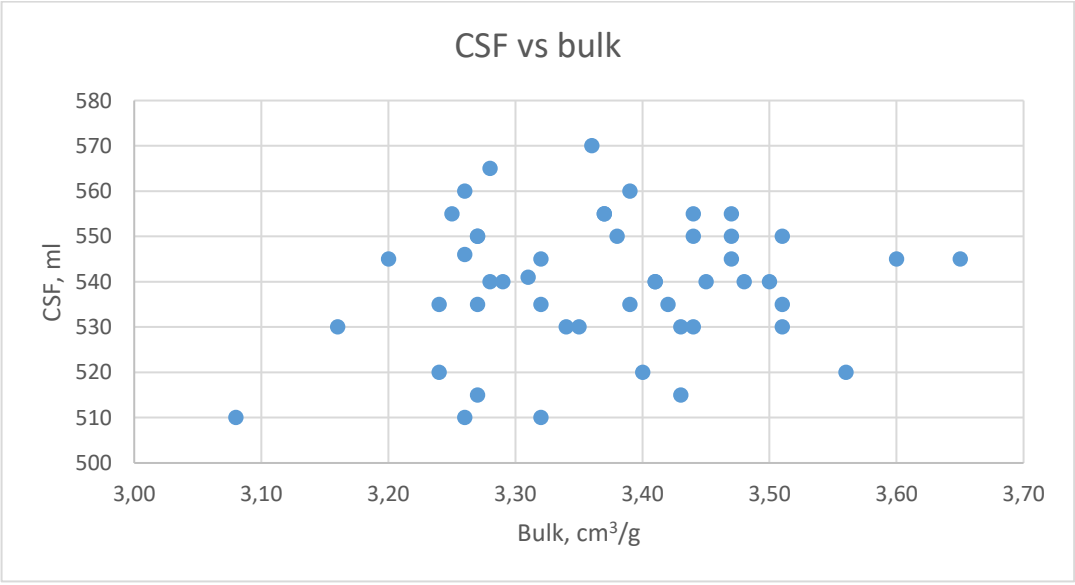


Figure 72 CSF values versus bulk values for BCTMP.

While CSF, shives content and bulk are important values considering the pulp quality, one of the most important value is the Scott Bond value (z-axis strength). This value represents the strength (J/m^2) needed to tear the sample surface in the direction of z-axis. As stated in section 5.5, the z-axis strength depends on the bonded area and the specific bonding strength between fibres. The bonded area is influenced by fibre flexibility and the amount of fines. Scott Bond values for BCTMP can be seen in Figure 73 (red line representing the blade change) and bulk values with Scott Bond values in Figure 74.

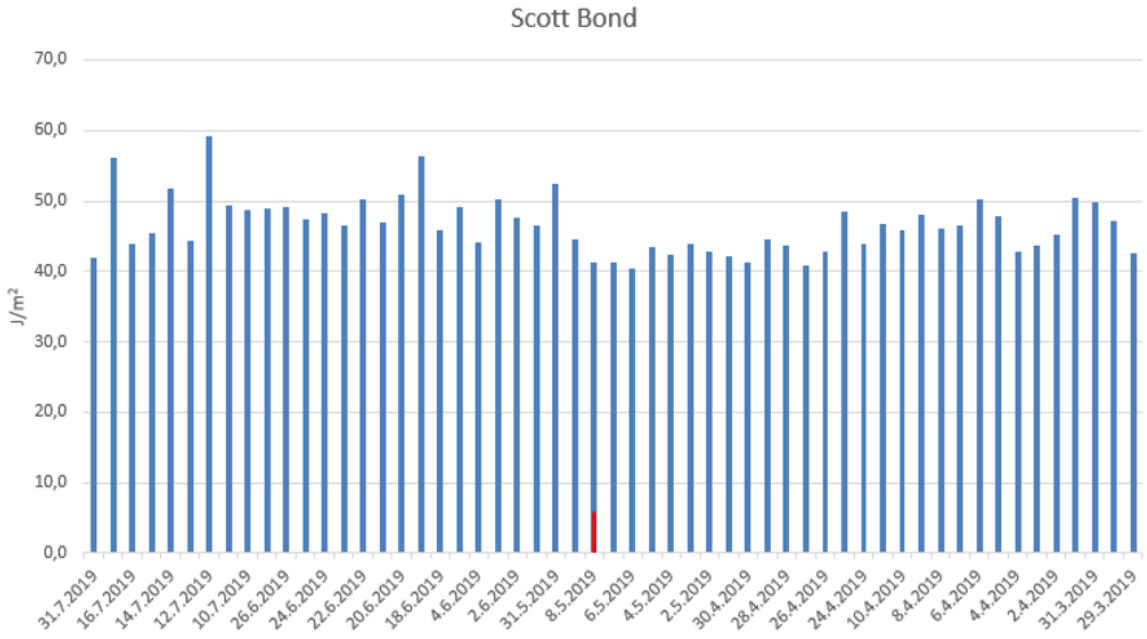


Figure 73 The Scott Bond values for BCTMP.

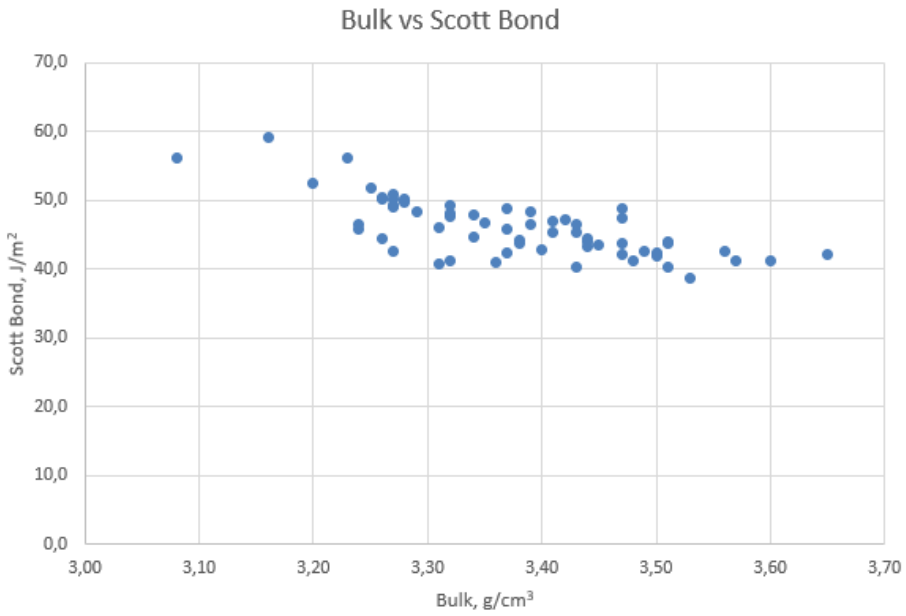


Figure 74 The bulk values versus Scott Bond values.

In longer periods of time there is significant variation within each value. This is because there is variation in process conditions and in the measurements themselves. Incorrect results can be obtained, because the measurements done are not constant as they are including the human factor and other factors influencing the gained results. One could determine the exact time of operation for certain quality level from the versus values, but maintaining optimal process conditions that prevail within these levels is difficult or even impossible. The blade change did not affect the pulp quality values; pulp quality had the same amount of variation compared to the situation with original refiner blades. The possible errors in measurements and results are discussed in the next section.

10 Error estimations

There is always a small error margin in every analysis made. The measured value is not exactly valid, but an estimation of the value that is being measured. Errors found in measurement can be classified as random and systematic errors. Systematic errors always include a pattern, that can be recognized and fixed. Random errors are harder to detect and fixed. Random error includes many independent factors. One cannot know the exact magnitude of the measurement error, so a measurements uncertainty margin is often applied (Taylor, 1999).

The greatness of the uncertainty margin states the reliability of the result; smaller the margin means more reliable result. When inspecting the uncertainty margin, one should take in consideration all possible factors that can have influence in the result. Common factors are for example the measurement method itself, process or measurement conditions, measurement equipment and the measurer (human) itself. Determining an actual error margin for the results in very difficult or almost impossible due to high amount of variables in the data and experiments.

The fines determination process started from consistency (the amount of solid particles) determination, where the sample consistencies in some cases were quite low. One could assume that analyses made from higher consistency samples are more reliable than the ones made from lower consistency samples, as the internal instruction method (''cup method'') is more suitable for higher consistencies. Higher consistency samples have consistency values up to 84 % while lower consistency samples can be less than 0,05%. It is only natural that the probability of error increases significantly in lower consistency values. The needed sample volume for lower consistencies is really high. Samples taken around the process had the same volume regardless from the consistency (~ 10L).

The errors that occurred in the consistency determination was clearly seen when building the Balas-model for the fines balance over the BCTMP process. Process streams with higher consistencies did not cause as much problems as the lower consistencies (filtrates) did. Some of the streams were not reasonable, so some estimations about the consistencies had to be made. However, as the problematic streams were mainly found in filtrate streams, the actual pulp flow was not influenced. One should also keep in mind that the balance model made with Balas is only a mathematic estimation of the process behavior; to obtain accurate results, every stream in the process should be measured (for example with equipment exploiting ultra sound). All process streams (pulps and filtrate) cannot be measured, but the ones that cannot be measured could be validated by certain mathematical approximations. Streams that include underpressure operations would probably be hard to measure, as the measurements in these cases often assume that the measured pipe is full (which is not the case in underpressure units).

One of the major issues in the fines fraction determination is considering the FS-5. FS-5 analyses the particle size from the particles' projected area (length or width based on the fines type). Definitely the biggest disadvantage considering the FS-5 is that it does not analyze flake-like and lamellar-like fines from the total amount of fines as all fractions (total, flake-like and lamellar-like fines) are measured form the total amount of solid particles. The vicinity of the results stays the same, but all in all it would be better if the fine types were analyzed from the total amount of fines. This of course means that the FS-5 should analyze all types of fines, not only flake-like and lamellar-like or alternatively fines that do not fulfill the specs for flake -and lamellar-like fines are categorized as ''other fine types'' in percentage. Also the results obtained from the FS-5 are not straightly comparable for example with the DDJ results. According to DDJ, pulp samples have fines content around 20 %. The FS-5 states that pulp samples have fines content in some cases over 50 %. At this point there is no existing correlation which could help to put the obtained results from FS-5 in proportion with the DDJ results. DDJ should give more realistic results when considering the total fines content as it gives the fines-to-fibers weight ratio in percentage. However, DDJ has very long analysis time for pulp samples and practically it is not reasonable to execute for filtrate samples.

11 Conclusions

The target of this thesis was to obtain information of fines types, fines generation mechanisms, fines behavior within the BCTMP process and fines effects on product (BCTMP) qualities. The goal of the experimental part of this thesis was to obtain the required information of fines behavior over the Joutseno BCTMP process via laboratory experiments and simulation. The fines balance was built based on obtained information about fines behavior using a Balas software. Results (balance) for disc filter and screw press 12 was represented as they are considered to be key unit operations considering the fines production. The experimental part included the laboratory experiments and a process trial with experimental blade type.

The amount of fines in pulp streams does not seem to have much difference when comparing fines content in late-process steps and fines content just after refining. Both FS-5 and DDJ analyses state that the fines content in main pulp stream (not including reject streams) does seem to stay relatively constant. The most interesting result is that bleaching does not seem

to have any influence on the fines content and morphology. One could assume that the structure and proportion would change, but this is not the case.

The amount of fines in reject stream is lower compared to the main pulp stream. This is because the screening units let the fines pass the screening mesh; higher proportion of fines is passing through to the accept flow thus reject flow is mainly consisted of longer fibres and fibre clusters that didn't pass the mesh. Both FS-5 and DDJ results support this theory. The amount of fines within the reject stream has way more variation compared to the main pulp stream. The amount of fines in some cases drop from ~ 45 % (reject accept flow) to ~ 15 % (pp reject flow). If fines would be treated in reject handling, it would be reasonable to treat the reject accept flow as it migrates into the main pulp accept flow.

CSF, shive, bulk and Scott Bond values were also inspected. CSF values have high variation (510 – 570 ml) as the results can vary significantly even between small time windows. This is because the process conditions and pulp quality in smaller time fragments is not constant. The shives values seemed to increase after the experimental blades were changed. There is a clear spike in shives content just after the experimental blade change (10 to 17 mg/g). Even though the refiner conditions and operation properties were optimized, the shives content stayed in higher levels compared to the levels before the blade changes. Bulk values dropped a bit after the experimental blade change. After the suitable refiner properties were obtained, bulk levels did rise back to the same level as they were before the blade change. Scott Bond values had no significant difference when inspecting the time before and after the blade change.

The corresponding charts for CSF, shives, bulk and Scott Bond illustrate the possible product qualities that can be achieved. However, determining the process conditions at certain quality point is quite hard and to keep the process in those conditions that produce that certain quality is really difficult or even impossible. The conditions and drivability for refiner J11 after the blade change was an issue; the pressures required to operate the refiner didn't stay in needed levels, temperatures tend to rise and the optimal consistency for the refiner feed was quite hard to find. Even though the blade type did not have influence on the fines content, major advantage was the lower specified energy consumption (~ 0,08 MWh/Adt in average).

Pulp and filtrate streams that have high fines production rate and are in key position considering the BTCMP process (such as disc filter and screw presses) should be investigated. If fines could be retented with retention agents in a key point of a process, the overall fines content would decrease. It would be desirable to have freshly generated fines influencing with the pulp alone. As fines are not treated in any way at this point, fines have achieved an equilibrium in the process. Fines circulating through the process within the filtrates do not enhance the final product properties. It is however unknown how retention agents or fillers are activated and how the mechanisms causing the fines retention in pulp is affected. Pulp retention capacity for fines was also obtained to be quite high already, so the actual benefit using retention agents should be investigated. It should be also noted that the actual fines production is relatively low in filtrates compared to pulp flows.

Another aspect would be trying to remove fines in whole. It is suggestable to investigate the actual effect of fines on consumption of bleaching chemicals. This experiment could be executed by taking a sample before the first bleaching stage (MC-bleaching) and removing fines from the sample (pulp). Fines free pulp would be bleached in laboratory scale in similar conditions with the right vicinity of bleaching chemicals. Fines absorption capacity and consumption difference of bleaching chemicals for fines rich and fines free pulp could be determined. Based on obtained results the methods for removing fines from the pulp and the cost-efficiency of the fines removal process could be studied.

12 References

Abbot, J., Hobbs, G. C., (1992). Influence of metal ions on two-stage peroxide bleaching of radiata pine TMP, *Journal of Pulp and Paper Science, 18 (2),* pp. 67-70.

Amiri, R., Gorres, J., Karnis, A., Wood, J. R. (1996). Mechanical pulp fines and sheet structure. *J Pulp Pap Sci*, 22, pp.J491-J496.

Asgari, F. and Argyropoulos, D. (1998). Fundamentals of oxygen delignification. Part II. Functional group formation/elimination in residual kraft lignin. *Canadian Journal of Chemistry*, 76(11), pp.1606-1615.

Azeez, A., Meier, D., Odermatt, J. and Willner, T. (2010). Fast Pyrolysis of African and European Lignocellulosic Biopulpes Using Py-GC/MS and Fluidized Bed Reactor. *Energy & Fuels*, 24(3), pp.2078-2085.

Bäckström, M., Kolar, M. C, Htun, M. (2008). Characterization of fines from unbleached kraft pulps and their impact on sheet properties. *Holzforsching, 62,* pp.546-552.

Bajpai, P. (2012). *Environmentally benign approaches for pulp bleaching*. 1st ed. Amsterdam: Elsevier, pp.205-225.

Bambrick, D. R. (1985). Effect of DTPA on reducing peroxide decomposition, *TAPPI Journal*, 68(6), pp. 96-100.

Barbe, M. C., Dessureault, S., Janknecht, S. (1993). Review of mechanical and chemi-thermomechanical pine pulping (1). *Paper Southern Africa 13(1):10*

Beath, L.R., Neill, M.T. and Pulpe, F.A. (1966): Latency in mechanical wood pulps, Pulp Paper Mag. Can. 67(10), T423.

Bian, Y., Ni, Y., Yuan, C., Heitner, C., Beaulieu, S. (2008). Improving TMP rejects refining through alkaline peroxide pretreatment: an opportunity for SCA paper? Pulp & Paper Canada, vol. 109, no. 1, p.23.

Blander, M., Ragland, K., Cole, R., Libera, J. and Pelton, A. (1995). The inorganic chemistry of wood combustion for power production. *Biopulp and Bioenergy*, 8(1), pp.29-38.

Boutelje, J. and Eriksson, 1. (1984): Analysis of lignin in fragments from thermomechanical spruce pulp by ultraviolet microscopy, Holzforschung 38(5), 249.

Brill, J. W. (1985). Effects of wood and chip quality on TMP properties. *Proceedings of 1985 International Mechanical Pulping Conference.* May 6-10, 1985, Stockholm, Sweden. SPCI. pp. 153-161.

Capretti, G., Westermark, U. (1988). Influence of ray cells on the bleachability and properties of CTMP and kraft pulps. *Nord Pulp Pap Res J,* 3, pp.95-99.

Carman, P. C. (1937). Fluid flow through granular beds. *Transactions, Institution of Chemical Engineers, London*, 15: 150-166, 1937.

Carrier, M., Loppinet-Serani, A., Denux, D., Lasnier, J., Ham-Pichavant, F., Cansell, F. and Aymonier, C. (2011). Thermogravimetric analysis as a new method to determine the lignocellulosic composition of biopulp. *Biopulp and Bioenergy*, 35(1), pp.298-307.

Chen, H., Park, A., Heitmann, J. A. (2009). Importance of cellulosic fines relative to the dewatering rates of fiber suspensions. *Ind End Chem Res, 48*, pp.9106-9112.

Cole, C. A., Hubbe, M. A., Heitmann, J. A. (2008). Water release from fractionated stock suspensions. Part 1 – effects of the amounts and types of fiber fines. *Tappi J,* 7, pp.28-32.

Colodette, J. L., Rothenberg, S., Dence, D. W. (1988). Factors affecting hydrogen peroxide stability in the brightening of mechanical and chemi-thermomechanical pulps. I: Hydrogen peroxide stability in the absence of stabilizing systems, J. Pulp Paper Sci: 14(6):J126

Daneault, C., Leduc, C. (1995). Bleaching efficiency of formamidine sulfidic acid (fas) in comparison to hydrosulfite, borohydride and peroxide in one and two stages, *Tappi J.* 78(7):153.

De Silveira, G., Zhang, X., Berry, R., Wood, J.R. (1996). Location of fines in mechanical pulp handsheets using scanning electron microscopy. J. Pulp Paper Sci. 22(9):J315-320.

Dhyani, V. and Bhaskar, T. (2018). A comprehensive review on the pyrolysis of lignocellulosic biopulp. *Renewable Energy*, 129, pp.695-716.

Ek, M. (2009). *Pulping chemistry and technology*. 2nd ed. Berlin: De Gruyter, pp.60-73.

Eklund, D., Lindström, T. (1991). Paper chemistry: An introduction. DT Paper Science Publications, Finland.

El-Sakhawy, M. (2005). Effect of bleaching sequence on paper ageing, *Polymer Degradation and Stability*, 87, pp. 419-423.

Fernando, D., Hafrén, J., Gorski, D., Daniel, G., Salomons, F. A. (2014). Fiber-and fine fractions-derived effects on pulp quality as a result of mechanical pulp consistency. *Wood Schi Technol*, 48, pp.737-753.

Ferritius, O., Moldenius, S., The effect of impregnation method on CTMP properties, *International Mechanical Pulping Conference Proceedings*, SPCI, Stockholm, p. 91.

Franzén, R. (1986). General and selective upgrading of mechanical pulps. *Nordic Pulp Paper Res.* J. 1(3):4.

Froschauer, C., Hummel, M., Iakovlev, M., Roselli, A., Schottenberger, H. and Sixta, H. (2013). Separation of Hemicellulose and Cellulose from Wood Pulp by Means of Ionic Liquid/Cosolvent Systems. *Biomacromolecules*, 14(6), pp.1741-1750.

Gehmayr, V., Schild, G. and Sixta, H. (2010). A precise study on the feasibility of enzyme treatments of a kraft pulp for viscose application. *Cellulose*, 18(2), pp.479-491.

Gharehkhani, S., Sadeghinezhad, E., Kazi, S., Yarmand, H., Badarudin, A., Safaei, M. and Zubir, M. (2015). Basic effects of pulp refining on fiber properties—A review. *Carbohydrate Polymers*, 115, pp.785-803.

Goring, D.A.I. (1963): Thermal softening of lignin, hemicellulose, and cellulose, Pulp Paper Mag. Can. 64(12), T517.

Gregersen, O. W. (1998). On the assessment of effective paper web strength, Doktor ingenior-avhandling, 76, Trondheim, Norway

Gregersen, O. W., Hansen, Å., Helle, T. (2000). The influence of shives on newsprint strength, J. of pulp and paper sci. 5(26): 176-179.

Gullichsen, J. and Fogelholm, C. (2000). *Chemical Pulping*. 6th ed. Helsinki: Fapet Oy & Tappi.

Gullichsen, J. and Paulapuro, H. (2000). *Papermaking*. Atlanta, Ga.: Tappi Press.

Gustafsson J, Lehto J, Tienvieri T, Ciovica L & Peltonen J (2003) Surface characteristics of thermomechanical pulps: the influence of defibration temperature and refining. Colloids and Surfaces A: Physicochemical and Engineering Aspects 225 (1–3): 95– 104.

Hache, M. J. A., Brundgard, J. R., Munroe, D. C., Teoderescu, G. (1994). The color stripping of office wastepaper with sodium hydrosulphite. *Pulp Pap- Canada* 95(12), 120-125.

Hardell, H.-L., Leary, G.J., Stoll, M. and Westermark, U. (1 980): Variations in lignin structure in defined morphological parts of spruce, Svensk Papperstidn. 83(2), 44.

Härkönen, E.J., Heikkurinen, A., Nederström, R. (1989). Comparison between different species of softwood as TMP raw material. *Preprints of 1989 International Mechanical Pulping Conference.* June 6-8, 1989, Helsinki, Finland. Vol. 2, pp. 390-397.

Haugan, M. and Gregersen, Ø (2006): Hydrogen peroxide bleaching of mechanical pulp fines, Nord. Pulp Paper Res. J. 21(1), 105-110.

He, Z., Ni, Y., Qian, X. (2005). The strength properties of bleached mechanical pulps from magnesium hydroxide-based peroxide bleaching process, *PAPTAC 91ST Annual Meeting, Montreal, Canada.* Book C, pp. 115-125.

Heitner, C., Argyropolous, D., Miles, K., Karnis, A., Kerr, R. (1993). Alkaline sulphite ultra-high-yield pulping of aspen chips: a comparison of steam explosion and conventional chemi-thermomechanical pulping, *J. Pulp Paper Sci.* 19(2): 58

Hemmes, J. L. (2013). Retention aids and drainage accelerators. *H. Holik (Ed.), Handbood of paper and board, Wiley-VCH Verlag, Weinheim*, pp. 295-300.

Honkasalo, J., Knuts, K. Laine, J.E. and Nygren-Konttinen, A. (1983): The fines fraction of mechanical pulp – A litterature review, Paperi Puu 65(11), 693-699.

Htun, M., De Ruvo, A. (1978). The implication of the fines fraction for the properties of bleached kraft sheet. *Sven Papperstidn, 81*, pp.507-510.

Htun, M., Engstrand, P. and Salmén, N.L. (1988): The implication of lignin softening on latency removal of mechanical and chemi-thermomechanical pulps, J. Pulp Paper Sci. 14(5), 109.

Hubbe, M. A, Heitmann, J. A. (2007). Review of factors affecting the release of water from cellulosic fibers during paper manufacture. Bioresources 2(3), pp. 500-533.

Hubbe, M. A. (2002). Fines management for increased paper machine productivity. *Proceedings of scientific and technical advances in wet end chemistry, Vienna, Austria.*

Hutterer, C., Kliba, G., Punz, M., Fackler, K. and Potthast, A. (2017). Enzymatic pulp upgrade for producing high-value cellulose out of a Kraft paper pulp. *Enzyme and Microbial Technology*, 102, pp.67-73.

Ibarra, D., Köpcke, V. and Ek, M. (2009). Exploring enzymatic treatments for the production of dissolving grade pulp from different wood and non-wood paper grade pulps 10th EWLP, Stockholm, Sweden, August 25–28, 2008. *Holzforschung*, 63(6).

Ilvessalo-Pfäffli, M.-S. (1977). The structure of wood. *In ''Wood chemistry''*(W. Jensen, ed.), 2nd ed., pp. 7-18. Text handb. Finn. Paper Eng. Assoc., Helsinki. (In Finn).

Janzon, R., Puls, J. and Saake, B. (2006). Upgrading of paper-grade pulps to dissolving pulps by nitren extraction: Optimisation of extraction parameters and application to different pulps. *Holzforschung*, 60(4).

Jones, H.W.H. (1966): Occurrence and removal of kink and curl from mechanical pulp fibres as related to paper properties, Pulp Paper Mag. Can. 67(6), T283.

Kallmes, 0. (1960): Distribution of constituents across the wall of unbleached spruce sulfite fibers, Tappi 43(2), 143.

Kangas, H. (2004). Surface chemical and morphological properties of mechanical pulp fines. *Nordic Pulp and Paper Research Journal*, 19(02), pp.191-199.

Kappel, J. (1999). Mechanical Pulps: from wood to bleached pulp, TAPPI Press, Atlanta.

Karlsson (2010). High consistency hydrogen peroxide bleaching of mechanical pulps with varying amounts of fines. Nordic Pulp and Paper Research Journal, 25(03), pp.256-268.

Kerekes, R.J. (2006): Rheology of fibre suspensions in papermaking: An overview of recent research, Nord. Pulp Paper Res. J. 21(5), 598.

Kleen, M., Kangas, H. and Laine, C. (2003): Chemical characterization of mechanical pulp fines and surface layers, Nord. Pulp Paper Res. J. 18(4), 361-368.

KnowPap.com. [online]. Available at: http://www.knowpap.com/.

KnowPulp.com. [online]. Available at: http://www.knowpulp.com/.

Korpela (2002). Improving the strength of PGW pine pulp by alkaline peroxide treatment. *Nordic Pulp and Paper Research Journal*, 17(02), pp.183-186.

Kouk, R.S., Meyrant, P. and Dodson, M.G. (1989): Hydrogen peroxide bleaching of spruce high-yield pulp at varying degrees of sulfonation, J. Pulp Paper Sci. 15(4), 151-157.

Krogerus, B., Tiikkaja, E. (2002). Fines from different pulps compared by image analysis, *Nord Pulp Pap Res J*, 17, pp.440-444.

Kubelka, P., Munk, F., Z. tech. (1931). Physik 12(11a): 593

Kurra, S., Lindholm, C.-A., Virkola, N., Effect of uneven impregnation in chemi-thermomechanical pulping, *1985 International Mechanical Pulping Conference Proceedings*, SPCI, Stockholm, p. 80.

Laivins, G. V, Scallan, A. M. (1996). The influence of drying and beating on the swelling of fines. *J Pulp Pap Sci, 22*, pp.J178-184.

Laivins, G. V, Scallan, A. M. (1993). The mechanism of hornification of wood pulps. *In Productions of Papermaking, Transactions of the Thenth Fundamental Res.* Symp., Oxford, U.K. pp. 1235-1260.

Law, K. -N and Valade, J.L. (1999). Properties of CTMP mixtures of aspen, birch and maple. *Pulp and Paper Canada.* 100.12. p 117-122.

Le Févre, G., Lamarche, Y. O., Lanry, É. (2001). Magnesium sulfate addition for refiner scale prevention in an alkaline peroxide mechanical pulping (APMP) process. *Proceedings of the Technical Association of the Pulp and Paper Industry*, 1-6.

Leduc, C. and Daneault, C. (2007): Impact of mechanical pulp fines on the efficiency of peroxide bleaching of TMP pulp, Cellul. Chem. Technol. 41(7-8), 399-404.

Lee, H., Hamid, S. and Zain, S. (2014). Conversion of Lignocellulosic Biopulp to Nanocellulose: Structure and Chemical Process. *The Scientific World Journal*, 2014, pp.1-20.

Lehto, J. (1995). Various poplar species as raw material for paper grade mechanical pulps. *Proceedings of 1995 International Mechanical Pulping Conference.* June 12-15, Ottawa, Canada, pp. 9-21.

Levlin J. (1999). General physical properties of paper and board, *Papermaking Science and Technology. Book 17, Pulp and Paper Testing.* Fapet, Helsinki, pp. 132-158.

Li, Y. (2014). Studies on Cellulose Hydrolysis and Hemicellulose Monosaccharide Degradation in Concentrated Hydrochloric Acid.

Liimatainen, H., Haapala, A., Niinimäki, J. (2009). Retention of PCC and GCC fillers on chemical pulp fines surfaces. *Tappi J, 8,* pp. 38-42.

Liimatainen, H., Taipale, T., Haapala, A., Niinimäki, J. (2008). Influence of mechanical pulp fines on clay retention. *Tappi J, 7,* pp. 10-16.

Lindholm, C. A. (1978). Modification of groundwood pulp through chemical treatment of the coarse fiber fraction. Part I. Effect on the sheet structure. *Pap Puu,* 60, pp.219-222.

Lindholm, C. A. (1980). Comparison of some papermaking properties of groundwood, pressure groundwood and thermomechanical pulp by means of artificial blends of pulp fractions. *Part 1. Primary results.* Pap Puu, 62, pp.593-606.

Lönnberg, B. (2009). *Papermaking science and technology*. Helsinki: Paperi ja Puu Oy.

Lumiainen, J. (1998). Papermaking part 1, vol. 8; Stock Preparation and wet end Ch. 4; Refining of chemical pulp.

Lundin, T., Batchelor, W., Fardim, P. (2008). Fiber trapping in low-consistency refining: new parameters to describe the refining process, s.I. Tappi Jr.

Luukko, K. (1998): On the characterization of mechanical pulp fines, Paperi Puu 80(6), 441-448.

Luukko, K. and Paulapuro, H. (1999): Mechanical pulp fines: Effect of particle size and shape, Tappi J. 82(2), 95.

Luukko, K., Kemppainen-Kajola, P., Paulapuro, H. (1997). Characterization of mechanical pulp fines by image analysis. Appita J, 50, pp.387-392.

Luukko, K., Maloney, T. C. (1999). Swelling of mechanical pulp fines. *Cellulose, 6*, pp.123-135.

Mark, R. E. (1984). Structure and structural anisotropy. V. Dimensional characterization of shives, slivers and fines. *Handbook of physical and mechanical testing of paper and paperboard*, Marcel Dekker, New York, USA.

Marton, R. (1964). Fiber structure and properties of different groundwoods. *Tappi, 47,* pp. 205A-208A.

Marton, R. (1964): Fiber structure and properties of different groundwoods, Tappi 47(1), 205A.

Melzer, J. (1985). Kinetics of bleaching mechanical pulps by sodium dithionite. In: International Pulp Bleaching Conference. CPPA Technical Section. Montreal. pp. 69–73.

Minor, L. J. (1994). Hornification – Its Origin and Meaning. *Progress in Paper Recycling,* pp. 94-95.

Mohan, D., Pittman,, C. and Steele, P. (2006). Pyrolysis of Wood/Biopulp for Bio-oil: A Critical Review. *Energy & Fuels*, 20(3), pp.848-889.

Moldenius, S. (1984). The effect of peroxide bleaching on the strength and surface properties of mechanical pulping, *J. Pulp Paper Sci,* 10(6): 172

Moss, P., Nieminen, K., Retulainen, E. (1993). Effect of fines on the properties of fibre networks. *C. F. Baker (Ed.), Products of papermaking, Pira International, Leatherhead, UK.* pp.727-770.

Muchorski, D. (2006). Tensile properties of paper and paperboard using constant rate of elongation apparatus, revision of T 494 om-01, *TAPPI* (2)

Müller, M., Czihak, C., Schober, H., Nishiyama, Y. & Vogl, G. (2000): All disordered regions of native cellulose show common low-frequency dynamics, Macromolecules, 33(5), 1834

Ni, Y., Ng, A. and Mosher, M. (1999): A model compound study –The formation of colored metallic extractive complexes and their effect on the brightness of TMP pulp, J. Wood Chem. Technol. 19(3), 213-223.

Nurminen, I and Sirviö, J. (2004). Systematic changes in paper properties caused by fines. *Pulp Pap Can,* 105, pp.39-42.

Odabas, N., Henniges, U., Potthast, A. and Rosenau, T. (2016). Cellulosic fines: Properties and effects. *Progress in Materials Science*, 83, pp.574-594.

Paavilainen, L. (1990). Importance of particle size-fiber length and fines – for the characterization of softwood kraft pulp, Pap Puu, 72, pp.516-526.

Paavilainen, L. (1993). Conformability – flexibility and collapsibility of sulphate pulp fibers. Paperi ja Puu 75(9-10), pp. 689-702.

Page, D.H. (1976): A Note on the cell-wall structure of softwood tracheids, Wood and Fiber, 7(4), 246.

Page, D.H. (1989): The beating of chemical pulps - The action and the effects, Papermaking Raw Materials, In Baker, C.F. and Punton, V.W. (ed.), Transactions of the 9th Fundamental Research Symposium, Cambridge, England Sept. 1989, Mech. Eng. Publ. Ltd. London, UK, pp.1-37.

Page, D.H., Seth, R.S., Jordan, B.D. and Barbe, M.C. (1985): Curl, crimps, kinks, and microcompressions in pulp fibers - their origin, measurement, and significance, Paper Making Raw Materials In Punton, V. (ed.), Transactions of the 8th Fundamental Research Symposium, Oxford, England Sept. 1985, Mech. Eng. Publ. Ltd., London, UK, pp. 183-227.

Pan, G. (2004). Relationship between dissolution of fiber materials and development of pulp strength in alkaline peroxide bleaching of mechanical pulp. *Holzforschung*, 58(4), p. 369.

Pandey, K. (1999). A study of chemical structure of soft and hardwood and wood polymers by FTIR spectroscopy. *Journal of Applied Polymer Science*, 71(12), pp.1969-1975.

Panshin, A. J, De Zeuuw, C. (1964). Textbook of wood technology, Vol 1, McGraw-Hill, USA.

Panula-Ontto, S., Fuhrmann, A., Robertsen, L. (2002). Effect of cell-wall thickness and fines on bleaching. *TAPPI international pulp bleaching conference, Portland, OR, US*, pp.161-169.

Paternoster, A., Van Camp, J., Vanlanduit, S., Weeren, A., Springael, J. and Braet, J. (2017). The performance of beer packaging: Vibration damping and thermal insulation. *Food Packaging and Shelf Life*, 11, pp.91-97.

Paulapuro, H and Vainio, A. K. (2007). Innterfiber bonding and fiber segment activation in paper. *Bioresources*, 2, pp.442-458.

Petit-Conil, M., Laurent, A. (2003). Bleaching behaviour of softwood TMP PGW or CTMP fibre fractions. *International mechanical pulping conference, Quebec city, Canada*, pp.105-114.

Putz, H. J. (1987). Upcycling of waste paper for use in high quality graphical papers by chemi-mechanical processing – mechanical treatment, p. 202. PhD thesis, Darmstadt University of Technology, Germany.

Rahkila, P., CMP/CTMP-nykytekniikka ja kemihierreprosessien ominaispiirteet, Insinöörijärjestöjen koulutuskeskus, Publication 75-86, p. III 1.

Reme, P. A., Helle, T. (2000). The fibre characteristics of shives initiating web rupture, Nordic Pulp and Paper Research J. 4(15): 287-291.

Retulainen, E., Luukko, K., Fagerholm, J., Pere, J., Laine, J., Paulapuro, H. (2002). Papermaking quality of fines from different pulps – the effect of size, shape and chemical composition. Appita J, 55, pp.457-460.

Richardson, J. D., Corson, S. R., Foster, R. S. (1992). Comparison of Scandinavian spruce and Radiata pine as raw material for high yield pulping. Appita 45(1): 33-37.

Roick, T., Schempp, W. and Krause, T. (1991): Mechanical pulp fines: some causes for their poor bleachability, Papier 45(10A), 23-26.

Roselli, A., Hummel, M., Monshizadeh, A., Maloney, T. and Sixta, H. (2014). Ionic liquid extraction method for upgrading eucalyptus kraft pulp to high purity dissolving pulp. *Cellulose*, 21(5), pp.3655-3666.

Rydholm, S. (1965). Pulping processes, Interscience Publisher, New York/London/Sydney, p. 896.

Salmén, N.L. and Olsson, A.-M. (1998): Interaction between hemicelluloses, lignin and cellulose: Structure-property relationships, J. Pulp Paper Sci. 24(3), 99.

Sampson, W. W., Kropholler, H. W. (1995). Batch-drainage curves for pulp characterization. *Tappi Journal 78(12)*, pp. 145-151.

Seccombe, R, & Crowe, R. (2007). A novel new non silicate stabiliser for the efficient bleaching of mechanical pulps, *Proceedings of 61st Appita Annual Conference and Exhibition*, 1, pp. 47-50.

Seth, R.S. (2006): The importance of fibre straightness for pulp strength, Pulp Paper Can. 107(1), T1

Seth, R.S., Francis, D.W. and Bennington, C.P.J. (1992): The effect of mechanical treatment during medium stock concentration fluidization on pulp properties, Appita J. 46(1), 54.

Sorvari, J., Sjostrom, E., Klemola, A. and Laine, J.E. (1986): Chemical characterization of wood constituents, especially lignin, in fractions separated from middle lamella and secondary wall of Norway spruce (Picea abies), Wood Sci. Technol. 20(1), 35.

Steenis, N., van der Lans, I., van Herpen, E. and van Trijp, H. (2018). Effects of sustainable design strategies on consumer preferences for redesigned packaging. *Journal of Cleaner Production*, 205, pp.854-865.

Stenius, P. (2000). *Forest products chemistry*. Helsinki: Fapet Oy, p.29.

Sundberg, A., Pranovich, A.V. and Holmbom, B. (2003): Chemical characterization of various types of mechanical pulp fines, J. Pulp Paper Sci. 29(5), 173-178.

Sundholm, J. (1999). Papermaking Science and Technology, Mechanical Pulping, Book 5.

Svensson, E., Hammar, L. -A., Htun, M. (1994) Some basic aspects on shives in low sulfonated thermomechanical pulps, Nordic pulp Paper Research J. 4(9):219-225

Taipale, T., Holappa, S., Laine, J. (2011). Isolation and characterization of cellulosic pulp fines and their interactions with cationic polyacrylamides. *J Dispers Sci Technol*, 32, pp.863-873.

Taylor, J. R. (1999). *An introduction to error analysis:* The Study of Uncertainties in Physical Measurements. University Science Books, pp. 94.

Techlabsystems.com. (2019). [online] Available at: https://www.techlabsystems.com/en/datasheets/pulp/cf_bauer_mcnett_fibre_classifier.pdf [Accessed 6 Apr. 2019].

Wakeman, R. J., Tarleton, E. S. (1999). Filtration: equipment, selection, modelling and process simulation. Elsevier Advanced Technology, Oxford, UK.

Wildfong, V. J, Genco, J. M., Shands, J. A., Bousfield, D. W. (2000). Filtration mechanics of sheet forming. Part II. Influence of fine material and compression. Journal of Pulp and Paper Science 26(8): 280–283.

Wood, J. R. (1996). Chip quality effects in mechanical pulping – a selected review. *Proceedings of TAPPI 1996 Pulping Conference.* Oct. 27-31, 1996, Nashville, TN, USA. TAPPI Press, Atlanta, GA, USA. Book 1, pp. 491-497.

Yoon, B.-H., Wang, L.-J. and Kim, G.-S. (1999): Formation of lignin-metal complexes by photo-irradiation and their effect on colour reversion of TMP, J. Pulp Paper Res. J. 25(8), 289-293.

Åkerlund, G., Jackson, M. (1984). The pulp of the future, *SPCI 1984 World Pulp and Paper Week Proceedings*, SPCI, Stockholm, p. 42.

Appendix

1. Laboratory experiment methods
2. Results

For consistency determination a MB internal instruction was applied. This method consists of sample weighting, filtration and drying. The steps can be seen in Figure 75.

Figure 75 The consistency determination for pulp samples. Can be also applied to filtrate samples. Consistency determination includes proper mixing and weighting of the sample (left), filtration (middle) and drying (right).

The weight of the sample is obtained before diluting (200-300 g). The weight of the diluted sample (additional water 1500 ml) is then obtained. Diluted sample is then mixed and smaller portion (250 ml) of the sample is put into a smaller container. This portion is filtrated through filtration paper using underpressure filtration. After filtration the sample is dried and weighted. The equation for consistency determination can be seen below:

$$C = \frac{100*(c-d)*b}{a*c} \quad (11)$$

where *a* is sample weight before dilution

b sample weight after dilution

c diluted sample weight used in filtration

d pre-weighted filtration paper

Appendix 1(2)

Fines determination for mechanical pulps was executed with DDJ; internal instruction and application of SCAN-CM 66:05. DDJ (Dynamic Drainage Jar) is designed for fines determination for pulp samples. The sample is weighted, diluted and filtrated through the wire screen (200 mesh) that is located on the bottom of the mixing tank. The agitator is constantly mixing the sample while water is added to the tank. Water is removed using the bottom valve located on the bottom of the mixing tank. Water is added to the sample until the filtrated water is clear. Fines pass through the wire screen, while fibres retain on the screen. Both materials are dried and weighted separately. The fines content is calculated and presented as a percentage of the oven-dry pulp of the sample portion. DDJ apparatus can be seen in Figure 77.

Figure 77 The Dynamic Drainage Jar (DDJ).

The amount of fines is calculated using the equation 12:

$$Fines\ \% = \frac{100*a}{a+b} \quad (12)$$

where a is the proportion of weighted oven-dry fines

b The proportion of weighted oven-dry fibre

The fibre fraction distribution analysis was executed with Valmet FS-5 fibre image analyzer. The sample is diluted based on the consistency before putting it into the analyzer. The FS-5 complies with following ISO -standards and gives the following results (Table XIII):

Table XIII The result obtained from Valmet FS-5 image analyzer.

Hot disintegration of mechanical pulp, ISO 5263-3:04
Fibre distribution, FS5, ISO16065-2:14
Arithmetic av. fibre length, mm
Length weighted av. fibre length, mm
Weight weighted av. fibre length, mm
Fiber curl, %
Kink index, 1/m
Fiber width, µm
Fibrillation, %
Length < 0.2 mm, %
Fines A (flake like), %
Fines B (lamellar), %

Even though the FS-5 gives several different results, only the results considering the fines fractions were exploited. The FS-5 can be seen in Figure 78 and example from graphical illustration of fibre distribution in Figure 79.

Figure 78 The Valmet fibre image analyzer.

Appendix 1(4)

Table XIV The methods used in laboratory experiments.

Pulp consistency	MB instruction
Turbidity	MB instruction
pH	MB instruction
Conductivity	MB instruction
Centrifugation	MB instruction
COD	MB instruction, based on SCAN-CM 44:97
Extractives	MB instruction
Total fines w/w %, DDJ	MB instruction, based on SCAN-CM 66:05
Hot disintegration of mechanical pulp	ISO 5263-3:04
Fibre distributions, FS-5	ISO 16065-2:14

Appendix 2(1)

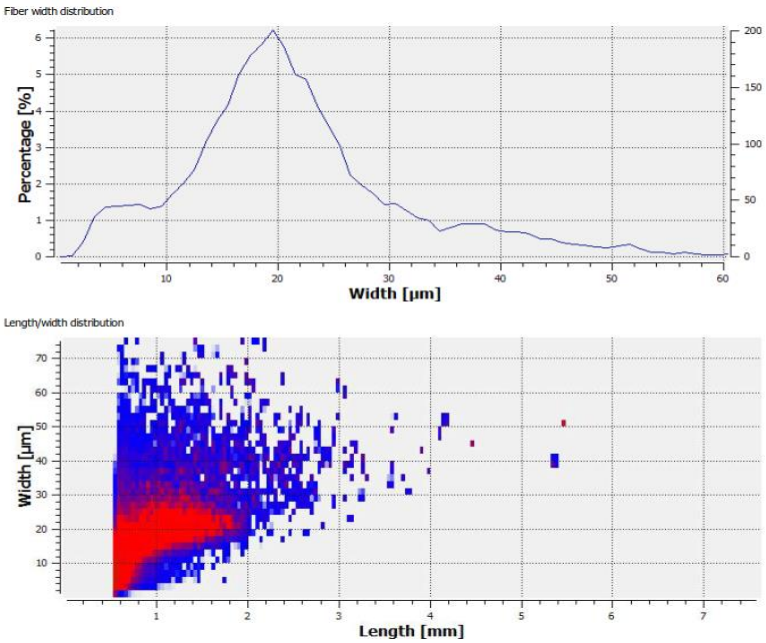


Figure 79 Example of the graphical illustration of fibre length/width distribution obtained from Valmet fibre image analyzer FS-5 (Refiner J11).

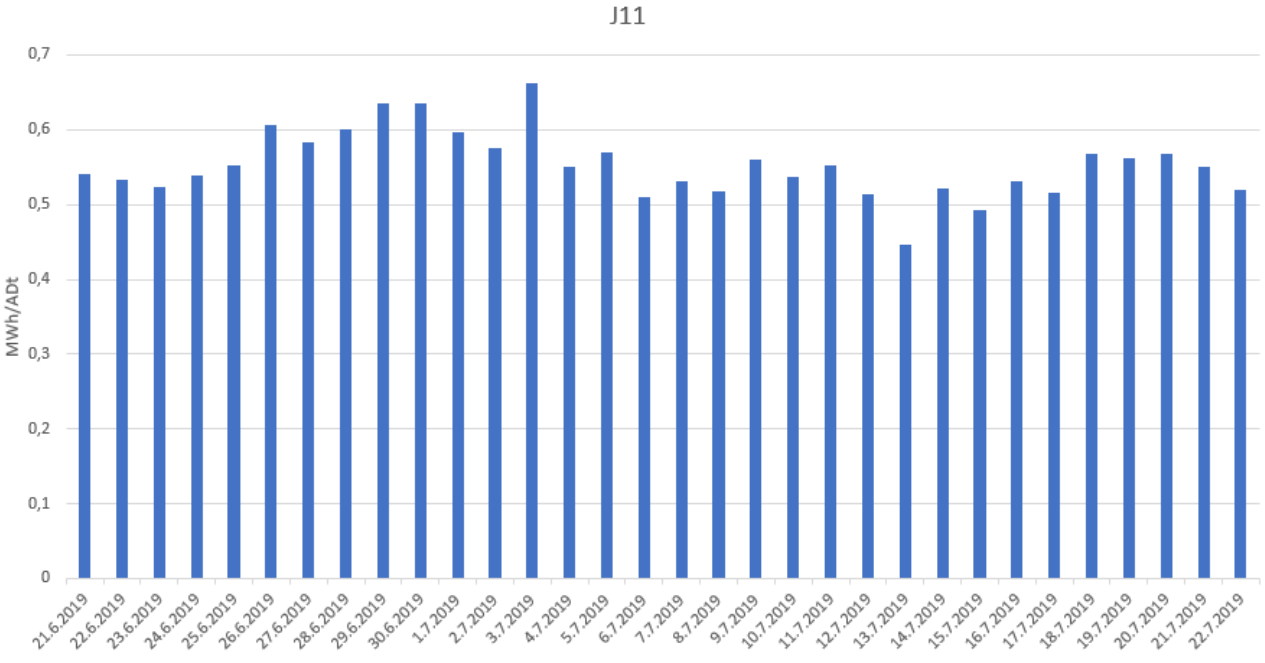


Figure 80 The specific energy consumption for the refiner J11.

Appendix 2(2)

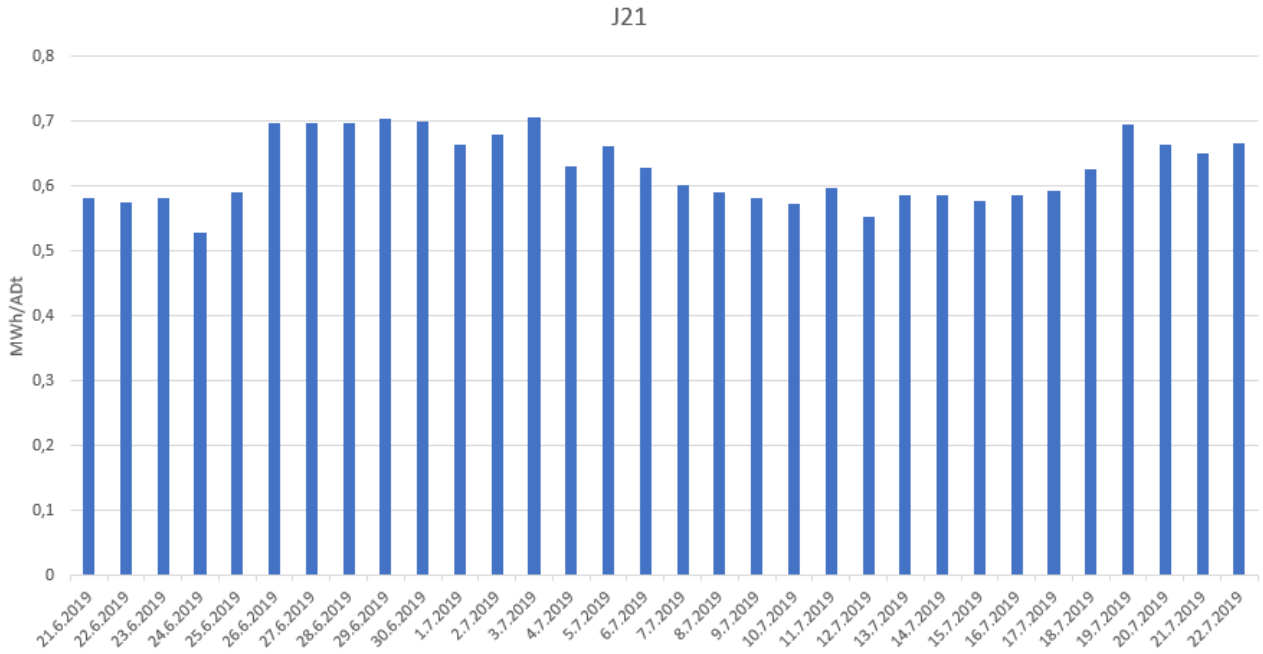


Figure 76 The specific energy consumption for the refiner J21.

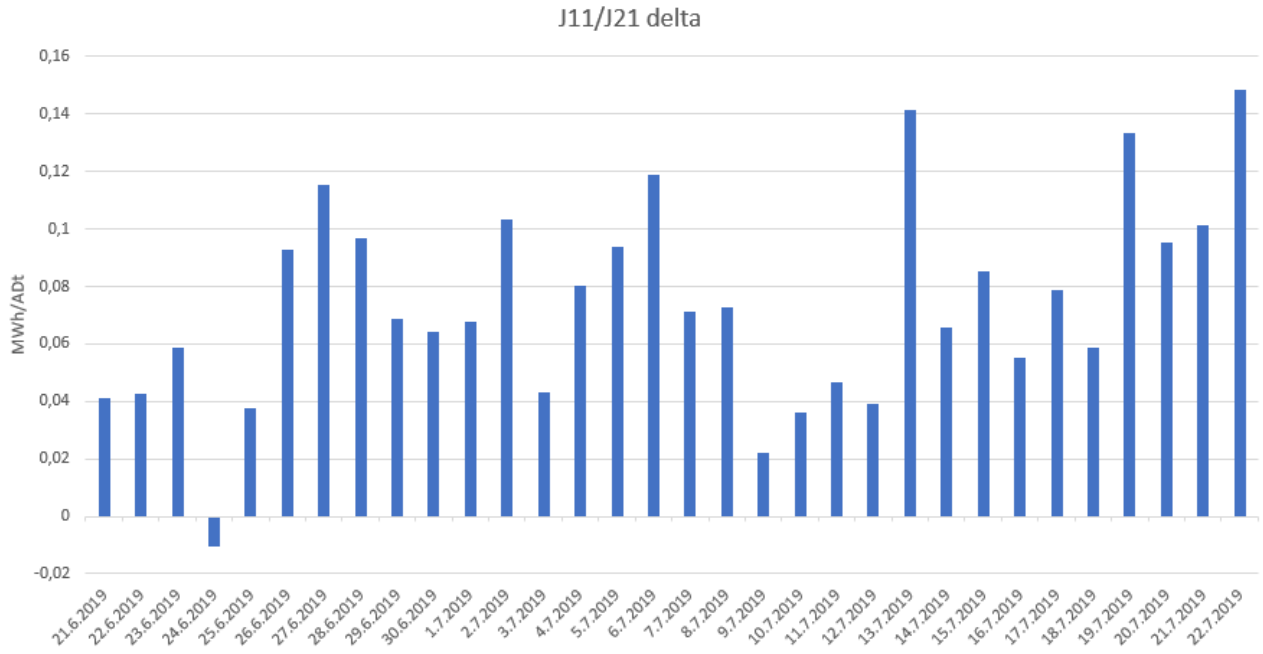


Figure 82 Specific energy consumption difference between refiners J11 and J21.

The energy consumptions were analyzed from 21 of June to 22 of July. It is clear that the experimental blade had severe effect on the grinding energy.

Appendix 2(3)

Table XV Results for all samples.

Sample	Solids (consistency), %		Fractions				Total flow	Fines		A (flake-like)		B (lamellar-like)	
	Measured	Balas	DDJ, w/w %	Fines < 0,2 mm	A (flake-like)	B (lamellar-like)	kg/s	Bdt/d	Adt/d	Bdt/t	Adt/t	Bdt/t	Adt/t
Chip water clarifier	0,16	0,158		92,7	86,4	7,79	155	19,863	22,070	18,505	20,561	1,669	1,855
Plug press 1	0,22	0,221		92,6	88,9	7,45	9,27	1,632	1,813	1,566	1,740	0,131	0,146
Press filtrate 1	0,22	0,205		91,4	84,4	7,8	20,2	3,509	3,899	3,241	3,601	0,299	0,333
Press filtrate 2	0,09	0,099		90,0	83,8	9,82	6,63	0,464	0,516	0,432	0,480	0,051	0,056
Evoparation feedstrain accept	0,11	0,081		96,6	95,6	19,84	66	6,059	6,733	5,997	6,664	1,244	1,383
Pure water	0	0		73,8	65,3	5,62	63	0,000	0,000	0,000	0,000	0,000	0,000
Steamwash water	0,01	0,012		78,8	70,1	9,54	9	0,061	0,068	0,054	0,061	0,007	0,008
Refiner 11 filtrate	0,17	0,177		96,1	94,6	14,9	5,5	0,771	0,856	0,759	0,843	0,119	0,133
Refiner 21 filtrate	0,19	0,208		96,9	94,5	6,85	5,46	0,869	0,965	0,847	0,941	0,061	0,068
Refiner blade water	0,01	0,01		91,8	89,7	18,7	8,3	0,066	0,073	0,064	0,072	0,013	0,015
Refiner 21	50,3	50,3	17,57	45,5	32,8	5,90	15,50	306,496	340,551	220,677	245,197	39,743	44,159
Refiner 11	48,5	48,5	16,79	47,2	33,0	5,47	15,5	306,570	340,633	214,209	238,010	35,528	39,476
Latency 1	2,48	2,3		48,5	34,3	6,22	504	523,766	581,963	370,632	411,814	67,172	74,635
Latency 2	1,5	1,63		48,1	33,5	5,61	718	447,584	497,316	312,099	346,777	52,203	58,003
Accept to disc	0,69	0,938	23,045	51,8	37,2	7,13	1271	533,571	592,856	383,182	425,758	73,443	81,604
Reject	1,94	1,91	12,19	39,9	26,3	5,41	154	102,993	114,437	67,939	75,488	13,965	15,516
Reject storage 1	1,49	1,94		34,6	22,4	5,01	212	94,430	104,923	61,189	67,987	13,673	15,193
Reject storage 2	1,91	1,94		34,7	22,2	5,35	212	121,398	134,887	77,667	86,297	18,717	20,797
Reject blowpipe	41,9	41,9		33,9	23,0	8,37	4,07	43,907	48,786	27,877	30,974	7,441	8,267
Pressed reject 1	41,3	41,6		29,8	18,9	5,05	4,13	42,738	47,486	26,881	29,867	6,912	7,680
Pressed reject 2	42	42		29,0	18,2	4,69	8,63	106,163	117,959	72,091	80,101	26,212	29,124
Reject press 2 filtrate	0,34	0,344		47,1	32,8	5,37	102	14,113	15,681	9,840	10,933	1,609	1,788
Refined reject	1,19	2,4		43,7	31,6	10,2	133,0	59,758	66,397	43,157	47,952	13,893	15,437
Reject accept	1,045	1,08	20,28	44,3	31,8	9,85	275	109,993	122,215	79,056	87,840	24,457	27,174
Reject's reject	1,62	1,64	9,79	33,2	22,4	8,61	27,1	12,593	13,992	8,504	9,449	3,266	3,629
Disc clear filtrate	0,01	0,012		87,6	80,6	9,12	404	3,058	3,397	2,814	3,127	0,318	0,354
Disc cloud filtrate	0,02	0,028		87,3	80,1	16,0	881,0	13,290	14,767	12,194	13,549	2,439	2,710
MC1	11,12	10,1		46,0	31,8	5,98	116	512,666	569,629	354,631	394,034	66,647	74,052
Masstower 1	8,4	9,79	20,41	46,8	32,6	6,22	120	475,033	527,814	330,696	367,440	63,135	70,150
Screw 11 filtrate	0,38	0,363	83,21	84,7	90,2	100	37,9	10,539	11,711	11,228	12,475	12,443	13,826
Screw 12 filtrate	0,27	0,298		90,0	85,7	7,84	41,7	8,755	9,728	8,338	9,264	0,763	0,847
Screw press 11	29,25	29,3	19,695	45,0	31,2	6,18	18,3	208,115	231,239	144,293	160,326	28,581	31,757
Screw press 12	28	28		46,1	32,3	6,57	21,7	242,010	268,899	169,354	188,171	31,018	34,464
MC bleaching	10,67	10,7		46,0	32,2	6,71	110	466,475	518,306	326,634	362,927	68,045	75,605
Twin wire press 11	45,15	45,2	20,32	45,8	32,0	6,44	12,8	228,690	254,100	159,983	177,759	32,156	35,729
Twin wire press 12	43,3	43		45,5	31,9	6,5	13,5	229,798	255,331	160,960	178,844	32,828	36,476
Twin wire press 11/12 filtrate	0,14	0,01		89,5	84,8	7,49	15	1,624	1,804	1,539	1,710	0,136	0,151
HC tower	37,6	37,4	19,65	46,8	33,0	6,95	31	471,313	523,681	332,134	369,038	69,992	77,769
HC bottom	36,95	37,4	19,565	45,7	32,3	6,54	31	452,279	502,532	319,564	355,071	64,724	71,916
MC4	12,31	12,7		46,3	32,7	6,21	92,5	455,506	506,118	322,101	357,890	61,095	67,883
Screw press 21	34,7	34,7	18,145	44,3	30,5	5,92	33,2	440,946	489,940	303,287	336,986	58,925	65,473
Screw press 21 filtrate	0,41	0,396		81,6	71,9	7,60	59,30	17,141	19,046	15,095	16,772	1,596	1,774
Screw press 22 feed	11,09	11,9		45,8	31,8	5,83	97,1	426,118	473,465	295,957	328,841	54,242	60,269
Screw press 22 filtrate	0,3	0,294		83,1	73,6	7,13	59	12,708	14,120	11,256	12,506	1,090	1,212
Screw press 22	29,9	29,9		42,9	28,7	5,47	38,1	422,248	469,164	282,384	313,760	53,839	59,821
MC5	12,03	12		45,4	31,5	6,36	94,8	447,346	497,051	310,285	344,761	62,668	69,631
Bleached mass	9,73	11,8	18,58	47,2	32,9	5,79	96,7	383,703	426,337	267,535	297,261	47,069	52,298
Twin wire press 21	44,35	44,4	18,665	44,8	31,0	6,36	12,8	219,733	244,148	152,195	169,105	31,194	34,660
Twin wire press 22	50,7	50,7	19,57	47,6	33,5	5,64	11,2	233,532	259,480	164,454	182,726	27,671	30,745
Twin wire press 22 filtrate	0,05	0,046		71,3	60,0	8,66	35,6	1,143	1,270	0,961	1,068	0,139	0,154
SVS1	0,31	0,329		66,1	60,4	75,7	37,1	14,075	15,639	12,853	14,281	16,121	17,912
SVS2	0,13	0,14		90,8	86,1	8,83	79,5	8,495	9,439	8,053	8,948	0,826	0,918
SVS3	0,37	0,375		81,0	71,1	8,67	83,3	18,229	20,255	15,997	17,774	1,951	2,168
SVS4	0,27	0,26		82,2	71,9	5,81	70,4	13,500	15,000	11,802	13,113	0,954	1,060
SVS5	0,09	0,083		85,8	77,3	7,06	70,4	5,231	5,812	4,714	5,238	0,430	0,478
Spraywater screen reject	0,03	0,028		62,6	48,6	3,28	78,4	0,368	0,409	0,286	0,318	0,019	0,021
Spraywater tank	0,01	0,01		91,9	89,2	11,4	22,7	1,196	1,329	1,161	1,290	0,148	0,164
Cloud filtrate tank	0,05	0,05		87,1	81,0	11,3	150,6	47,391	52,657	44,072	48,969	6,148	6,832
Clear filtrate tank	0,03	0,012		84,3	79,5	9,06	1259,5	8,828	9,808	8,321	9,245	0,949	1,054
Clear water tower	0,05	0,036		75,1	62,8	10,3	404,0	2,041	2,267	1,707	1,897	0,279	0,310
Circulate water tower	0,01	0,012		91,0	86,3	7,66	62,9	1,541	1,712	1,461	1,624	0,130	0,144
PP dilute water	0,12	0,148		79,4	72,3	12,6	196,0	46,430	51,588	42,272	46,969	7,380	8,200
BCTMP (bale)	84,69	84,55	16,75	45,3	31,5	5,98	564	444,170	493,522	308,860	343,177	58,634	65,149
PP reject	0,855	0,721	2,205	12,1	9,5	3,49	13,4	0,214	0,237	0,168	0,187	0,062	0,068

Table XVI Results using the experimental blades in refiner 11.

	Refiner 11		**Refiner 21**		**Refiner 11**
	Sample 1	Sample2	Sample 1	Sample2	Original
Length < 0.2 mm, %	48,8	46,8	43,5	42,7	47,2
Fines A (flake like), %	34,9	33,0	29,6	28,9	33,0
Fines B (lamellar), %	5,65	4,65	3,68	3,62	5,47