



**APPLICABILITY OF FIBROUS AND SIZE INDEX TO CHARACTERIZE
MICROFIBRILLATED CELLULOSE, FIBER BLENDS, AND PAPER
PROPERTIES**

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ABSTRACT

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Applicability of fibrous and size index to characterize microfibrillated cellulose, fiber blends, and paper properties

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Microfibrillated cellulose (MFC) has a broad particle size range. In papermaking, MFC is often mixed in a pulp suspension with polymers. Analyzing pulp suspensions that contain a wide range of components becomes challenging for optical measurement, but measurement efficiency can be enhanced using tube flow fractionation. The fraction data obtained from optical measurement can be further analyzed using fibrous and size indexes.

This thesis presents a study that explores the applicability of fibrous and size indexes in characterizing MFC. The research methodology involved analyzing fiber blends and correlating the results with paper properties. Additionally, two grades of MFC, commercial (MFC1) and research-grade (MFC2), were compared to identify potential differences in index distributions and particle size.

The findings of this study validated the potential of fibrous and size indexes to characterize multicomponent suspensions. Adding cationic starch and CPAM to the pulp suspension reduced the fibrous index, with the extent of reduction correlating to the chemical dosage. On the other hand, the addition of MFC increased the proportion of fines fraction observed in the fibrous index distribution, leading to enhanced tensile strength in the resulting paper. These results suggest that the fibrous index could be used as an indicator for evaluating either the tensile strength or tear strength of paper, depending on the desired paper property.

TIIVISTELMÄ

Lappeenrannan–Lahden teknillinen yliopisto LUT

LUTin insinööritieteiden tiedekunta

Kemiantekniikka

Ella Tirronen

Kuitumaisuus- ja kokoindeksin soveltuvuus mikrofibrilloidun selluloosan, kuituseosten ja paperin ominaisuuksien karakterisointiin

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Mikrofibrilloidulla selluloosalla (MFC) on laaja partikkelikokoalue. Paperinvalmistuksessa MFC sekoitetaan usein sellun joukkoon polymeerien kanssa. Kuituseosten analysointi, jotka sisältävät laajan valikoiman erilaisia komponentteja, on haastavaa optisella mittauksella, mutta mittauksen tehokkuutta voidaan parantaa käyttämällä putkivirtaukseen perustuvaa fraktiointia. Optisella mittauksella saatu fraktiodata voidaan edelleen analysoida käyttäen kuitumaisuus- ja kokoindeksejä.

Tämä diplomityö esittää tutkimuksen, joka tutkii kuitumaisuus- ja kokoindeksien soveltuvuutta MFC:n karakterisointiin. Tutkimusmenetelmänä oli kuituseosten analysointi ja tulosten korrelointi paperin ominaisuuksiin. Lisäksi verrattiin kahta MFC-laatua, kaupallista (MFC1) ja tutkimuslaatua (MFC2), tunnistamaan mahdollisia eroja indeksijakaumissa ja partikkelikoossa.

Tämän tutkimuksen tulokset vahvistivat kuitumaisuus- ja kokoindeksien potentiaalia monikomponenttisten seosten karakterisointiin. Kationisen tärkkelyksen ja CPAM:n lisääminen sellun joukkoon laski kuitumaisuusindeksiä, mikä korreloi kemikaalien annostuksen kanssa. Toisaalta MFC:n lisääminen lisäsi hienoainesfraktion osuutta indeksijakaumassa, mikä johti paperin lopullisen vetolujuuden parantumiseen. Nämä tulokset viittaavat siihen, että kuitumaisuusindeksiä voitaisiin mahdollisesti käyttää indikaattorina paperin joko vetolujuuden tai repäisyjuuuden arvioimiseen, riippuen halutusta paperin ominaisuudesta.

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Savonlinna, May 2024

Ella Tirronen

SYMBOLS AND ABBREVIATIONS

Roman characters

A_n	area of the test piece	mm^2
d_b	bulk density	g/cm^3
g	grammage of the sheet	g/m^2
m	mass of the test piece	g
V_A	attractive interaction energy	J
V_R	repulsive interaction energy	J
V_T	total interaction energy	J

Greek symbols

μDP	depolarized light amount	
μ_{ext}	extinction coefficient	
δ_b	mean bulking thickness	μm

Abbreviations

AFM	Atomic Force Microscopy
CMC	Carboxymethyl Cellulose
CNC	Cellulose Nanocrystals
CNF	Cellulose Nanofibrils
CNM	Cellulose Nanomaterials
CPAM	Cationic Polyacrylamide
CS	Cationic Starch
DFA	Dynamic Fractional Analysis
DLS	Dynamic Light Scattering

DP	Degree of Polymerization
EVOH	Ethylene Vinyl Alcohol
FBA	Flow Based Analysis
FE-SEM	Field Emission Scanning Electron Microscopy
FI	Fibrous Index
MFC	Microfibrillated Cellulose
NCC	Nanocrystalline Cellulose
NFC	Nanofibrillated Cellulose
NIR	Near Infrared
OTR	Oxygen Transmission Rate
PAE	Cationic Polyelectrolyte, Polyamidoamine-Epichlorohydrin
SC	Super Calendered
SEM	Scanning Electron Microscope
SI	Size Index
TEM	Transmission Electron Microscope
Vis	Visible

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1 Introduction

Establishing reliable monitoring systems for quality control, prediction of network properties, and developing new products becomes crucial when scaling up micro and nanocellulose production from the laboratory to an industrial level. The current analysis technologies require modification and development for industrial deployment. Therefore, there is an urgent need to get a deeper insight into the micro and nanofibril morphology and particle characterization.

As the size and shape of fine materials significantly impact product properties, numerous techniques have been developed to characterize them. According to Larsson et al. (2019), these methods can be categorized into high-precision morphology characterization and rapid characterization of indirect morphology-related properties. High-precision morphology characterization methods, such as microscopic imaging, have great accuracy. Still, they have difficulty determining simultaneously the length and the width of a high aspect ratio particle, such as microfibrillated cellulose (MFC). These methods are also time-consuming and raise an uncertainty of whether the microscopic image accurately represents the overall characteristics of the bulk material. The more rapid characterization methods indirectly related to the morphology include turbidity, rheology, water retention value, specific surface area measurements, and properties of MFC films.

Valmet has introduced a tube flow fractionator combined with a fiber analyzer. The fractionation phenomenon is based on hydrodynamic size separation and camera detection. As the measurement is image-based, it can give both size and shape data for every particle. Törmänen (2021) developed an enhanced analysis technique for fractionation data in measuring pulp sample suspensions. The analysis is called dynamic fractional analysis (DFA) and has been tested by measuring sample consistencies and observing particle changes during the pulp refining. Based on DFA algorithms, fibrous index, and size index are obtained and used to indicate the progress of micronization reliably.

This thesis aims to validate the indices' applicability in studying the fingerprint of heterogeneous fibers like MFC and observing the factors related to fiber network formation. The final goal of the thesis is to create a tool that can be used to predict and monitor the quality characteristics of the paperboard product during the manufacturing process. Previous

studies suggest that MFC enhances the strength of paper. This thesis also investigates the impact of additional additives like cationic starch and cationic polyacrylamide (CPAM) on forming fiber-fines flocs. The difference between the two MFC qualities is compared with chemical additives. Fractionation measurements are done to characterize heterogeneous pulp particles and flocs, and the suitability of DFA-based indexes is studied.

1.1 Target of the work

The thesis aims to answer whether paper or paperboard quality can be predicted using fibrous and size indices of heterogeneous pulp particles and flocs. The object is to establish essential factors that correlate MFC particles and fiber-fines flocs' structural morphology and physicochemical properties to fiber network properties.

The literature part of the thesis emphasizes the structural and rheological properties of MFC. The properties and applications of MFC are mainly examined from the perspective of paperboard manufacturing and papermaking applications. The literature also focuses on the current MFC characterization methods and introduces recent, more selective measurement methods. The experimental part of the thesis consists of three main parts: characterization of microcellulose, characterization of pulp suspensions, and laboratory sheet trials. The experimental part can be divided into three parts:

1. Applicability of fibrous and size index to characterize microcellulose
2. Applicability of fibrous and size index to characterize pulp suspensions
3. Correlating particles to fiber network properties and the final product

The flocculation of MFC suspensions is studied with a Valmet fractionator. The suspensions are made using bleached birch pulp and two MFC grades, commercial quality and non-commercial quality. CPAM and cationic starch are used as retention chemicals. Laboratory sheets are made with a 3-5 wt% composition of MFC. Laboratory sheet testing includes the subsequent measurements: basis weight, thickness, formation, tensile strength, tear strength, and retention. Fibrous and size indices are employed to assess the morphological properties of heterogeneous pulp suspensions and characterize white water's fiber or fines content.

Literature part

2 Cellulose

Cellulose is the most dominant component of wood. Typically, cellulose constitutes approximately 40-45% of the dry weight in most wood species. In addition to cellulose, wood contains hemicellulose, lignin, and extractives. The share of hemicellulose in wood is approximately 20-30%, and the share of lignin is from 20% to over 30%, depending on the wood species. Wood also contains a small proportion of various extractives, usually less than 10%. (Sjöström, 1993) Cellulose is divided into amorphous and crystalline regions. Regions in low order are called amorphous, and areas in high order are called crystalline. The mechanical properties of natural fibers rely on the organization of these regions and the geometrical conditions of cellulose. (Kalia et al., 2011) Cellulose consists of fibrils. The most primitive fibrils are about 100 nm long and 1.5-3.5 nm wide. Fibrils continue to form fiber bundles or microfibrils, which are 10-30 nm wide. In addition, microfibrillar bands are formed, which are about 100 nm wide and hundreds of nanometers or even a few micrometers long. (Rojas, 2016)

Most of the cellulose is in the secondary cell wall of the plant cell. Regardless of the plant type, the structure of a plant cell is similar. Plant cells consist of the middle lamella, primary, secondary, and warty walls. The first layer is the middle lamella, which binds plant cells together. The next layer is the primary cell wall, which is thinner than the secondary cell wall. The secondary cell wall is divided into three sublayers (S1, S2, and S3), where S2 is the thickest layer, varying between 2-4 μm . The warty wall is located in the innermost part of the plant cell. (Sjöström, 1993; Rojas, 2016) Figure 1 shows a simplified structure of a plant cell.

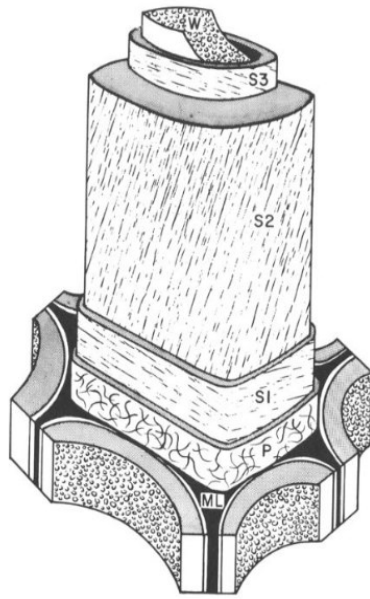


Figure 1. The simple structure of a wood cell illustrates the middle lamella (ML), primary wall (P), secondary wall (S1, S2, S3), and warty wall (W). (Adapted from Sjöström, 1993)

2.1 Nanocellulose

Nanocellulose is a term used to describe cellulosic material with a particle diameter between 1-100 nm (TAPPI Standard WI-3021). Nanocellulose can be categorized into three primary types: cellulose nanofibrils, cellulose nanocrystals, and bacterial cellulose. Many different terms have been used for these in the literature. The most common terms for nanofibrils are nanofibrillated cellulose (NFC) and microfibrillated cellulose (MFC). The terminology for nanocrystals is also very extensive. Some terms used are nanocrystalline cellulose (NCC) and cellulose whiskers, but many variations exist. (Osong et al., 2016; Lavoine et al., 2012; Kangas, 2014) Figure 2 shows the classification of cellulosic nanomaterials based on their nanoscale or microscale. Nanofibrils are usually 20-40 nm in diameter and have a length of several micrometers. Nanocrystals are a bit smaller in size. The width is typically 2-20 nm, and the length can vary between 100-600 nm to over one micrometer. Bacterial cellulose consists of microfibrillar bands approximately 20-100 nm in width. Microfibrillar bands are formed from finer nanofibrils with a 2-4 nm width. (Kangas, 2014)

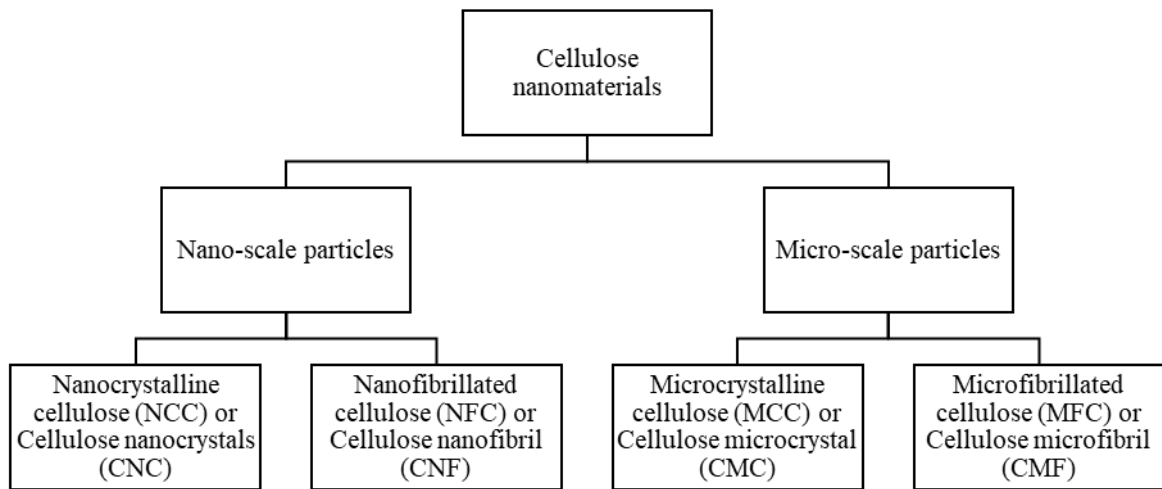


Figure 2. Hierarchical levels of cellulose nanomaterials. (Adapted from Osong et al., 2016)

Herrick and Turback were the first to produce nanofibrils mechanically using a high-pressure homogenizer. Since then, many different methods, such as grinding and microfluidization, have been developed.

Cellulose nanocrystals are commonly produced through acid hydrolysis, involving the dissolution of the amorphous regions of cellulose and replacing them with releasing crystalline areas. The most effective chemical to modify cellulose fibers to needle-like particles via acid hydrolysis is sulfuric acid. The cellulose material, hydrolysis conditions, and ionic strength affect the nanocrystals' dimensions. (Dufresne, 2012) Since nanocrystals have a high crystallinity (62-90%), they are not as flexible and branched as nanofibrils (Kangas, 2014).

Bacterial cellulose differs from cellulose nanofibrils and nanocrystals by its production method. A specific bacterium, e.g., *acetobacter xylinum*, is used to produce bacterial cellulose via biosynthesis, which results in a unique gel-like material with excellent mechanical and physical properties. Mechanical endurance arises from bacterial cellulose's high specific surface area and porosity. Because of the high specific surface area and porosity, bacterial cellulose is also a very hydrophilic and water-retaining material. (Osong et al., 2016; Kangas, 2014)

3 Microfibrillated cellulose

Microfibrillated cellulose (MFC) was discovered by Turbak et al. in the early 1980s. Wood was the first cellulosic material to produce MFC and is still the primary source. Several industrial fiber companies, such as Borregaard and UPM, produce MFCs. (Lavoine et al., 2012) The use of MFC in various applications is due to its favorable properties, such as high strength, low weight, and biodegradability (Siró & Plackett, 2010). The growing interest in MFC can be seen in the increased number of patents and publications since the early 1980s. Figure 3 presents the number of published works discovered from 1983-2022 using the keyword “microfibrillated cellulose.”

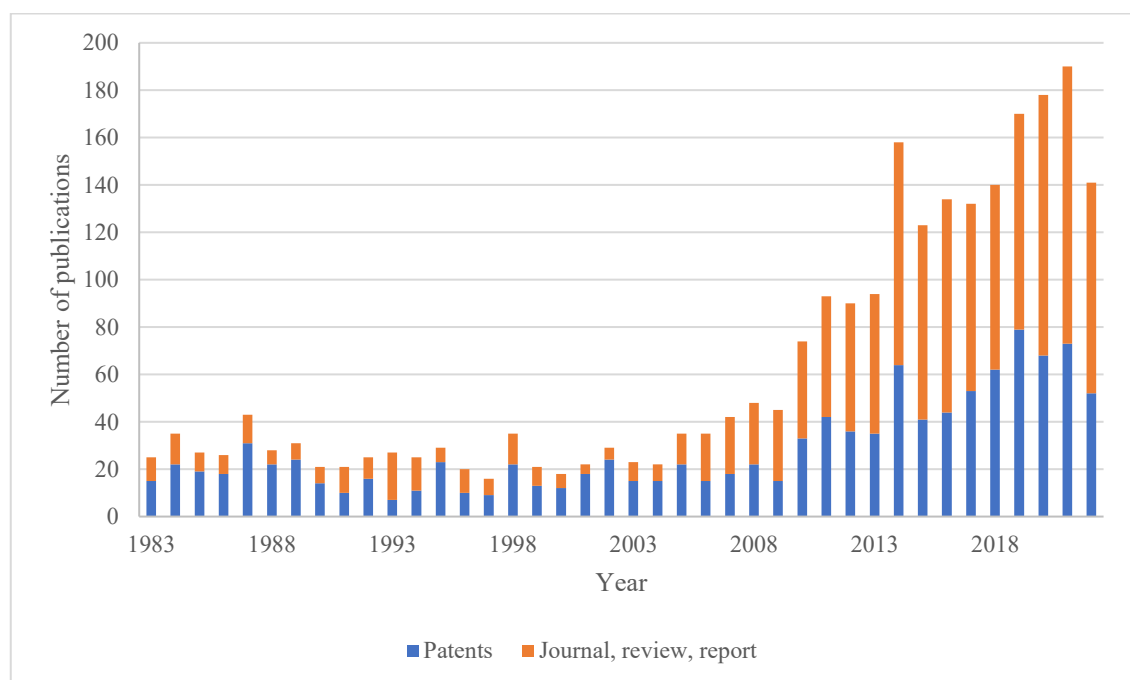


Figure 3. The number of published works and patents discovered from 1983-2022 with the keyword “microfibrillated cellulose.” Data analysis was conducted using SciFinder (CAS) on 28 September 2023.

Overall, there is an increasing demand for wood-based celluloses in various sectors, such as the building, furniture, and pulp and paper industries, which has led to innovations. Therefore, microfibrillated cellulose can be produced from almost any cellulosic fiber source. For example, the suitability of non-wood sources, e.g., agricultural crops, has been tested as a source of MFC. The structure of MFC varies little depending on the material source and the production methods. (Lavoine et al., 2012) For instance, Iwamoto et al. (2007) produced 20-50 nm wide MFC fibers through grinding, whereas Abe et al. (2007) were able to make 15 nm wide MFC fibers with a similar method. These conventional methods to produce MFC yield inhomogeneous material.

3.1 Structure of MFC

Microfibrillated cellulose has a complex structure because it can contain coarser particles, such as fiber fragments and fibers, and nanoparticles, such as nanofibrils and fibrillar fines. However, MFC materials produced correctly consist mainly of nanostructures, specifically nanofibers. (Cinar Ciftci et al., 2020; Larsson et al., 2019; Chinga-Carrasco, 2011) Microfibrils are formed during a mechanical process where the high shear force splits the cellulose fibrils along its longitudinal axis, which is the reason for the high specific surface area of MFC fibers. (Thomas, 2013) The diameter of microfibrils usually ranges from 20-60 nm, and the length is typically a few micrometers. These flexible and long microfibrils form a web-like structure, a unique property of MFC. Unlike cellulose nanocrystals (CNC), microfibrillated cellulose is divided into amorphous and crystalline parts. (Lavoine et al., 2012) The structure of cellulose fiber and microfibrillated cellulose are shown in Figure 4.

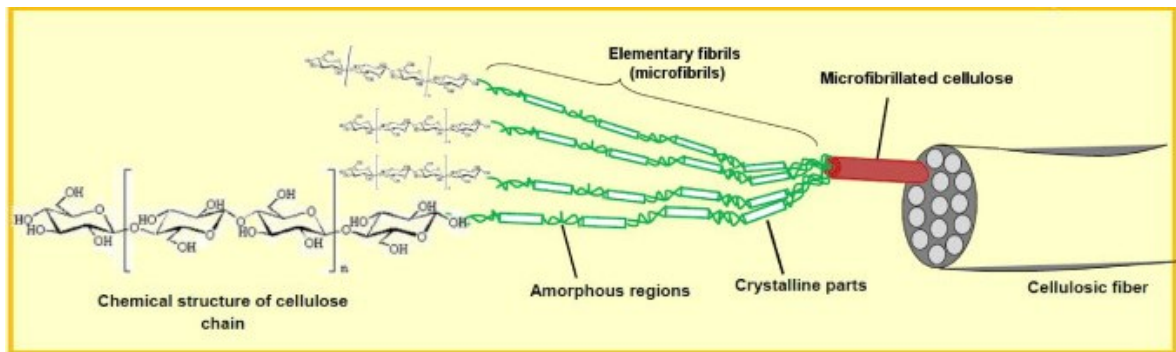


Figure 4. Structure of cellulose fiber and microfibrillated cellulose. (Adapted from Lavoine et al., 2012)

3.2 Production of MFC

Mechanical treatment is the most used processing method to produce MFC from wood fibers. The most conventional mechanical treatments are homogenization, microfluidization, and grinding (Nechporchuk et al., 2016). Many other mechanical methods produce MFC, such as cryo-crushing, ultrasonication, electrospinning, and steam explosion. Usually, a chemical or enzyme treatment precedes mechanical processing. The most applied pretreatments incorporate alkaline acids, enzymatic hydrolysis, and ionic liquids. (Balakrishnan & Thomas, 2021) The mechanical treatments and pre-treatments to produce MFC are shown in Table 1.

Table 1. Treatment approaches for MFC production. (Lavoine et al., 2012; Osong et al., 2016; Nechyporchuk et al., 2016)

Mechanical treatments	Chemical/Enzymatic pre-treatments
Homogenization	TEMPO-mediated oxidation
Microfluidisation	Periodate-chlorite oxidation
Grinding	Carboxymethylation
Refining	Alkaline extraction
Cryocrushing	Enzymatic hydrolysis
Ultrasonication	
Electrospinning	
Steam explosion	

Pre-treatments are typically incorporated with mechanical treatment to reduce energy consumption. They also improve the efficiency of the fibrillation process. (Osong, 2016) Pre-treatments can be chemical or enzymatic. The most used pre-treatment method is TEMPO oxidation. In their study, Syverud et al. (2011) noticed that the TEMPO-treated fibers were more homogeneous after the same mechanical treatment than non-pre-treated fibers. Periodate-chlorite oxidation has been developed alongside TEMPO oxidation. For example, Liimatainen et al. (2012) used the method to enhance the fibrillation of hardwood fibers. Enzymes can be used as an alternative to chemical pre-treatment methods. Pääkkö et al. (2007) noticed that using enzymes before mechanical treatment improved the fibrillation process, decreased fiber clogging, and saved the energy consumption needed.

Homogenization can be done using homogenizers or microfluidizers, as seen in Figure 5. The principle of homogenizer is to expose the wood fiber to very high shearing forces caused by the reciprocating mechanical movement of valves. In MFC production through homogenization, fiber suspension undergoes a high-pressure pumping process and passes through a spring-loaded valve assembly. The rapid opening and closing of the valve expose the fibers to significant pressure drops, resulting in shearing and impact forces. These forces lead to extensive microfibrillation of the cellulose fibers. The number of homogenization cycles and the pressure applied determines the fibrillation level. Higher pressure results in greater disruption efficiency during each pass through the equipment. (Kargarzadeh et al.,

2018) A microfluidizer is an alternative method of homogenization. The fiber suspension passes through a geometrical interaction chamber (e.g., Y or Z-shaped) with high pressure and shear forces, which causes fibrillation. (Kargarzadeh et al., 2018; Nechyporchuk et al., 2016)

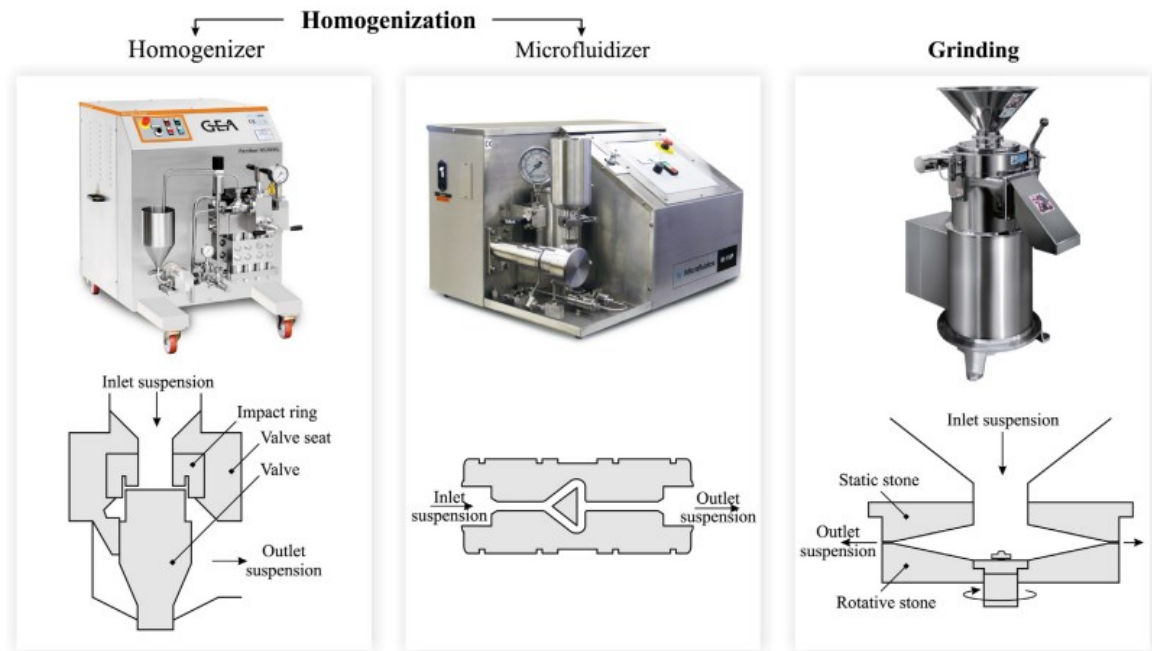


Figure 5. Conventional mechanical processes for cellulose nanofibrils production. (Adapted from (Nechyporchuk et al., 2016)

Grinding is another commonly used mechanical method to produce MFC. The grinding of the fibers occurs between two specially made discs, one of which is stationary and one of which is rotating. Throughout the process, the high shear forces break down the cell wall structure, which leads to nanosized fibers. The fibrillation degree depends on the distance of the discs from each other, the structure of the discs, and the frequency of grinder passes. (Kargarzadeh et al., 2018) Supermasscolloiders or Masuko grinders, as seen in Figure 5, are the most used grinders. Masuko Sangyo Co. Ltd., Japan, pioneered building and selling this equipment, hence the name. The supermasscolloider is based on ultra-fine friction grinding. It breaks down fibers using frictional forces and the powerful impact generated by the grinding action of the rotor against the stator. (Osong et al., 2016; Nechyporchuk et al., 2016)

3.3 Applications of microfibrillated cellulose

In general, nanocellulose has achieved significant progress in products attained from forests, particularly in papermaking, coatings, and films. A critical factor in this progress is its use to enhance the strength of paper and board products when wet and dry. Specifically, MFC is employed due to its impact on final products' mechanical and barrier properties within the pulp and paper sector. (Osong et al., 2016) Previously, the energy costs related to material production hindered the ability of many companies to scale up and commercialize their MFC production, but the problem has now been slightly alleviated. (Ålander et al., 2017) Nanocellulose technology has prompted various companies to invest in developing innovative products for the market, as demonstrated in Table 2.

Table 2. Production pilot plant facilities of cellulose nanostructured materials. (Adapted from Miller, 2014)

<i>Industry or university</i>	<i>Country</i>	<i>Announced production amount (Dry solid content)</i>
University of Maine	USA	1 ton/day
Nippon paper	Japan	150 kg/day
Borregaard	Norway	100 kg/day
Innventia AB	Sweden	100 kg/day
NamiCell	France	100 kg/day
Oji Paper	Japan	100 kg/day
FPIinnovations	Canada	n/a
Stora Enso	Finland	n/a
UPM Kymmene Ltd	Finland	n/a
Daicel	Japan	Lab-scale
Luleå University of Technology	Sweden	Lab-scale
US Forest Service, Forest Products Laboratory	USA	Lab-scale
JRS	Germany	n/a
Omya	Swiss	n/a
BASF/Zelpho	Germany	n/a
CelluComp	UK/Scotland	n/a
InoFib	France	n/a
EMPA	Swiss	15 kg/day
VTT	Finland	15 kg/day
PFI	Norway	15 kg/day

3.3.1 Papermaking applications

The paper and board industry has recognized the potential of microfibrillated cellulose for many years. The primary and most significant application of MFC on a large scale is as a strength enhancer in papermaking. Furthermore, MFC can enhance paper gloss and minimize paper grammage. (Osong et al., 2016) Two factors can explain the ability of MFC to act as a strengthening agent. First, the high surface area of MFC allows it to promote adhesion effectively. Densifying the fiber network increases the bonding between fibers and the total bonded area. Secondly, the long microfibrils form entangled networks embedded with larger fibers, and together, they improve the mechanical properties of paper. (Zambrano et al., 2020)

Literature is filled with research articles where MFC as a paper-strengthening agent has been studied (Saito & Isogai, 2015; Ahola et al., 2008; Eriksson et al., 2005; Taipale et al., 2010; Ankerfors et al., 2014). Saito and Isogai (2005) have studied the wet strength property of MFC in tissue paper, paperboard, and other paper applications. Ahola et al. (2008) continued to study the effect of cellulose nanofibrils with cationic polyelectrolyte (PAE) to improve paper strength. The mechanical properties of paper have also been experimented with using multilayering of cationic and anionic starch by Eriksson and his team (2005).

Many have reviewed using retention aids with microfibrillated cellulose and nanofibrillated cellulose in papermaking. Four main polyelectrolytes are used with MFC: (i) carbohydrates, e.g., cationic starch (CS); (ii) polyvinylamines (PVA); (iii) polyacrylamides, e.g., c-PAM and (iv) cationic polymers with quaternary ammonium, e.g., polyamidoamine-epichlorohydrin (PAE). (Zambrano et al., 2020) Merayo et al. (2017) have studied the retention of nanoparticles in the fiber network in the presence of cationic polymers. Research shows that MFC addition into a pulp slurry containing polyelectrolytes increases flocculation and flocs' stability and is an essential factor affecting retention. This is due to hydrogen bonds created by MFC and CS. MFC and polyelectrolytes also regulate the floc stability. The floc size has been shown to increase when PVA is added.

In their study, Ankerfors et al. (2014) used microfibrillated cellulose to enhance the strength of filled papers in a pilot scale. The results showed that adding 2.5-5.0 wt-% of MFC improved the mechanical properties of filled papers with a 20-35 wt-% filler content. The mechanical properties were further enhanced when MFC was combined with cationic starch.

It was also concluded that the filler content could be raised from 20 to 33 wt-% without negatively affecting tensile strength when adding 5 wt-% of MFC and 2 wt-% of cationic starch.

Taipale et al. (2010) studied papermaking properties from pulp suspensions when different MFC grades were combined. They found that drainage reduces during papermaking when the amount of MFC is increased significantly. The drainage could be manageable when MFC is added with cationic polyelectrolytes. Although MFC alone was shown to reduce the drainage rate during papermaking, it significantly improved the mechanical properties of paper.

3.3.2 Coatings and films

MFC, as a coating additive in paper and cardboard applications, e.g., food packaging, is gaining attention. The reason for this “greener,” more sustainable trend comes from the European Union level, which aims to increase the use of more environmentally friendly solutions, such as eco-efficient packages. It is believed that wood-based celluloses can replace petroleum-based polymers. (Osong et al., 2016) Typically, paper materials undergo coating to enhance their surface characteristics and print quality. Another application is to improve the material’s barrier properties, such as water vapor, oxygen, grease, or oil, as Nygård (2011) mentioned. Her thesis studied the use of coating paper substrates with MFC.

Syverud and Stenius (2009) were among the first researchers to report the results linking MFC and barrier properties. They used bleached spruce sulfite pulp to make MFC films and measured their oxygen permeability. The films' thickness was approximately 20-33 μm . The measured oxygen transmission rate (OTR) values of MFC films revealed that the thickness of MFC films appears to be comparable to that of established synthetic polymer films due to their nanoporous and dense fiber network.

Lavoine et al. (2011) investigated cardboard's strength properties and barrier characteristics with MFC coating. Their study showed that MFC improved the mechanical properties of the cardboard, but the barrier properties remained almost unchanged. Ankerfors (2012) examined the mechanical properties of MFC films and reported that MFC enhanced the

tensile strength by over 50%. In addition, the strain at break was improved by 226% and Young's modulus by 61% by adding MFC into the films.

4 Pulp suspension components

Pulp suspensions can contain various particles: long and short wood fibers, fines particles or fibrils, and fillers or other chemical substances. Everett (1972) defines suspension as where "solid particles are dispersed in a liquid." A colloidal suspension consists of particles that fall within the colloidal size range. Pulp suspensions are processed at different mass consistencies (C_m), the mass of fibers divided by the total suspension mass (Derakhshandeh et al., 2011). Kerekes et al. (1985) categorized these consistencies into several ranges:

- Low consistency ($C_m=0-8\%$): The suspension resembles a mix of water and fibers.
- Medium consistency ($C_m=8-20\%$): Achieved by dispersing a mat formed by vacuum filtration of low consistency suspension.
- High consistency ($C_m=20-40\%$): Created by mechanically removing water from a medium-consistency suspension.
- Ultra-high consistency ($C_m>40\%$): Obtained through evaporative drying.

Fibers

Wood fibers are composed of cellulose fibrils wound in spirals. Fiber flocculation arises typically from mechanical forces and colloidal forces. Mechanical mechanisms can be divided into mechanical linking forces and elastic interlocking mechanisms, as presented in Figure 6. The mechanical linking prevents the relative movement of fibers with coarse surfaces and irregular equilibrium shapes, which causes variations in the fiber mass space. The elastic interlocking prevents the relative motion of fiber with friction and contact forces. The fibers are held in strained configurations with at least three contact points. (Schmid & Klingenberg, 2000) According to Kerekes et al. (1985), the role of mechanical forces in fiber

flocculation becomes essential, especially in suspensions with a high concentration of fibers having a high aspect ratio.

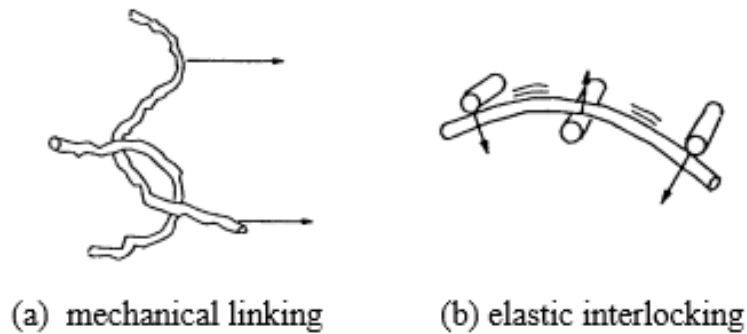


Figure 6. Fiber flocculation by mechanical forces (a) mechanical linking and (b) elastic interlocking. (Adapted from Schmid & Klingenberg, 2000)

The colloidal forces can be described by the DLVO theory, named after its founders, Derjaguin, Landau, Verwey, and Overbeek. The theory is built on two forces: van der Waals forces and electrical double-layer forces. It incorporates the influences of van der Waals forces and electrostatic repulsion from overlapping the double layers of counterions. Adding attractive and repulsive components determines the overall energy of interaction between two surfaces or particles. (Liang et al., 2007) This can be defined with Equation 1 as follows:

$$V_T = V_A + V_R \quad (1)$$

Where,

V_T = Total interaction energy

V_R = Repulsive double layer interaction energy

V_A = Attractive London-van der Waals energy

Van der Waals forces draw similar surfaces together, creating attraction, while interactions within the electrostatic double layer result in repulsion between surfaces carrying the same charge. Due to its slightly negative charge in an aqueous environment, MFC experiences repulsion between distanced fibers when the electrolyte concentration is low, owing to the electrostatic double layer. In contrast, attractive van der Waals forces become significant at closer distances. Flocculation can also result from non-DLVO interactions, such as steric

and electrosteric interactions. These interactions take place when polymers or polyelectrolytes are added to the suspension. (Karppinen et al., 2012)

Fines

Papermaking pulps contain varying amounts of fine materials, significantly differing from the fiber fractions. Fines are typically particles that pass through the 200—or 100-mesh wire of a Bauer-McNett fractionator or similar device, with a median size of a few micrometers. The largest fine particles are fiber fragments, while the smallest are fibrils or parts of fibrils, some of which may be smaller than 1 μm . Fines consist of cellulose, hemicelluloses, lignin, and extractives in proportions similar to other fiber fractions. (Retulainen et al., 1998)

There are two main types of fiber fines: primary and secondary. Primary fines are created during pulping and bleaching, where harsh treatments break them from the cell wall. These fines usually have a flake-like structure due to their origin from the compound middle lamella, ray cells, and parenchyma cells, with only small amounts of fibrillar material present. Secondary fines are made during pulp refining, where mechanical treatment breaks some cell wall parts into tiny, fibrillated pieces. Both types are found in papermaking, but they affect paper quality differently. With their larger surface area and bonding ability, secondary fines improve the paper's strength but make dewatering more difficult in the forming section. Primary fines mainly affect the paper's appearance and can also cause dewatering; sometimes, the paper's strength is worse. (Fischer et al., 2017)

MFC

MFC fibers form a complex fiber network that flocculates in water suspensions. The flocculation of pulp suspensions has been widely studied, but the flocculation of MFC suspensions has yet to be studied. The floc structure of MFC suspension can be compared to a pulp suspension to a certain extent. MFC and pulp fibers differ in their smaller dimensions and higher aspect ratios. (Karppinen et al., 2012)

Flocs can be noticed on a suspension at rest or under shear. In a state of rest, flocs can be characterized as bundles of fibers, i.e., areas in the fiber network with high fiber density. Due to shearing forces, the fiber network gradually breaks, and the size of the flocs decreases

the higher the shear force. (Karppinen et al., 2012) Fiber flocculation can be separated into macroscopic scale and molecular scale. Macroscopic scale is referred to when the flocs are formed mechanically. Here, the fibers collide and entangle each other under aqueous suspension flow. Molecular scale is when particles about 1-100 nm apart from each other have colloidal interactions resulting from interfibrillar dispersion and electrostatics. (Saarikoski et al., 2012) Cohesive forces and the number of contacts between fibers determine the floc strength (Karppinen et al., 2012).

The flocculation occurs already at low concentrations and leads to a suspension with high viscosity. Viscosity decreases as the shear rate increases, a phenomenon known as shear-thinning. Pääkkö et al. (2007) have documented that MFC creates a gel-like formulation even at 0.125% concentration. The strong MFC fiber network is probably due to fibril aggregates partially disintegrated and entangled during MFC production. The inherent fiber network forms a stronger MFC gel than gels formed solely due to weaker hydrogen bonds between water and fibrils.

Adding polymers to MFC/water suspensions can induce the degree of flocculation. Karppinen et al. (2011) studied MFC suspensions when adding carboxymethylcellulose (CMC), cationic polyacrylamide, and cationic starch. The studies showed that CMC reduced the gel-like properties of MFC and shear-thinning behavior. Cationic polyacrylamide and cationic starch, on the other hand, enhanced the strength of the gel while preserving its shear-thinning properties.

The properties of MFC suspensions are significantly influenced by their fibrillation degree and possible chemical modifications. Chemical pre-treatments, such as TEMPO-mediated oxidation, form anionic groups that promote repulsion between nanofibrils and allow easier fibrillation. Consequently, these treated MFC suspensions contain minimal residual macro-fibers and appear translucent gels. In contrast, unmodified MFC suspension appears as white gels, with smoothness varying based on the presence of residual macro-fibers and fine particles. (Raynaud, 2017)

5 Paperboards

There are many types of paperboards on the market. Paperboards can be divided according to the manufacturing process, pulp composition, or product end use (Häggblom-Ahnger & Komulainen, 2006). Paperboards are mainly classified into cartons-, containers-, and special boards. The classification of paperboards is shown in Figure 7. The basis weight of paperboard is generally higher than that of paper, approximately 150 g/m^2 . Paperboards are most often used for packaging, so they are expected to have good strength properties. (Kiviranta, 2000)

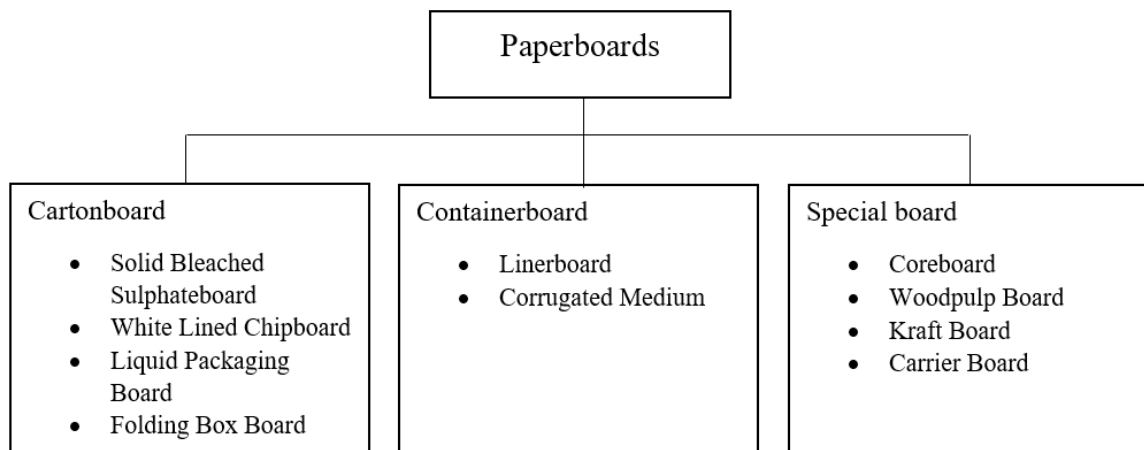


Figure 7. Paperboards classified. (Adapted from Kiviranta, 2000; Knowpap, 2023)

5.1 Paperboard making

The production of paper and board does not significantly differ from each other. The main difference between board and paper is that boards are often multi-layered, and their basis weight is often higher than that of papers. Board making consists of several process steps, which can be divided into stock and water systems, board machines, finishing, and extrusion coating. (Knowpap, 2023)

Stock preparation occurs between the pulp mill and the paper mill. It involves several essential steps, including the disintegration and defibration of pulps, refining, pulp cleaning, proportioning, recovery of fibers and solids, and maintaining buffer and disturbance

balancing chests between the pulp mill and the paper machine. Short circulation is an integral part of stock and water systems. Short circulation in papermaking refers to the stage where water, filtering through the wire, dilutes the stock before it reaches the head box. Within the mill, this short circulation occurs between stock proportioning and the headbox of the paper machine. The most critical tasks of short circulation are to dilute stock into headbox consistency, remove impurities and air, enhance the efficiency of fiber and filler material usage, improve the web particle size distribution for optimal results, reduce fluctuations in consistency and pressure, and measure and blend dyes, filler materials, and chemicals. The circulation water systems in the mill are made to enhance the economy of the process materials by improving solid recovery. (Knowpap, 2023) The stock and water systems of a typical paper mill are presented in Figure 8.

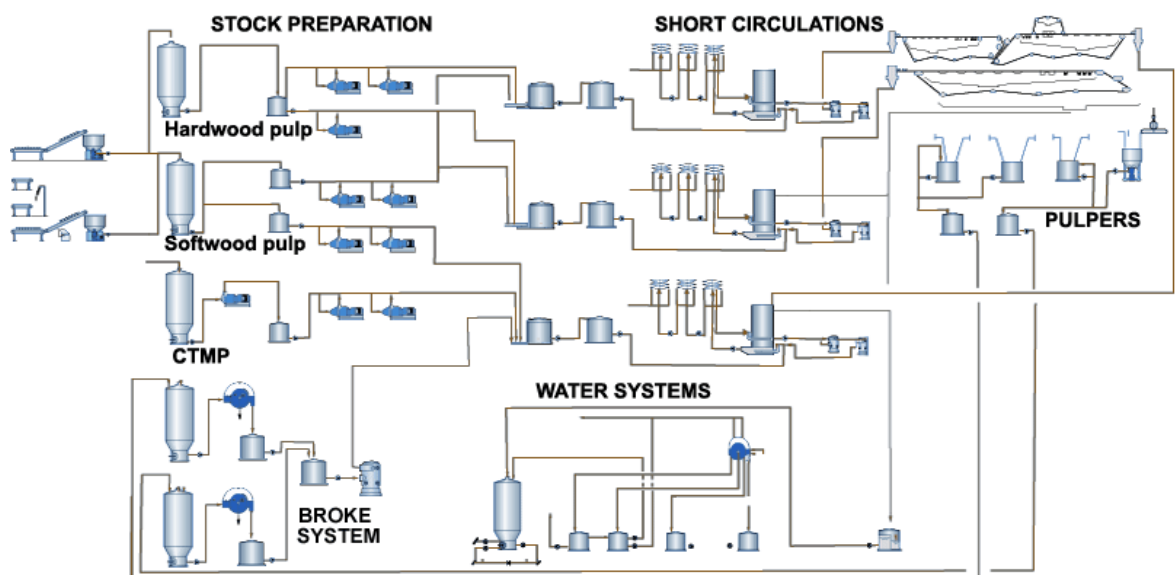


Figure 8. Process diagram of stock and water systems in a paper mill. (Knowpap, 2023)

Web forming occurs in paper machines. The web forming includes a headbox, wire section, press section, and drying section, as shown in Figure 9. The primary purpose of the headbox is to ensure even distribution of the stock suspension across the entire width of the wire section. This takes place in three stages. Initially, the cross-direction distributor evenly spreads the mix across the machine width. Pressure drop elements are then introduced to smooth out the flow profile in the cross-direction. Finally, the headbox nozzle produces the

ultimate jet that is delivered. (Paulapuro, 2000) Typical stock suspension in the headbox is from 0.5 to 1.0% (Knowpap, 2023).

The wire section is after the headbox. The primary purpose of the wire section is to remove water from the stock suspension to form a wet web (Paulapuro, 2000). Additionally, the wire section generates hydrodynamic solid forces within the web, ensuring the prevention and dispersion of floc formation and effectively regulating dewatering and hydrodynamic forces, maintaining uniform and desired fiber and filler retention levels. After the wire section, the dry content of the web is approximately 17-20%. The press section further extracts water from the web, leading to a 35-50% dry content. The objective of the drying section is to reduce the moisture content of the wet web (with a solids content ranging from 40-50%, depending on the board grade and press type used) received from the press section. This drying process aims to attain and sustain the necessary properties for the final board. The primary mechanism involved in drying is the evaporation of water. (Knowpap, 2023)

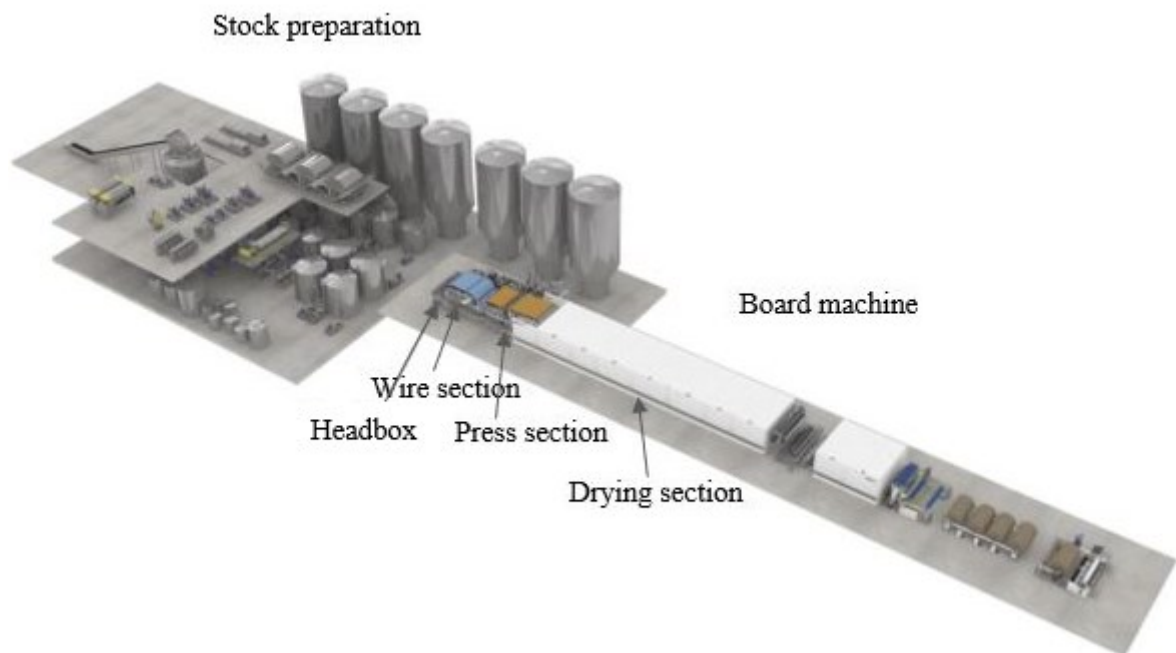


Figure 9. Web forming in board machine. (Adapted from Knowpap, 2023)

After the paper or board machine operation, the finishing process varies according to grade requirements. Common finishing methods for all grades are reeling and winding. Additionally, based on the product type, the finishing techniques can include surface sizing, which is prevalent in fine papers, coated raw papers, and boards. The coating is applied to

printing papers and certain types of boards. Uncoated SC grades undergo finishing through calendering. The coating is used for specific liquid packaging boards, where the surface is coated with plastic and aluminum extrusion. (Knowpap, 2023)

5.2 Properties of paperboards

Paperboards are distinguished from other packaging materials by their excellent strength properties, lightness, and recyclability. Paper and paperboard properties can be classified roughly into the following categories: basic-, optical-, strength-, surface-, and special properties. (Knowpap, 2023)

As mentioned previously, good mechanical properties are essential to cartonboard. However, the requirements for different properties depend on the product applications. For example, printing papers require good surface properties, such as smoothness. On the other hand, food packages require unique properties such as odor and taste. (Knowpap, 2023) The following chapters will discover the basic and strength properties of papers and paperboards.

5.2.1 Basic properties

Basis weight refers to the mass of paper or paperboard per square meter, measured in grams (g/m^2). Typically, the basis weights of papers range between 28-150 g/m^2 . Cartonboards that are multi-layered can have a basis weight from 100 g/m^2 to even 600 g/m^2 . (Häggblom-Ahnger & Komulainen, 2006) Variations in the basis weight impact many other characteristics of the paper. Differences in fiber and additive quantities mainly cause them. Furthermore, paper machine operations and recipe changes can indirectly influence paper quality. A decrease in basis weight can lead to reduced thickness, stiffness, strength, and opacity. (Knowpap, 2023)

Paper thickness is determined by the distance between the surfaces within a paper or paperboard. When measured on an individual sheet, it's called sheet thickness. Stack thickness, on the other hand, represents the thickness of a single sheet calculated from the combined thickness of multiple sheets stacked atop one another. (Häggblom-Ahnger & Komulainen, 2006; Knowpap, 2023)

The structural properties of paper are density and bulk, which can be calculated from thickness and basis weight. Density is calculated by dividing basis weight by thickness; its unit is kg/m^3 . Bulk is an inverse value of density, and its unit is cm^3/g . For paper and cardboard, the desired characteristic is typically low density, meaning high bulk, provided other critical properties are sufficient. High bulk correlates with good opacity, high stiffness, high compressibility, and high tear strength, among other qualities. (Hägglom-Ahnger & Komulainen, 2006)

5.2.2 Strength properties

Tensile strength refers to the maximum rate at which a sheet of paper or board can be stretched in the surface direction without breaking. Papers generally have tensile strengths between 1 and 10 kN/m , while cardboard can have tensile strengths above 10 kN/m . From the stress-strain curve, it is possible to calculate, in addition to tensile strength, the strain at break, or the percentage elongation of the paper until rupture (%), the tensile energy absorption, or the total energy used for stretching before fracture per unit area (J/m^2), and the tensile stiffness, or the maximum slope of the stress-strain curve expressed in the unit kN/m . (Hägglom-Ahnger & Komulainen, 2006) A schematic of a stress-strain curve from paper is illustrated in Figure 10. Fiber strength affects the tensile strength of paper, but it is primarily determined by the extent of bonding between fibers (Levlin & Söderhjelm, 1999).

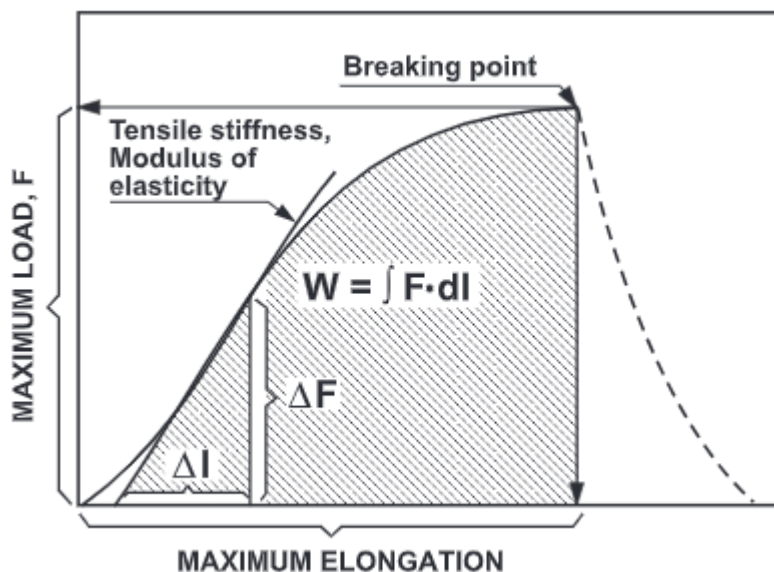


Figure 10. Stress-strain curve of paper. (Levlin & Söderhjelm, 1999).

Tear strength is determined by the force needed to create a particular tear size. The cross-directional tear strength of paper is employed to assess its resilience against faults. (Knowpap, 2023) The tear strength is influenced by the fiber length, fiber strength, and degree of bonding between fibers (Hägglom-Ahnger & Komulainen, 2006). Greater tear strength is achieved with longer and stronger fibers. In situations with low bonding, an increase in bonding leads to enhanced tear strength. On the contrary, when bonding is already high, tear strength is predominantly determined by the strength of the fibers. (Levlin & Söderhjelm, 1999).

6 Pulp measurement and characterization

Pulp characterization can be roughly divided into quantity or quality assessment. A quantity measurement ideally gives consistent results despite variations in quality, while a quality measurement should be unaffected by quantity. Quantity-like properties, such as consistencies or concentrations, describe the pulp slurry itself, not its fibers, particles, or hand sheet. Quality-like properties reflect specific characteristics of the pulp slurry derived from the properties or presence of individual particles. (Törmänen, 2021)

Traditionally, pulp fiber length is measured using a laboratory method called projection, as outlined in TAPPI Standard T 232. Another approach involves fiber classification using a set of at least four screens with progressively smaller openings, following TAPPI Standard T 233. The Bauer-McNett type is a commonly used instrument for this purpose. Fiber length can be automatically measured in a diluted solution using optical methods. (Biermann, 1996) Optical parameters are employed to define the characteristics of either single particles or a group of particles in a suspension. The primary physical phenomena employed in optical measurements of pulp processes include absorption, scattering, and depolarization. (Törmänen, 2021)

6.1 Optical measurement used in this work

The optical measurement technique used in this study involves continuously monitoring material flow through a cuvette within the fractionator system. This process is illustrated in Figure 11. Light-emitting diodes (LEDs) emitting visible and near-infrared wavelengths are employed as light sources. The beams from two LEDs are combined using a 50/50 beam splitter and directed through the sample in the cuvette. (Törmänen, 2021)

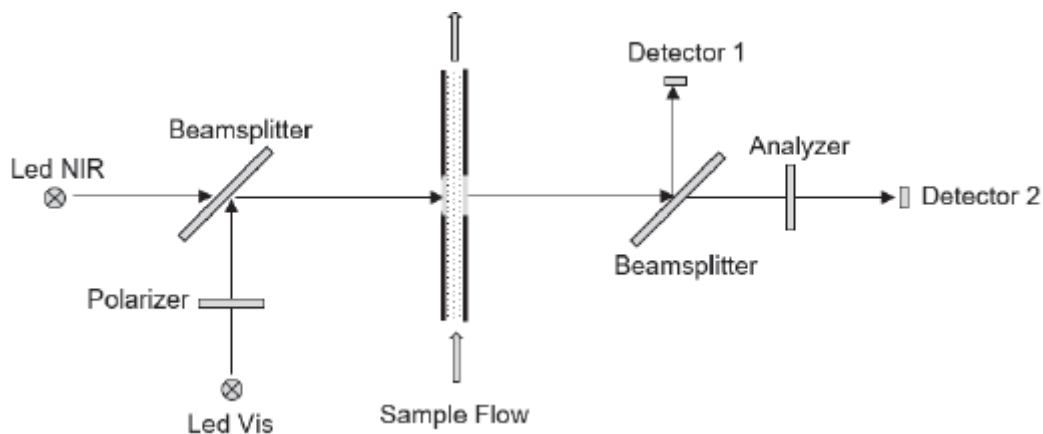


Figure 11. The optical measurement system consists of led-light sources and scattering optics. (Törmänen, 2021)

Detector 1 measures extinction for both wavelengths and assesses depolarization. Depolarization is also measured by both detectors 1 and 2 on separate paths. Afterward, the dark values from both detectors are removed. The extinction or attenuation coefficient gauges how much light dims as it travels through a substance. This dimming occurs due to two factors: absorption, where the material absorbs light energy, and scattering, where light changes direction upon encountering solid particles within the substance. (Törmänen, 2021)

In substances like pulp slurry, scattering primarily causes light to diminish, with its intensity decreasing as the number of particles in the substance increases. For instance, wood fibers and other particles in the slurry can deflect light from its original path, leading to a decrease in intensity detected. This process is the foundation for measuring consistency based on light attenuation: as the substance becomes denser, more particles scatter light, resulting in a weaker light signal. (Törmänen, 2021)

Light polarization refers to how the strength of the electric field of light changes based on the direction perpendicular to its path. The light is polarized linearly when the electric field oscillates in one direction. On the other hand, depolarization measurement refers to when linearly polarized light encounters the crystalline structures in cellulose within wood fibers, causing it to lose its polarization. (Törmänen, 2021)

6.2 Characterization of MFC fibers

Various techniques, either employed individually or in combination, have been utilized to characterize MFC. The final product and its requirements determine to a great extent what properties of the material are studied. The morphology of MFC fibers is typically examined by microscopy. The advantage of microscopy is its high accuracy, but they only consider particles more significant than the resolution of the equipment. In addition, they have difficulty simultaneously determining the length and the width of a high aspect ratio particle, such as MFC. (Cainglet et al., 2023) Microscopic techniques rely heavily on the operator and typically involve analyzing a limited sample size (Gamelas et al., 2015). Alongside microscopic techniques, the MFC characterization can be conducted using more rapid methods indirectly linked to the morphology, such as rheology, dynamic light scattering, surface area, and MFC film properties. (Larsson et al., 2019)

Scanning electron microscope (SEM)

SEM imaging is a measurement used to image and observe micro- and nanostructural surfaces of various materials. The image is obtained by scanning an electron beam on the sample's surface (Figure 12 b) (Ul-Hamid, 2018). According to Kangas et al. (2014), the resolution of SEM imaging is between an optical microscope and TEM and AFM. They demonstrated that the microscope could observe cellulosic material from millimeters to nanometer scales. Therefore, SEM imaging has been widely applied by many researchers.

Abe et al. (2007) measured the fibril size of cellulose nanofibrils (CNF) using the FE-SEM imaging method. They had two different CNF samples that were pretreated by freeze-drying and oven-drying. Both samples gave similar measurement results for 15 nm diameter particles. Chinga-Carrasco et al. (2013) studied the structure of unbleached and osmium

tetroxide (OsO₄) treated MFC combined with a mixture of bleached and TEMPO-treated MFC grades. The results obtained by SEM, FE-SEM, and laser profilometry proved that the different MFC qualities had different morphology and surface chemistry.

The sample preparation is essential in SEM imaging, especially when the samples are wood fibers. Wood fibers are radiation sensitive, thermally unstable, and poor conductors. Generally, the pretreatment of cellulosic fibers is done by different drying methods, such as air-, freeze-, or super-critical point drying. Nonetheless, drying has been noticed to affect the fiber structure by causing shrinkage and collapsing. (Osong et al., 2016) This is called aggregation or hornification, resulting in fiber aggregates and fibrillation loss. Hornification is one of the main challenges in commercializing powder-like MFC. (Silva et al., 2021)

Transmission electron microscope (TEM)

Figure 12 a) The transmission electron microscope uses transmitted electrons to image samples. TEM has a high resolution, which can be reported from angstroms (0.1 nm) to even subangstroms. Compared to SEM or AFM, the sample thickness in TEM imaging is thinner, usually below 100 nm. This will ensure that the electrons penetrate through the sample, but it is also a drawback of the measurement. As in SEM imaging, TEM also requires an adequate sample preparation. Generally, TEM grids are used to pretreat fiber particles in a liquid solution. (Luo, 2016)

TEM measurement has also been widely used in characterizing nanocelluloses. For example, Ankerfors et al. (2012) used TEM to analyze modified MFC. The MFC fibers were pretreated with carboxymethyl, followed by a high-pressure microfluidization. The diameter of these treated MFC fibers varied between 5-15 nm and had a length of over one micrometer.

Atomic force microscope (AFM)

As presented in Figure 12c), atomic force microscopy is a high-resolution microscope that can observe a three-dimensional (3D) material's structure even on a nanometer scale. It can image various materials, from synthetic to natural, and hard or soft. Typically, the samples are examined in air, but in some cases, the measurement can be conducted under a vacuum

or liquid environment. The measurement operation is based on surface forces, made using a sharp probe that touches the surface. AFM differs from SEM or TEM in its measurement technology since it does not use light or electrons to image materials. (Haugstad, 2012) AFM does not require special sample preparation, such as staining or dehydration. Although AFM can reach a high resolution even at the nanometer scale, the drawback is that it does not provide information about the structure or chemical composition of the analyzed material. Therefore, AFM could be referred to as a very high-resolution profilometer. (Luo, 2016)

The MFC morphology using AFM has been studied by Andresen et al. (2006). They used unmodified MFC from softwood sulfite pulp. The results revealed that MFC is a heterogeneous material consisting of thinner fibrils and fibril bundles. Ahola et al. (2008) studied the structure of two modified MFC qualities, unlike Andresen. The MFC types differed by raw material sources, production methods, and hemicellulose content. The first MFC was produced from sulfite pulp with a significant amount of hemicellulose. The second MFC was produced from dissolving pulp and contained less hemicellulose. In addition, the second MFC was produced using carboxymethylation, which forms charged groups on the MFC surface. The results showed that the first MFC had a more apparent fiber network, whereas the second MFC formed denser and smoother films. Siró & Plackett (2008) have also studied these MFC modification techniques. They obtained similar results where the chemically charged MFC formed finer and homogeneous films. On the other hand, the charged nanofibers were revealed to have some larger aggregates in the MFC films.

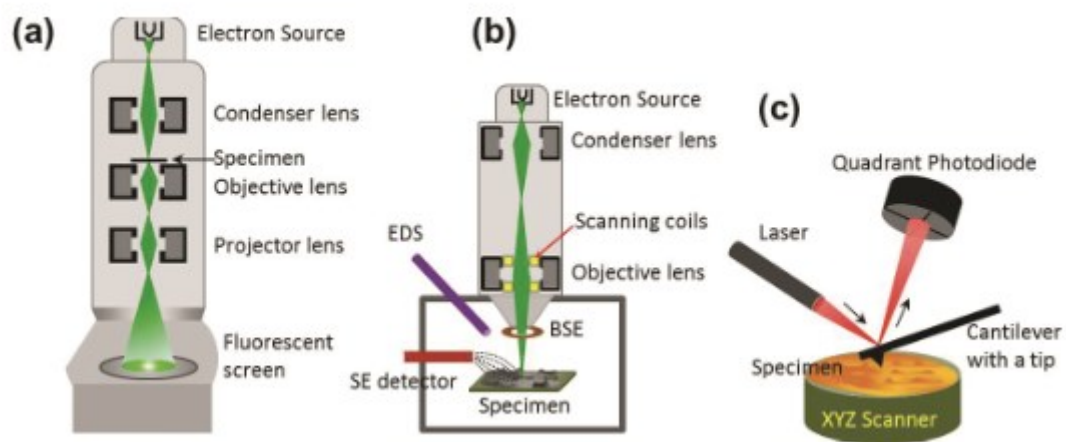


Figure 12. Comparison of imaging techniques: (a) TEM, (b) SEM, and (c) AFM. (Adapted from Luo, 2016)

Degree of polymerization

There are many different analysis methods for describing the chemical structure of MFC. The length of cellulose chains, known as the degree of polymerization (DP), is closely tied to the shape of nanofibers and has been used to describe the degree of fibrillation. Longer fibrils are linked to higher cellulose DP. Typically, the polymerization degree of MFC is determined by the viscometry method following ISO standard 5351. The degree of polymerization varies depending on the raw material. For instance, sulfite pulp usually has a DP of 1200–1400. However, isolating nanofibers mechanically can reduce the polymerization degree by about 30–50%. Depending on the fiber treatment methods, MFC may have an even lower polymerization degree. (Siró & Plackett, 2010) Iwamoto et al. (2007) observed a reduction in the polymerization degree of MFC from 770 to 550 after the grinding process. A higher polymerization degree is advantageous for MFC fibers, as it is associated with enhanced tensile strength, as Henriksson et al. (2007) indicated. The polymerization degree can also be used to evaluate the transparency of MFC material since high fibrillation forms optically non-reactive fibrils with low light scattering value (Chinga-Carrasco, 2011).

Surface area

High specific surface area is an essential characteristic of MFC. Typically, modeling tools are employed to evaluate this property, utilizing parameters like length and diameter. The obtained measurement is often an estimate. The BET method was used to determine the surface area of MFC. (Lavoine et al., 2021) The BET method was developed by Brunauer, Emmett, and Teller in 1983 and is based on gas adsorption. The technique requires a completely dry sample, which poses a challenge due to the significant aggregation, also called hornification, of MFC during the drying process. As a result of drying, the specific surface area is reduced, which results in an underestimation of the value. Some methods have been developed to maintain the fiber structure, such as solvent exchange and critical point drying. (Moser et al., 2016)

Rheology

When studying the rheological properties of cellulose nanomaterials, researchers typically either examine gelation using viscometric measurements or explore liquid crystallinity and ordering properties through rheological characterization (Foster et al., 2018). Such rheological properties are gel-forming, shear-thinning, and yield stress. (Kataja et al., 2017). Shear-thinning occurs when the floc structure changes with the shear rate (Saarinen et al., 2014). The rheology of a nanocellulose suspension is sensitive to many external influences, such as pH, solids content, ion concentration, and temperature. In addition, many other factors can have a minor effect, such as particle dimensions, aspect ratio, fibrillation degree, and surface charge. MFC imposes a challenge on rheological measurements since it is a heterogeneous material composed of at least two phases and behaves non-linearly. (Schenker et al., 2019) MFC rheology can be measured with traditional rotational rheometers. However, they tend to cause wall depletion, which can be problematic for flow measurements. A depletion layer develops when fibers and flocs move away from the walls during flow, and shear mainly happens in this fiber-poor layer. However, when making oscillation measurements in the linear viscoelastic region with low stresses and strains, issues with wall depletion are anticipated to be reduced. (Karppinen, 2014)

Dynamic light scattering

Dynamic light scattering (DLS) determines the hydrodynamic "apparent particle size" of particles in suspension. This technique measures the changes in scattered light intensity over time as particles undergo Brownian motion. Due to the unique shape of nanocellulose particles, which are elongated like rods or fibrils and have different diffusion rates in different directions, DLS measurements cannot directly tell us about the length or cross-section of the particles. Additionally, since the diffusion of rod-shaped particles depends on their orientation, the distributions observed in DLS cannot be directly connected to particle size distributions. Therefore, it is recommended to use light scattering as a relative measurement complemented by microscopy. (Foster et al., 2018) Besides particle size evaluation, dynamic light scattering has been used to study particle size aggregation and gelation of nanocellulose in water, as Fall (2013) reported.

MFC films

MFC has proven to have excellent film properties, such as high strength due to the large aspect ratio and excellent oxygen barrier properties due to its partial crystallinity. (Rodionova et al., 2012) MFC films are typically made either by casting or vacuum filtration. Water extracted from the MFC gel forms a network of cellulose nanofibers held together by hydrogen bonding between the fibers. This process leads to the creation of films that are both stiff and strong. The microscopic examination of MFC film surfaces is often used to describe their fibrillar nature. (Siró & Plackett, 2010) The most typical properties describing films include mechanical-, optical-, and barrier properties.

Larsson et al. (2019) studied MFC films' mechanical properties from different fractions. Mechanical testing was performed using analysis, including tensile strength, thickness, strain at break, and Young's modulus. The study concluded that producing durable films is primarily about decreasing the presence of larger particles rather than increasing the quantity of smaller particles, as mechanically strong films were formed by every fraction except the coarsest one.

The transparency of MFC films is measured through optical properties. Nanocellulose fibers, with diameters much smaller than visible light wavelengths, can reduce light scattering through dense packing or scatter light forward. This results in transparent films, distinct from traditional paper. The excellent transparency of nanocellulose films makes them attractive for various applications, prompting recent studies on light transmission through these films. The optical properties are impacted by surface roughness and fiber aggregates. Taking additional steps to homogenize the material improves the optical transparency of MFC films by minimizing the presence of fiber clusters. (Kumar et al., 2014) The light transmittance of MFC films can be measured with spectrophotometers.

The barrier properties of MFC films can be tested in several ways. The degree of crystallinity is a significant contributor to the structure and barrier properties of the films since the possibility of other molecules passing through crystalline parts of the network is low. Therefore, it has been generally concluded that high crystallinity equals good barrier properties. (Kumar et al., 2014; Padberg et al., 2016) MFC films have proven to have excellent oxygen barrier properties, but the water vapor barrier properties are poor due to the hydrophilic feature of the material. (Kumar et al., 2014) Oxygen transmission rate (OTR)

and water vapor transmittance are typical methods to characterize these properties (Rodionova et al., 2012).

7 Fractionation

Fractionation can enhance the analysis of pulp suspensions that contain a wide range of particles. Different methods exist to separate MFC, the easiest being centrifugation to isolate nanosized particles from larger fibril aggregates and fiber fragments. More advanced methods are membrane filtration and sieving. However, accomplishing this task is challenging because most small MFC particles tend to create gel-like films. (Larsson et al., 2018) A new fractionation approach was developed for MFC by Larsson et al. (2018) that combines both filtration and centrifugation. The size distributions of each fraction were analyzed with scanning electron microscopy. Later, the same method was also used by Ciftci et al. (2020) to tailor the rheological properties of MFC.

Other fiber fractionation methods include pressure screening, and hydrocyclones operated on an industrial scale. In their study, Madani et al. (2011) used four hydrocyclone stages to fractionate MFC. Their hydrocyclone was 10 mm in diameter and operated at 5 bars with a feed flow rate of 4.2 l/min. Their accept-reject ratio was 6 to 4. The reject fraction was collected after each pass, and the fibril length distribution was measured. The MFC was then subjected to re-fractionation through the hydrocyclone. Seifert et al. (2023) used pressure screens to fractionate pulp. The reject stream consisted of long and coarse particles, and the accept stream of short fibers and fines.

Special laboratory equipment has also been developed for fiber fractionation. For example, the Bauer McNett type of fiber length classification method determines the weighted average fiber length of a pulp (Tappi standard T 233 cm-15). Nowadays, more advanced fiber fractionation equipment is on the market, based on tube-flow fractionation and ultra-high definition camera technology.

7.1 Tube flow fractionation

Since micro and nanocellulose production is shifting from laboratory to industrial scale, there will be a more urgent demand for selective measurements of heterogeneous raw materials. Within this framework, selectivity refers to the measurement apparatus's ability to remain unaffected by changes in non-targeted parameters. As mentioned in previous chapters, microfibrillated cellulose has a broad particle size range, including nanofibrils and more fiber-like particles. Quite often, MFC suspensions are also mixed with polymers. Achieving selective measurement becomes challenging when a sample contains a mix of these components in varying proportions. This difficulty is particularly pronounced in optical measurement methods, where the distinct responses of different components pose a significant challenge. (Törmänen, 2021)

Examining multicomponent samples like pulps through fractional analysis provides valuable insights into their properties and particles. This method offers unique information that is challenging to acquire through other means, such as determining mass fractions of pulp or filler, assessing the content of attached and free ink in deinked pulp, and examining several characteristics of particles through image analysis. A simple and rapid yet less familiar technique for categorizing pulp particles based on their dimensions is tube flow fractionation. In this method, particles are separated in a continuous water flow. In the tube flow method, particles are fractionated along the tube length, causing the largest particles to gather at the leading edge of the flow plug. In contrast, the smallest particles accumulate at the trailing edge. (Laitinen et al., 2011)

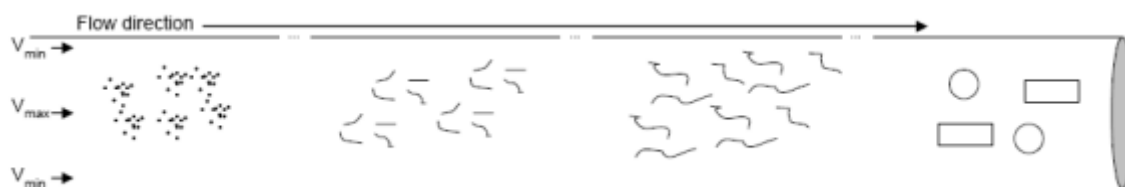


Figure 13. Principle of tube flow fractionation. (Adapted from Laitinen et al., 2011)

A schematic of the tube flow fractionation method is shown in Figure 13. Particles are initially distributed randomly when the sample is fed into the tube. Once the flow begins, the mild turbulence occurring during the transition flow regime causes particles to shift

randomly within the flow. The hypothesis suggests that tiny particles floating near the tube wall may not be readily captured by the more rapid central flow, lingering in the region where the velocity of the flow is lower. While large particles can also flow near the tube wall, their greater size enables them to be more readily recaptured by the faster middle flow. Particles with elongated dimensions, like fibers, or multiple long dimensions, like paper flakes, are more likely to be captured by the faster central flow than particles with shorter dimensions, like fines. As a result, larger particles tend to accumulate at the leading edge of the flow. Consequently, larger particles are prone to collect at the front end of the flow and are the first to exit the tube. (Laitinen et al. 2011)

8 Dynamic fractional analysis (DFA)

The dynamic fractional method (DFA) is a new measurement method that dynamically analyzes the fractionation data of pulp suspensions. Valmet utilized the technique with a fractionator fiber analyzer. The DFA method combines tube flow fractionation and optical measurements to obtain more precise information from the nature of the pulp suspension than the previously known flow-based analysis (FBA) method. The advantage of DFA is that it does not require information on the fluid properties, such as flow velocity and water temperature, unlike the FBA method, where the sample quality is a static flow-based factor. Therefore, the dynamic way of analysis enables the measurement of the quality of the fractionated sample simultaneously with the quantity. Quantitative properties of the sample include, for example, sample concentration. In the DFA method, quality is represented by the fibrous index, while the variable μ_B describes the balanced concentration indicating quantity. Extinction and depolarization signals are primary indicators of quantity. (Törmänen, 2021)

8.1 Fibrous index

The fibrous index is a new term that can be used to measure fiber suspensions. The effectiveness of the index relies on the unique response of signals to various components in the sample. Intact fibers generate a robust depolarization signal compared to the extinction

signal, maintaining a high fibrous index. On the contrary, fines and fillers yield the opposite effect, resulting in a low fibrous index. Thus, in tube flow fractionation, the fibrous index shows if the substance in the flow is made up of fine particles or fibers. The fibrous index (FI) is a ratio of depolarization to extinction coefficient signals, indicating the fibrous nature of the sample, as seen in Equation 2.

$$FI = \frac{\mu_{DP}}{\mu_{ext}} \quad (2)$$

Where,

μ_{DP} = Amount of depolarized light

μ_{ext} = Extinction coefficient

The DFA approach simultaneously assesses the qualitative and quantitative aspects of the fractionated sample flow. In this context, the fibrous index characterizes the quality, while the variable μ_B serves to quantify the balanced concentration. A higher fibrous index at the beginning of the flow reveals the presence of fibers, and this index decreases as the flow continues, which indicates a decrease in fibrous properties at the measurement point. As seen in Figure 14 a), at the initial sample stage where fibers are present, the depolarization reading is significantly stronger than the corresponding extinction signal. The signal intensity order shifts as the sample transitions from fibers to fines, occurring around a flow point of 18 600 ml. The fibrous index from the same sample as a function of flow is shown in Figure 14 b). The index number directly shows how fibrous a sample point is. A higher value means a more fibrous sample. As we approach the fines fraction, the fibrous index drops to approximately 1, and extinction and depolarization signals become similar. A small fibrous index number suggests the sample is primarily non-fibrous, such as fines or fillers during that flow period. (Törmänen, 2021)

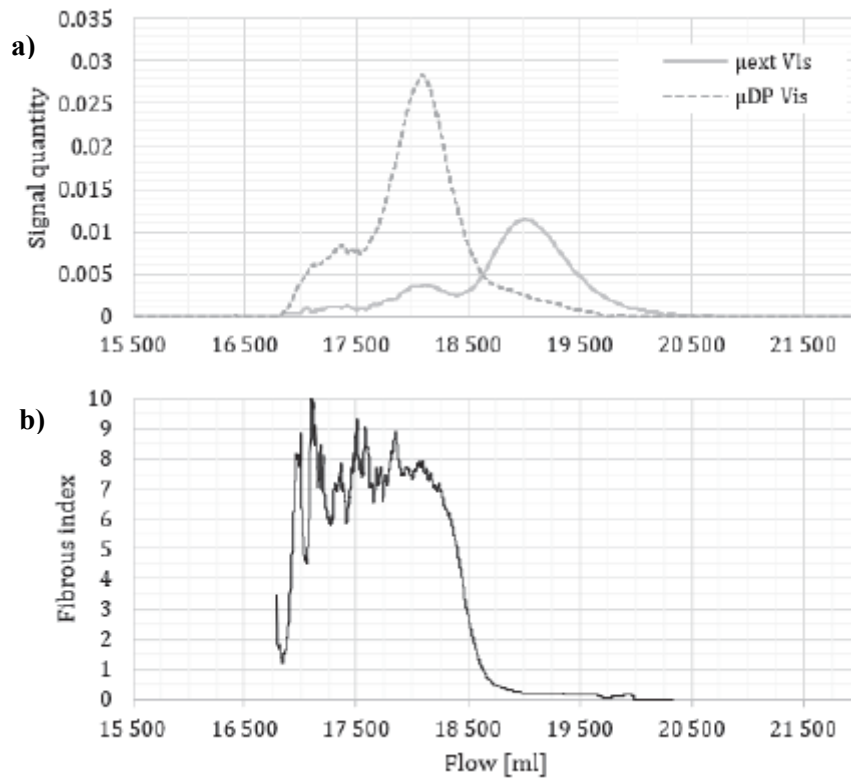


Figure 14. a) Extinction coefficient and depolarization signals as a function of flow, and b) fibrous index as a function of flow. (Törmänen, 2021)

8.2 Size index

Another new term, the size index (SI), is the ratio of extinction coefficients at long and short wavelengths. A long wavelength (Vis) emphasizes large particles, such as fibers, and a short wavelength (NIR) emphasizes small particles, such as fines. The size index primarily characterizes the particle dimension closest to the wavelength. For non-fibrous particles, such as fines and fillers, it represents the length, width, and depth dimensions parallel to the particle. For fiber particles, it means the cross-sectional dimensions. The size index can be calculated from Equation 3.

$$SI = \frac{\mu_{ext(NIR)}}{\mu_{ext(Vis)}} \quad (3)$$

Where,

$\mu_{ext(NIR)}$ = Extinction coefficient at near infrared wavelength

$\mu_{ext(Vis)}$ = Extinction coefficient at visible wavelength

Calculating the size index distribution can involve covering all particles in the measurement. When the aspect ratios of particles are similar, the size index is considered the primary measurement. However, a pulp sample typically includes fibers and fines with various aspect ratios, which can cause the size index data to overlap. For this reason, it is difficult to distinguish whether the numerical value is because of the fiber's cross-sectional dimension or the fines' proportions. To address this issue, the size index can serve as an additional measurement for the fibrous index, which helps to identify whether the measured particles consist of fibers or fines, allowing separate size index distributions for fiber and fine fractions. (Törmänen, 2021)

The distribution figures provide insights into the process status, which is particularly beneficial for process operators. By examining the distribution plot, one can promptly observe the fibrous index distribution of the measured sample and, if required, the fractional size index distribution. (Törmänen, 2021)

9 Conclusions of literature part

Microfibrillated cellulose is an emerging raw material in many industrial applications due to its unique properties and ability to replace environmentally harmful chemicals. MFC can be used in papermaking, coatings, and films. In papermaking, MFC can be used as a strength agent like starch. Ankerfors et al. (2014) noticed that even a 2.5-5.0 wt-% addition of MFC improves the mechanical properties of papers. Typically, MFC is produced mechanically by homogenization or grinding. Mechanical treatment is usually combined with a chemical pre-treatment to enhance fibrillation and reduce energy consumption.

Many different characterization methods have been utilized in analyzing the structure of MFC, the most common being high-precision microscopes, such as electron microscopies and scanning probe microscopy. Some other measurements used to describe MFC properties that are indirectly linked to its morphology are, e.g., polymerization degree, surface area, dynamic light scattering, rheology, and measurements related to MFC films. The most typical properties describing films include mechanical-, optical-, and barrier properties.

It has been studied that MFC has a broad particle size range that includes both nanofibrils and fiber-like particles. In papermaking, MFC is often mixed in a pulp suspension with polymers. Characterization of pulp suspensions can be divided into quantity and quality assessment. A quantity measurement ideally gives consistent results despite variations in quality, while a quality measurement should be unaffected by quantity. Quantity-like properties, such as consistencies or concentrations, describe the pulp slurry itself, not its fibers, particles, or hand sheet. Quality-related aspects show us specific pulp qualities based on its individual particles.

Optical parameters can be employed to define the characteristics of single particles or a group of particles in a suspension. However, obtaining a selective measurement becomes challenging when samples mix these components in varying proportions, especially in optical measurement methods where different component responses pose significant challenges. It has been studied that a tube flow fractionation before optical measurement can enhance the analysis of pulp suspensions that contain a wide range of particles. Valmet has recently developed a dynamic fractional analysis, which has been tested for R&D purposes. The dynamic fractional analysis method, shortened as DFA, combines tube flow fractionation and optical measurements to obtain more precise information about the nature of the pulp suspension.

Experimental part

10 Materials and methods

The experimental part consists of laboratory sheet trials and fractionation measurements. Suspensions for laboratory sheets and fractionation measurements were prepared using hardwood pulp, circulated water, and MFC. Cationic starch was used as a strength additive together with MFC. CPAM was used as a retention system. The data from the fractionator was analyzed using dynamic fractional analysis (DFA) from optical measurement signals

provided by Valmet Fractionator equipment. All the experiments were done at the Xamk Fiber Laboratory research unit in Savonlinna.

The laboratory sheets trials aimed to study the effect of two MFC qualities and their dosage amounts on paper strength. The impact of chemical dosage amounts was also investigated. The purpose of the fractionation measurements was to find applications for the fibrous index and size index from the papermaking industry. The laboratory sheet suspensions were analyzed with a Valmet Fractionator to study whether the fibrous and size indexes could be connected to paper properties. The applicability of fibrous index and size index was also studied in white waters from laboratory sheet making.

10.1 Used materials

A specific Finnish mill provided bleached birch kraft pulp and circulating water. Two companies provided MFCs for the trials. A commercial MFC producer company provided MFC1, and a Finnish company provided MFC2 for R&D purposes. The MFC2 sample is used as a secondary MFC grade in this work. Both MFC samples were made from softwood. Before making the laboratory sheets and suspensions, MFCs were diluted using deionized water from ~2% and ~4% to 0.4% with a magnetic stirrer.

A Finnish chemical supplier supplied cationic starch in powder form. The starch was prepared for a solution by cooking. Using a heat plate, two grams of cationic starch were diluted into 400 ml of deionized water and warmed to 90°C. The blend was allowed to cook for 15 minutes while continuously stirring. The solution was allowed to cool to room temperature.

CPAM was provided by a specific Finnish chemical supplier in a solid form and prepared for a solution afterward. 0.125 grams of CPAM was added to 500 ml of deionized water while continuously stirring with a magnetic stirrer. Mixing was slowed, and the CPAM was allowed to dissolve for at least 2 hours before use.

The materials were kept at a cold temperature of approximately 4°C, besides CPAM, made separately for each day, and starch, stored at room temperature. Storage time for circulated water before the laboratory sheets were 3-7 days, and before fractionation tests, 11 days.

10.2 Methods

Laboratory sheets were done using two different MFC grades and chemical amount variations. Two levels were chosen for each variable: high (+) and low (-). The chosen MFC1 was a high-quality grade, and MFC2 was a low-quality grade. The laboratory sheet pulp suspensions were analyzed using Valmet fractionation equipment. Methods for suspension preparation, laboratory sheet making and testing, and fractionation analysis are described in this chapter. Table 3 contains the compositions of pulp suspensions.

Table 3. Compositions of the pulp suspensions.

Test point	Pulp (g. abs. dry)	MFC grade	MFC wt%	Cationic starch kg/t	CPAM (g/t)
1	1.63				
2	1.63			2	150
3	1.63			6	600
4	1.63	MFC1	3		
5	1.63	MFC2	3		
6	1.63	MFC2	5		
7	1.63	MFC1	5		
8	1.63	MFC1	3	2	150
9	1.63	MFC1	3	6	600
10	1.63	MFC1	5	2	150
11	1.63	MFC1	5	6	600
12	1.63	MFC2	3	2	150
13	1.63	MFC2	3	6	600
14	1.63	MFC2	5	2	150
15	1.63	MFC2	5	6	600

10.2.1 Suspension preparation

The pulp was mixed with circulating water for sheet formation and other measurements using a 550 rpm magnetic stirrer for 1 minute. Then, MFC was introduced and mixed for 30 seconds. Then, cationic starch was added through a syringe and stirred for 30 seconds. Finally, CPAM was incorporated and stirred for only 2 seconds to prevent floc breakage.

The object was to produce sheets with a basis weight of 60 g/m² using bleached birch pulp. The amount of MFC, CS, and CPAM varied. Laboratory sheets were done using 3 wt% and 5 wt% of MFC, 2 kg/t and 6 kg/t of CS, and 150 g/t and 600 g/t of CPAM.

10.2.2 Fiber properties

Fiber properties were analyzed using the Valmet fractionator fiber analyzer, as seen in Figure 15. The measurement sequence is divided into a separation cycle and a fractionation cycle. In separation, the sample is circulated through a looped fractionating hose until the water in the hose returns to the water tank. The sample's flow rate, pressure, temperature, and optical properties are monitored throughout the separation cycle. Measurement signals are regularly recorded, and the results are stored. When the flow rate reaches the required volume, the sample is directed for discharge, starting the fractionation process. Fractionation ends when the final volume is reached. The device waits until the discharge volume is reached, then directs the flow back to the water tank. After analysis, the computer calculates the results, and a final rinse is done. (Valmet, s.a.)



Figure 15. Valmet fractionator.

The fractionator measures the share of fractions, fiber dimensions, fines, flocs, fibrillation, kinks, and curl. The measurement is based on the ability of the UHD camera to detect fractionated particles. According to Table 4, fiber properties were measured using a fractionator and FS5 fiber analyzer from MFC samples. Property of fractions 1-5 as a percentage of length-weighted distribution was measured using FS5, and other properties were measured using a fractionator. In addition, the fibrous and size indexes of samples were derived from the recorded measurement signals as a function of sample consistency. The composition of white water was also measured with a fractionator.

Table 4. Valmet fractionator and FS5 fiber analyzer definitions.

<i>Property</i>	<i>Definition</i>
Fiber length Lc(l) ISO, mm	Length-weighted average fiber length, ISO 0.2-7.0 mm
Fiber width, μm	Length-weighted average fiber width
Fines A, %	Flake-like fines (type A) as percentage of the projection area of measured particles. Particles shorter than 0.2 mm.
Fines B, %	Lamella-shaped fines (type B) as percentage of length. Particles with width less than 10 μm and length over 0.2 mm. The sum length of these particles is divided by the sum length of all measured particles longer than 0.2 mm, and then multiplied by 100.
Fines, %	Fines as percentage of arithmetic distribution
f1...f5(l), %	Fractions 1–5 as a percentage of length-weighted distribution. Fraction 1: 0–0.2 mm, width $\geq 10 \mu\text{m}$ Fraction 2: 0.2–0.6 mm, width $\geq 10 \mu\text{m}$ Fraction 3: 0.6–1.2 mm, width $\geq 10 \mu\text{m}$ Fraction 4: 1.2–2.0 mm, width $\geq 10 \mu\text{m}$ Fraction 5: 2.0–3.2 mm, width $\geq 10 \mu\text{m}$

10.2.3 Laboratory sheet making

Laboratory sheets were prepared following the ISO 5269-1 standard. After the suspension preparation, the sample was transferred into the laboratory sheet former (165 x 165 mm), where regular tap water was filled to the mark less than halfway down the former. The rest of the water used to form the sheet was circulating water. The air agitator was turned on, and 10 seconds after completing the agitation, the drainage valve was opened. On top of the sheet, one new blotting paper and four used blotting papers were placed. The sheet was rolled with a couch roll six times and transferred from the wire. Each sheet was placed between a drying plate and a new blotter before wet pressing. Figure 16 demonstrates the magnetic stirrer and sheet former.



Figure 16. Magnetic stirrer (left) and sheet former (right).

The sheets were pressed for five minutes under 410 kPa. Then, the blotters were changed to dry blotters, and the sheets were pressed again for two minutes at 410 kPa. After wet pressing, the sheets were dried under standard conditions at 23°C and 50% relative humidity overnight. The sheets were separated from the pile while remaining between the drying plate and a blotter to avoid shrinkage.

10.2.4 Laboratory sheet testing

The measurements were performed under standard conditions at 23°C and 50% relative humidity. Before testing, the samples were kept in a conditioning room for at least 4 hours, following ISO 187 guidelines. Table 5 shows the specific measurements and standards utilized.

Table 5. Used measurements and standards in laboratory sheet testing.

<i>Property</i>	<i>Equipment</i>	<i>Measurement method/standard</i>
Grammage	-	ISO 536:2019
Thickness	L&W Micrometer 250	ISO 534:2011
Formation	Pixact Paper Analyzer V700	-
Tear strength	L&W Tearing Tester 009	ISO 1974:2012
Tensile strength	L&W Tensile Tester 066	ISO 1924-2:2008

Grammage was determined from every sheet by ISO 536:2019 standard from Equation 4.

$$g = \frac{m}{A} = 10^6 \quad (4)$$

Where,

m = mass of the test piece

A = Area of the test piece

The bulking thickness was measured after the grammage from a pack of six sheets by ISO 534:2011 standard. The measurement was taken from six different points on the sheet pile. Bulk density was calculated from grammage and thickness with Equation 5.

$$d_b = \frac{g}{\delta_b} \quad (5)$$

Where,

g = grammage of the paper

δ_b = mean bulking thickness

Tensile strength was measured using the ISO 1924-2:2008 standard on 10 test pieces cut to 15 mm width from six sheets.

Tear strength was measured by ISO 1974:2012 standard. Two rectangular samples were cut from six sheets. The width of each sample was 50 mm \pm 2 mm, and the length was 62 mm \pm 0.2 mm. The samples were randomly assembled into sets of four before measurements.

11 Results and discussion

The following chapters present results from laboratory sheet testing and fractionation analyses. Dynamic fractional analysis (DFA) was used to analyze the data from fractionator measurements using fibrous and size indices. The DFA method was applied to analyze fines, fiber suspension properties, and white waters. Fractionator UHD and FS5 fiber analyzer were used as a reference measurement to study MFC samples and compositions of pulp suspensions mixed with fines and chemicals.

11.1 Fibrous and size index in MFC characterization

The MFC qualities used in the laboratory experiments were measured using a Valmet fractionator and FS5 fiber analyzer. The MFC qualities in the results are indicated as MFC1 and MFC2. The MFC1 sample is commercially available, and the MFC2 sample is produced for research and development purposes. Table 6 shows the fiber properties of MFC grades.

Table 6. Fiber properties of two MFC grades determined by fractionator and FS5.

Sample	Fractionator and FS5 UHD results					
	Lc(n) ISO mm	Fiber width um	Fines A %	Fines B %	Fines %	Fiber fraction 0.00-0.20 mm %
MFC1	0.046	4.19	98.15	69.16	99.91	96.4
MFC2	0.12	9.22	67.2	25.36	97.68	61.3

The fiber properties of MFC1 and MFC2 were different. The fiber length and width of MFC1 were lower compared to MFC2. The ISO fiber length of MFC1 was 0.046 mm, whereas the ISO fiber length of MFC2 was 0.12 mm. The fiber width of MFC1 was 4.19 μm , while the fiber width of MFC2 was 9.22 μm . The number of flake-like fines (type A) in MFC1 was 98%, and in MFC2, 67%. The number of lamella-shaped fines (type B) in MFC1 was 69%, and in MFC2, 25%. Fraction 0.00-0.20 mm fines was also more significant in MFC1 at 96% compared to MFC2 at 61%. The share of over 65% of fiber fraction 0.00-0.20 mm fines was considered as MFC during the experiments. Therefore, MFC2 did not quite meet the definition.

The MFC qualities used in the laboratory sheet-making and fractionator analyses were observed through fibrous and size indexes. The fibrous index describes the quality of the sample. The higher the fibrous index, the more fibrous the sample. A lower fibrous index indicates that the sample is a more fines-like material. Fibrous index values between 0-1 are roughly categorized into fines, and fibrous index values between 1-10 are classified into a fibrous material. Figure 17 shows a fibrous index of MFC qualities. The size index describes different-sized particles in a sample. Different peaks in the size index graph represent particles of various sizes. Figure 18 shows the size index of MFC qualities.

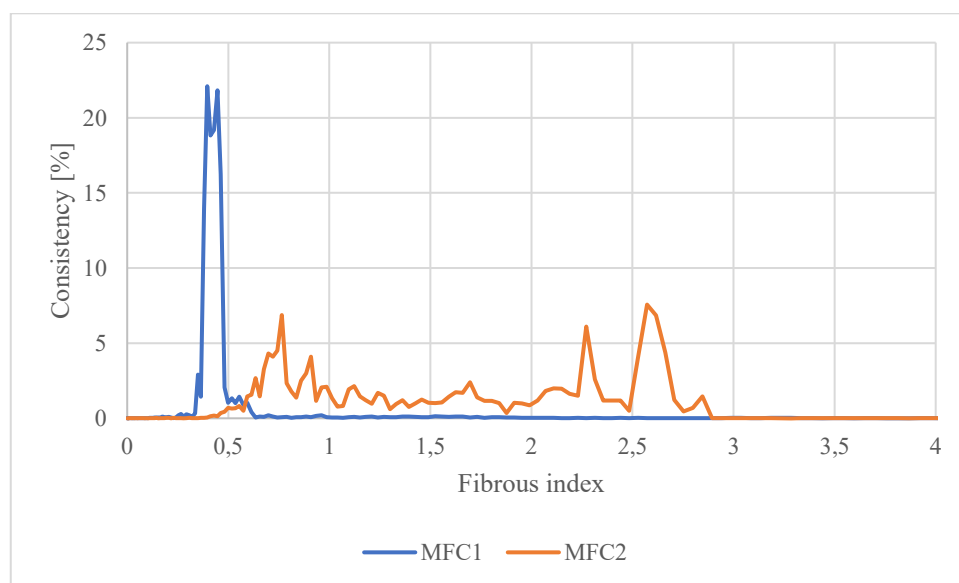


Figure 17. Fibrous index of MFC qualities. MFC1 is of commercial quality, and MFC2 is of non-commercial quality.

As seen from the results, the fibrous index of MFC1 was more uniform than that of MFC2. MFC1 is the commercial grade, and MFC2 is the non-commercial grade. The fibrous index value of MFC1 was approximately 0.4, whereas the fibrous index values for MFC2 were between 0.5 and 2.8, having a much more significant deviation. The fibrous index verifies that MFC1 was a more homogeneous material than MFC2. MFC2 contains some fibrous material, indicated by index values above 1. Therefore, it is still on its way to homogeneity.

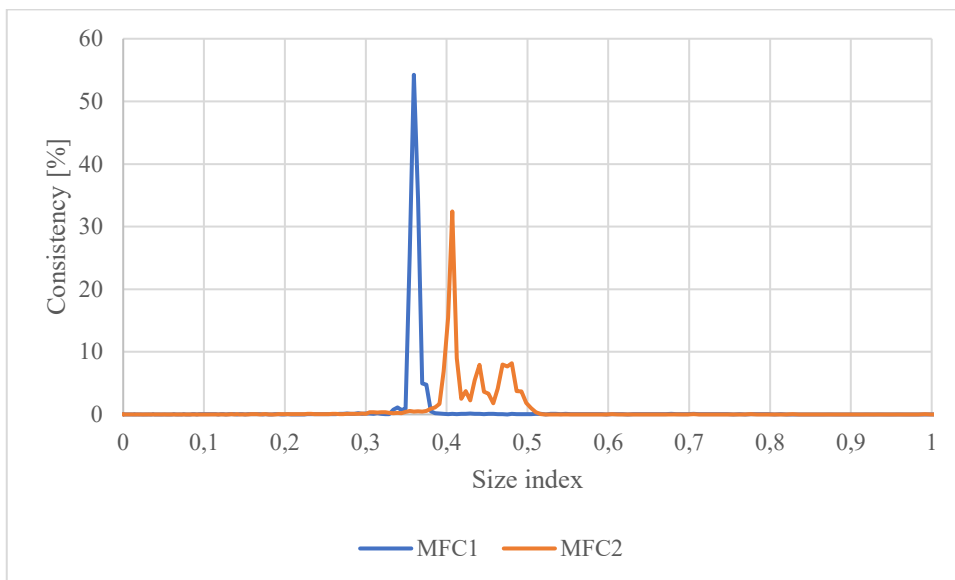


Figure 18. Size index of MFC qualities. MFC1 is of commercial quality, and MFC2 is of non-commercial quality.

The size index of MFC qualities also showed that MFC1 is more homogeneous than MFC2. The size index peak for MFC1 was approximately 0.35, whereas the size index of MFC2 was formed from three distinct peaks. Therefore, the size index of MFC2 suggests that the sample contained three different-sized particles, while MFC1 contained mainly one kind of particle. The size index values of MFC2 were higher than MFC1, indicating that the particles were coarser than commercial MFC. The indices of two MFC qualities were compared to fractionator UHD images, shown in Figure 19.

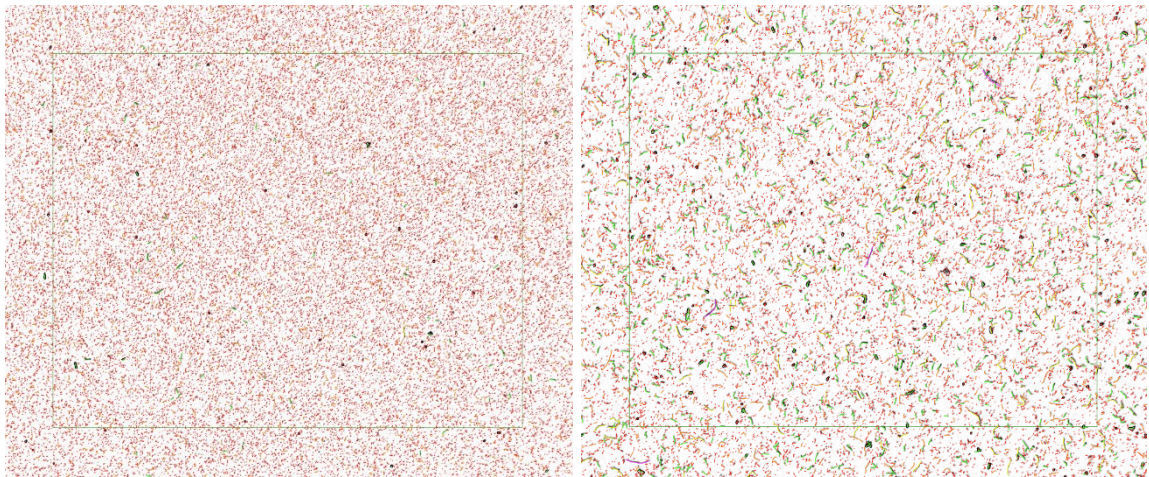


Figure 19. UHD images of MFC qualities. Left: MFC1 and right: MFC2.

The UHD images were taken from the same water flow point of 18 500 ml during fractionation. The red color in the figure presents fines, and the green colour presents fibers. As the figure shows, MFC1 contained primarily fines, while MFC2 contained fines and fibers. The resolution limit of the fractionator UHD camera was also studied using the MFC1 grade since the particle size was smaller in diameter in the MFC1 grade compared to the MFC2 grade. For this purpose, the size index was compared to fiber width, measured with UHD. Based on previous experiments, the ability of a UHD camera to separate particles ends at a size index of 0.3. However, this has not yet been scientifically verified. Figure 20 shows the size index as a function of the fiber width in the MFC1 sample.

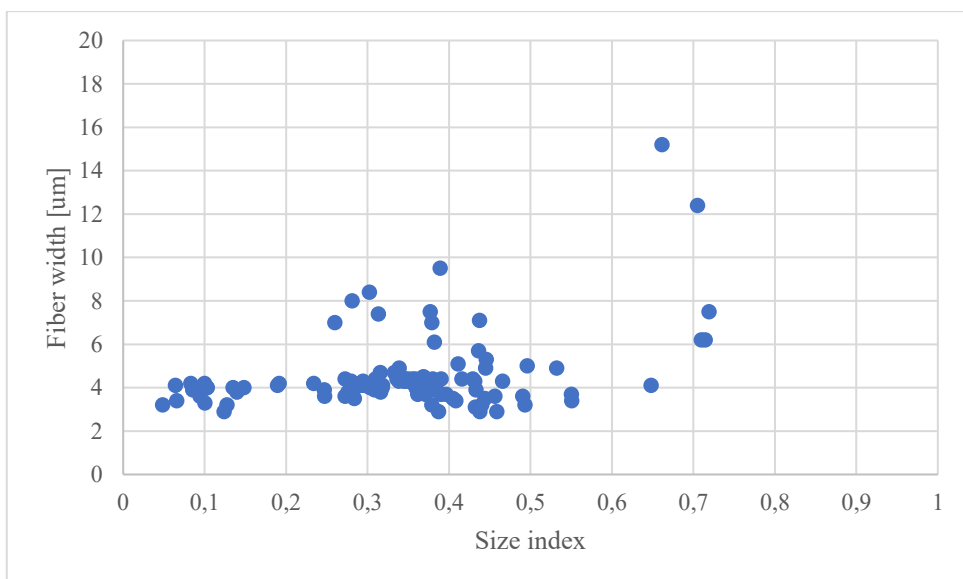


Figure 20. Fiber width as a function of size index in MFC1 sample.

The figure shows that the size index decreased below 0.1, but the fiber width remained constant between size indices 0.05 and 0.3. This could indicate the UHD resolution limit, where the camera cannot recognize the smallest particles visible in the size index.

11.2 Fibrous and size index in suspension characterization

The fibrous index was applied to analyze different pulp suspensions with chemical additives. All the fractionator fiber results are presented in Appendix 2. Figure 21 shows the fibrous index of pure birch pulp and the fibrous indices of two pulp suspensions to which chemicals have been added at two different dosage levels. In Figure 22, the fibrous index of pulp suspension with a 5 wt% MFC addition is shown, as well as the fibrous indices of two other suspensions to where chemicals, in addition to 5 wt% of MFC, have been added at two different dosage levels. The chemicals used in Figure 21 were cationic starch and CPAM. The MFC used in Figure 22 was the MFC1 grade.

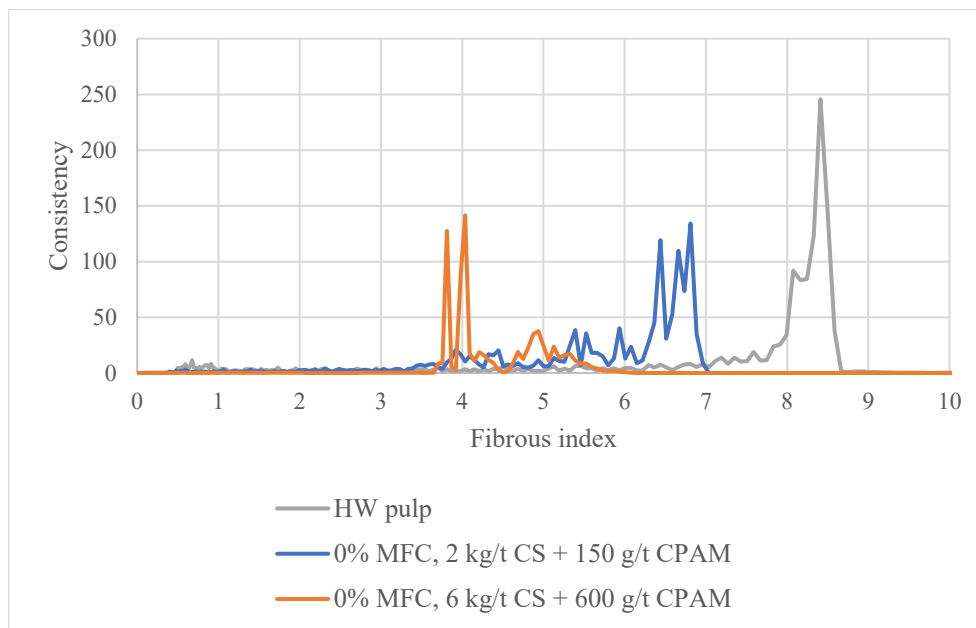


Figure 21. Fibrous indices of pure HW pulp and pulp-chemical blends without MFC.

The fibrous index was the highest in a pure HW pulp sample and lowest in a sample that contained the most chemicals. Thus, the addition of chemicals decreases the fibrous index value. This might be because pure fibrous material decreases when additives promoting fiber flocculation are introduced into the sample. The impact of chemical addition is also reflected

in the changes in the fines fraction, i.e., index values ranging from 0 to 1. In Figure 21, it can be observed that the fibrous index of the HW pulp sample was more visible within the 0-1 range, but the same phenomenon was not observed in samples containing chemicals. This may be because the amount of free fines in the sample decreases as the fines adhere to fibers due to the effect of chemicals. Figure 22 shows the fibrous index of pulp samples when MFC is added.

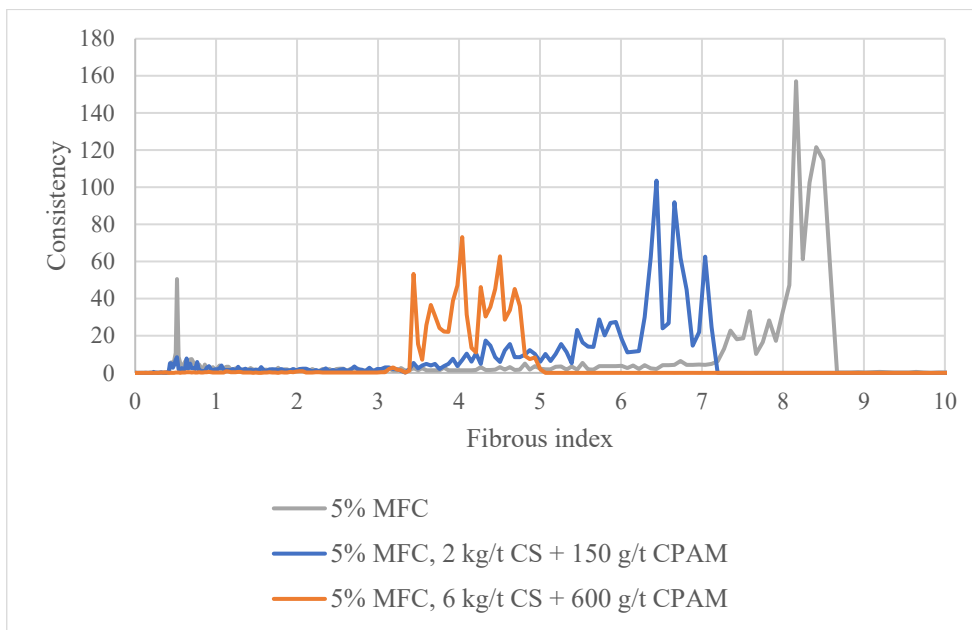


Figure 22. Fibrous indices of pure HW pulp and pulp-chemical blends with 5 wt% MFC.

As seen from the figure, the effect of chemical addition to the fibrous index was the same as in the previous Figure 21. The most significant difference between the images is observed in samples that did not contain CS and CPAM. Adding MFC to HW pulp created a peak in the fines fraction, around the 0.5 index value. This peak likely represents MFC, which is not as strongly attached to fibers as in the presence of chemicals, as seen from UHD images in Figure 23. The index peak also corresponds to Figure 17, which shows the fibrous index of pure MFC1 quality, approximately 0.45. The fibrous and size indices of pulp samples containing only MFC are presented in Appendix 1. Both MFC grades at two concentrations (3 wt% and 5 wt%) are also shown. Another observation in the figure is that the fines fraction index values in the range of 0-1 were more visible even when adding chemicals, unlike in Figure 21. This may be attributed to the addition of MFC, leading to an increase in the total fines content in the sample, as seen from UHD images in Figure 24.

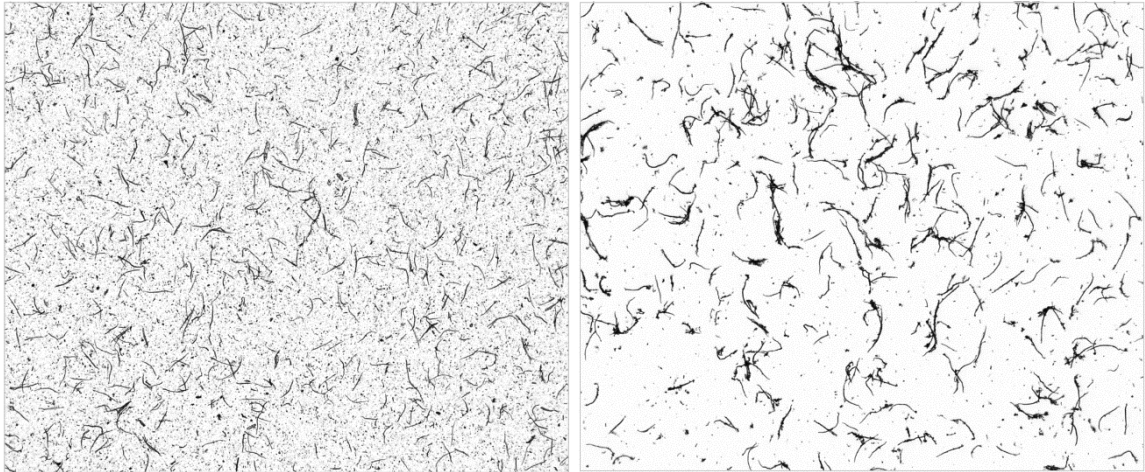


Figure 23. Fractionator UHD images from samples containing 5% MFC. Left: 0% chemicals and right: 6 kg/t CS and 600 g/t CPAM.

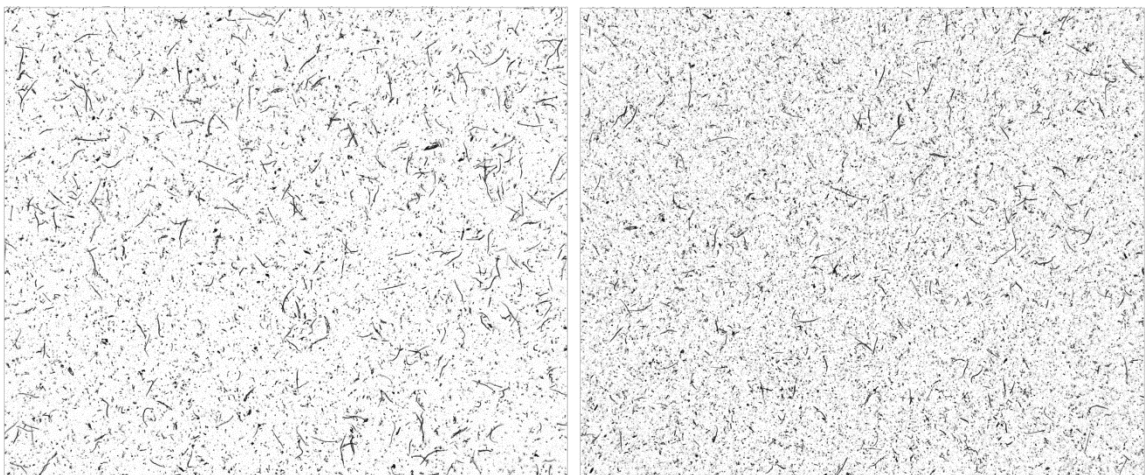


Figure 24. Fractionator UHD images from samples containing 2 kg/t CS and 150 g/t CPAM. Left: 0% MFC and right: 5% MFC.

11.2.1

Fractions

Different fraction results were analyzed using the fibrous index and size index. The fractions were categorized into fines and fiber fractions. Within the fiber fractions, there were three distinct groups: fibers with a fibrous index ranging from 1 to 5, fibers with a fibrous index between 5 and 10, and fibers with a fibrous index of 1 to 10. The fiber fraction that contains values between 1-10 includes all fibrous material in a sample. The fines fraction was

characterized by fibrous index values falling between 0 and 1, consisting of all fines-like material. Figure 25 shows the average fibrous index across various fractions of pulp samples.

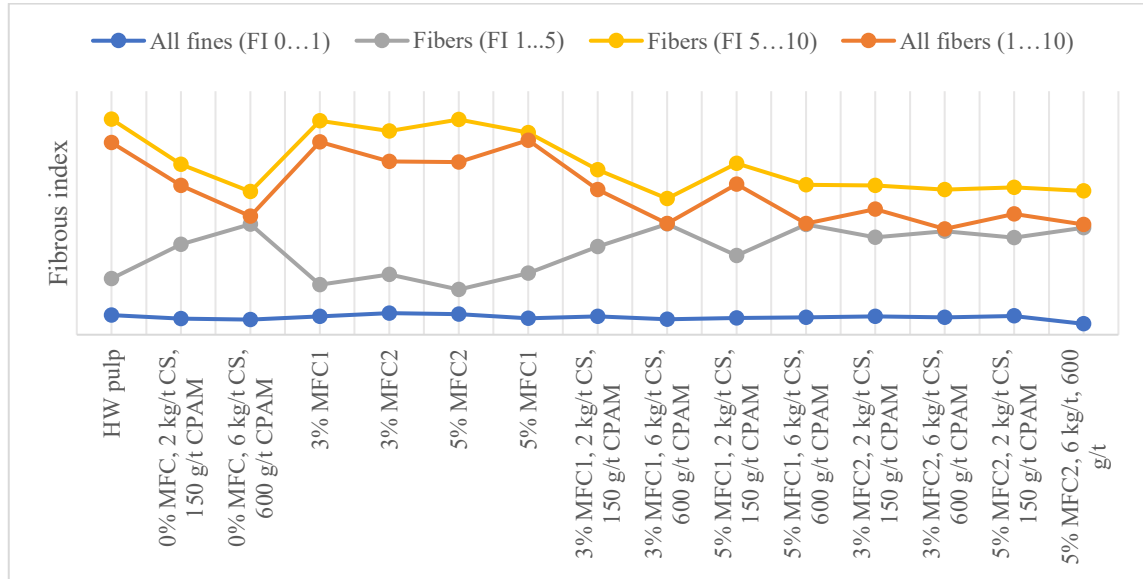


Figure 25. The average fibrous index values in different fractions.

The fibrous index values showed minimal changes among different test points in the fines fraction. Trends in fiber fractions with fibrous index values between 5-10 and 1-10 were consistent, but the trend for the fiber fraction with fibrous index values between 1-5 was the opposite. In other words, for fiber fractions with fibrous index values between 5-10 and 1-10, the fibrous index decreased when a polymer was added to the pulp suspension and was highest without any additives or with only MFC addition. For the fiber fraction with fibrous index values between 1-5, the fibrous index increased when a polymer was added, reaching the highest values with the highest polymer dosage. This fiber fraction with fibrous index values between 1-5 likely represents the most significant impact of the polymer. Adding polymer to the pulp suspension causes fiber flocculation, as illustrated in Figures 21 and 22, where the effect of polymers on the fibrous index distribution was shown. With the highest polymer amount, index values fall within the fibrous distribution range of 3-5. From Figure 25, the highest fibrous index was in the fraction with fibrous index values between 5-10. This fraction likely represents fibers with little or no polymer, as demonstrated in distribution graphs 21 and 22. The size index of different fractions is shown in Figure 26.

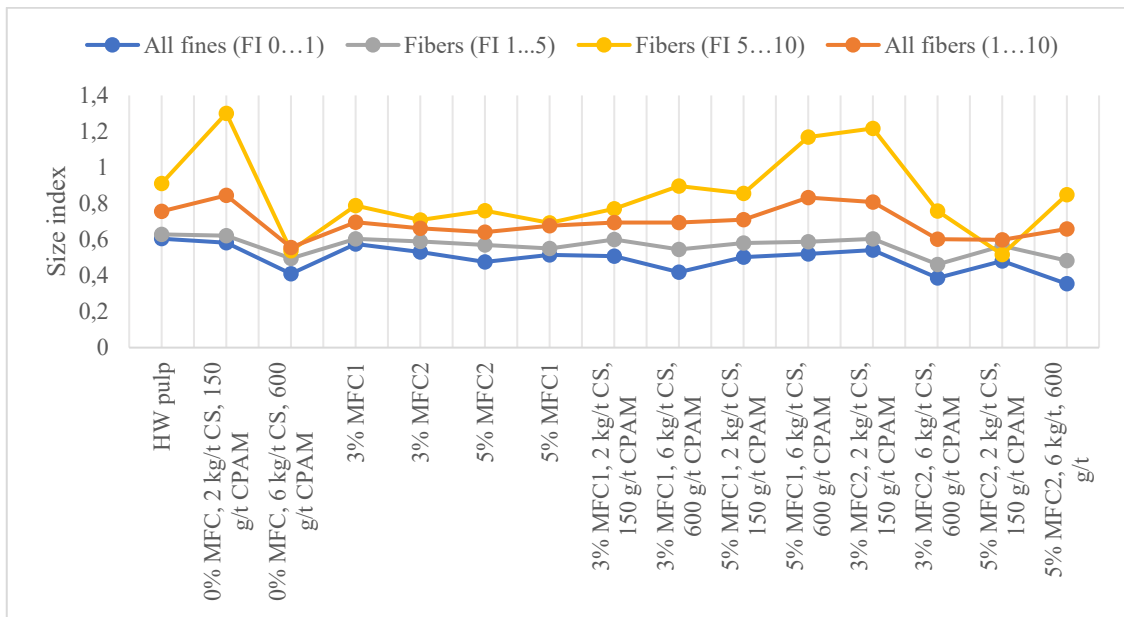


Figure 26. The average size index values in different fractions.

As seen in the figure, adding MFC did not decrease the size index, contrary to what one might expect with adding fines. In fact, the reference sample, pure HW pulp, had a slightly higher size index than samples containing only MFC. A significant increase in polymer content reduced the fines fraction's size index, which could be explained by the decrease in free fines in the sample as they adhered to fibers. On the other hand, reducing the size index in fines fraction does not seem to increase the size index in other fractions that one might think. The consistency values of fines and fibers in different fractions are shown in Figure 27.

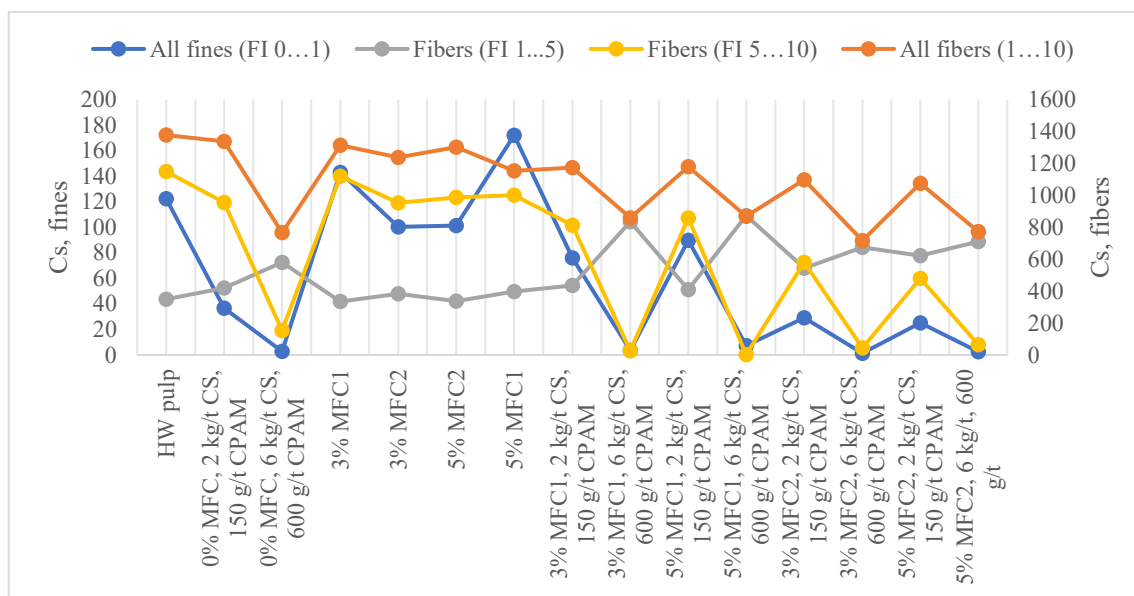


Figure 27. The average consistency in different fractions.

The figure shows that, except for the fraction with consistency values between 1-5, the consistency values decreased when a high polymer dosage was added. The number of fines (fines fraction 0-1) and pure fibers (fiber fraction 5-10) decreased significantly when a high polymer dosage was added to the pulp suspension, while the consistency values of fiber fraction 1-5 increased. Again, this most likely shows how fines are attached to fibers due to the effect of starch and CPAM. From the figure, it can also be seen that the consistency values in the fines fraction are higher when MFC1 is used instead of MFC2. This may be due to particles containing MFC1 being much smaller than particles containing MFC2, as indicated in Table 6.

11.3 Paper properties

The study examined how various variables affect paper properties, presenting the findings in index form. This format involves dividing the strength property by the average grammage of the sheet. All the results were compared to a reference point (HW pulp) where no MFC or chemicals were used. In addition to paper strength properties, the basic properties and paper formation results are presented in Appendix 3. The results compared the significance of additives on paper strength by varying the dosages of MFC and chemicals. The additives used include MFC, cationic starch, and CPAM. Additionally, the study compares the impact of two different qualities of MFC on the strength of paper. Finally, efforts were made to

align the strength index values of paper with the fibrous index and identify correlations between two different index values.

11.3.1 Effect of chemical additives

The effect of chemical additives on paper properties was studied from laboratory sheets using varying additive dosages. The additives used in the sheets were microfibrillated cellulose (MFC), cationic starch (CS), and cationic polymer (CPAM). The MFC used in this section was commercial MFC grade (MFC1). The MFC dosages were 0 wt%, 3 wt%, and 5 wt%. The cationic starch dosages were 2 kg/t and 6 kg/t. The CPAM dosages were 150 g/t and 600 g/t. MFC and cationic starch were used as strength enhancers, and CPAM was used as a retention agent. All the results are presented in index form. Figure 28 shows the tensile indices.

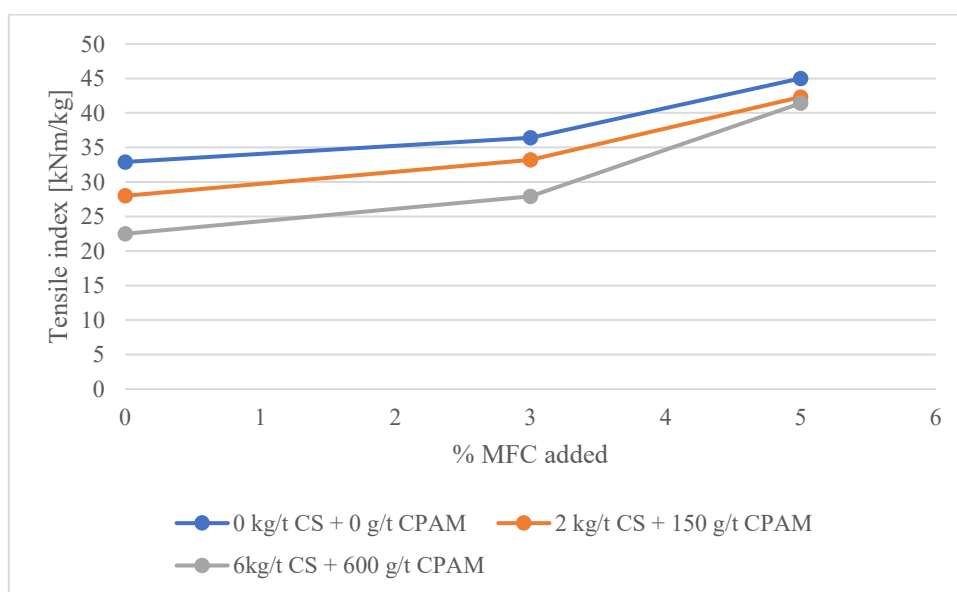


Figure 28. Tensile indices of samples with and without MFC, CS, and CPAM.

The figure shows that the paper's tensile strength improved the more MFC was added to the pulp sample. The best tensile strength was achieved by adding only MFC to the pulp sample without CS and CPAM. The worst tensile strength was achieved when the highest amount of CS and CPAM was used. The paper tear indices are presented in Figure 29.

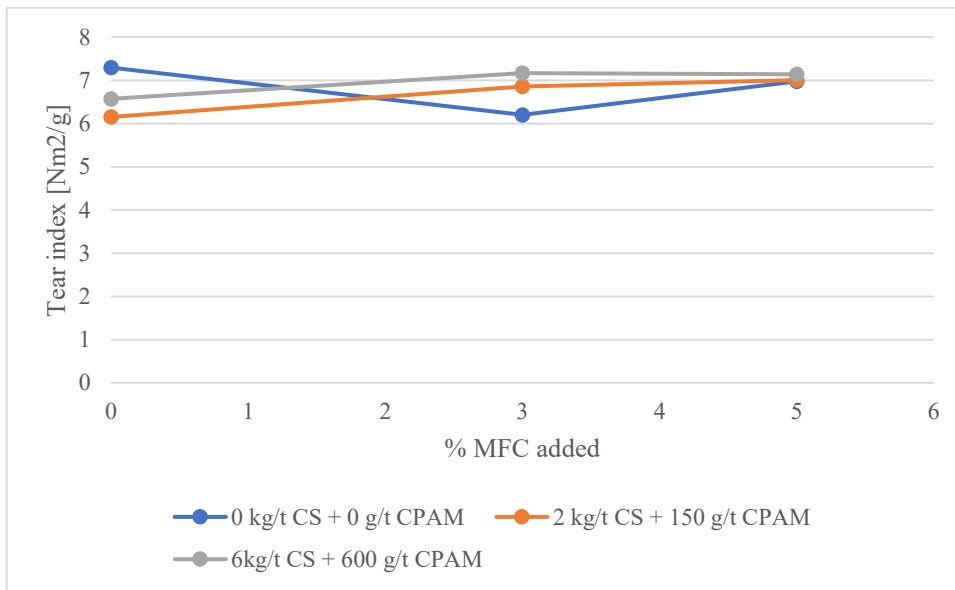


Figure 29. Tear indices of samples with and without MFC, CS, and CPAM.

A pure pulp sample without MFC, CS, or CPAM achieved the highest tear strength. The tear index improved as more starch and CPAM were used with MFC. Adding 3 wt% MFC improved tear strength when the sample contained CS and CPAM. However, the addition of 5 wt% MFC no longer affected tear strength.

11.3.2 Effect of MFC qualities

The effect of two different MFC qualities in paper properties was studied separately and with CS and CPAM. The MFC dosages were 3 wt% and 5 wt%. All the results are presented in index form. Figure 30 shows the tensile indices.

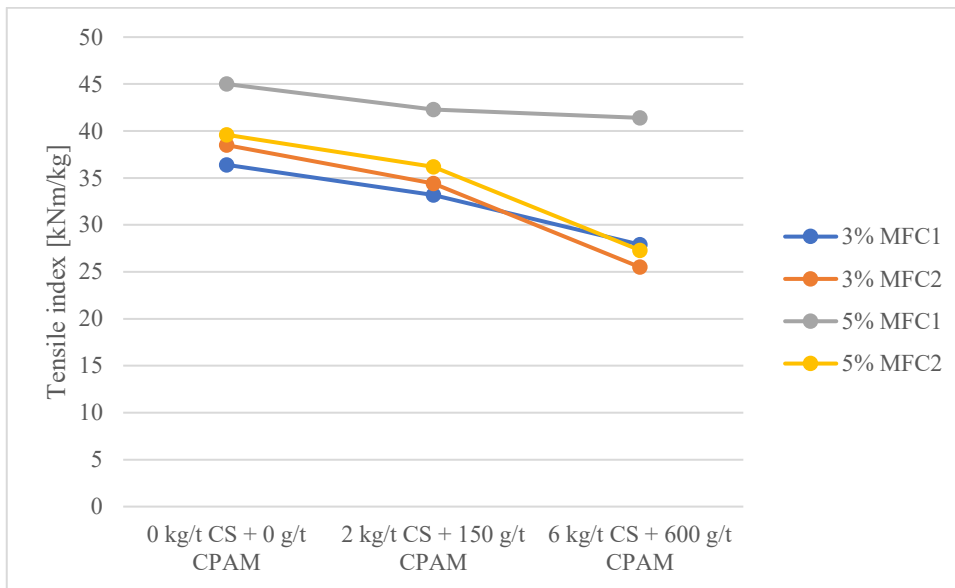


Figure 30. Tensile indices of samples containing 3 wt% and 5 wt% of both MFC grades.

The best tensile strength was achieved with a commercial grade of MFC and a higher dosage. Increasing the amount of MFC from 3% to 5% had a more pronounced impact on paper tensile strength when using MFC1 rather than MFC2. In other words, increasing the MFC2 dosage does not seem to improve strength as effectively as increasing the MFC1 dosage. Notably, the same strength was achieved using either 3 wt% MFC1 or 5 wt% MFC2. Tensile strength decreases when either type of MFC is used in the sample with the addition of CS and CPAM. The cationic polymer forms larger flocs, weakening the formation (Karhu, 2017). This leads to weaker areas in the paper, which may be reflected in the tensile strength results. The sheet formation images are shown in Figure 31 to illustrate the effect of CS and CPAM on sheet formation.

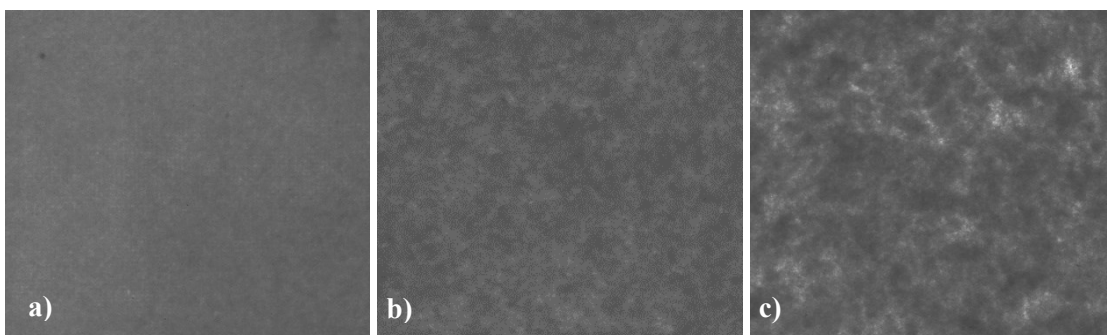


Figure 31. Sheet formation images of a) HW, b) 5 wt% MFC, and c) 5 wt% MFC, 6 kg/t CS+600 g/t CPAM.

The formation images show that white spots are highest on the sheets where MFC and CS with CPAM are used. However, the addition of MFC alone has already begun to form spots. Figure 32 shows the impact of MFC grades on tear strength.

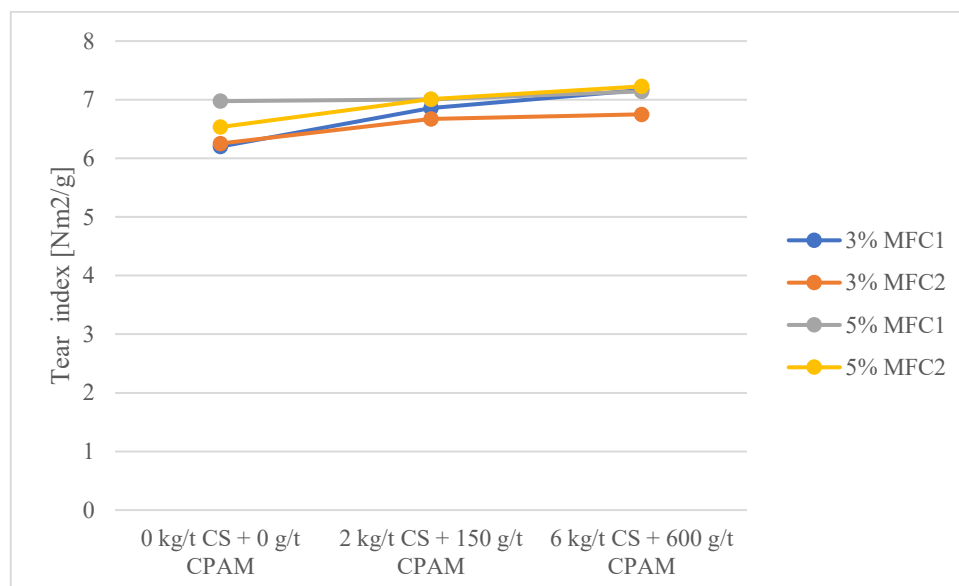


Figure 32. Tear indices of samples containing 3 wt% and 5 wt% of both MFC grades.

The impact of MFC grade on tear strength was less significant than on tensile strength. Without CS and CPAM, tear strength was practically the same when using a 3 wt% MFC dosage, regardless of its grade. However, with 5 wt% MFC, the same tear strength was achieved, regardless of the used MFC grade. Unlike tensile strength, adding CS and CPAM slightly improved tear strength. Interestingly, the same tear strength was achieved with 3 wt% MFC1, 5 wt% MFC1, or 5 wt% MFC2 when the CS and CPAM dosage was at its highest.

11.4 Fibrous index in paper properties characterization

In pulp suspension characterization, the fibrous index decreased as more CS and CPAM were added to the suspension. A paper properties study showed that increased chemical dosage decreased the tensile strength of papers. However, the increase in MFC dosage improved tensile strength. The best tensile strength results were obtained using 5 wt% MFC1. The effects of additive usage on tear strength were the opposite. The study showed

that adding CS and CPAM slightly improved papers' tear strength. However, the best tear strength was achieved using no MFC, CS, or CPAM.

The correlation between paper strength and the fibrous index was studied from samples containing different MFC qualities from 0 wt% to 5 wt%. The chemical increase was also studied from 2 kg/t cationic starch and 150 g/t CPAM to 6 kg/t cationic starch and 600 g/t CPAM and compared to sample points where no chemicals were used. In Figure 33, tensile indices are shown as a function of fibrous indices, presented as consistency-weighted average results.

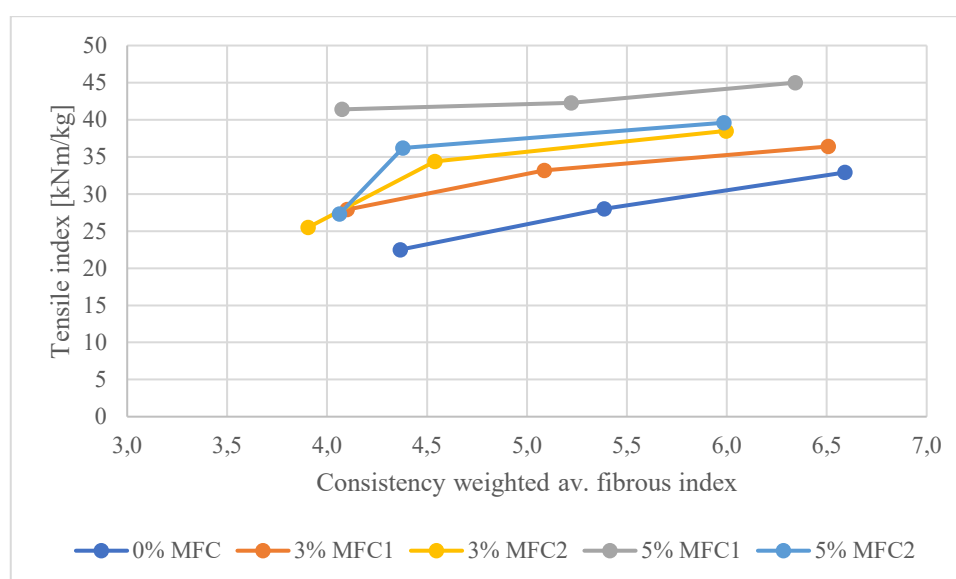


Figure 33. The tension index as a function of the consistency-weighted average fibrous index. The test points from right to left: 0 kg/t CS + 0 g/t CPAM, 2 kg/t CS + 150 g/t CPAM, and 6 kg/t CS + 600 g/t CPAM.

The tensile index decreases simultaneously with the fibrous index. Adding cationic starch and CPAM decreases tensile strength and lowers fibrous index values regardless of the MFC type or dosage. Therefore, the fibrous index could be used as an indicator to describe the effect of polymer addition on paper strength rather than the effect of MFC. However, further conclusions would require more measurements and test points. The tear indices as a function of fibrous indices are presented in Figure 34.

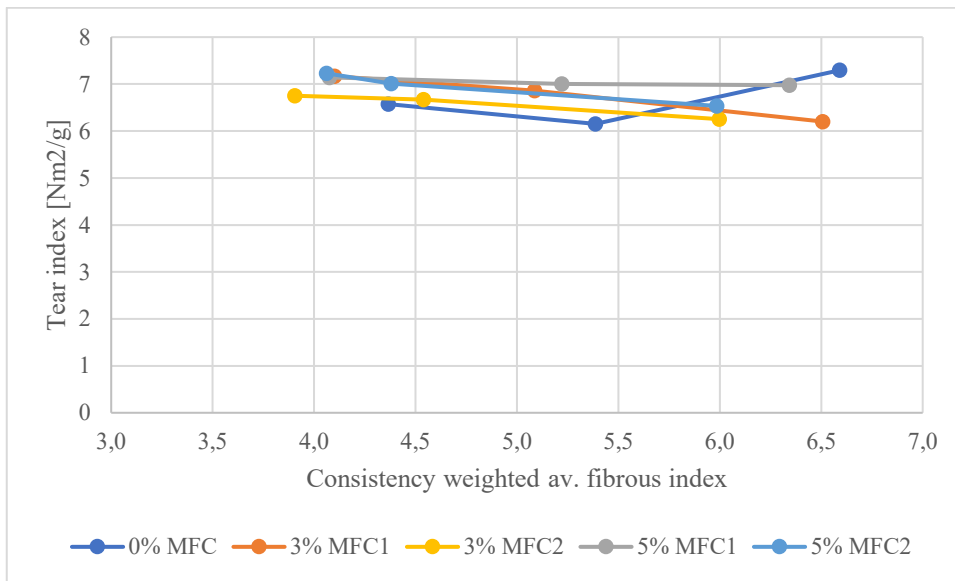


Figure 34. Tear index as a function of consistency weighted average fibrous index. The test points from right to left: 0 kg/t CS + 0 g/t CPAM, 2 kg/t CS + 150 g/t CPAM, and 6 kg/t CS + 600 g/t CPAM.

Overall, the tear indices of samples increase while the fibrous index decreases. An exception is a test point where no MFC, CS, or CPAM were used. Adding cationic starch and CPAM increases tear strength slightly and again, lowering the fibrous index values. Therefore, a lower fibrous index would indicate a better tear strength in this case. However, as mentioned earlier, further conclusions require more experiments.

11.5 Fibrous and size index in white water analysis

The applicability of the fibrous and size indices was tested in white waters. After forming the sheets, white waters were collected from 12 test points. Figure 35 shows the fibrous indices of white waters in the fines and fiber fractions separately. The mean values of fibrous indices are weighted by consistency. The fines fraction considers index values between 0 and 1, and the fiber fraction considers index values between 1 and 10.

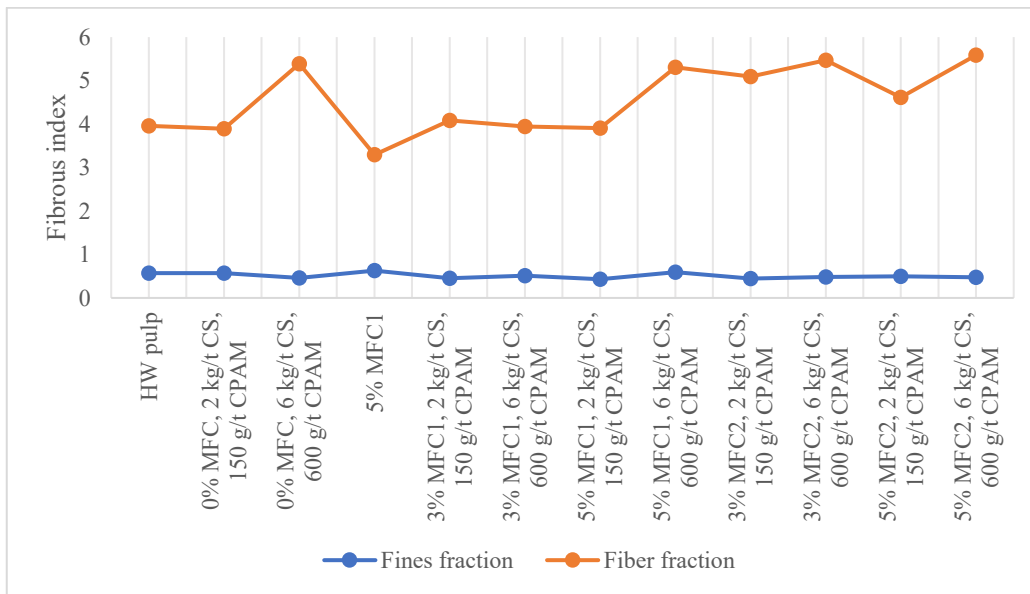


Figure 35. The average fibrous indices of white waters in fines fraction and fiber fraction.

The figure shows that the fibrous indices of white waters in fines fraction remained on the same level regardless of the analyzed sample. The fibrous indices of white waters in fiber fraction showed more variation between different samples. The highest fibrous index values are measured from samples with the highest chemical amount. The lowest fibrous index is calculated from a sample containing only MFC. This is the opposite result compared to pulp suspension samples. Because of a very dilute sample, an error in an optical measurement is possible. Figure 36 shows the size index values of white waters in fines fraction and fiber fraction separately.

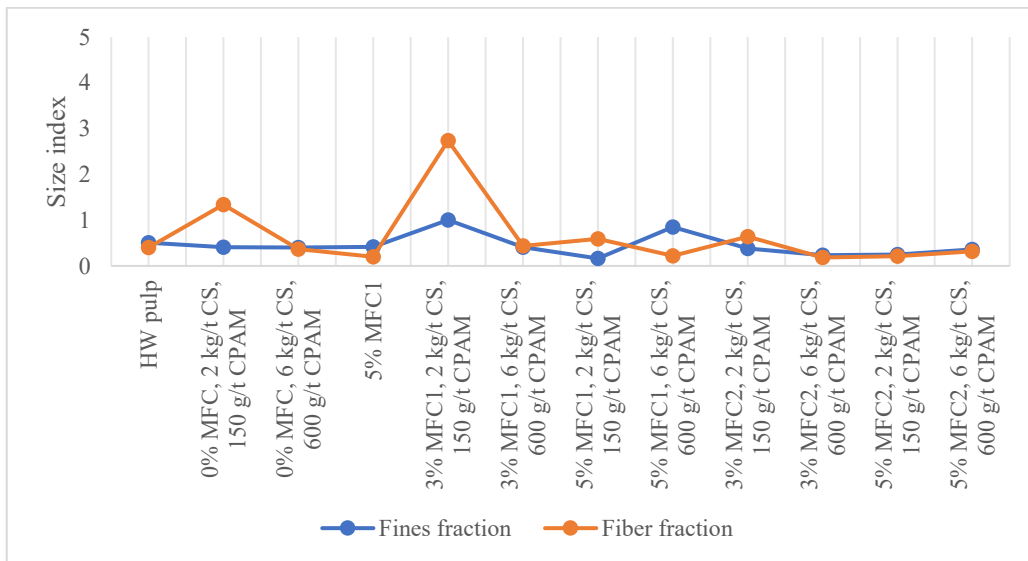


Figure 36. The average size indices of white waters in fines fraction and fiber fraction.

The size index values of white waters in fines fraction showed no regularity in the results. The size index values of white waters in fiber fraction indicated that the largest particles were in a sample containing a bit of MFC and chemicals (3wt% MFC1, 2 kg/t CS, and 150 g/t CPAM). The hypothesis was that a greater chemical addition would increase the size index when forming fiber-fines agglomerates. The size index values are very close to zero, which can cause an error in optical measurement. Figure 37 shows the turbidity of white waters relative to the consistency of fines fraction calculated from the mean values of the fibrous index. The turbidity was measured from white waters as a reference to the consistency of the fines fraction.

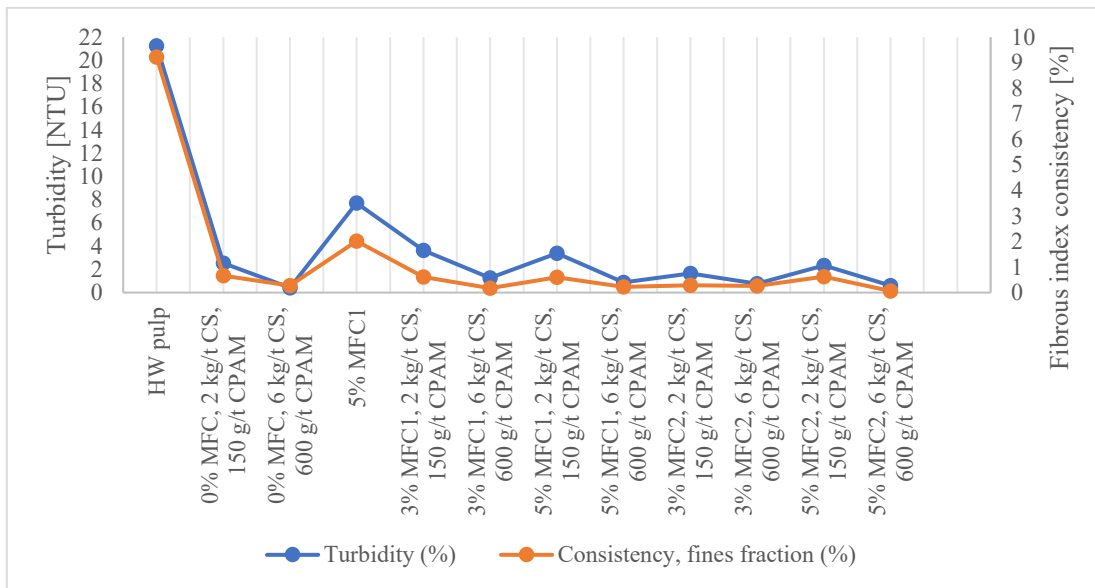


Figure 37. Turbidity of white waters relative to average consistency of fines fraction calculated from the fibrinous index.

The figure shows that the white water's turbidity correlates to the fines fraction's consistency. The highest turbidity and consistency were measured from white water using a pure pulp sample with no additives. Increasing the amount of chemicals reduces the fines in white water, as observed in the decrease of turbidity and consistency of fines fraction. The quantity of fines was also visible in pure HW sample but invisible in other samples where additives were used. MFC alone without chemicals does not seem to bind fines as effectively to the fibers as with chemicals, as evidenced by an increase in turbidity and consistency measurements.

12 Conclusions

The fibrous and size indexes were found to characterize very different qualities of MFC. Index distributions showed that the commercial grade MFC used in the study was more homogeneous than the research grade quality. The dispersion of fibrous index values was significantly higher with the research-grade MFC2 compared to the commercial MFC1. Fibrous index values ranging from 0-1 can be divided into fines, while values 1-10 belong to fibrous material. According to this division, the MFC1 quality contained only fines, whereas the MFC2 quality contained both fines and fibrous material. UHD images from both MFC grades also demonstrated this. The size index also indicated that MFC2 contained particles of different sizes, while MFC1 consisted of only one size. The ability of the size index to identify fines was further compared to the UHD camera's ability to image fibers. The parameter selected was fiber width, which was compared as a function of the size index. This study chose commercial MFC (MFC1) as the MFC grade because it was more uniform and had finer particle size than MFC2. The results showed that the fiber width remained almost unchanged at approximately 4 μm , but the size index decreased below 0.1. It has been tested that the resolution limit of the UHD camera corresponds to a size index of approximately 0.3, suggesting that the size index may better identify micro- and nanocellulose grades containing fines particles than the UHD camera.

The study also examined the suitability of the fibrous and size indexes for analyzing various fiber blends. Adding cationic starch and cationic polymer to the pulp suspension reduced the fibrous index more as the dosage of chemicals increased. This is likely because the fibers flocculate due to the influence of starch and polymer, reducing the amount of pure fibrous material and smooth fibers in the sample and decreasing the fibrous index. It was also evident from the fibrous index distributions that adding chemicals to the fiber sample affects the fines fraction, reducing and even removing its proportion. This is likely because starch and polymer bind any free fines to the fibers. Adding MFC to the pulp suspension increased the proportion of fines fraction observed in the fibrous index distribution. Without cationic starch and CPAM, a 5 wt% MFC amount appeared to form a clear peak in the fines fraction, but no peak in the index distribution was formed when chemicals were present.

Fibrous and size indices were examined more closely to characterize various fiber blends fraction by fraction. This was done by weighting the index values by consistency and calculating the averages of the index values for each test point in different fractions. Index values ranging from 0-1 represented the entire fines fraction, while values from 1-10 represented the entire fiber fraction. Additionally, the fiber fraction was further divided into two fractions, one with index values between 1-5 and the other with index values between 5-10. Fibrous index distribution results by fraction showed consistent trends for the fiber fractions 5-10 and 1-10. In other words, adding starch and CPAM to the fiber blend lowered the fibrous index. Conversely, the trend for the fiber fraction 1-5 was the opposite, meaning that adding starch and CPAM to the fiber blend raised the fibrous index. The polymer's effect on the fiber blend is more apparent in the fiber fraction, with fibrous index values ranging from 1-5. Size index distribution results by fraction showed that 6 kg/t of cationic starch and 600 g/t of CPAM mainly decreased the size index of the fines fraction, which is likely explained by fines adhering to the fibers. However, this effect was not reflected in the size indices of the fiber fractions, from which one would have expected to see an increase in size index due to fiber-fines flocculation.

The consistency, i.e., the amount of fines and fibrous material at each test point, was also examined fraction by fraction. The results showed that the quantities of all other fractions decreased when the polymer was added except for the fiber fraction 1-5. A high chemical dosage, namely 6 kg/t of cationic starch and 600 g/t of CPAM, was most noticeable in reducing fines fraction and fiber fraction 5-10, which describes pure fibers. This most likely presents how free fines are attached to fibers due to the effect of starch and CPAM and how the fiber agglomeration is shown in fiber fraction 1-5 increase.

The impact of different variables on paper properties was investigated. Tensile strength improved as a function of MFC amount when it increased from 0 wt% to 5 wt%. Adding MFC to the pulp sample without starch and CPAM achieved the highest tensile strength. Tensile strength improved when starch and CPAM were added to the pulp sample, but the effect of polymers was smaller than that of MFC. Without MFC, the tensile strength of the paper decreased as more CS and CPAM were used. Commercial MFC (MFC1) improved paper strength more than MFC2 quality. The results showed that the same tensile strength was achieved either by using 3 wt% of MFC1 or 5 wt% of MFC2. The differences in tear strengths between different test points were more minor than in tensile strengths. Unlike

tensile strengths, adding chemicals slightly improved papers' tear strengths. The best tear strength was achieved without MFC, CS, and CPAM. Interestingly, the same tear strength was achieved either by using 3 wt% of MFC1 or 5 wt% MFC1 or 5 wt% MFC2.

The correlation between paper strength and fibrous index was investigated. The results indicated that tensile strength decreases as the fibrous index decreases when starch and CPAM are added to the fiber blend. Conversely, the tear strength of the paper increases as the fibrous index decreases when starch and CPAM are added to the fiber blend. Thus, the fibrous index could potentially be used as an indicator for evaluating either the tensile strength or tear strength of paper, depending on which paper property is targeted. However, this area requires further experiments and test points to draw more significant conclusions. Three levels of variables are not yet sufficient but provide a basis for further research. The next phase of the study could be an optimization phase, where the effects of different chemical amounts on strength and fibrous index would be examined. It would be interesting to see how the fibrous index detects differences in fiber blends when chemical dosages are fine-tuned rather than examining extremes.

Laboratory sheet water analysis was also experimented with using the fibrous and size indexes. The indices were divided into fines fraction and fiber fraction. Changes in the fibrous index in the fines fraction were not as significant as in the fiber fraction. The highest fibrous indices were exhibited in samples containing the most starch and CPAM. This contradicts fiber blend samples. The size index results of the white waters were not very consistent. The size indices of the fiber fraction in the white waters indicated that sheets with a smaller amount of additives contained the largest particles. The hypothesis was that a higher chemical dosage would increase size indices as fiber flocculation occurs. Nevertheless, the white waters were so diluted that errors in indices based on optical measurement were possible. On the other hand, the fines fraction of the white waters correlated with turbidity measurement. The fines fraction and turbidity were highest in the pure fiber and MFC samples. The addition of starch and CPAM reduced the amount of fines in white water. Thus, adding MFC to the pulp suspension without chemicals does not appear to adhere to the fibers as effectively as when chemicals are present.

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Appendices

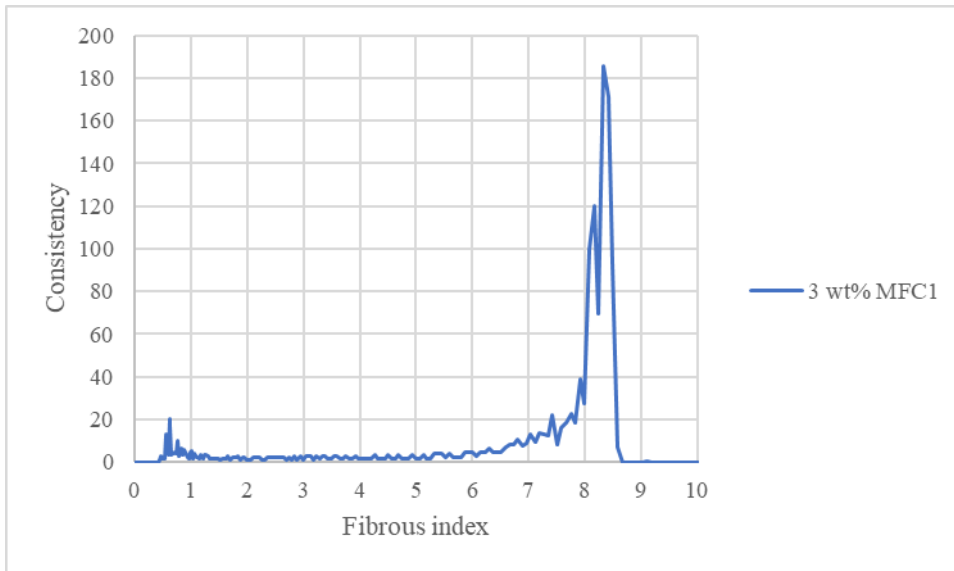


Figure 38. Fibrous index of pulp sample containing 3 wt% MFC1 grade.

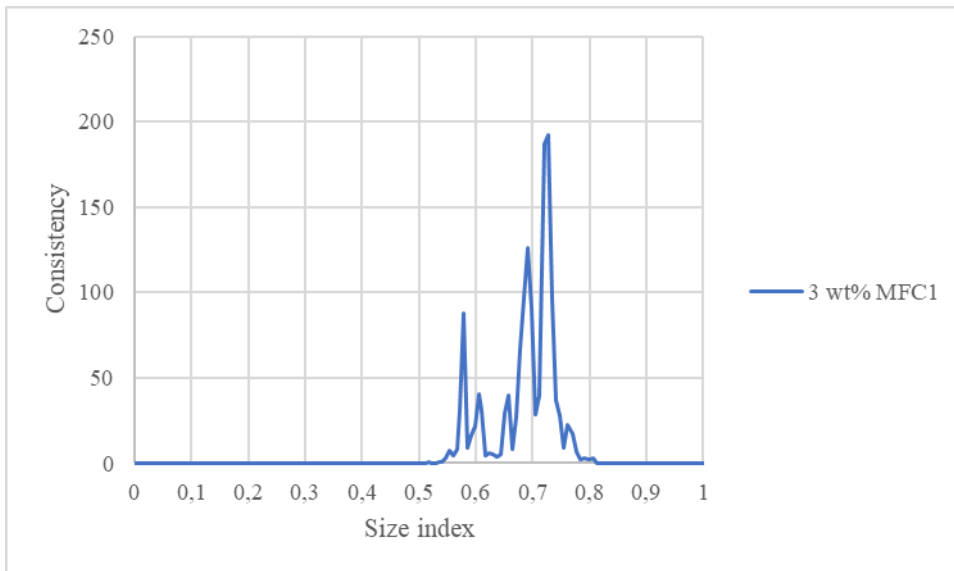


Figure 39. Size index of pulp sample containing 3 wt% MFC1 grade.

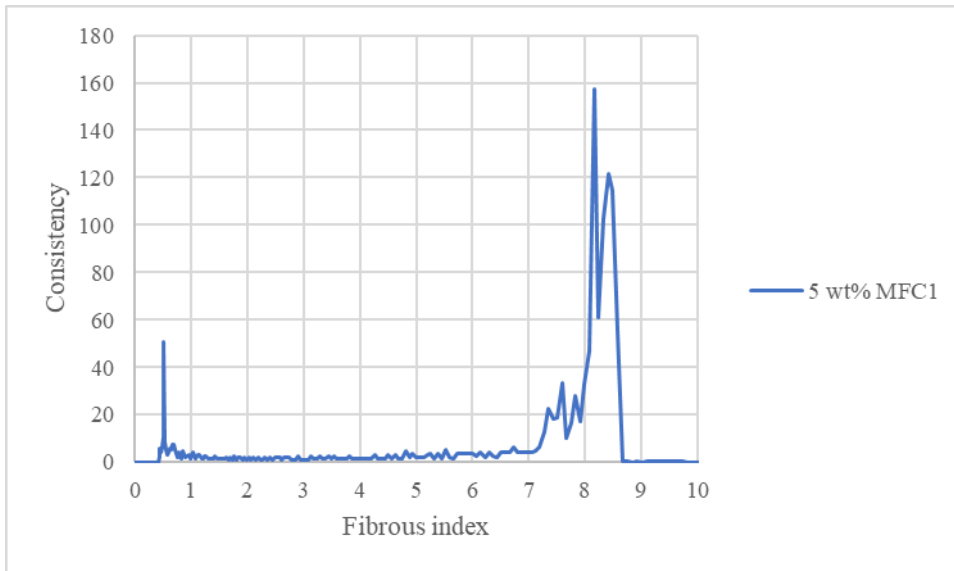


Figure 40. Fibrous index of pulp sample containing 5 wt% MFC1 grade.

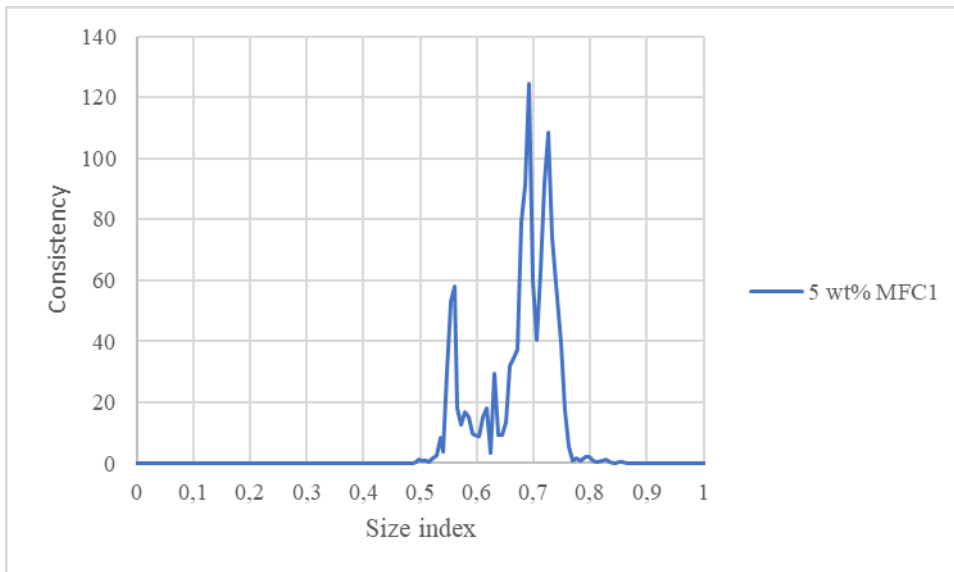


Figure 41. Size index of pulp sample containing 5 wt% MFC1 grade.

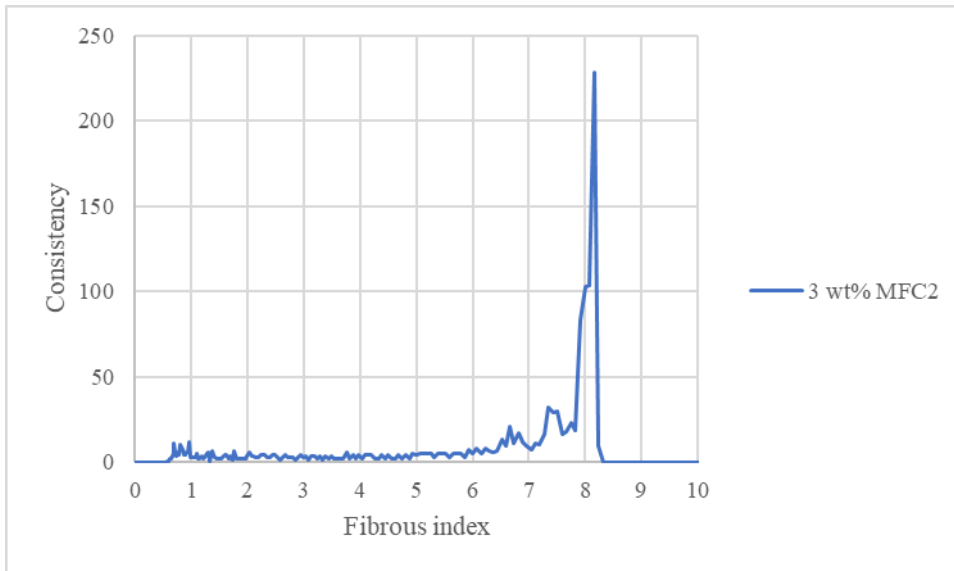


Figure 42. Fibrous index of pulp sample containing 3 wt% MFC2 grade.

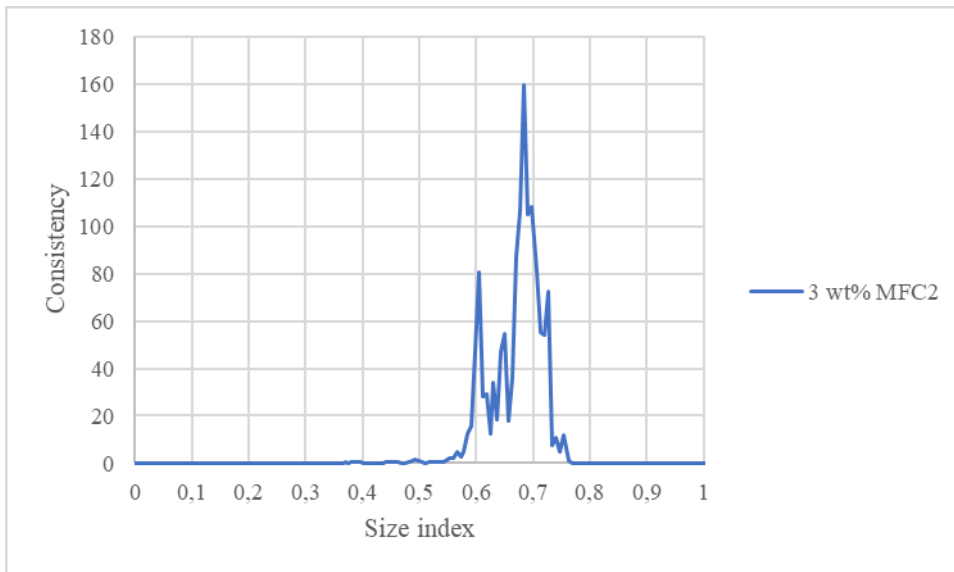


Figure 43. Size index of pulp sample containing 3 wt% MFC2 grade.

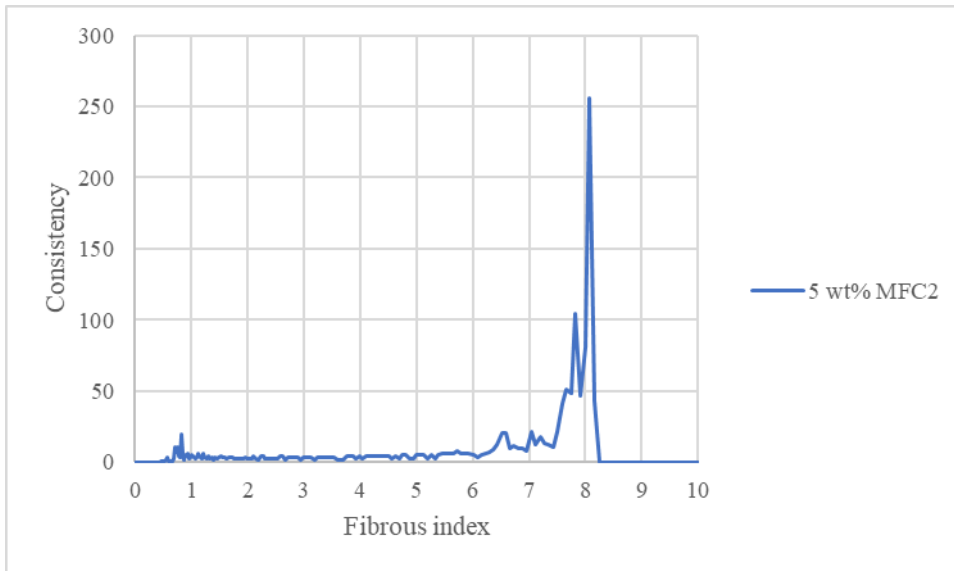


Figure 44. Fibrous index of pulp sample containing 5 wt% MFC2 grade.

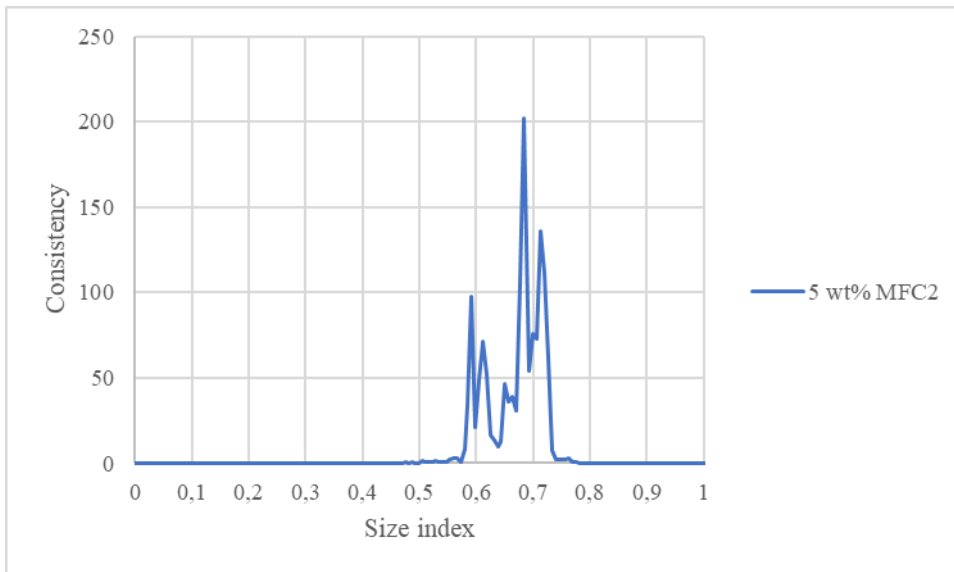


Figure 45. Size index of pulp sample containing 5 wt% MFC2 grade.

Appendix 2 (1/2)

Table 7. Fractionator results of pulp suspensions.

Sample point	FR1 %	FR2 %	FR3 %	FR4 %	FR5 %	Lc(n) ISO mm	Lc(l) ISO mm	Lc(w) ISO mm	Fiber width um	Curl %
HW pulp	2.88	32.91	35.75	26.95	1.50	0.065	0.555	1.153	17.26	11.83
0% MFC, 2 kg/t CS, 150 g/t CPAM	21.18	40.45	25.39	11.94	1.04	0.067	0.513	1.107	19.42	11.24
0% MFC, 6 kg/t CS, 600 g/t CPAM	85.96	1.49	1.71	5.10	5.75	0.139	0.722	1.121	26.55	10.72
3% MFC1	2.33	29.98	36.44	29.90	1.35	0.054	0.408	1.091	15.11	11.73
3% MFC2	2.38	29.72	39.65	26.88	1.38	0.056	0.403	1.086	15.58	12.03
5% MFC1	2.64	27.84	34.65	33.43	1.44	0.146	0.797	1.160	20.55	11.39
5% MFC2	2.51	30.13	38.94	27.24	1.18	0.066	0.541	1.168	17.49	11.86
3% MFC1, 2 kg/t CS, 150 g/t CPAM	20.95	38.70	23.69	15.58	1.08	0.054	0.410	1.049	17.08	11.24
3% MFC1, 6 kg/t CS, 600 g/t CPAM	82.90	9.45	1.73	2.53	3.39	0.106	0.658	1.131	25.83	11.53
5% MFC1, 2 kg/t CS, 150 g/t CPAM	17.77	37.51	24.92	18.80	1.01	0.056	0.448	1.066	17.13	11.07
5% MFC1, 6 kg/t CS, 600 g/t CPAM	74.91	16.47	3.76	2.22	2.64	0.089	0.608	1.114	25.50	11.32
3% MFC2, 2 kg/t CS, 150 g/t CPAM	27.98	37.17	23.14	10.60	1.10	0.064	0.461	1.060	19.52	11.34
3% MFC2, 6 kg/t CS, 600 g/t CPAM	85.01	1.10	2.08	5.37	6.44	0.130	0.706	1.181	28.55	11.57
5% MFC2, 2 kg/t CS, 150 g/t CPAM	29.77	36.46	22.55	10.21	1.01	0.063	0.444	1.044	19.31	11.30
5% MFC2, 6 kg/t CS, 600 g/t CPAM	84.04	4.36	1.50	4.41	5.69	0.120	0.659	1.089	26.60	11.22

Appendix 2 (2/2)

Table 8. Fractionator results of pulp suspensions.

Sample point	Kink 1/m	Kink 1/1000 fibers	Fibrillation %	Fines A %	Fines B %	Fines %	Particle count n	Count [flocs] n/1000
HW pulp	3914	2970	0.94	26.21	0.45	95.37	375031	0
0% MFC, 2 kg/t CS, 150 g/t CPAM	4123	2845	1.66	30.37	0.41	94.88	539783	0.1
0% MFC, 6 kg/t CS, 600 g/t CPAM	4526	3244	1.05	17.44	0.11	85.12	66700	0.3
3% MFC1	3842	2643	0.70	38.95	1.10	96.86	115739	0.1
3% MFC2	3898	2542	2.06	40.65	1.31	96.56	121373	0.1
5% MFC1	3930	3031	0.62	8.92	0.33	84.53	125888	0.1
5% MFC2	3971	2961	2.34	28.70	0.62	95.35	135176	0
3% MFC1, 2 kg/t CS, 150 g/t CPAM	4108	2723	1.02	37.13	0.68	96.54	672041	0.1
3% MFC1, 6 kg/t CS, 600 g/t CPAM	4686	3309	0.92	21.08	0.16	89.69	204115	0.5
5% MFC1, 2 kg/t CS, 150 g/t CPAM	4041	2798	1.00	32.27	0.72	96.25	669323	0.1
5% MFC1, 6 kg/t CS, 600 g/t CPAM	4726	3298	1.11	23.58	0.20	91.92	357092	0.5
3% MFC2, 2 kg/t CS, 150 g/t CPAM	4243	2755	0.97	33.26	0.72	95.23	644206	0.2
3% MFC2, 6 kg/t CS, 600 g/t CPAM	4849	3359	1.69	18.64	0.15	86.17	93618	0.5
5% MFC2, 2 kg/t CS, 150 g/t CPAM	4227	2662	1.04	34.01	1.05	95.25	655781	0.2
5% MFC2, 6 kg/t CS, 600 g/t CPAM	4769	3243	1.31	19.98	0.23	87.37	117285	0.6

Appendix 3 (1/2)

Table 9. Paper properties of the samples.

Sample point	Grammage (g/m ²)	Thickness (um)	Density g/cm ³	Total retention %	Tensile index kNm/kg	Tea index J/kg	Tear strength mN
HW pulp	50.3	70.8	0.71	84.64	32.9	489	367
0% MFC, 2 kg/t CS, 150 g/t CPAM	54.6	77.1	0.71	89.91	28.0	421	336
0% MFC, 6 kg/t CS, 600 g/t CPAM	56.5	86.0	0.66	92.33	22.5	146	371
3% MFC1	57.6	89.4	0.64	95.52	36.4	701	357
3% MFC2	56.6	85.5	0.66	93.03	38.5	718	354
5% MFC1	54.9	74.8	0.73	91.84	45.0	859	383
5% MFC2	57.4	87.4	0.66	95.30	39.6	696	375
3% MFC1, 2 kg/t CS, 150 g/t CPAM	50.9	71.5	0.71	84.62	33.2	396	349
3% MFC1, 6 kg/t CS, 600 g/t CPAM	58.2	83.3	0.70	95.04	27.9	270	417
5% MFC1, 2 kg/t CS, 150 g/t CPAM	56.0	76.6	0.73	93.19	42.3	790	392
5% MFC1, 6 kg/t CS, 600 g/t CPAM	57.0	77.4	0.74	93.66	41.4	612	407
3% MFC2, 2 kg/t CS, 150 g/t CPAM	57.0	79.6	0.72	93.66	34.4	587	380
3% MFC2, 6 kg/t CS, 600 g/t CPAM	61.9	88.6	0.70	99.71	25.5	204	418
5% MFC2, 2 kg/t CS, 150 g/t CPAM	58.9	83.9	0.70	98.67	36.2	432	413
5% MFC2, 6 kg/t CS, 600 g/t CPAM	61.6	88.9	0.69	99.86	27.3	240	445

Appendix 3 (2/2)

Table 10. Paper formation properties of the samples.

Sample point	Variance gray level	Skewness	Kurtosis	Number of dark spots	Number of dark spots (m ²)	Number of white spots
HW pulp	1321242	-0.37	8.5	66	6147	247
0% MFC, 2 kg/t CS, 150 g/t CPAM	2231713	0.50	4.8	13	1254	419
0% MFC, 6 kg/t CS, 600 g/t CPAM	6899207	1.34	8.0	3	247	850
3% MFC1	497169	-0.11	5.1	105	7455	53
3% MFC2	517512	-0.03	3.9	97	9020	118
5% MFC1	610002	-1.14	30.4	59	5437	364
5% MFC2	492674	0.03	4.4	116	10719	168
3% MFC1, 2 kg/t CS, 150 g/t CPAM	1910420	0.50	4.4	25	2293	401
3% MFC1, 6 kg/t CS, 600 g/t CPAM	4257684	1.04	6.2	6	587	623
5% MFC1, 2 kg/t CS, 150 g/t CPAM	955717	0.53	4.2	32	2935	332
5% MFC1, 6 kg/t CS, 600 g/t CPAM	2421614	0.56	4.3	13	1236	438
3% MFC2, 2 kg/t CS, 150 g/t CPAM	1026208	0.53	4.1	10	958	480
3% MFC2, 6 kg/t CS, 600 g/t CPAM	7523020	1.43	8.6	4	402	656
5% MFC2, 2 kg/t CS, 150 g/t CPAM	1595520	0.64	8.6	27	2471	360
5% MFC2, 6 kg/t CS, 600 g/t CPAM	6101369	1.21	7.6	9	803	646