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Fines Characterization and their Impact on Technological Properties in Paper-Making Applications

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Abstract

Fines are an inevitable but undefined part of chemical and mechanical pulps. The amount and character of this material is typically not monitored, despite the fact that in particular fibrillated fines greatly affect paper properties due to their large surface area and high water absorption capacity. Monitoring of fines properties is challenging for several reasons related to the characteristics of fines. They are small in size, incorporate a heterogeneous mixture of different morphological entities and show high water absorption capacity. Thus, hardly any analytical method is able to fully capture the properties of this material.

The subject of this thesis was the development of stable, reliable and quantifying methods for the characterization of fines with the aim that the measured properties reflect the effect of this material on the pulp and paper properties. Two methods have been developed, one for the assessment of morphology and one for water absorbency. These methods include the characterization of the most important properties of fines with respect to their effects on the technological properties of papermaking: microfibrillation and swelling.

In addition a systematic investigation was carried out to clarify, which differences in fines character due to (a) refining (mechanical modification), (b) different pulping processes (kraft and sulfite) and (c) cationization (chemical modification) occur. Refining conditions had a major impact on the microfibrillation of fines. Fines from the kraft process affect paper properties to a higher degree than sulfite fines, mainly due to increased microfibrillation and swelling, while cationization, bonding of cationic charges to fines, affect network properties as dewatering and porosity, induced by charge interactions.

Overall, this dissertation provides fundamental new knowledge of the relationship between the character of fines and their technological properties in papermaking. The developed methods allow an in depth characterization of fines and thus provide a tool to generate added value for this unique material in the future.

Kurzfassung

Feinstoffe sind ein unvermeidlicher, aber undefinierter Teil des Zellstoffes. Die Menge und der Charakter dieses Materials wird typischerweise nicht überwacht, ungeachtet der Tatsache, dass insbesondere fibrillierte Feinstoffe aufgrund ihrer großen Oberfläche und der besonders hohen Wasserabsorptionskapazität Papier- und Zellstoffeigenschaften in hohem Maße beeinflussen. Die Überwachung der Feinstoffqualität ist aus mehreren Gründen schwierig, die im Wesentlichen mit dem Charakter dieses Materials zusammenhängen. Sie sind klein, enthalten eine heterogene Mischung verschiedener morphologischer Einheiten und weisen eine hohe Wasseraufnahmekapazität auf. Somit ist kaum eine Analysenmethode in der Lage, die Eigenschaften dieses Materials abzubilden.

Der Gegenstand dieser Arbeit war daher die Entwicklung stabiler, zuverlässiger und quantifizierender Verfahren zur Charakterisierung von Feinstoffen, wobei die gemessenen Eigenschaften die Wirkung dieses Materials auf die Zellstoff- und Papiereigenschaften abbilden sollten. Zwei Methoden, eine für die Beurteilung der Morphologie und eine für die Wasseraufnahmefähigkeit von Feinstoffen, wurden entwickelt. Diese Methoden umfassen die Charakterisierung der wichtigsten Eigenschaften von Feinstoffen in Bezug auf ihre Auswirkungen auf die technologischen Eigenschaften bei der Papierherstellung: Mikrofibrillierung und Quellung.

Zusätzlich wurde systematisch untersucht welche Unterschiede im Feinstoffcharakter aufgrund von (a) Mahlung (mechanische Modifizierung), (b) unterschiedlichen Aufschlussverfahren (Kraft- und Sulfitaufschluss) und (c) Kationisierung (chemische Modifikation) auftreten.

Die Mahlbedingungen zeigten einen großen Einfluss auf die Mikrofibrillierung von Feinstoffen, Feinstoffe aus dem Kraft Prozess beeinflussen die Papiereigenschaften stärker als Sulfitfeinstoffe, hauptsächlich aufgrund höherer Mikrofibrillierung und Quellung, während Kationisierung, die Bindung kationischer Ladungen an Feinstoffe, Einfluss auf Netzwerkeigenschaften wie Entwässerung und Porosität durch Ladungswechselwirkungen aufweist.

Insgesamt bietet diese Dissertation grundlegende Kenntnisse über den Zusammenhang zwischen dem Charakter der Feinstoffe und ihren technologischen Eigenschaften in der Papierherstellung. Die entwickelten Methoden ermöglichen eine detaillierte Charakterisierung von Feinstoffen, und liefern das Werkzeug um in Zukunft einen Mehrwert für dieses einzigartige Material zu generieren.

Acknowledgements

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Which should be not taken for granted is the assistance provided by the laboratory personal, whom I want to thank all and mention here only Adelheid Bakhshi, so that the list will not extent too long. For dealing with bureaucracy and their help in administrative matters I would like to thank the secretariat with the mention of Claudia Bäumel.

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In the end I would like to thank my parents, who looked after so I will learn something useful and for the opportunity to attend university and find out what I really like to do.

List of Publications

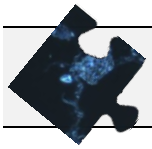
I Mayr, Melanie, Eckhart Rene and Bauer Wolfgang (2017) "Improved Microscopy Method for Morphological Characterisation of Pulp Fines." *Nord. Pulp. Pap. Res. J.* 32 (2): 244–52. doi:10.3183/NPPRJ-2017-32-02-p244-252.

II Mayr, Melanie, Eckhart Rene, Winter Heribert and Bauer Wolfgang (2017). "A Novel Approach to Determining the Contribution of the Fiber and Fines Fraction to the Water Retention Value (WRV) of Chemical and Mechanical Pulps." Cellulose 24 (7): 3029-36 doi:10.1007/s10570-017-1298-6.

III Mayr, Melanie, Thaller Andreas, Eckhart Rene and Bauer Wolfgang (2017) "Characterization of Fines Quality and Their Independent Effect on Sheet Properties." Transactions of the 16Th Fundamental Research Symposium Held in Oxford: September 2017, 299–322.

IV Mayr, Melanie, Odabas Nora, Eckhart Rene, Henniges Ute and Bauer Wolfgang (2017) "Cationization of Lignocellulose as a Means to Enhance Paper Strength Properties." BioResources 12 (4): 9338–47. doi:10.15376/biores.12.4.9338-9347.

Table of Contents



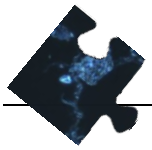
1. INTRODUCTION

1.1. Motivation

Paper is made from wood fibers. Apart from these fibers also other components are contained in a paper sheet, having a significant influence on the product properties. Chemical additives are used for multiple purposes as e.g. to enhance strength, improve dewatering during sheet forming and increase the hold back (retention) of the stock components on the forming wire, to just give some examples. Apart from these chemical additives mineral fillers and fine cellulosic material - so called fines - are determining the product properties as well. Chemical additives and mineral fillers, are added in a defined quantity, while cellulosic fines are produced during pulping and mechanical treatment of the fibers. Consequently they are an inevitable, but undefined part of the papermaking furnish. Their quality and quantity is not considered in common practice, although it is known that fines show distinctly different properties compared to fibers. Routinely only whole pulp (containing fibers and fines) properties are determined, for example drainability, in order to control product quality. This approach allows a monitoring and control of pulp quality in production, but does not give any information which properties of the final product such as strength or porosity are influenced by fibers and fines to what extent. As fines show distinctly different behavior than fibers due to their differences in morphology and chemistry, measuring only standard pulp properties may be insufficient to forecast paper quality. Further a differentiation into fibers and fines and a more detailed evaluation of fines properties may be of interest with respect to the following exemplary topics:

- annual fluctuations of pulp quality
- removal or addition of fines in the process
- influence of fines on process steps (e.g. bleaching chemical demand, dewatering)
- optimization of stock composition and refining strategy
- comparative evaluation of different pulp qualities
- application of fines as an additive outside the paper industry

And indeed it was shown in many studies that fines have a great influence on the papermaking process and paper properties. So why are fines properties not monitored in production and seldom considered in scientific studies?

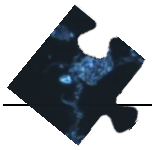


First of all fines are an inherent part of the papermaking furnish. The quantity cannot be controlled exactly and they are always together with fibers. Thus they have to be isolated before characterization. Further the term 'fines' denominates quite a small, heterogeneous material, showing a high water absorption capacity. These properties make sample preparation tedious. While the character of fibers can be assessed by a number of methods, the small size, high water absorption capacity and heterogeneity of the fines are challenging in this respect.

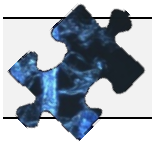
Scientific studies characterizing fines properties frequently lack to find the connection between fines characteristics and paper properties. Partly the reason is, that fines quality frequently is only evaluated qualitatively, for example through visual comparison of light microscopy images. Another reason is that the available methods give unreliable or incomplete data with important information missing. To meet these challenges, novel methods for fines characterization have been developed in this thesis. The obtained fines characteristics were linked to paper properties using a trial setup designed especially for the purpose to isolate the impact of fines characteristics on paper properties. Mechanical modification (refining) and chemical modification (cationization) of fines was studied to investigate the potential with regards to technological properties of fines in papermaking.

1.2. Scope of this thesis

In this thesis the major focus is not on the investigation of whole pulp properties, but on the distinction between fibers and fines. Fiber characteristics can be assessed quite well using partly standardized routines, while methods for fines characterization - especially the morphology of fines - are not readily available, tedious or give just qualitative information. A description of available characterization methods and an overview of definitions of fines categories as well as the findings and challenges in fines characterization are reviewed in *Chapter 2*. Technological properties of fines in papermaking are the topic of *Chapter 3,* summarizing which properties are affected by fines and why fines have an impact on technological properties. Further a brief introduction of strategies how to influence the character of fines is given. The development of quantitative, comparatively fast and reliable methods for fines characterization is elaborated in *Chapter 4* and in *Paper I* and *Paper II. Chapter 5* and *Paper III* discuss whether the developed fines characterization methods are significant and allow a more detailed information regarding their technological influence in paper making applications. Using a sophisticated trial plan considering various refiner settings and pulp types, properties of fines were investigated applying the newly developed besides standard methods and relating these characteristics to the independent impact of fines on pulp and paper properties. Apart from the evaluation of characterization methods for



fines, this setup allowed to highlight the differences between fibers and fines from the sulfite and the kraft pulping process. On the basis of these results the window of operation for quality variation of chemical pulp fines in industrial refining is discussed. Refining is only one option to influence paper properties by internal and external fiber fibrillation, but also by the production of secondary fines. Apart from this mechanical modification, the effect of a chemical modification, precisely cationization of fines, was investigated and is presented in *Chapter 6* and *Paper IV*. Cationization was also carried out on fibers before refining in order to study how this affects the morphology of the fines produced in refining.



2. FINES CHARACTERIZATION

The high diversity of material belonging to the category pulp fines led to a wide range of different definitions. An overview of these definitions used in literature is given in *Chapter 2.1.* Besides the inhomogeneity of fines, there are further challenges when it comes to fines characterization as explained in *Chapter 2.2.* In this chapter an overview of chemical and morphological characterization methods of fibers and fines is given to emphasize where the differences between the characterization of those materials are. When it comes to fines characterization, morphological characterization is the part that differs most from fiber characterization. *Chapter 2.3* then discusses the state of the art in morphological evaluation methods and *Chapter 2.4* on the characterization of fines swelling a characteristic also related to morphology.

2.1. Fines Definition

Fines can be defined according to their size, origin and morphology as summarized in Table 2-1. Pulp fines are most commonly defined according to their size as all particles in a papermaking furnish passing through a 200 mesh screen (76 µm hole diameter; SCAN-CM 66:05). Fiber analyzers define all particles smaller than 200 µm in length as fines (ISO 16065-2); larger particles are considered fibers, giving a sharp cut-off. Besides these two standard classifications authors have also used other size definitions and methods in their work. Therefore, whenever fines are addressed in literature, one has to keep in mind that the respective definitions may vary and direct comparison may be difficult.

In addition to the size definition chemical pulp fines are further distinguished in primary and secondary fines according to their origin (see *Figure 2-1 b,c*). Primary fines are those fines present after the pulping and bleaching process prior to refining. These fines mainly consist of ray cells, parenchyma cells, fragments of the middle lamella and only a small portion of fibrils. Secondary fines contain fibrillated and lamellar material originating from the fiber wall, as a result of mechanical forces acting on a fiber during beating (Krogerus, B., Fagerholm, K., and Tiikkaja 2002). Fines after the refining stage in industrial papermaking, contain always primary and secondary fines. Microfibrillated cellulose (MFC) is also mentioned in this context, as size and morphology can be rather similar to fines (see *Figure 2-1* and *Figure 2-2*) as of course it is also produced from cellulosic sources by various chemical and mechanical treatments.

Table 2-1: Definition of fines according to their size (blue), origin (green) and morphology (red).

Particles passing a 200 mesh	Definition (SCAN-CM 66:05) for obtaining a fines fraction with the Britt Dynamic Drainage Jar (BDDJ) or Bauer McNett Classifier
Particles with length smaller than 200µm	Definition (ISO 16065-2) for flow cell based fiber analyzers
Primary fines	Fines present in pulp prior to refining
Secondary fines	Fines present in pulp produced during refining
Fines after refining	Including primary and secondary fines
Microfibrillated cellulose (MFC)	Fine material produced by various mechanical and chemical treatments from pulp and pulp fibers or other cellulosic materials
Flour stuff	Definition for mechanical pulp components: parenchyma and ray cells, fiber pieces
Slime stuff	Definition for mechanical pulp components: fibrillar and lamellar fines
Flake-like	Definition for mechanical and chemical pulp components: parenchyma and ray cells, fiber pieces
Fibrillar	Definition for mechanical and chemical pulp components: fibrillar and lamellar fines
Crill (old definition (Steenberg, et al. 1960))	Material not entangled in a plug flow
Crill (current definition (e.g. Osong et al. 2014))	Material only detectable under illumination with UV light

While for chemical pulp the morphology of the fines can be roughly related to their origin and to different process steps, mechanical pulp fines are more heterogeneous in morphology and origin and are produced in one process step by mechanical action. Brecht and Klemm (1953) defined flour stuff (non - fibrillar) and slime stuff (fibrillar) as different morphological entities in mechanical pulp fines (see *Figure 2-1 a*). A similar definition, valid for chemical and mechanical pulp fines was introduced by Luukko et al. (1997): Flake-like material (non-fibrillar) contains fiber wall fragments, thick lamellae and ray and parenchyma cells, whereas fibrillar material contains fibrils and thin lamellae, as well as fibrils that are attached, for example, to a fiber wall fragment.

Another category used in literature when referring to the fine fiber fraction is crill, defined as the part of cellulosic material that does not necessarily become entangled in the plug of fibers during plug flow (Steenberg et al. 1960; Sandgren and Wahren 1960). Their experiments conducted based on this definition, showed that crill of chemical pulps consists mainly of slender fibrillar particles and for PGW, including both flour stuff and slime stuff (see *Table 2-1*). Today crill is understood differently than in this early definition. The crill measurement implemented in some fiber analyzers identifies material as crill, that only is detected under illumination with UV light (Osong et al. 2014). This material is related to thin fibrils (Williamson and Back 2014).

a.) Pressurized ground wood (PGW)

b.) Bleached softwood kraft (BSK) primary fines

c.) Bleached softwood kraft (BSK) secondary fines

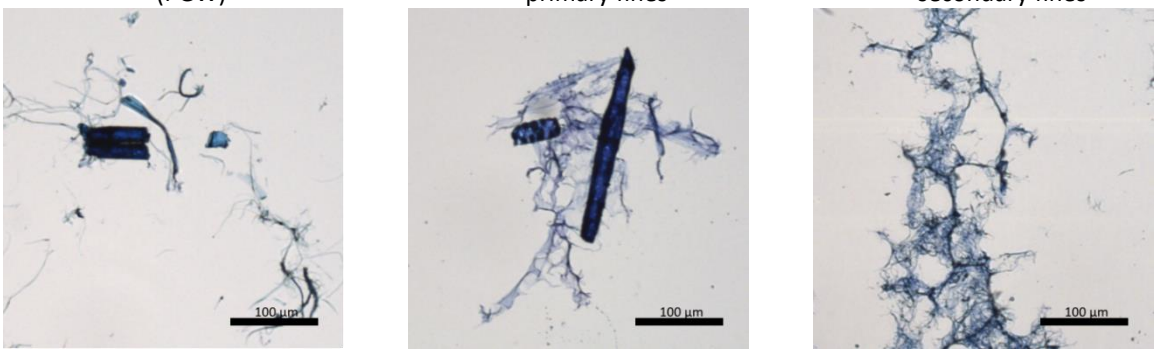


Figure 2-1: Microscopic images of fines of different origin
PGW fines (a), BSK primary fines (b), BSK secondary fines (c)

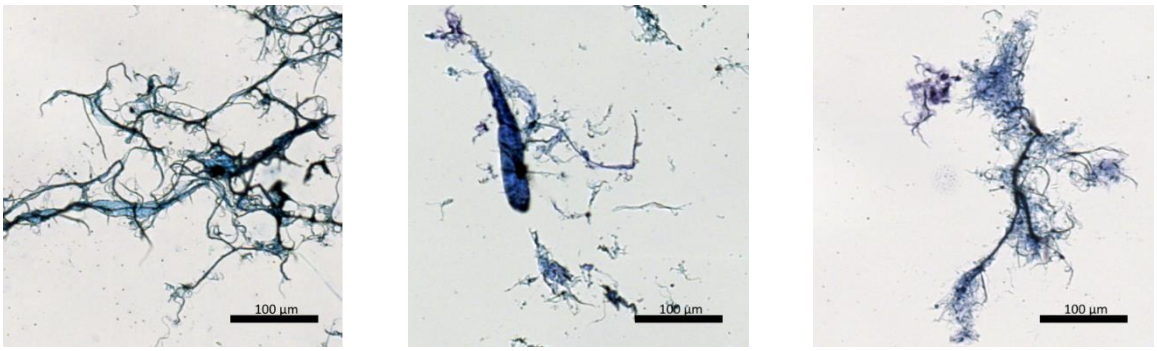


Figure 2-2: Microscopic images of microfibrillated cellulose (MFC) from different cellulosic sources

2.2. Challenges in fines characterization

As both fibers and fines originate from wood, they consist of the same chemical components. Thus chemical characterization identifying the content, type and distribution (surface/bulk) of those chemical components is similar for fibers and fines (see *Figure 2-3*). Sample preparation of fines, showing high dewatering resistance, may be more challenging when filtration processes are required. When drying is required, fines form a much denser network than fibers, which might lead to an issue of accessibility in chemical characterization.

Morphological characterization - the description of the characteristics of the solid form - of course is different for fibers and fines (see *Figure 2-3*). Fibers are rod shaped particles having a lumen, surrounded by a fiber wall. Fines do not have a fiber wall or a lumen. Because of their different origins (ray cells, parenchyma cells, fibrils) fines show much higher heterogeneity in

shape and optical properties. Together with their small size, broad size range and high water absorption capacity it is therefore challenging to obtain reliable and quantitative information regarding their morphology.

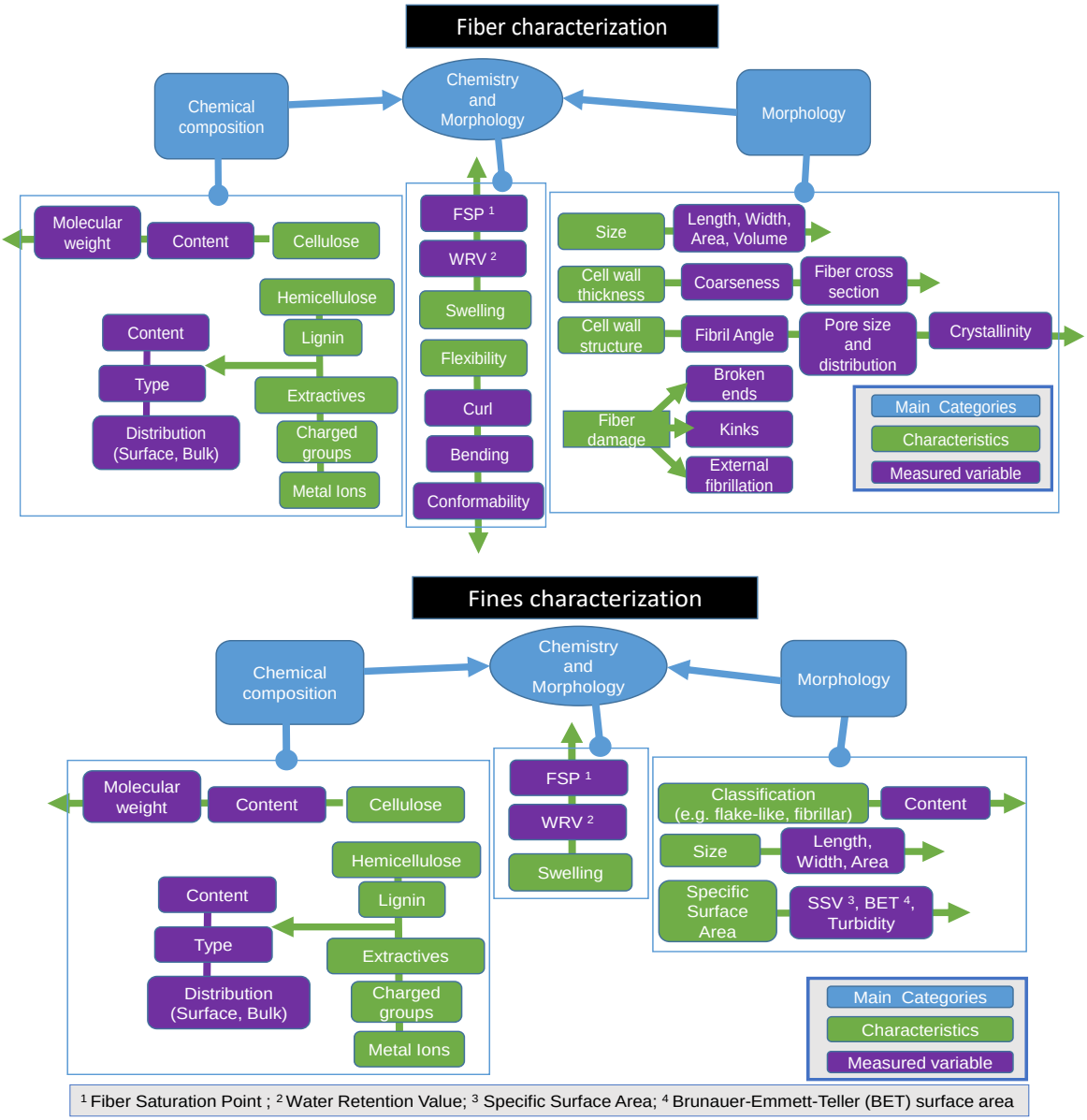
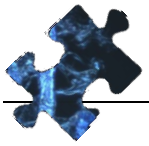


Figure 2-3: Overview of measured characteristics and variables for the characterization of fibers and fines structured in the categories chemical composition and morphology. Intermediate of these main categories, characteristics depending on both, chemistry and morphology, are listed.

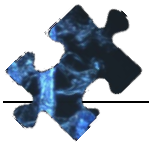


2.3. Morphological characterization

For fibers most of morphological characteristics are obtained using flow cell based fiber analyzers, giving information regarding e.g. size, cell wall thickness, fiber damage and flexibility (curl). Fines morphology is also accessed with such analyzers. Usually only the fines content in a certain pulp fraction is evaluated, depending strongly on the resolution of the fiber analyzer and the optical properties (refractive index, color) of the fines fraction (Hyll 2016). Therefore other methods for morphological characterization of fines were developed, summarized in a review by Hyll (2015). These methods can be roughly categorized in gravimetric and optical methods.

Gravimetric methods are used to isolate the fines fraction for further characterization, but also to measure the weight of different size classes obtained by screening techniques, tube flow fractionation or sedimentation. These techniques are limited in resolution based on, e.g. the number of screens and have other restrictions as well. For example whether a particle contributes to one or another class is not only dependent on particle size but also on shape, flexibility and swellability of the particle.

Optical methods can be roughly grouped in imaging and non-imaging methods. Non–imaging methods are based on different interactions of particles and light such as e.g. attenuation, scattering or reflectance. In comparison to imaging methods, they can operate over broader size ranges and allow a higher resolution. Given the heterogeneous optical and morphological nature of pulp fines, imaging methods are considered to be advantageous compared to non-imaging methods. Although lower in resolution, particle properties can be assigned to a single particle, allowing the distinction of particles for example by shape or gray tone. Flow imaging techniques work with particles suspended in water and acquire the images from a flowing suspension for example with traditional fiber analyzers or as recently published in an image stream flow cytometer (Hyll et al. 2016), a device using different light sources to obtain additional information dependent on chemical composition. As already mentioned fines suspended in water tend to swell and thus give no true information about size. Even more important, they show too low contrast for accurate detection in imaging methods because their refractive index is close to that of water and the particles might be too small to be resolved by the used cameras. To overcome this limitation crill measurement is implemented in flow cell analyzers. The crill technique is a non-imaging optical approach, determining the so called crill value or crill quota relating the response of particles suspended in water exposed to IR light to the additional response of these particles exposed to an UV light source. UV light has a shorter wavelength compared to IR light and therefore on the one hand of course gives response to smaller particles, but more important also to particles



with a refractive index closer to water. This feature is also applied in systems using dynamic light scattering (DLS) to be able to detect such particles. The advantage of the crill technique is the easy and fast measurement which is useful for process control as shown in an implementation to follow the fibrillation progress in MFC production (Osong et al. 2014). Still it remains unclear, how much of the "invisible" material in imaging techniques is detectable using this technique and which morphological character(flake – like, fibrillar) the material defined as crill has, as no information on the structure (size and shape) of the fine material is given.

Static microscopy is a further imaging technique and acquires images from particles fixed on a sample holder. Compared to flow cell based systems, sample preparation is more tedious and prone to errors because of manual sampling. The advantage of a static microscopy approach is that the sample is analyzed in dry state, thus swelling does not influence detection (contrast) or size measurement. Luukko et al. (1997) introduced such a method predominately applied for mechanical pulp fines to distinguish between the character of fines - flake-like (low/not bondable) and fibrillar material (bondable) - based on the differences in gray tone values of the captured images. Although implemented, size characterization was not applied for mechanical pulp fines. The content of fibrillar material seemed to be the only meaningful parameter considering paper (strength) properties. Retulainen et al. (2002) on the other hand developed a method applied for chemical pulp fines, capable to measure size and shape parameters but did not distinguish between flake-like and fibrillar material.

Based on this background, we decided that static microscopy, combining Luukko's approach differentiating between the character of fines and the method of Retulainen, measuring size and shape would be a good scientific approach to learn more regarding the morphological impact of fines on paper properties.

2.4. Swelling

A property of fibers and fines related to morphology, but also to chemistry, is swelling. Lignocellulosic fibers and fines swell in water, because of charged groups, dissociated in water. . This groups are part of the solid cellulosic matrix, thus the charges are fixed and cannot move. Charged groups are located on the surface of fibers and fines (primary wall, microfibrils) but also in the bulk phase (fiber wall, macrofibrillar backbone of fines). If now the concentration of charges in the bulk phase is higher than in the surrounding liquid, an osmotic pressure difference arises. This pressure difference is balanced by the bulk phase absorbing water and thereby 'diluting' the charges in the fiber wall (Scallan 1983). Therefore swelling not only depends on the charges in the bulk phase, but also on the properties of the surrounding aqueous environment, such as the pH

(dissociation) and conductivity of the water phase, the types of counterions of the charged groups and addition of chemical additives (Scallan 1983; Scallan and Grignon 1979; Stone et al. 1968; Strom and Kunnas 1991). All of these influences are of chemical nature.

Apart from charges and the properties of the surrounding liquid the uptake of water is limited by the solid matrix of fibers and fines, hindering an unlimited dilatation. Therefore Stone and Scallan (1967) defined regions of a fiber with different water holding capacities, illustrated in *Figure 2-4.* Even the cell wall of a fiber is heterogeneous and shows differences in water uptake, basically distinguishing between cell wall water (V_C), water in fiber lumen (V_L), water entrapped in external fibrils (V_F) and water held between interstices of fibers (V_I). In a strict sense also the cell wall, external fibrils and fines comprise of regions with different water holding capacity. This is important background information considering that most of the measurement methods applied only give a summarized parameter for such a heterogeneous system. Especially fines can take up three times more water compared to their corresponding fibers (Laivins and Scallan 1996).

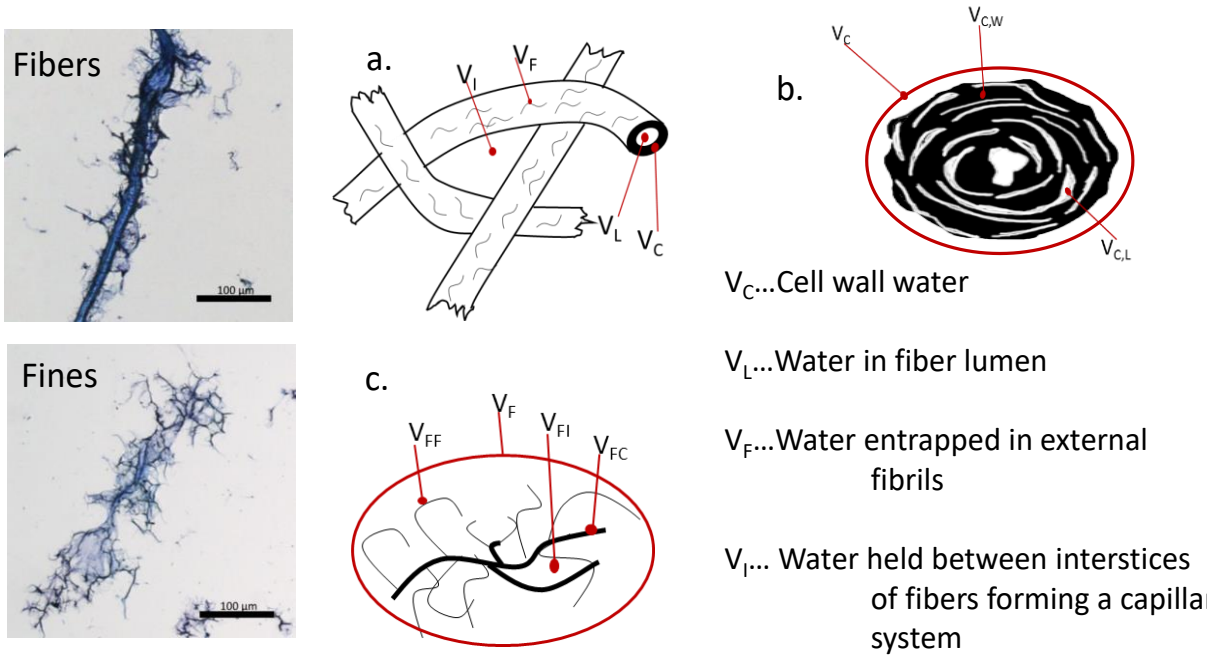
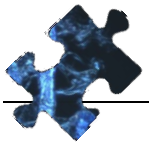
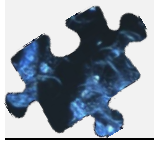


Figure 2-4: Illustration of regions in fibers and fines with different water retention capacities
(a) Regions of a fiber adapted from Stone and Scallan (1967). *Subdivision into (b) regions of different swelling in cell wall and (c) regions in external fibrils and fines.*



Various methods are applied to characterize the swelling behavior (Berthold and Salmén 1997; Hui, Liu, and Ni 2009; Stone and Scallan 1967; Wang, Maloney, and Paulapuro 2003), but the most prominent ones are the fiber saturation point (FSP) and the water retention value (WRV). In FSP measurement, a weighed quantity of wet pulp of known moisture content is immersed in a dilute aqueous solution of a high molecular weight dextran polymer (approximately 1wt% in water). The polymer molecules are large in size and cannot enter porous regions. Thus water contained in the pores will lead to a change in the polymer concentration. The FSP, which can be understood as the amount of water in the cell wall, is then determined based on Stone and Scallan (1967). WRV measurement has a quite different principle. The WRV is a standardized centrifugation technique (ISO 23714:2014), determining the water retained in a fiber pad after the application of centrifugal forces under defined conditions. Controversial discussion were going on whether the one or the other method describes best the ability of fibers and fines to swell (Hui et al. 2009; Maloney et al. 1997; Scallan and Carles 1972). However WRV, compared to FSP, is a relatively fast and accurate measurement and is most frequently applied nowadays and standardized. When it comes to the measurement of fines showing high dewatering resistance, nevertheless this method is not applicable under standardized conditions, as a filtration process is required. Several authors adapted the procedure for fines measurement by changing measurement conditions (Bäckström, Kolar, and Htun 2008; Cheng et al. 2010; Hii et al. 2012). Different measurement conditions lead to differences in the absolute value. As fines are part of the papermaking furnish, it is of interest to relate and compare swelling of fines and fibers using one evaluation routine in order to evaluate the impact of these fractions, which would not be possible using different methods for fibers and fines.



3. TECHNOLOGICAL PROPERTIES OF FINES IN PAPERMAKING

A short introduction to the importance of fines and their influence on technological properties in papermaking is presented in *Chapter 3.1* in order to give an overview which properties are influenced by fines. How the character of fines is related to their impact on paper properties is reviewed in *Chapter 3.2*. *Chapter 3.3* presents two approaches to influence the character of fines on the one hand by mechanical and on the other hand by chemical modification.

3.1. Importance of fines for papermaking applications

Chemical pulps as used in papermaking contain between 5 and 15% fines in mass, depending on the wood source (e.g. hardwoods contain more primary fines than softwoods) as well as on the refining strategy. Mechanical pulps can contain up to 40% of fines (Retulainen et al. 2002; Retulainen, Moss, and Nieminen 1993). Both chemical as well as mechanical pulp fines play an important role regarding sheet consolidation, initial wet web strength, pressing and drying, further converting steps (e.g. coating, calandering etc.) and finally the properties of the final paper product (see *Table 3-1*).

Table 3-1:Effect of fines on pulp and sheet properties (Retulainen et al. 1993)

Property	Effect	Property	Effect
Drainage Resistance	++	Folding endurance	+
Wet web strength	+	Air permeability	--
Sheet density	+	Specific bond strength	
Shrinkage potential	+	-primary fines (flake – like)	-
Tensile strength	+	-secondary fines (fibrillar)	+
Elongation	+	Light scattering	
Tensile stiffness	+	-chemical pulp fines	(-)
Tear strength	-	-mechanical pulp fines	++
Compression strength	+	Fiber rising/Linting	-

Due to their small size and their slender fibrillar structure, especially fibrillar fines show a high specific surface area additional increased by the tendency to swell when suspended in water. Because of the better conformability and larger surface area compared to fibers even small quantities of fines have a high impact on paper properties (Brecht and Klemm 1952; Sandgren and Wahren 1960; Bäckström, Kolar, and Htun 2008; Retulainen et al. 2002; Sirviö and Nurminen

2004; Kibblewhite 1975; Paavilainen 1990). Especially fibrillar fines increase tensile strength and z-strength (Pruden 2005; Retulainen 1992). Nanko & Ohsawa (1989) identified a bonding layer between two bonding fibers in refined chemical pulps. When secondary fines are present this layer's thickness increases, while it is reduced when the fines are removed and thus only external fibrils attached to the fibers participate in the bonding layer formation. Macrofibrils (thick bundles of microfibrils) form a network structure and microfibrils seem to fill the space between the macrofibrils. It is suggested that the microfibrils are predominately contributing to bond strength. Further, secondary fines were found to cover the surface of fibers, as they are attracted to the fibers by capillary forces thereby also covering the edges of the fiber bonds. Apart from forming a surface layer, fines fill voids and form film-like structures between fibers (Belle et al. 2015). These possible locations of chemical pulp fines are illustrated in *Figure 3-1*. One can imagine that the presence of fines thereby results in a higher bonded area and better stress distribution in sheets containing fines (Nanko and Ohsawa 1989; Pruden 2005; Retulainen 1992). It is also suggested that fines have a higher impact on bonding than external fibrils still connected to the fibers (Paavilainen 1990; Retulainen 1992), probably because they are free to move to any position in the fiber web. Together with tensile strength, density is also increased by the addition of fines, pulling fibers closer together by capillary forces and filling up voids. Air permeability is reduced for similar reasons and dewatering resistance is increased (Sirviö and Nurminen 2004). Dewatering resistance is increased even further because of the high swelling ability of fines (Paavilainen 1990). Light scattering was found to be improved by mechanical pulp fines and primary chemical pulp fines, more precise flake-like fines, but reduced for refined chemical pulp fines (secondary fines) as more interfaces are created by the stiffer mechanical pulp fines whereas they are reduced by the flexible, fibrillar secondary fines of chemical pulps (Luukko 1999).

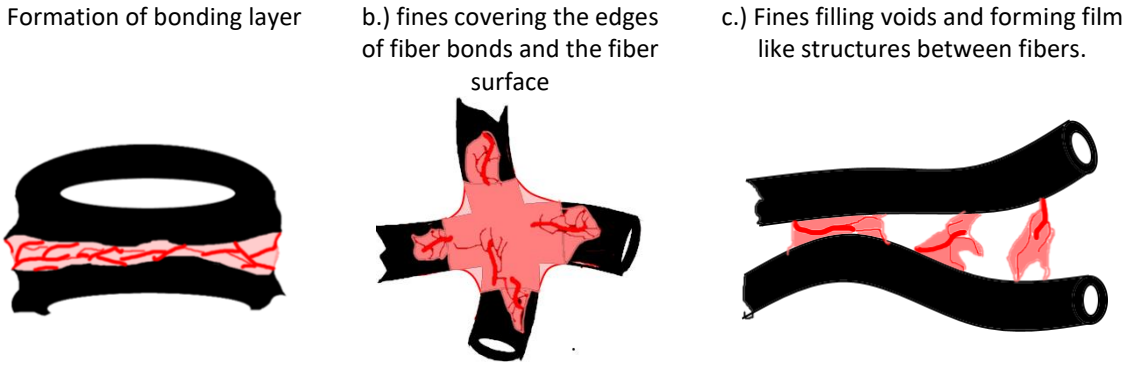


Figure 3-1: Possible locations of (chemical pulp) fines in the fiber network

3.2. Character of fines and paper properties

It is common knowledge that fibrillar fines influence paper properties mainly due to their large surface area, swelling ability and high conformability (see *Chapter 3.1*). Nevertheless a quantification of these effects and the connection of fines characteristics and paper properties was seldom investigated. A detailed investigation was only performed for mechanical pulp fines, where the relation between fibrillar content of fines, sheet density, paper strength properties, as well as the connection between flake content and optical properties were illuminated (Brecht and Klemm 1952; Luukko 1999; Luukko and Maloney 1999; Luukko and Paulapuro 1999; Sirviö and Nurminen 2004). Of course also attempts were made to quantify the differences in the behavior of chemical pulp fines. Nevertheless, due to insufficient differentiation in quality and quantity of fines and/or a too high diversity of different types of chemical pulp fines as well as the fact that either fines were characterized or the effect of fines on paper properties, without combining both, only a qualitative information can be provided for chemical pulp fines. In this section a review of these findings is given.

Primary fines have a lower impact on paper properties than secondary fines (Giner-Tovar et al. 2015), again attributed to the higher swelling ability of secondary fines (Bäckström et al. 2008). Differences in swelling, extractive content and specific surface area of fines from different wood sources and pulping processes were found to be related to strength development of sheets (Retulainen et al. 2002; Spence et al. 2010; Stone, Scallan, and Abrahamson 1968). Sub fractionation of chemical pulp fines showed that the impact of the obtained fractions on tensile strength is differing depending on morphology and chemical composition (Retulainen et al. 2002). Differences in quality and quantity of secondary fines were observed when using different refining aggregates (Kibblewhite 1975; Lindqvist et al. 2012). It was found that the particle size and quantity of secondary fines is related to the fibril angle. A low fibril angle leads to the production of coarser fines (Paavilainen 1990).

3.3. Strategies to influence fines character

3.3.1.Refining (mechanical modification):

Refining is the conventional approach to influence pulp properties. Due to the refining action mainly four different mechanisms - internal fibrillation, external fibrillation, fiber shortening and fines production - occur.

Internal fibrillation results from compression forces that the fiber flocs are exposed to during refining (*Figure 3-4*). Delamination of the fiber wall leads to a flexibilization and allows straightening of the fibers. Due to the internal space created, swelling is promoted. These effects lead to a collapse of the fiber (*Figure 3-2*). External fibrillation, fiber shortening and fines production (*Figure 3-3*) is more pronounced in abrasive refining (Cuberos-Martinez and Won Park 2012; Kibblewhite 1975; Suchart 2014), where the fiber flocks are exposed to edge forces and shear forces between rotor and stator, for example in conventional industrial disk refiners (*Figure 3-4*).

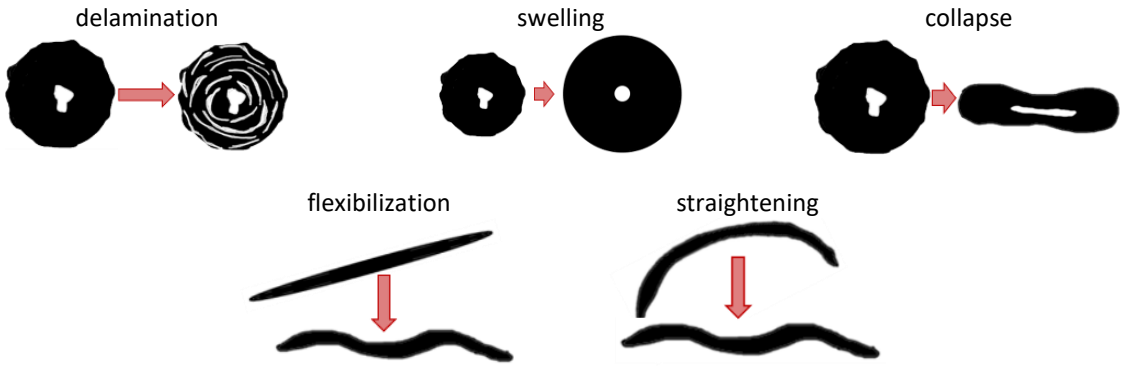


Figure 3-2: Internal fibrillation (delamination, swelling, collapse, flexibilization, straightening) as a consequence of compressive refining

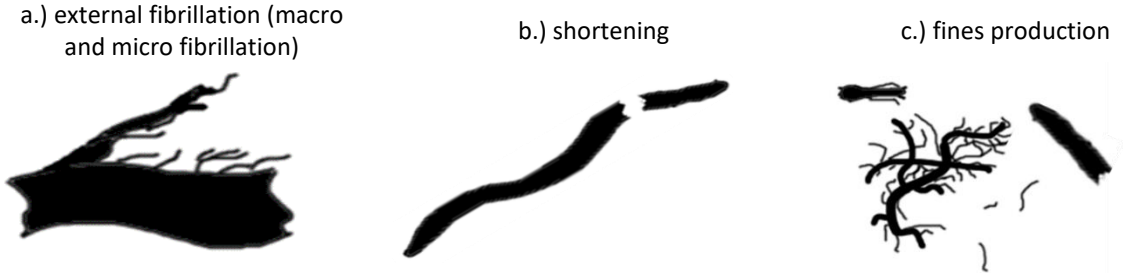


Figure 3-3: a.) external fibrillation; b.) shortening; c.) fines production as a consequence of abrasive refining

In characterization of refiner performance two parameters, specific edge load (SEL) or specific surface load (SSL) and specific energy consumption (SEC) are frequently used. Unfortunately these parameters are a combination of three variables (flow rate, refining pressure, geometry of the fillings), making it difficult to discuss refining action on this basis. Considering different forces acting on a fiber floc in a conventional disk refiner (see *Figure 3-4*), it will depend on the ratio and magnitude of these forces how fiber and fines properties develop, i.e. how distinct each of the four mechanisms are (*Figure 3-2, Figure 3-3*). Compression forces are only transferred to the fibers when the refiner gap is rather narrow (see *Figure 3-5*). Thus, depending on a compression index, refining can be categorized in brushing, squeezing and cutting (Antensteiner 2002).

More fines will be produced the more impacts occur and the higher the shear forces acting on the fibers are. Coarser fines will be produced at higher compression forces, together with high shear forces. Also fiber pieces produced by fiber shortening will be part of the fines fraction, defined by all particles passing a 200 mesh screen. In general more flexible fibers (springwood vs. summerwood) and fibers with a higher bonding ability in the cell wall (kraft vs. sulfite) produce less (mass percent) but finer fines at a given refiner setting (Page and Grace 1967).

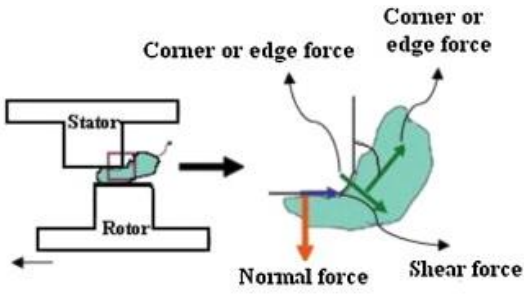


Figure 3-4: Forces acting on a fiber floc in a conventional disk refiner
(Cuberos-Martinez and Won Park 2012)

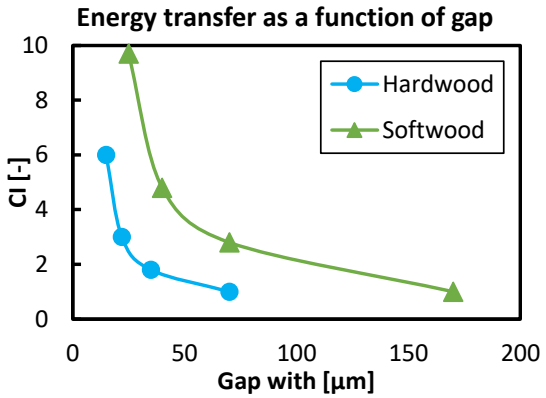


Figure 3-5: Energy transfer on the fiber floc in refining expressed by the compression index (CI) as a function of the gap clearance. CI represent the normal forces acting on the fiber floc (Antensteiner 2002)

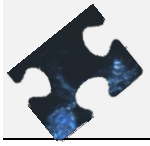
3.3.2.Cationization (chemical modification):

In the 1980s the research group around Gruber at TU Darmstadt started a row of investigations on cationization of pulp fibers. They studied reaction efficiency and kinetics, different cationization protocols with varying chemicals and the effects of cationized fibers on pulp

and paper properties (Granzow and Ott 1996; Gruber and Granzow 1996; Käufer and Krause 1984; Krause et al. 1981). They found a reduction in refining energy consumption, a retention and flocculation effect, improved sizing efficiency and improved paper strength.

Cationization means to covalently bind a cationic functional group to the cellulose chain. Cationization using glycidyltrimethylammonium chloride (EPTMAC) under alkaline conditions take place on the surface and in the bulk phase of the fiber similar to the more frequently cited tempo oxidation (Gamelas et al. 2015). Gruber (2002) stated therefore a spacer effect responsible for lower refining resistance and higher strength properties due to fiber flexibilization and higher conformability by the charge induced swelling, similar to the findings of Zhao et al. (2016) inducing negative charges by tempo oxidation. Others stated the effect to be related to the improved fines retention and the cationic functionalities taking part in fiber bonding (Montplaisir et al. 2006). Pelton (2004) studied the effect of cationic functionalities on soluble dry strength agents and concluded that these dry strength additives force strength, because of their hydrophilic nature and not due to the cationic functionalities. The latter improving only the retention of the soluble polymers in the wet end. Nevertheless cationic functionalities reacted to solid particles might act differently. The electrostatic interaction between positively charged fibers and negative charged fibers might bring them into closer contact and thereby facilitate bonding. Cationic charges on fines might bring an even higher effect, because of the much higher surface area of fines.

The study of the basic effects of cationic functionalities on fibers did not allow a clear separation between changes in structural properties (flexibility, fines production) and changes in chemistry (charges) related to technological properties in papermaking. As fines are already considered quite flexible material, cationic modification of those may give a clearer image which properties are affected directly by the charged groups.



4. METHOD DEVELOPMENT FOR FINES CHARACTERIZATION

4.1. Microscopy method for morphological characterization of pulp fines (*Paper I*)

Motivation

Flow cell based fiber analyzers as for example the L&W Fibertester$^+$ (FT$^+$) are traditionally used for fiber morphological characterization. The FT$^+$ has a resolution of 3.3 µm/pixel, analyses up to 1000 particles per minute and has a large enough image frame (8.1x6.8 mm) to analyze fibers and fines without prior fractionation. The operators have to place a 0.1 to 0.2 g dry sample diluted in 200-400 ml water in the 'auto sampler' (*Table 4-1*). Thus fiber analyzers theoretically would present a quick, quite accurate method for morphological analysis of fines. In *Figure 4-1* images of bleached softwood kraft (BSK) primary and secondary fines captured by the FT$^+$ are shown. Applying the threshold (segmentation criteria), a gray-tone value of 200, used in the device, the material is separated from the background as illustrated in the bottom row. The turquoise areas present the detected particles, which are then further processed by the implemented image processing routine and size (length and width) of each connected element is calculated.

Table 4-1: Comparison between operation and measurement conditions of the FT$^+$, (flow cell based fiber analyzer) and the static light microscope for characterization of fines.

		Fibertester$^+$	**Microscope**
Resolution:	µm/pixel	3.3	0.86 (0.43/1.72)
Sample:	-	wet sample	dry sample
Analyzed particles:	-	7000 – 100000	7000 – 70000
Sample mass:	g dry	0.1 - 0.2	0.01
Duration:	min	10 - 20	20
Image frame:	mm	8.1 x 6.8	1.4 x 1.0
Particles	-	fibers, fines	fines

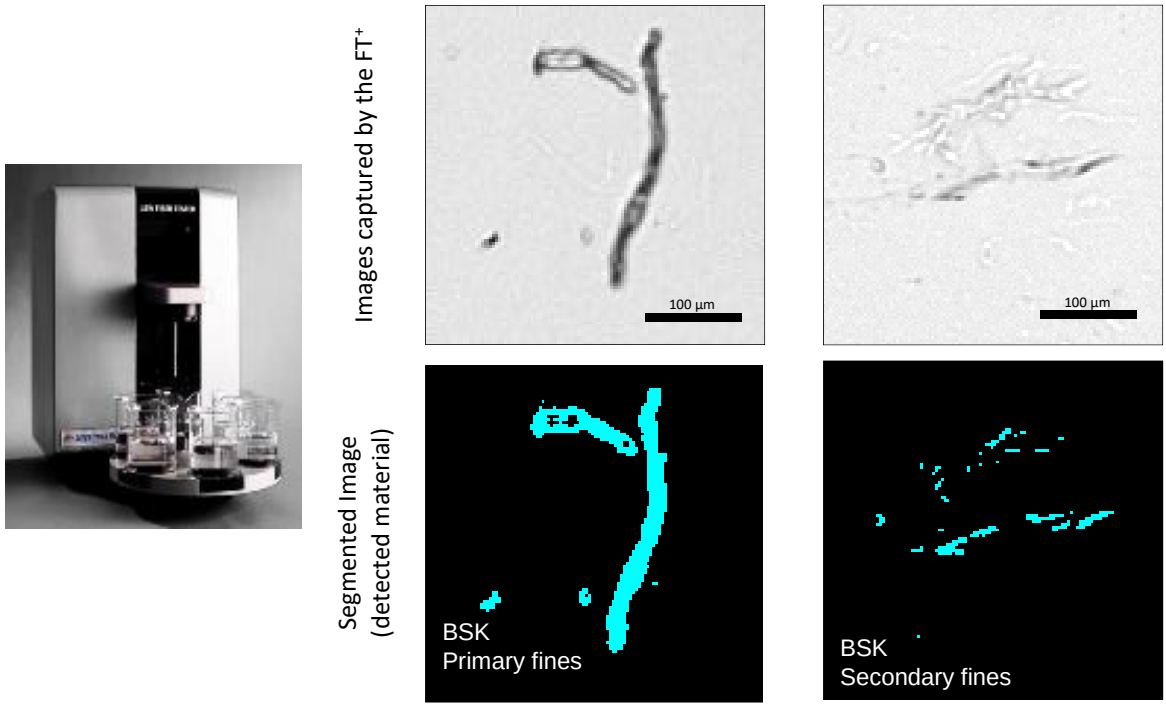


Figure 4-1: Image segmentation L&W Fibertester+
First row: Exemplary image of bleached softwood kraft (BSK) primary fines (middle) and BSK secondary fines (right); Second row: Detected material (turquoise). Secondary fines show incomplete detection.

The FT+ detects primary fines sufficiently well, but only part of the secondary fines are visible because of the high swelling of the fines in water. Also primary fines contain some swellable material, which is not recognizable in the captured images. As especially this swellable part of the fines fraction is of special interest with regard to the effects of fines on paper properties, another characterization method had to be found.

Method development

Static microscopy was the method of choice. Compared to fiber analyzers, the microscope has a higher resolution (0.86 µm/pixel) with the compromise that the size of the captured images is smaller, not allowing fiber analysis in parallel (see *Table 4-1*). Therefore the fines fraction has to be isolated prior to analysis. The most important feature of the static light microscopy method is, that the particles are analyzed in dry state and thus swelling is not an issue anymore. Also a statistical significant number of particles can be analyzed in the same time as for the FT+ (see *Table 4-1*). The crucial and time consuming point in this method is the sample preparation.

Staining of fines is necessary to enhance contrast for an accurate detection of the quite thin fibrils. Methylene blue (1wt% in water) was used for this purpose as already suggested by Luukko

et al. (1997) and Retulainen et al. (2002), added to the fines suspension. Nevertheless the dye did not adhere uniformly. Especially thin fibrils of bleached chemical pulps showed insufficient dye adsorption. Most probably because methylene blue as a basic dye adheres to anionic groups (Fardim and Holmbom 2003), which are less concentrated on these thin, swollen structures. This problem was solved by adding a tall oil emulsion to the fines suspension in addition to the dye. More details regarding the staining method are described in *Paper I*. After this dyeing procedure, three droplets of the prepared suspension were placed on a microscope slide and fixed with a cover glass before drying on a heated plate. Observation under the microscope showed that the tall oil droplets in the tall oil – water emulsion, attract methylene blue probably due to the carboxyl groups of fatty acids contained in the tall oil. During the drying process, water evaporates and tall oil droplets together with the dye adhere to the fines and form a film on the fines surface. 700 to 800 images were captured automatically. The material on one microscope slide represents one sample. Exemplary images are illustrated in *Figure 4-2*. Even thin fibrils are visible, only possible because of the tall oil addition.

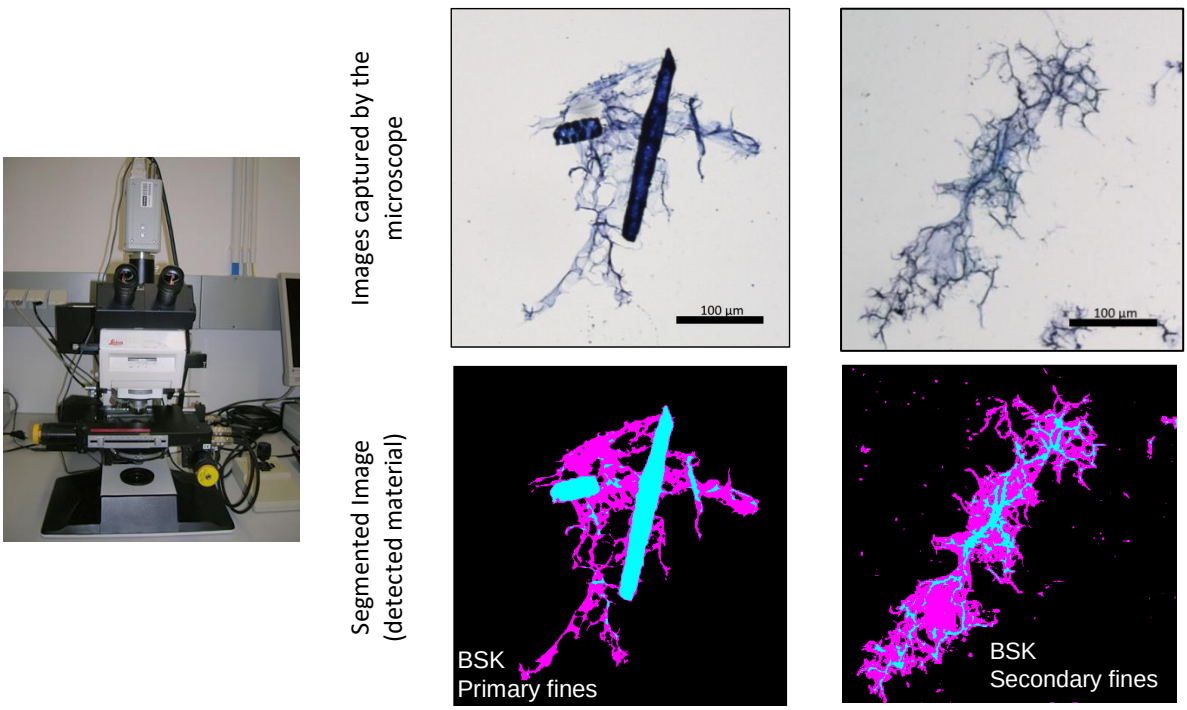


Figure 4-2: Image segmentation microscopy
First row: Exemplary image of bleached softwood kraft (BSK) primary fines (middle) and BSK secondary fines (right); Second row: Detected material: Fibrillar fines (magenta), flake-like fines (turquoise).

Image processing is described in detail in *Paper I*. The key issue is the segmentation into flake-like (low bondable fines) and fibrillar material (bondable fines) as illustrated in *Figure 4-2*. Flake-like material, consisting of ray cells, parenchyma cells, the macrofibrillar backbone of fibrillar fines and fiber fragments and fibrillar fines (microfibrils) can be evaluated separately. Apart from the fibrillar content, the percentage of fibrillar fines related to all detected fines in the sample, size and shape of the detected particles are measured. The size is measured by the circle equivalent diameter (CED), being the diameter of a circle equivalent to the area of the particle. Shape was calculated as length to width ratio also known as aspect ratio (see *Paper I*). Because each single particle is measured also size distributions can be obtained. Finally a morphological description of fines is achieved with respect to their differences in technological properties.

Example

In *Figure 4-3* results from the microscopy method are compared to FT^+ results. As the FT^+ has deficiencies in the detection of swellable fibrillar fines, only the flake-like material identified in the microscopy method is considered in this comparison. Mechanical pulp fines (PGW) and chemical pulp fines (BSK primary fines), show comparable size distributions applying these two methods. This not only underlines the reliability of the microscopy method, but also shows that flake-like fines do not significantly swell in aqueous media. Further results demonstrating the applicability of the methods are presented in *Paper I*.

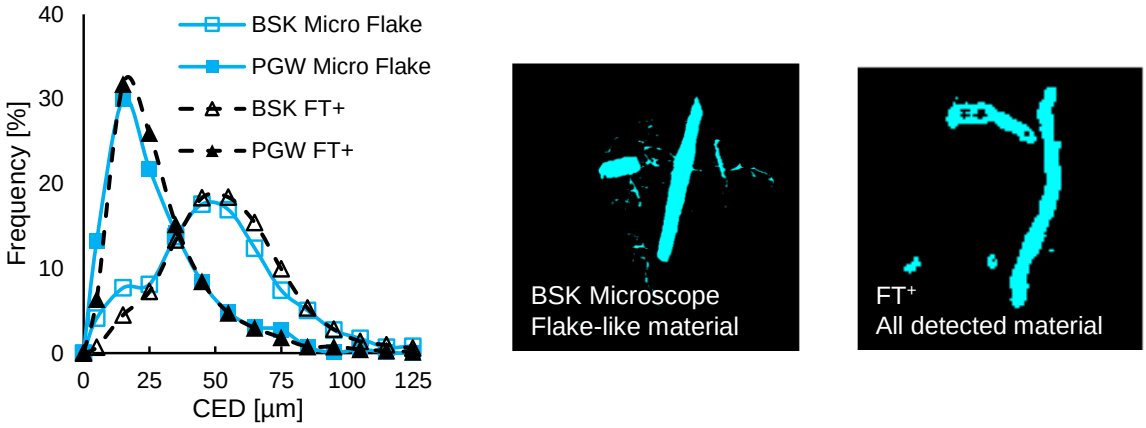


Figure 4-3: Comparison of size distributions for flake-like material
Size distribution, microscopy method (full line) and FT^+ (dashed line) for BSK fines (hollow symbols) and PGW fines (full symbols).

Summary

The microscopy method compared to traditional flow cell based analysis allows the detection of fibrillar fines as it is independent from differences in the swelling tendency and color of fines. The applied staining method results in complete detection of fines and allows a reproducible size measurement, which is not influenced by the optical properties of especially swollen fines. Slight drawbacks of the method are the rather tedious sample preparation and possible errors caused by the manual handling procedure.

4.2. Water retention value (WRV) of fibers and fines (*Paper II*):

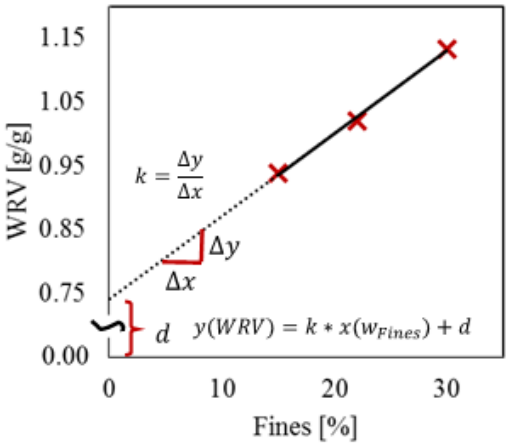
Motivation

Among other factors, the ability of fibers and fines to swell is influenced by the pulping process. The WRV of a sulfite pulp might be similar to the WRV of a kraft pulp, but the underlying reason for this similarity is different: After pulping, sulfite fibers show a higher swelling potential (measured as WRV or FSP) than kraft fibers (Lindström et al. 1986). For the corresponding fines fractions are opposite with sulfite fines showing a lower swelling tendency than kraft fines (Stone et al. 1968). An explanation is that sulfite fibers swell more because of poor adhesion and cohesion of the lamellae in the fiber wall and therefore have a larger inner structure compared to kraft fibers (Page 1983; Stone et al. 1968). Probably kraft fines swell more, because of their finer structure compared to the coarser sulfite fines. So there are different reasons and regions in the fibers and fines which swell, as already mentioned in the introduction section (see *Chapter 2.4*). It seems logical that these differences also lead to different effects on paper properties. Therefore it is important to consider fibers and fines separately regarding their swelling tendency. Available methods to characterize swelling for fibers are different than for fines not allowing a direct comparison of absolute values and thus swelling of fibers and fines and their respective effect on paper properties is difficult to assess based on comparable values.

Method development

Based on the standard WRV method (ISO 23714:2014) a method allowing the determination of the WRV of fines and fibers as well as their contribution to pulp properties has been developed. The developed method is described in detail in *Paper II*. The idea is that each component (fibers and fines) has an intrinsic water retention capacity. Based on the knowledge that fines show a higher WRV than fibers, it is expected that WRV increases linearly when the fines content is

increased, as depicted in *Figure 4-4*. The linear equation (*Eq. (4-1)* obtained from this relationship was solved according to the two boundary conditions: $w_{Fines} = 0\%$ (100% fibers) and $w_{Fines} = 100\%$ to determine the WRV of fibers (WRV_{Fiber}, *Eq. (4-2)* and the WRV of fines (WRV_{Fines}, *Eq. (4-3)*). WRV_{Pulp} was calculated using Eq. (4-4) based on the values for WRV_{Fines}, WRV_{Fiber} and the gravimetric fines content (w_{Fines}) measured for the original pulp. The contribution of fibers and fines to WRV_{Pulp} can also be determined by this approach.



$$WRV_{Pulp} = k * w_{Fines}[\%] + d \quad (4\text{-}1)$$

$$w_{Fines} = 0\% \rightarrow \mathrm{WRV}_{Pulp} = d \triangleq WRV_{Fiber} \quad (4\text{-}2)$$

$$w_{Fines} = 100\% \rightarrow WRV_{Pulp} = k * 100 + d \triangleq WRV_{Fines} \quad (4\text{-}3)$$

$$WRV_{Pulp} = WRV_{Fiber} * (1 - w_{fines}) + WRV_{Fines} * w_{fines} \quad (4\text{-}4)$$

Figure 4-4: Linear relationship between fines content and WRV

Example

Comparing the water retention of unrefined and refined bleached kraft (BSK) and bleached sulfite pulp (BSSU), the latter shows a higher WRV_{Pulp} in the refined and unrefined state (*Table 4-2*). Using the method described in *Paper II* to evaluate WRV of fibers and fines separately, sulfite fibers show a higher WRV compared to kraft fibers, but kraft fines have a higher WRV than sulfite fines. Thus there is an opposite effect for the fines fraction, which would not have been obvious just measuring the WRV of whole pulp.

Table 4-2: Gravimetric fines content and WRV for fibers, fines and pulp determined by the novel method. Exemplarily result for unrefined and refined bleached softwood kraft (BSK) and bleached softwood sulfite (BSSU).

	Fines content [%]	WRV [g/g] novel method		
		Fiber	Fines	Pulp
SBK (unref)	4.9	0.73	2.75	0.83
SBK (ref)	7.7	1.05	3.37	1.22
SBSU (unref)	4.4	1.05	2.35	1.10
SBSU (ref)	11.5	1.15	2.91	1.36

The differences between refined kraft and sulfite pulp are shown in *Figure 4-5* in more detail. The initial WRV_{Fiber}, the WRV of the fiber fraction before refining, has a larger share in sulfite pulp with 68 %, while the corresponding share of the fines fraction is lower with 8% compared to the kraft pulp. In this example, BSSU produces more fines than BSK. Although secondary BSSU fines show a lower WRV_{Fines} compared to the secondary kraft fines, the impact of fines on the WRV of the pulp (ΔWRV_{Fines}) is higher because of the higher amount of fines produced. All in all WRV is influenced by refining to a higher extent in kraft pulping, showing that mainly the development of the fibers (ΔWRV_{Fiber}) is responsible.

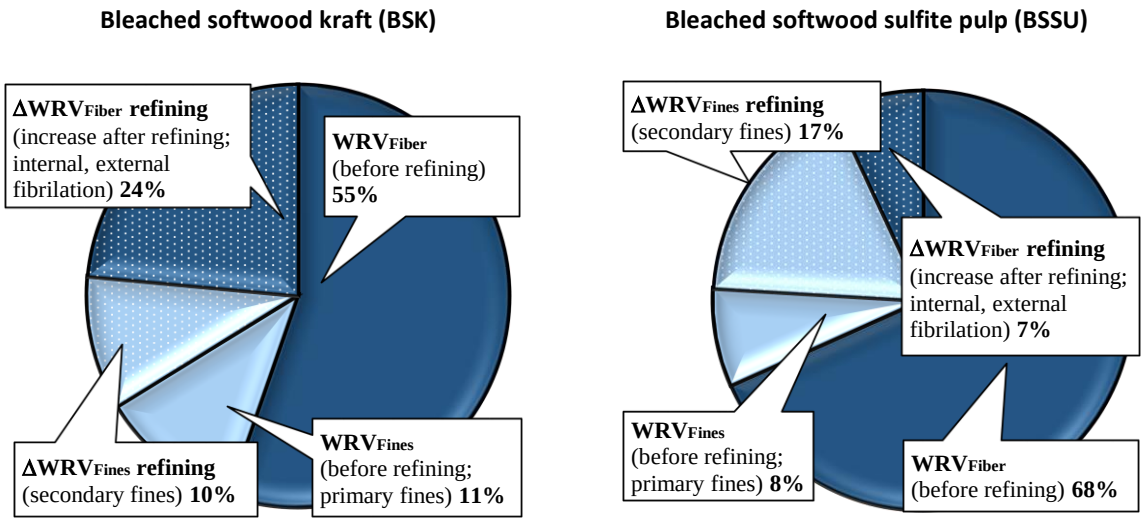


Figure 4-5: Composition of WRV_{Pulp} after refining for kraft pulp and sulfite pulp.

Summary

Nearly all processes in pulping and stock preparation, such as bleaching, drying or refining, influence the amount of water retained in a pulp measured by the WRV. The simple method presented allows separate determination of the WRV of pulp fibers and fines. The contribution of fibers and fines to the water holding behavior of a given pulp can thus be calculated using the standardized WRV measurement procedure. This is seen as an advantage over alternative methods applied to determine the WRV of cellulosic fines, which require modifications to the standard procedure and therefore are not directly comparable. The example of the development of WRV with refining underlines the value of the novel approach. While the overall increase of the WRV of a pulp can be measured using the standardized procedure, the novel approach, in addition, allows us to differentiate between WRV_{Fiber} and WRV_{Fines}, and thus to show the contribution of each fraction to the water holding behavior. This valuable information allows a more targeted process and product optimization.

5. CHARACTER OF CHEMICAL PULP FINES INFLUENCED BY REFINING

This chapter covers different aspects related to the character of chemical pulp fines influenced by refining. Assuming that applying different refiner settings to the very same pulp, yields different pulp character and thus also differences in the character of the produced fines, a setup was designed varying refiner settings for bleached softwood kraft (BSK) and bleached softwood sulfite pulp (BSSU). To assign changes in pulp and paper properties exclusively to changes in fines character a methodology was developed to isolate the impact of fines from the simultaneously changed fiber character. This methodology including a sophisticated experimental setup, data processing and interpretation of the results is described in *Paper III* and briefly summarized in *Chapter 5.1*.

In *Chapter 5.2* the interrelation between fines characteristics measured with the novel characterization methods (see *Chapter 4*) as well as with commonly used ones (gravimetrical fines content and crill) with the impact on pulp and paper properties is discussed. Why some of the characteristics represent the effect of fines on technological properties in paper making and others not is reflected based on descriptive models showing which aspect of the fines character is captured by the applied method.

Based on these observations *Chapter 5.3* focusses on pulp and paper properties affected by the changes in fines character for each pulp source (BSK and BSSU) separately (see also *Paper III*) Further differences of BSK and BSSU fines are compared to the differences of BSK and BSSU fibers. This comparison enables to identify properties affected predominately by morphology and those affected by the differences resulting from the pulping process. *Chapter 5.4* then deals with applying this knowledge with respect to the state of the art industrial refining process.

5.1. Method for the evaluation of the influence of fines character on technological properties (*Paper III*)

Refining exerts several different actions on the fibers and not only the development of fiber properties but also the amount and character of fines produced is influenced by the applied refiner settings (see also *Chapter 3.3*). These multiple changes in fiber as well as fines properties make it difficult to assign the impact on pulp and paper properties to the one or the other fraction.

To isolate the effect of either fibers or fines on pulp and paper properties a methodology was developed and applied to bleached softwood kraft (BSK) and bleached sulfite pulp (BSSU). These pulps were refined at different refiner settings (SEL, SEC) in a conventional industrial single disk refiner to obtain fibers and fines with a different character. The actual parameters varying in industrial refining operation are usually the specific energy consumption (SEC) and the flow rate, based on these the specific edge load (SEL) can be calculated. SEC and SEL are the most commonly used parameters to describe refining action. The refiner settings are given in *Table 5-1* in blue for the BSK pulp and in green for the BSSU pulp. Lower SEC values are depicted in lighter color and the higher ones in darker color. In *Figures 5.1 to 5.10* presenting the data only the numbers from 1 to 10 were used. Abbreviations used in *Paper III* are also given in *Table 5-1*. Refining condition number 9 is not included in the following discussion, because the amount of sample produced was too low to evaluate the properties of fibers and fines.

Table 5-1: Refiner settings for the production of different fines characters; BSK (blue); BSSU (green); low SEC (light); high SEC (dark)

Nr.	Abbreviation Paper III	Pulp	Specific energy consumption (SEC) [kWh/t]	Specific edge load (SEL) [Ws/m]	Flow rate [l/s]
1	HS_1	BSK	150	0.79	21.4
2	HS_2	BSK	150	1.02	27.6
3	HS_3	BSK	200	0.79	16.0
4	HS_4	BSK	200	1.02	20.7
5	HS_5	BSK	200	1.37	27.8
6	HE_1	BSSU	90	0.51	23.0
7	HE_2	BSSU	90	0.79	35.6
8	HE_3	BSSU	130	0.51	15.9
9	*HE_4*	*BSSU*	*130*	*0.78*	*24.3*
10	HE_5	BSSU	130	1.02	31.8

After refining the pulps were fractionated using a laboratory pressure screen (Jagiello 2017) in a fiber and a fines fraction. The latter is defined as all particles passing through a 100 µm hole screen. The obtained fractions were recombined to a whole pulp fraction in a ratio of 91% fibers and 9% fines using various fiber and fines fractions obtained at different refining conditions as illustrated in the trial matrix (see *Figure 5-1*). Handsheets were prepared from these blends using white water recirculation to obtain sheets with a stable and defined fines content(Giner-Tovar et al. 2015). The sheets were wet pressed right after sheet formation to minimize differences that might be caused by capillary forces during sheet consolidation and in order to better mimic

industrial papermaking conditions. Also differences in optical properties and in tear resistance induced by fines only develop when sheets are pressed. Pulp and sheet properties were tested according to standard procedures described in *Paper III*.

				Fines fractions								
				SEC		SEC			SEC		SEC	
				1	2	3	4	5	6	7	8	10
Fiber fractions	SEC	SEL	3									
			5									
	SEC	SEL	8									
			10									

Figure 5-1: Sample matrix for blending fibers and fines with different character induced by refining conditions
BSK (blue); BSSU (green); low SEC (light colors); high SEC (dark colors), SEL increases within one SEC setting from left to the right. Nine different fines fractions (horizontal) were combined with four different fiber fractions (vertical). The reference point is marked in red.

The influence of the fiber and fines fraction on pulp and sheet properties was derived from comparing the different blends. Each column in *Figure 5-1* represents blends with the same fines character but different fiber character. Each row represents blends with the same fiber character but different fines character. In principle only one row respectively one column would be needed to describe the changes due to fines respectively fiber character. But a high variability in the measurement results is observed, when using this approach. This variability is caused probably by using only long fibers resulting in a rather poor formation of the handsheets which in addition might be influenced by the variation of fines character. To improve the accuracy and the reliability of the results therefore properties from more fiber and fines blends were taken into account by applying a data processing routine described in *Paper III*.

To give example on how the derived data are to be interpreted the results after data processing of the drainage resistance are shown in *Figure 5-2* . The isolated impact of fines of different character (left) and fibers (right) on the drainage resistance of a blend containing 91% fibers and 9% fines is depicted. The BSK fractions are shown in blue and BSSU fractions in green. The labels on the x-axis are indicating the different refiner settings (see *Table 5-1*) applied to achieve the variations in fiber and fines character. For an easier estimation of the magnitude of impact, relative values are shown on the y-axis, obtained by dividing the absolute value of the given data point by the value of the reference point highlighted red in *Figure 5-1* and also shown in red

in the top right corner of *Figure 5-2* (in this case 21.1 ° SR). Multiplication of the relative values with this reference value give the absolute value of the property. All relative data and the absolute value for the reference point derived from this trial matrix are given in the Appendix. The results in *Figure 5-2* show, for example, that exchanging 9% fines of character 1 (refiner settings) by fines of character 2 increases drainage resistance by 40%. BSK (blue) and BSSU (green) fibers show about the same impact on drainage resistance (see right side of *Figure 5-2*), while BSK fines fractions increase drainage resistance to a higher extent than BSSU fines fractions, indicated in *Figure 5-2* with the bars of BSK fines projecting beyond the horizontal dashed red line depicting a relative value of 1.0. As the main topic of this thesis was to investigate the influence of fines, discussions in the next chapters are mainly focused on fines and apart from the comparison of sulfite and kraft process (see *chapter 5.3.2*), the results for the influence of fibers in *Figure 5-2* and in the *Appendix* are only given for the sake of completeness.

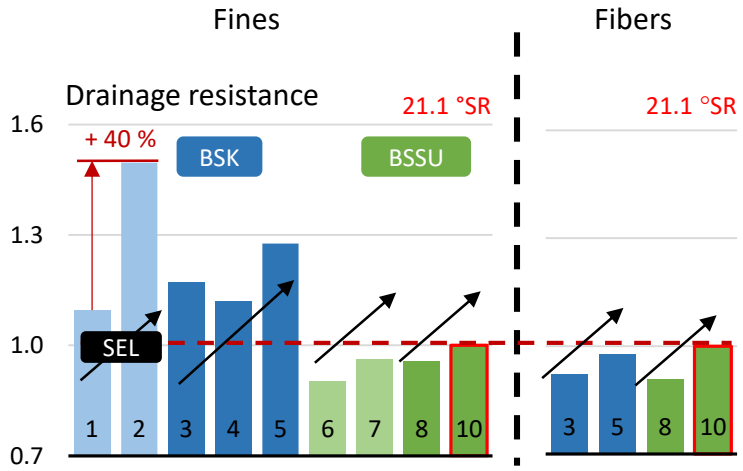
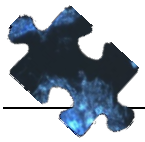


Figure 5-2: Impact of character change of fibers and fines on drainage resistance
Independent impact of 9% fines (left) and 91% fibers (right); BSK fractions in blue; BSSU fractions in green; x-labels represent the different refiner settings (see Table 5-1) also marked by the lighter (lower SEC) and darker color (higher SEC). Within one color SEL increase from left to right as marked by the black arrows.



5.2. Interrelations of fines characteristics and pulp and paper properties

In this chapter the interrelations between the characteristics of fines and their effect on technological pulp and paper properties are analyzed. Why some characteristics are related to the effect of fines on technological properties in paper making and others are not is discussed based on descriptive models showing which aspect of the fines character is captured by the applied method. The pure fines fractions (particles passing a 100µm hole screen) obtained from the BSK and BSSU pulp at the different refiner settings were characterized via the secondary fines content (gravimetrically) and the crill measurement (see also *Chapter 2.3*) as well as by the two novel methods - the WRV of fines and the microscopy method measuring the percentage of fibrillar fines in the fines fraction, expressed as the fibril area (see *Chapter 4*). The results obtained by these four characterization methods are presented in *Figure 5-3* to *Figure 5-6* together with an illustration showing which aspect of the fines character is captured by the applied characterization method. In the illustrations ray and parenchyma cells as well as coarse fiber fragments are depicted in black color; the macrofibrillar backbone (condensed coarse fibril bundles) is presented in dark red, while the microfibrillar part of fines is presented in light red. When a mass related characteristic of the fines fraction is measured with the applied method (secondary fines content and WRV) the differences in the material character are shown as circles. When an area or percentage related characteristic of the fines fraction (Crill, fibril area) is determined the different classes of fines are drawn in the same way as they appear under the light microscope. The size of the circles or images indicates the relative contribution of this component to a certain characteristic. When these characteristics are expressed as a ratio, this is indicated by the black division mark in the respective illustrations.

These four characteristic properties of the fines fractions (i.e. secondary fines content, crill, WRV and fibril area) influenced by the different refiner settings are then compared to the isolated impact of the fines fraction on the paper strength properties Scott Bond and tensile index (*Figure 5-7*). As at all only nine different fines characters are evaluated including two pulp sources with distinctly different properties (BSK and BSSU), a correlation matrix would not allow a fair comparison, due to the limited number of measurement points as well as the irregular distribution of measured values, clustered for BSK and BSSU fines fractions. Therefore bar diagrams were used for the comparison and discussion of different fines characters. If a method is capable to describe an important characteristic property of the fines fraction responsible for paper strength, the trends in strength properties should show a similarity to the trends of this characteristic property.

In a first step each characteristic property of the fines fraction is interpreted and in a second step it will be discussed why some characteristics explain the impact of fines on strength properties while others do not.

The secondary fines content (*Figure 5-3*) represents the mass percentage of secondary fines in the pure fines fraction, containing primary fines (already present prior to refining) and secondary fines (produced during refining). Overlapping circles in the illustration indicate that the different constituents of secondary fines cannot be measured separately and thus only provide an average of these constituents. Secondary fines consist of a microfibrils (light red) connected to a macrofibrillar backbone (dark red) and thus cannot be separated when measuring the mass of the fines fraction. Primary fines (black) are already present prior to refining and therefore can be determined separately.

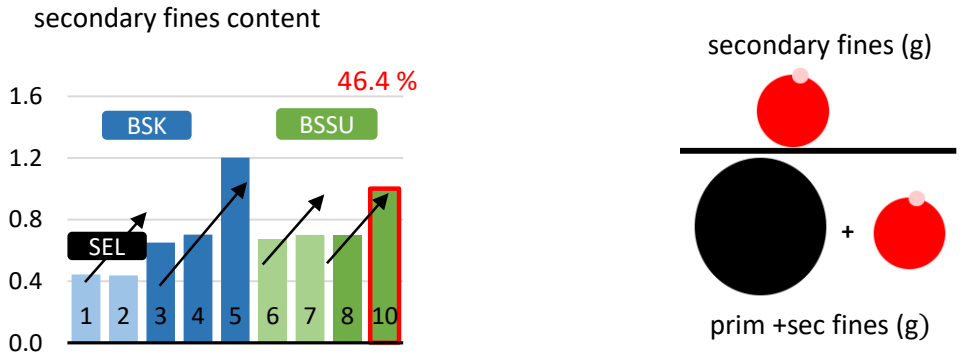


Figure 5-3: (left): Secondary fines content of pure BSK (blue) and BSSU (green) fines fractions produced by the variation of refiner settings ; lower SEC (light color), higher SEC (dark color), increasing SEL from left to right for each color block indicated by black arrows;
(right) Image illustrating the measured characteristic: primary fines predominately contain ray and parenchyma cells (black), secondary fines containing macrofibrillar backbone (dark red) and microfibrillar parts (light red), circles show that the weight is measured, overlapping circles indicate that the weight of these two parts can only be determined as a sum parameter. The size of the circles indicates the contribution of the different constituents to the measured characteristic.

The crill value (also crill or crill quota (Lorentzen & Wettre), KFP (PulpEye)) defines the ratio between the response of particles suspended in water exposed to UV light and the response of these particles exposed to IR light in a flow cell based system, as illustrated in *Figure 5-4*. Because of the shorter wavelength UV light is capable to resolve smaller particles and particles with a refractive index closer to water, therefore giving a higher response than the IR light. Under response basically adsorption and scattering of light can be understood. Unfortunately an exact definition how the crill quota is determined is not available.

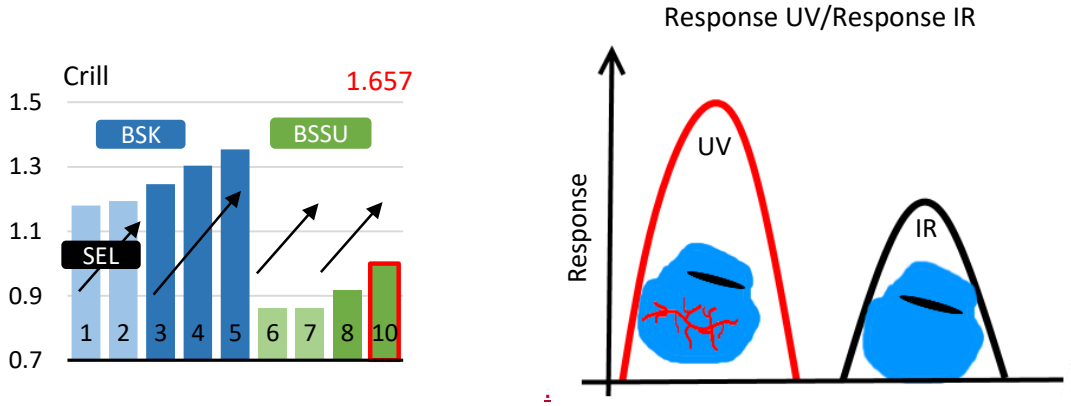


Figure 5-4: (left) Crill value of pure fines fractions, explanation of graph see Figure 5-3
(right) Image illustrating the measured characteristic: Crill is determined by the ratio between the response of particles illuminated with an UV light source and an IR light source (right), particles are suspended in water illustrated by the blue background. Results indicate that under illumination with IR light mainly primary fines (black) are detected, while the UV light having a shorter wavelength is also capable to respond to the macrofibrillar backbone of secondary fines (dark red); results indicate that microfibrillar fines are also invisible to UV light.

The water retention value (WRV) is defined as the amount of water retained in the fines fraction after the application of centrifugal forces (*Figure 5-5*, see also *Chapter 4.2*). Microfibrillar fines (light red circle) retain the highest amount of water (indicated in blue filling the circle) per unit mass, because there is less hindrance for them to swell and expand compared to the more condensed macrofibrillar backbone (dark red). The ray and parenchyma cells (black) retain the lowest amount of water relative to their mass (see *Figure 5-5*). Only an average WRV is determined, because the different constituents cannot be evaluated separately, indicated by the overlapping circles in the illustration.

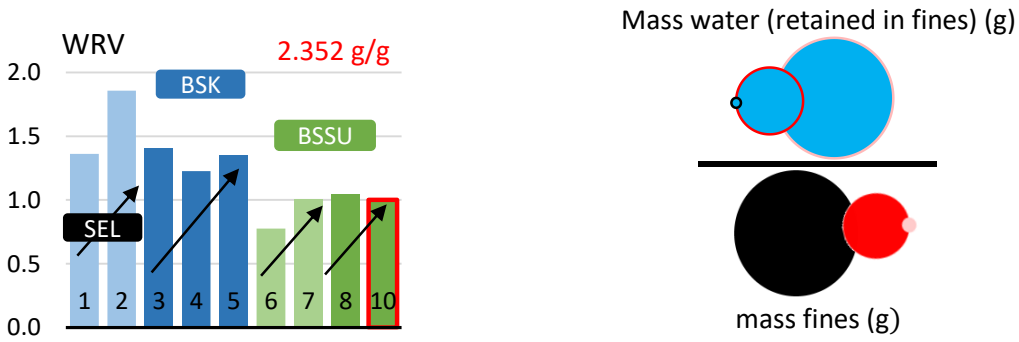


Figure 5-5: (left) WRV of pure fines fractions, explanation of graph see Figure 5-3.
(right): Image illustrating that the WRV is calculated by the mass of water retained in the fines fraction divided by the mass of fines, The size of the circles indicate that the highest amount of water per mass unit is retained by microfibrillar fines (light red circle), while the lowest one is for ray and parenchymacell contained in primary fines (black circle). Overlapping circles indicate that only an average of the different constituents can be measured.

The fibril area is calculated as a percentage of the area of microfibrillar fines (light red) divided by the whole area of the fines, containing microfibrillar fines, macrofibrillar backbone (dark red) and ray and parenchyma cells (black) as illustrated in *Figure 5-6.* Microfibrillar fines are separated from the other fines fractions by the image processing routine described in *Chapter 4.1*. Based on the measurement of area, microfibrillar fines yield a high contribution to the fines fraction in comparison to their low contribution to the mass of this part of the fines fraction (see *Figure 5-3*).

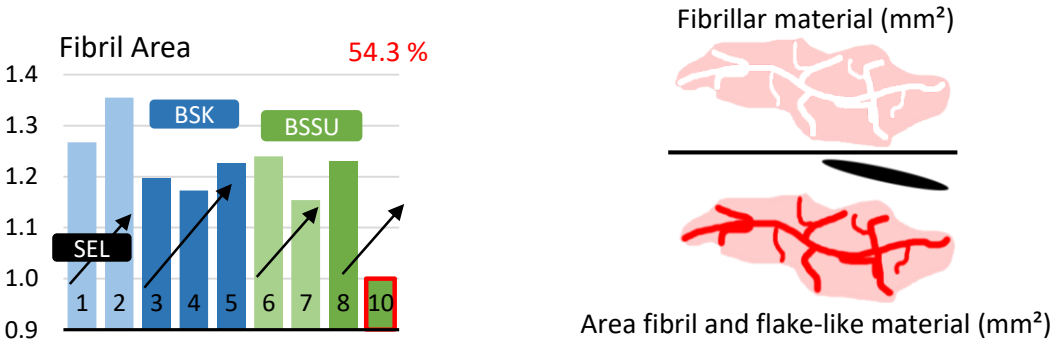


Figure 5-6: (left) Fibril area of pure fines fractions, explanation of graph see Figure 5-3.
(right) Image illustrating the calculation of fibril area: Fibril area is defined as the area of microfibrillar fines (light red) divided by the area of all constituents in the fines fraction. Based on area microfibrillar fines yields a high contribution to the fines fraction, indicated by the area size of the different constituents in the illustration.

The fact that each characteristic property describes a different aspect of the fines fraction is obvious when comparing the results of the analyzed fines obtained at the different refiner settings characterized by the described methods (graphs on the left in *Figure 5-3* to *Figure 5-6*). WRV and fibril area are capable to predict the impact of fines character on paper strength properties (*Figure 5-7*) as can be observed by the similar trends of these characteristics and strength properties. Already Nanko and Ohsawa (1989) suggested microfibrillar fines as being predominately responsible for the bonding ability of chemical pulp fines due to their high conformability and surface area. This characteristic is directly determined measuring the fibril area of fines and also captured by the measurement of WRV, due to the fact that the water retention capacity of the fines fraction is dominated by microfibrillar fines (*Figure 5-5*). The correlation between WRV and fibril area holds as long as the WRV of the macrofibrillar backbone, which has also a large contribution to this characteristic, did not change significantly. This seems to be the case for BSSU fines (green bars) showing different trends in Fibril Area and WRV (*Figure 5-5* and *Figure 5-6*).

It is often stated that secondary fines are those predominately responsible for bonding. Thus a higher secondary fines content should lead to an increase in paper strength properties. The changes in character of secondary fines originating from the microfibrillar fraction nevertheless are not captured by this gravimetrical method due to the low mass contribution of the microfibrillar fraction to the fines fraction (*Figure 5-3*). This mass might only change insignificantly or in a different direction while the surface and therefore the fibril area can vary quite significantly (e.g. compare *Figure 5-3* to *Figure 5-6*). Therefore strength properties are poorly related to the secondary fines content when the the fibril area of fines varies.

The crill technique is capable to capture an additional part of fines invisible to conventional flow cell based imaging systems. Which category of the fines fraction is exactly detected is not entirely clear. This technique is based on the scattering and absorption of light when it interacts with a particle, thus changes in detection of scattered and absorbed light should be related to surface and volume and therefore also to fibril area, if microfibrillar fines are detected by this method. Comparing fibril area and crill (*Figure 5-6* and *Figure 5-4*) no such a correlation can be found. Especially when comparing BSK fines character 1 and 2, where clearly an increase in microfibrillation as well as WRV was observed, yielding a significant difference in strength properties. Contrary crill measurement indicates that these two fines characters are similar.

Crill results resembles more the trends in secondary fines content (*Figure 5-3*). Therefore crill seems merely to measure the macrofibrillar backbone of secondary fines, but fails to detect the microfibrillar fraction. Considering that the crill value is related to the particle surface and the measurement is performed in the wet stage it is also related to swelling and WRV (*Figure 5-5*). The more swollen the macrofibrillar backbone of fines, the higher the surface and therefore the higher the crill value explaining the offset between BSK (blue) and BSSU (green) fines in the crill measurements compared to the secondary fines content.

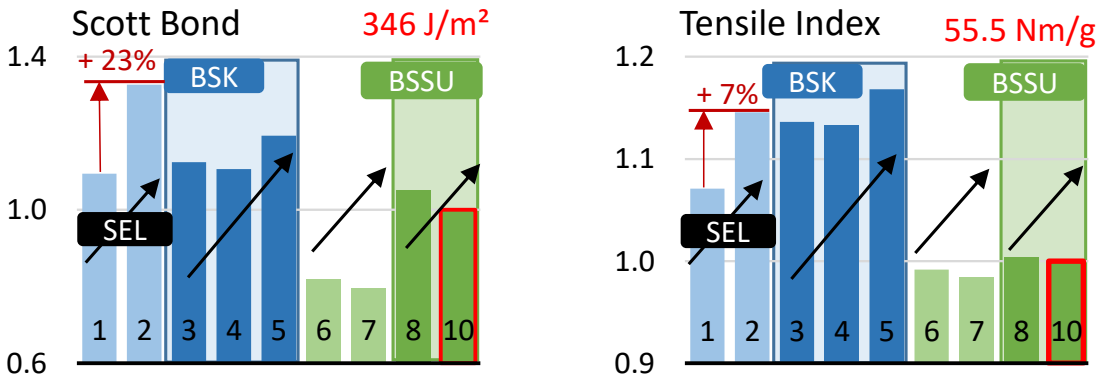


Figure 5-7: Impact of changing the character of fines (9%) on strength properties; Scott Bond (left), Tensile Index (right); BSK fractions in blue; BSSU fractions in green; x-labels represent the different refiner settings (see Table 5-1) also marked by the lighter (lower SEC) and darker color (higher SEC). Within one color SEL increase from left to right as marked by the black arrows.

5.3. Impact of fines character on pulp and paper properties

5.3.1. Impact of fines

In the previous chapter strength properties were compared to fines characteristics. In addition to strength properties also other technological properties are affected by the changes in fines character as elaborated in *Paper III.* In the following chapter only the two parameters most affected by the fines character, drainage resistance and air permeability, together with the impact of fines character on strength properties are discussed. Given the trial setup investigating different pulp sources (BSK and BSSU) and distinguishing between fibers and fines allows also to compare the changes arising from exchanging fines from one pulping process by the fines from the other one and the exchanging fibers from the different pulping processes.

Scott Bond and tensile index (*Figure 5-7*) values resulting from the exchange of fines character show similar trends, mainly related to the fibril area and WRV of those fines fractions. Comparing Scott Bond and tensile index in detail, only fines produced at the same specific energy consumption (SEC) show the same trend (e.g. light blue or dark blue). Secondary fines comprise of microfibrils connected to a macrofibrillar backbone. Although the microfibrils might be the fraction enabling close contact and bonding, the macrofibrillar backbone will also play a role for tensile index. This macrofibrillar backbone can be up to 100µm or longer and consists of oriented, condensed microfibrils. It is reasonable to assume that it is predominately oriented in plane, thus

contributing more to tensile index (were the force is applied in plane) than to Scott Bond (where the force is applied out of plane). Higher compression forces are acting on the fibers in refining at higher applied specific energy consumption. The macrofibrillar backbone of fines might be also flexibilized by this compression forces similar to fibers although on a much smaller structural level. Fibers become more flexible, due to delamination of the fiber wall and therefore are capable to form more contact points. After drying the delaminated fiber wall forms a continuous structure again, so that the entire fiber cross section is loaded when force is applied in tensile measurement. Also the macrofibrillar backbone of fines, comprising of condensed and oriented microfibrils, might be delaminated to some extent enabling better contact. Thus for higher SEC for BSK fines (dark blue) a higher tensile index is achieved than would be expected from the Scott Bond results. For BSSU fines this is different. At higher SEC (dark green) tensile index remains the same as for the lower SEC, although Scott Bond increases. This behavior might be related to the fact that BSSU fibers and probably also fines in general have a weaker structure and already reached the maximum stress level before break.

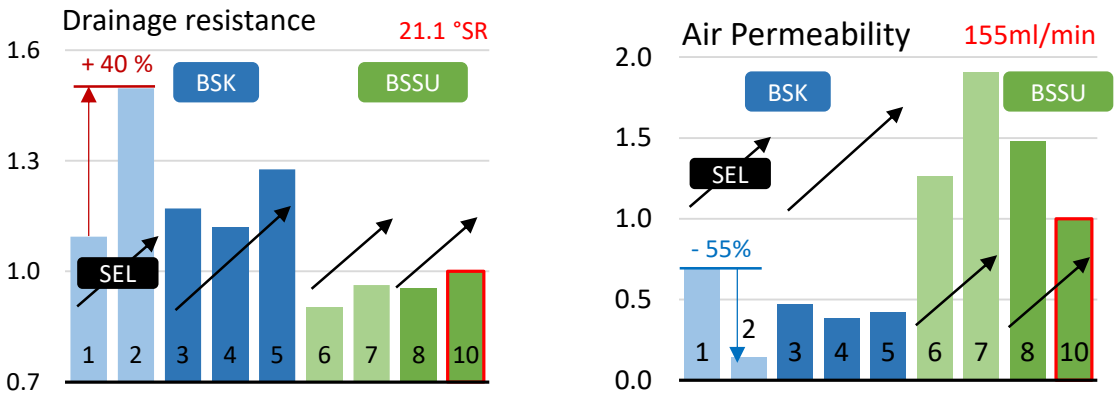


Figure 5-8: Impact of changing the character of fines (9%); Drainage resistance (left), Tensile Index (right); BSK fractions in blue; BSSU fractions in green; x-labels represent the different refiner settings (see Table 5-1) also marked by the lighter (lower SEC) and darker color (higher SEC). Within one color SEL increase from left to right as indicated by the black arrows.

The impact of fines character on drainage resistance shows a similar trend as the WRV (see *Figure 5-5*) of the fines fraction for both BSK and BSSU fines. Therefore it can be argued that the dominant reason for increasing drainage resistance is the swelling of fines rather than their size or secondary fines content. Fines in general close the porous sheet structure, thereby reducing air permeability. The impact of BSK fines (blue) on air permeability is much larger than for BSSU fines (green), indicating that BSK fines bind more sufficiently. The fines fraction with the highest Scott Bond value (refiner setting 2) shows the lowest air permeability. Opposite to drainage resistance

dominated by the swelling of fines air permeability is influenced by additional parameters that also might be related to the size and location of fines in the sheet.

Which properties are now influenced the most by the change in the fines character due to the variation of the refiner settings? For a detailed comparison all properties are shown in the appendix. The difference in the pulp and paper properties due to the variation of fines character by refiner settings is given as a percentage in the diagrams (*Figure 5-7* and *Figure 5-8*). The highest impact was observed in air permeability (-55%) and drainage resistance (+40%), while the influence on Scott Bond was by +23% and on tensile index +7% when fines obtained at refiner setting 1 were exchanged by fines obtained at refiner setting 2. Similar findings were reported by Retulainen, et al. (1993), who did not investigate the effect of changing the fines character, but the effects fines have on the fiber network in general. They also concluded that the impact of fines on tensile index is low in relation to the impact on drainage resistance and air permeability.

5.3.2. Impact of fines and fibers from different pulp sources

In the previous section the effect on pulp and paper properties by changing the fines character due to different refiner settings was discussed. In this section the impact on pulp and paper properties by exchanging fines from different pulp sources (BSK and BSSU) or exchanging fibers (BSK and BSSU) are compared. In *Figure 5-9* the influence on dewatering resistance by exchanging 9% BSSU fines by 9% BSK fines or 91% BSSU fibers by 91% BSK fibers is presented. Thus the impact of fiber type (BSK and BSSU) and the impact of fines type (BSK and BSSU) on sheet properties can be compared. The mass fractions (9/91) are typical for standard paper making furnishes. As only fibers using refiner settings 3 and 5 for BSK (see *Table 5-1*) and 8 and 10 for BSSU were used in this setup, also for the fines only the four corresponding fines fractions at these refiner settings were selected. First the mean values for BSK fibers and fines (3 and5) indicated by the blue rectangle in *Figure 5-9* and for the BSSU fibers and fines (8 and10) indicated by the green rectangle were determined. Then the change in drainage resistance influenced by exchanging either 9% fines or 91% fibers of BSSU by BSK was determined as a percentage of the value of the BSSU drainage restistance. In this example the exchange of 9% BSK fines for 9% BSSU fines results in a 25% higher drainage resistance (see left side of *Figure 5-9*). Exchanging 91% of BSSU by BSK fibers however showed no significant change in drainage resistance (see right side of *Figure 5-9*).

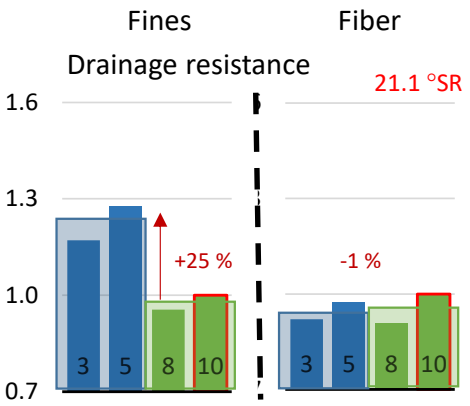


Figure 5-9: Example of the effect of changing either fines or fiber type on drainage resistance. When 9% BSSU fines are replaced by BSK fines, the drainage resistance is increased by 25%. Replacing 91% BSSU fibers by BSK fibers leads to a reduction of drainage resistance of only 1%.

In *Table 5-2* the differences of the exchange of BSSU fines and fibers by BSK fines and fibers for the other measured pulp and paper properties are presented with the most significant changes highlighted in red. A large impact on air permeability is evident where BSK fines showed 64% lower values than BSSU fines indicating a high degree of closing the sheet. Contrary the BSK fibers produced at the same refiner settings even improve air permeability by 9%, which is not so significant when considering the much higher impact of fines on this property. Higher tensile index is achieved when BSSU fibers or fines are replaced by the corresponding BSK fractions. Tear strength is reduced by 8% with the introduction of BSK fines, but on the other hand BSK fibers improve tear by about 43% compared to BSSU fibers. Tensile energy absorption (TEA) is increased by 21% when BSSU fines are exchanged by BSK fines and by 39% when BSSU fibers are exchanged by BSK fibers.

Summarizing the results, the exchange of BSSU fibers by BSK fibers mainly influence paper strength properties such as tear, tensile, E-modulus and elongation, while the exchange of BSSU fines by BSK fines mainly influences drainage resistance of the furnish but especially air permeability of the paper in a negative way. The exchange of BSSU by BSK fines also has a positive effect on Scott Bond and tensile index, which in the case of Scott Bond is higher than the effect of the exchange of fibers.

Change in property exchanging BSSU by BSK [%]		
	Fines	**Fibers**
WRV [g/g]	7	-5
Drainage resistance [°SR]	**25**	**-1**
Density [g/cm³]	1	-1
Opacity	-4	0
Air Permeability [ml/min]	**-64**	**9**
Tensile Index [Nm/g]	**15**	**24**
Elongation [%]	6	13
E-Modul [N/mm²]	3	12
TEA [J/g]	**21**	**39**
Scott Bond [N/mm²]	13	0
Tear Strength [mN]	**-8**	**43**

Table 5-2: Comparison of properties of BSK and BSSU fines and fibers. The change in property replacing either 9% BSSU fines by 9% BSK fines or replacing 91% BSSU fibers by 91% BSK fibers is show; compare also Figure 5-9.

5.4. From theory to the state of the art industrial process:

In the presented investigations the effect of fibers and fines on sheet properties was decoupled and a constant amount of 9% fines was used in all pulp blends. In industrial refining processes the final properties are determined by the character but also the amount of fibers and fines. Increasing SEC or SEL will increase the impact on the fibers, which can be observed by the increase in the fibril perimeter of the fibers (see *Figure 5-10, left*), a measure for the impact of refining action on the fibers. A larger impact on the fibers will lead to higher paper strength at least at these levels of refining. In parallel also a higher amount of fines is produced (see *Figure 5-10, right*) at increased energy input. Thus the final sheet will contain more fines when applying higher SEC and SEL, which is in contrast to our investigations where always a constant amount of 9% fines was used. Due to their higher surface area and WRV a given amount of fines has a higher impact on paper properties than the same amount of fibers. These two effects, the higher impact on the fibers and the higher amount of fines in the sheet, add up and thus finally lead to the highest strength properties for the highest applied SEL and SEC although our investigations showed that microfibrillation and therefore the impact on bonding of fines is higher at lower SEC. If the character of fines would altered in the same direction at highest SEL and SEC most probably there would even be a higher improvement in strength properties. On the other hand also a higher impact on drainage resistance and air permeability would have to be accepted.

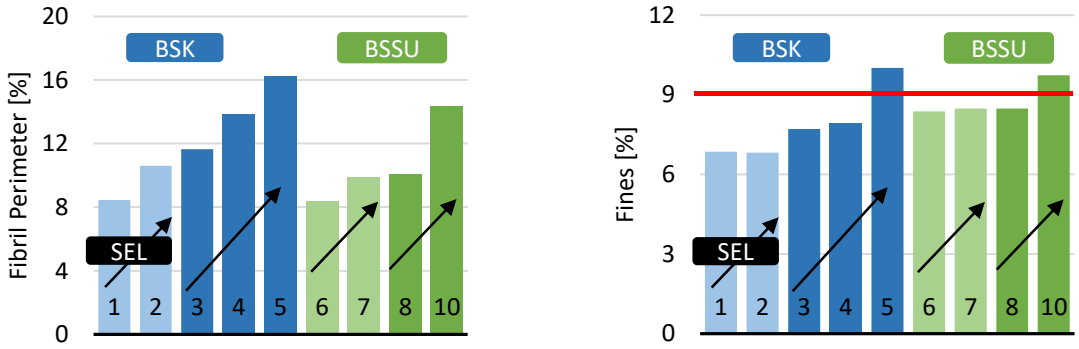
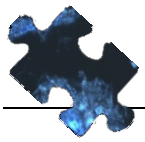


Figure 5-10: Development of fibers and fines applying the different refiner settings (see Table 5.1). Fibril Perimeter (left) is a measure for the external fibrilation or the impact transferred to the fibers in refining. The actual fines content (right) applying these refiner settings increase similar to the fibril perimeter. In our investigations the fines content was held constant at 9% as marked by the red line.

There might be a certain window of operation concerning the control and regulation of technological properties by the fines character for example by using different refiner plates or serial connection of refiners. Nevertheless in state of the art refining technology higher impact on fibers will lead to an increase in fines production and to coarser fines. Taking this under account exchanging and blending of different pulp types will be more efficient to regulate technological properties. Still a targeted production and use of fines shows potential as the character of this material has a great influence on technological properties in papermaking. However such a control of properties by the variation of fines character and amount can only be achieved by uncoupling fiber treatment in refining from fines production. Therefore an alternative refining technology would be needed. Another approach might be a separation of the fines fraction from the pulp furnish after refining, followed by targeted addition.

5.5. Summary

In the approach presented in this thesis the impact of fines character was isolated from the impact of fibers on technological properties. Different methods to analyze the fines character were compared allowing on the one hand to identify what is really measured by these different methods. On the other hand it was shown that especially microfibrillar fines have a high impact on bonding. But also the macrofibrillar backbone was found to influence the tensile index. Similar to internal fibrillation of the fibers it is difficult to access direct information regarding the character of the macrofibrillar backbone of fines. The measurement of WRV in combination with the measurement of fibril area of fines proofed to be useful as an indirect approach.



The character of fines changes significantly when applying different refiner settings, because the forces acting on the fiber structure will determine the development of the character of fines. It was shown that besides an increase in secondary fines content, the typically used refining parameters SEC and SEL provide no information on the character of produced fines. Further BSSU and BSK fines as well as fibers have considerably different impact on technological properties, probably mainly resulting from differences in the fiber wall structure originating from the different pulping processes.

Current industrial refining processes do not allow to decouple fiber treatment from fines production. Despite the observed differences in fines character it is therefore only possible to control pulp and paper properties by targeted use of fines to a very limited extent. Alternative refining methods and/or separation and targeted addition of fines would be needed to open up new possibilities to better use of the potential of fines in current papermaking processes. One option to selectively add fines to the papermaking furnish is the introduction of microfibrillated celluloses (MFC), which could also benefit from the use of the presented characterization methods.

6. CHARACTER OF CHEMICAL PULP FINES INFLUENCED BY CHEMICAL MODIFICATION (*PAPER IV*)

The character and the resulting technological properties of fines influenced by mechanical modification by refining were discussed in the previous chapter. In this chapter the influence of a chemical modification – in this case cationization - of fines on technological properties is evaluated. In *Chapter 6.1* the cationization protocol is introduced briefly. *Chapter 6.2* deals with the effects of positive charged fines on pulp and paper properties. In addition to the content covered in *Paper IV* in *Chapter 6.3* the influence of refining of cationized fibers on the morphology of the produced fines is discussed.

6.1. Cationization of fines

The cationization procedure is described in detail in *Paper IV*. Basically EPTMAC (2,3-Epoxypropyl trimethyl ammonium chloride) is added to bleached softwood kraft (BSK) primary fines in suspension (1%) and reacted for 15 hours at 40°C under alkaline conditions (see also Odabas et al. 2016; Odabas 2016). Finally cationic functional groups are bound covalently to the cellulose molecules (see *Figure 6-1*). In parallel the chemical is also consumed by water. A degree of substitution, of 0.034 was achieved for the fines, similar as for cationic wet end starch.

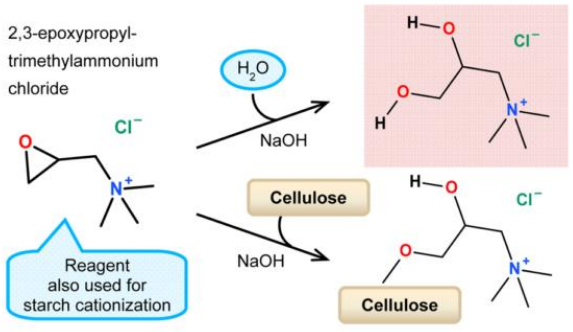


Figure 6-1: Cationization reaction of cellulose with EPTMAC (2,3-epoxypropyltrimethylammonium-chloride) and side reaction with water (Odabas et al. 2016).

6.2. Impact on sheet properties (*Paper IV*)

Sheet preparation and testing is described in detail in *Paper IV*. In principle 5% cationized BSK fines were added to refined fibers with fines included (A,B), to refined fibers with fines removed (C) as well as to unrefined fibers (D). The pulp and paper properties resulting from these combinations were compared to references (Ref AB, C, D) adding 5% unmodified BSK fines instead of the cationized ones (*Figure 6-2, Figure 6-3*).

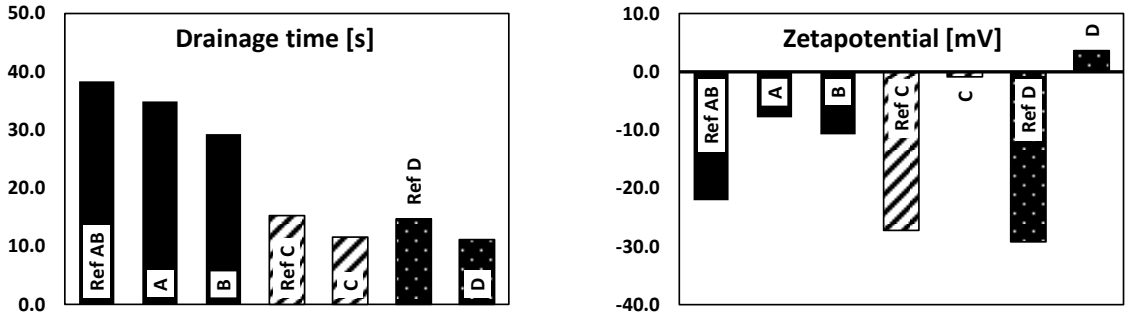


Figure 6-2: Pulp properties: Drainage time (left) and Zeta-potential (right); References (Ref. AB,C,D) contained unmodified fines and (A-D) cationic fines replacing the unmodified fines; black bars: fines were added to refined pulp (fibers + fines); striped bars: fines were added to refined fibers (fines removed); dotted bars: fines were added to unrefined fibers.

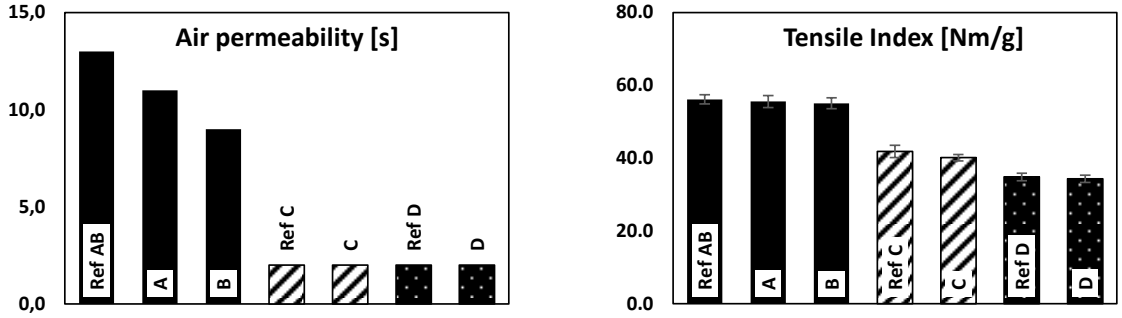


Figure 6-3: Paper properties: air permeability measured in Gurley seconds (left) and tensile index (right); References (Ref. AB,C,D) contained unmodified fines and (A-D) replacement of unmodified fines by cationic fines; black bars: fines were added to refined pulp (fibers + fines); striped bars: fines were added to refined fibers (fines removed); dotted bars: fines were added to unrefined fibers.

No significant effect on paper strength properties was observed when adding cationic (A-D) in place of unmodified fines (Ref AB – D) (see *Figure 6-3 right*). Dewatering and air permeability was improved for all blends with cationic fines compared to their references, regardless whether cationic fines were added to unrefined, refined fibers or refined fibers plus fines (*see Figure 6-2 left and Figure 6-3 left*). The reason that there is no difference visible in air permeability comparing C and D with their references, is the measurement limit of the device.

The changes in air permeability and dewatering can be explained by electrostatic interactions between positive charged groups on the cationic fines and negative charged groups on fibers and in case of A and B also on unmodified fines. The order of addition plays a role. A higher effect on air permeability and dewatering was achieved when the cationic fines were added prior to the unmodified ones, which was the case in trial B. The cationic fines then would adhere to the negative charged fibers followed by the adherence of anionic fines added afterwards. In trial A cationic fines were added to the suspension with unmodified fines already present, thus cationic charges are neutralized by flocculation with unmodified fines present in the pulp, which presumably led to a reduced attachment to the fibers. These cases are illustrated in *Figure 6-4.*

Strength was not improved by cationic fines although some studies of cationic modification of fibers showed different results (Gruber 2002; Krause, Käufer, and Schemp 1981; Ma et al. 2010; Montplaisir, Chabot, and Daneault 2006). Based on the findings of this study, the improvement of strength properties by the cationization of fibers or the whole pulp seems to results from side effects rather than from an effect that can be directly assigned to the cationic charges. Higher strength might be achieved due to the improved retention of fines in cationicly modified pulps. Cationic modification not only takes place on the surface of the fiber but also in the bulk. Due to this effect, fibers become more flexible, implicating that more interfiber joints can be formed. This flexibilization due to cationic charges is termed as a spacer effect (Gruber 2002).

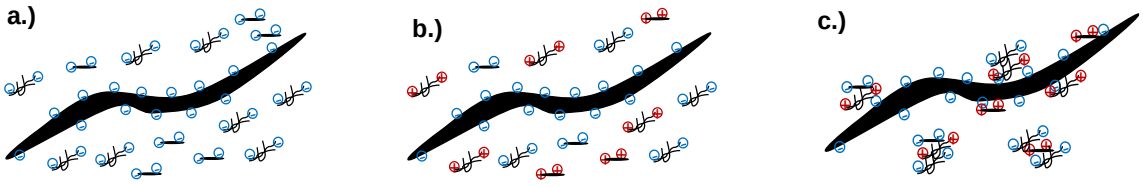


Figure 6-4: Illustration of pulp suspension containing fibers and (a) unmodified fines; (b) addition of cationic fines and (c) its effect on flocculation, leading to lower dewatering resistance and air permeability

6.3. A combination: Cationization and refining:

Direct cationic modification of fines did not change the morphology of those fines as illustrated in *Figure 6-5*. For cationized fibers an improvement in tensile index was reported and related to the aforementioned spacer effect. Compared to unmodified fibers, cationic fibers would have more loosely bonded areas within the fiberwall and also on the fiber surface as illustrated in *Figure 6-6*. Refining BSK fibers cationized with EPTMAC (DS 0.035) and unmodified fibers with a Valley beater for 30 minutes and subsequent fractionation of the fines fraction showed a distinct difference in morphology comparing fines from cationized fibers to fines from unmodified fibers (see *Figure 6-7*).

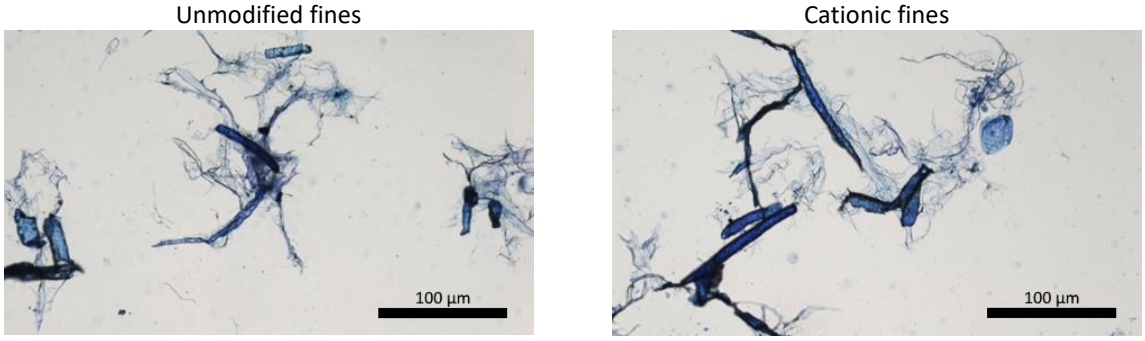


Figure 6-5: Microscope images of unmodified (reference) fines and cationic fines.

As the refining treatment was the same for the unmodified and cationized fibers, this difference can be exclusively related to the spacer effect of cationic groups in the fiberwall creating predetermined "breaking points". The changes in morphology were quantified with the microscopy method (see *Paper I*). Size distributions indicated a larger size of fibrillar material and smaller size of flake-like material, both contributing to the higher fibril area achieved for these cationic fines produced by refining cationized fibers compared to the fines produced applying the same refining conditions to a reference pulp shown in *Figure 6-8*.

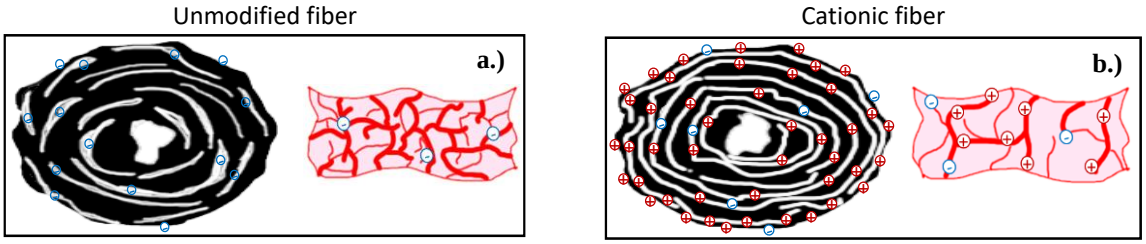


Figure 6-6: Illustration of fiber cross-section and the possible effect of charges on the topology of the outermost fiber wall; tightly bound areas (dark red), loosely bound areas (light red); unmodified fibers negatively charged (left), and cationized fibers (right), proposed effect of cationic charges acting as a spacer in the fiber wall.

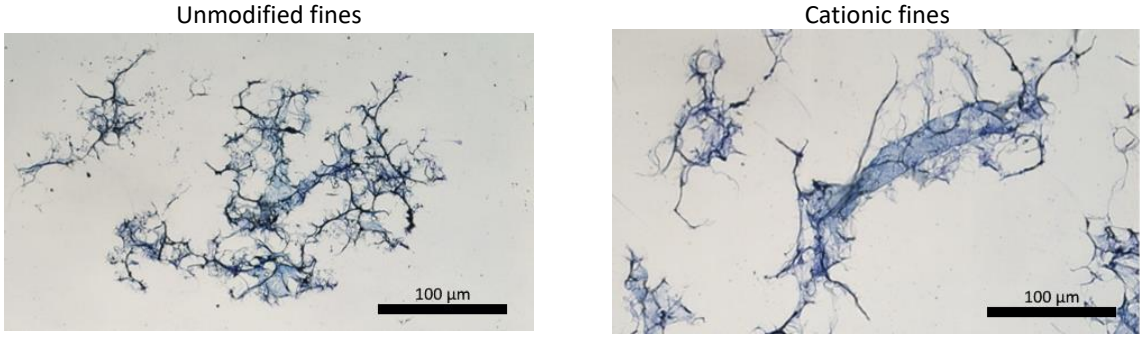


Figure 6-7: Morphology of fines originating from refining unmodified (reference) BSK fibers (left) and BSK fibers cationized prior to refining (right).

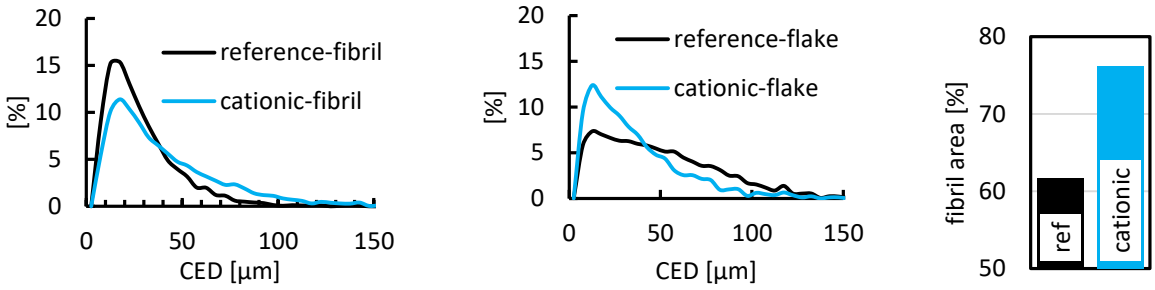


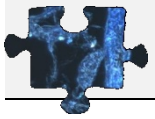
Figure 6-8: Particle size distribution of fibrillar material (left) and flake-like material (middle), fibril area (right); unmodified (reference) fines black, cationic fines (blue). Cationic fines show larger fibrillar material and smaller flake-like material as well as a higher fibril area compared to the reference

6.4. Summary

Cationization of the fines fraction of pulp showed no impact on paper strength when these cationized fines were added as an additive to unmodified fibers and fines, but a reduction in drainage time and a higher air permeability was observed. These effects were related to

electrostatic interactions between the negatively charged unmodified material and the cationized fines. It was concluded that cationic groups itself per se do not contribute to paper strength.

Cationization of fibers prior to refining changes the morphology of the produced fines. These changes in morphology were related to the so-called spacer effect introduced by cationic groups in the fiberwall, weakening bonds and thereby creating predetermined "breaking" points different to the unmodified fibers. These differences in morphology of fines most probably will affect paper strength properties, as it was shown in *Chapter0* and *5.3* that higher fibrillation of unmodified fines improves strength.



7. CONCLUSIONS AND OUTLOOK

7.1. Methods for fines characterization

Two methods for fines characterization were developed: A microscopy approach for the evaluation of the morphology of fines (*Paper I*) as well as a novel approach for the measurement of the WRV of fines. (*Paper II*). These two methods are applicable for all types of pulp fines independent of differences in color, swelling, charges or the pulping process. Also application of these two methods to microfibrillated celluloses (MFC) is possible. These two methods allow to relate fines characteristics to their impact on technological properties in papermaking, contrary to established methods such as crill, which seems to fail in detecting microfibrillar material, or secondary fines content, which describes the fines fraction gravimetrically but fails in distinguishing between the macrofibrillar backbone and microfibrils. The characterization methods and related technological pulp and paper properties are summarized in *Figure 7-1.*

A high surface area and strong swelling behavior are the characteristics of fines affecting pulp and paper properties. These properties can only be determined by the developed methods. For other applications also characteristics such as crill or secondary fines content are of relevance. Application of these four methods in the characterization of the fines fraction of a given pulp allows a thorough description, as only the combination of these methods allows a detailed analysis of the character of the fines fraction. These methods also should have a high potential in describing the properties of MFC qualities, allowing a targeted development of this material, which shows similar characteristics compared to the fines fraction in conventional paper pulps.

The determination of fibril area via the microscopy method is of special importance as it is capable to distinguish between macrofibrillar and microfibrillar fines and gives a quantitative, reliable information on the degree of microfibrillation, which was shown to have a large impact on pulp and paper properties. Microfibrillation is also influenced by mechanical treatment of fibers in refining with and without the combination with chemical modification (cationization). Generally chemistry of pulp fibers is influenced throughout the whole pulping process and differences in mechanical treatment occur when refiner settings are changed by e.g. use of refiner or refiner plate designs. Unfortunately the influence of these changes in process parameters on pulp and paper properties is currently only monitored by investigation of the whole pulp comprising fibers and the fines fraction. A detailed morphological characterization of the fines

fraction would help to establish a better knowledge of the effects of either mechanical or chemical treatment not only on fines, but also on fibers, as the morphology of fines is related to chemistry and morphology of the fibers, as obvious from the changes occur in fines morphology when fibers were cationized prior to refining.

Besides the fibril area the microscopy method is capable to determine other morphological parameters of fine material, similar as a fiber analyzer does for fibers. These additional possibilities were only touched by measuring aspect ratio and size after separation into flake-like and fibrillar parts of fines. There are also other aspects, as measuring the size, shape and solidity of an entire connected fine particle, which might be relevant e.g. for barrier properties and coverage. The manual sample handling still limits the abilities of this microscopy approach, as achieving a homogeneous distribution and optimum concentration of fine material deposited on a glass slide is challenging. Automatization of this procedure would open further possibilities for a more accurate and in depth characterization of the fines fraction of pulps.

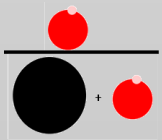
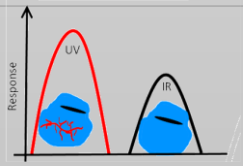
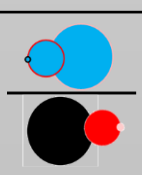
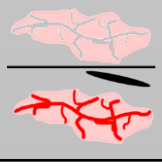
	Unit	Illustration	Description	Related Properties
Secondary fines content	%		Mass of secondary fines related to total fines	
Crill	-		Additional response (Scattering/Absorption) of UV related to IR	
WRV	-		Mass water retained per mass of dry sample	• Drainage resistance • Tensile Index • Scott Bond • Air Permeability
Fibril Area	%		Percentage of area microfibrillar fines divided by total fines	• Tensile Index • Scott Bond

Figure 7-1: Summary of characterization methods for fines and pulp and paper properties related to the measured characteristics.

7.2. Properties of fines in paper making applications

Fines are affecting pulp and paper properties mainly due to their high surface area and swelling behavior. The first aspect leads to improved bonding and therefore fines have a higher impact on tensile index and Scott Bond compared to fibers. Swelling also has a positive effect on strength development by increasing the surface and conformability of the fines. In addition swelling increases drainage resistance and decreases air permeability. The impact on these properties is further increased due to the small size of fines. They are capable to fill even the smallest spaces, where fibers are not able to have an influence due to their much larger size. Fines allow dense packing similar to the densest sphere packing concept, which can only be achieved when smaller spheres are filling up void spaces. This feature further enables fines to improve bonding strength while increasing sheet density (see Figure 7-2). These properties of fines were already investigated e.g. by Retulainen et al. (1993), while a more in depth differentiation of the influence of fines character is missing. Fines character was studied in this thesis regarding three different aspects:

- Influencing the fines character by applying different refiner settings (*Paper III*)
- Comparison of fines and fibers from different pulping processes (BSK and BSSU)
- Cationic modification of fines (*Paper IV*)

For a given pulp source, varying the refiner settings yields fines with differences in their character regarding microfibrillation. An increase in microfibrillation can be linked to pulp and paper properties and shows similar effects on technological properties in papermaking than when fines were compared to fibers (see *Figure 7-2*). A higher degree of microfibrillation increases strength properties but in parallel also deteriorates drainage resistance, while lowering air permeability. Thus microfibrillation is a key characteristic of the fines fraction.

The comparison of BSK and BSSU fibers and fines leads to an interesting conclusion. While exchanging BSSU fines by BSK fines yields a higher drainage resistance and lower air permeability, due to higher swelling and microfibrillation of BSK fines, these effects are not seen exchanging BSSU fibers by BSK fibers. Only the effect of the material itself yielding higher tensile index for using either BSK fibers or fines instead of the corresponding BSSU fraction remains. Consequently on the one hand the effect of fines on pulp and paper properties seems to be coupled to inherent material properties and on the other hand to the potential of fines being capable to occupy spaces where fibers are hindered by their size and lower conformability.

Apart from different pulping processes cationization of fines changes also the material chemistry, while not influencing the morphology. Due to cationic-anionic charge interactions inducing flocculation, adding cationic fines compared to the unmodified ones bring a reduction in drainage resistance accompanied by an increase in air permeability, while no effect on strength properties was observed (see Figure 7-2).

	Fines compared to fibers	Increase in micro fibrillation	BSK instead of BSSU fines	BSK instead of BSSU fibers	Cationic fines compared to unmodified
WRV	+ +	+ +	+	~	-
Drainage resistance	+ +	+ +	+ +	~	- -
Density	+	~	~	~	~
Air Permeability	- -	- -	- -	~	+ +
Tensile Index	+	+	+ +	+ +	~
Scott Bond	+ +	+ +	+	~	~
Tear strength	-	-	-	+ +	~

Figure 7-2: Properties of fines in papermaking classified in different categories compared against each other. (+) indicates an increase, (-) decrease in a property and (~) that the property is not influenced. The influence of fines on drainage resistance is highlighted in red as drainage resistance, independent of the paper grade, is always targeted to be on a low level. The impact on tensile index is highlighted blue as an improvement in tensile index is always seen positive.

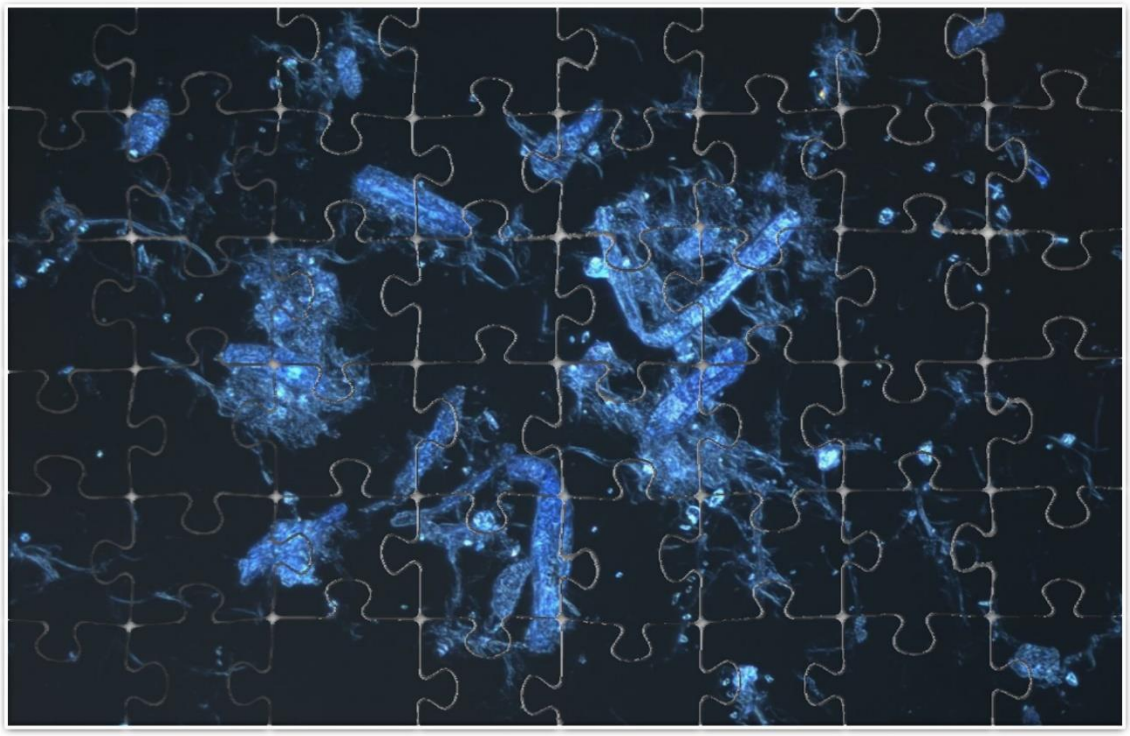
In paper industry required properties are defined by the paper grade, depending on the application. Independently, dewatering is always aimed to be fast in order to be able to increase machine speed. Achievement of high strength properties or equal strength properties at lower material input are further aims independent of the paper grade to be produced, reasoned by runability issues in paper production and further converting steps, as well as the end use of the product. When it comes to the fines fraction in pulps high strength can be obtained adding fine material, but only by compromising dewatering (*Figure 7-2*). In a simplified approach therefore strength is easier to generate by exchanging the pulp grade (BSK vs. BSSU) than by addition of a higher quantity or more fibrillated fines. As fines nevertheless have the unique property to be able to occupy spaces a fiber is too large for, they generate increase in strength an equal amount of

fibers would not be capable of. Thus when BSSU pulp is exchanged by BSK a higher amount or higher fibrillated BSK fines would lead to an additional improvement. The generation of highly fibrillated fines with a limited effect on drainage resistance might be possible by cationizetion of fibers prior to refining or by the addition of MFCs. As shown in *Chapter 6.3* these fines produced from cationized fibers show an increase in microfibrillation. Combining cationization with microfibrillation might level out the unwanted increase in drainage resistance, while still improving strength properties in sheets were those fines could be added as an additive.

A targeted production of fines shows potential as the character of this material has a great impact on the final pulp and paper properties (*Figure 7-2*). However such a control of properties by the variation of fines character and amount can only be achieved by uncoupling fiber treatment in refining from fines production. Therefore an alternative refining technology would be needed allowing the treatment of fibers without fines production and a targeted dosage of tailored fine material, such as MFC produced in a separate aggregate. In addition to the capability to tailor fines properties this approach would also lead to stronger fibers, as these fibers would no longer be weakened by the abrasion of material from the fiber wall. Hence this approach would imply the development of an entirely novel refining strategy, another approach could be the separation of the fines from the fiber fraction after refining, followed by systematic addition.

Thus pulp fines and their “relative” MFC are interesting materials, characterized by a high water absorption capacity, high surface area and aspect ratio while relatively small in size. These materials might however not be able to unfold their full potential when simply applied in the paper making furnish as their high swelling potential is an unwanted side effect. Their high surface area might be more beneficial when fines would be used as a carrier, for example for fillers in papermaking, but also for other applications outside the paper industry. The high water absorption capacity of fines implies also absorption of any other hydrophilic liquid. This characteristic might be useable as a separation technique, for example to separate miscible or fine distributed liquids. The potential of MFC and fines as reinforcing additive in composites is already a topic in research as the high aspect ratio of this material has the potential to yield high strength. Due to their characteristics fibrillar fines and relatecd MFC products might be applicable as an additive in barriers, making especially use of their heterogeneous but at the same time connected appearance. The macrofibrillar backbone has a stabilizing and self-retaining functionality and the microfibrils are cross-linking and form a network.

In this thesis novel methods capable to characterize all types of pulp fines were established. The effects of fines character on pulp and paper properties were thoroughly investigated and led to a better understanding of this material. So to summarize we can complete this puzzle:



But more puzzles have to be solved in order to make use of the full potential of this material, such as establishing a feasible separation technology, capable to separate fibers and fines or to develop a novel refiner concepts capable to uncouple fiber treatment from fines production, aiming for a better control of paper properties in parallel to an ecological and economical improvement.

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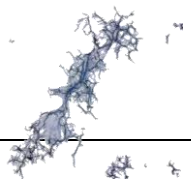

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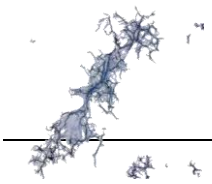

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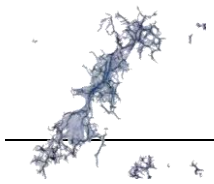

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APPENDIX

Supplementary information to Chapter 5

Property	Unit	Fines										Fibers					Reference
		1	2	3	4	5	6	7	8	10	3	5	8	10	
Density	g/cm³	1.01	1.01	1.02	1.01	1.02	1.04	1.02	1.02	1.00	0.99	0.99	1.00	1.00	0.66
Opacity	-	0.98	0.96	0.97	0.98	0.96	1.01	1.00	1.01	1.00	1.01	0.99	1.00	1.00	61.42
Scattering Coefficient	-	0.95	0.93	0.92	0.95	0.92	1.01	1.00	1.01	1.00	1.10	1.07	1.03	1.00	18.38
Absorption	-	0.96	0.97	0.94	0.89	0.91	0.96	0.98	1.04	1.00	0.61	0.58	0.89	1.00	0.255
Air Permeability	ml/min	0.69	0.14	0.47	0.38	0.42	1.26	1.91	1.48	1.00	1.53	1.11	1.43	1.00	155.62
Tensile Index	Nm/g	1.07	1.15	1.14	1.13	1.17	0.99	0.98	1.00	1.00	1.23	1.26	1.01	1.00	55.49
Elongation	%	1.12	1.12	1.03	1.12	1.08	0.96	0.96	0.99	1.00	1.16	1.10	1.00	1.00	2.579
E-Modul	N/mm²	1.02	1.05	1.07	1.03	1.07	1.14	1.02	1.08	1.00	1.08	1.14	0.98	1.00	5.014
TEA	J/g	1.21	1.27	1.16	1.29	1.25	0.95	0.93	0.99	1.00	1.41	1.37	1.00	1.00	1.019
Scott Bond	J/m²	1.09	1.33	1.12	1.11	1.19	0.82	0.80	1.05	1.00	0.93	1.01	0.94	1.00	346.11
Elmendorf	mN	0.93	0.84	0.92	1.03	0.89	0.99	1.07	0.97	1.00	1.54	1.41	1.06	1.00	225.68
WRV	g/g	1.04	1.10	1.05	1.04	1.07	0.95	0.99	0.99	1.00	0.90	0.94	0.93	1.00	1.228
Drainage resistance	°SR	1.09	1.50	1.17	1.12	1.28	0.90	0.96	0.95	1.00	0.92	0.98	0.91	1.00	21.08
Zetapotential	mV	0.68	0.65	0.66	0.79	0.65	0.87	0.76	0.88	1.00	0.97	0.92	0.99	1.00	-23.29

Publications

I Mayr, Melanie, Eckhart Rene and Bauer Wolfgang (2017) "Improved Microscopy Method for Morphological Characterisation of Pulp Fines." *Nord. Pulp. Pap. Res. J.* 32 (2): 244–52. doi:10.3183/NPPRJ-2017-32-02-p244-252.

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Improved microscopy method for morphological characterisation of pulp fines

Melanie Mayr, Rene Eckhart and Wolfgang Bauer

KEYWORDS: Morphology, Fines, Microscopy, Flow cell analyzer, Size, Shape, Image analysis

ABSTRACT: It is widely accepted and discussed in the literature that not only fiber properties but also fines properties determine the final paper quality. While fiber morphology is well studied, morphological characterization of fines is usually restricted to the quantity of fines in a certain pulp since it is quite difficult to measure detailed morphological properties of the fines. They have a broad size range, a high surface area, show different optical properties within the fines fraction and are irregular in shape. In this article an optical method is introduced which allows the evaluation of differences in the morphology of fines. Quantitative information regarding particle size and shape can be obtained. The effect of optical properties on size measurement of different types of fines is minimized by a special sample preparation technique. The results of the new method are compared to those of a commercial flow cell based fiber analyzer. It was found that the flow cell analyzer failed in the detection of a large portion of fibrillar fines.

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Introduction

Fiber morphology of paper pulps has a significant influence on the properties of the final product and can be described well using a number of commercially available fiber analyzers. In the past several researchers have shown that not only fiber but also fines properties determine the final paper quality (e.g. Bäckström et al. 2008; Chauhan et al. 2012; Ferreira et al. 2000; Htun and Ruvo 1978; Lin et al. 2007). Fines are most commonly defined as all particles in a papermaking furnish able to pass through a 200 mesh screen (76 μm hole diameter) according to SCAN-CM 66:05. Fines definition with commercially available fiber analyzers is different, categorizing particles smaller than 200 μm in length as fines (ISO 16065-2). Fines are further distinguished in primary and secondary fines (Krogerus, et al. 2002). Primary fines are those fines present after the pulping and bleaching process and mainly consist of ray cells, parenchyma cells, fragments of the middle lamella and only a small portion of fibrils. Secondary fines are fines produced during refining and fibrils are the main component. Because of their different nature, they have different effects on paper properties. Primary fines are acting more or less as fillers and contribute to optical properties (Yin, et al. 2013) whereas fibrillar secondary fines have a strong impact on strength properties (Lin et al. 2007; Bäckström, et al. 2008; Yin et al. 2013). Typically both primary and secondary fines are found in a pulp fraction and cannot be evaluated separately. Further primary fines also include fines with fibrillar nature as well as secondary fines include fiber fragments. For these reasons the classification into primary and secondary fines is not precise enough when it comes to analytical characterization of fines. Distinguishing between flake–like and fibrillar material is a more appropriate definition considering the properties of fines. Besides the differences in morphology, these two categories differ in their chemical composition (Retulainen et al. 2001; Mosbye 1999; Kangas and Kleen 2004; Bäckström et al. 2008), swellability (Luukko, Maloney 1999; Mosbye 2003) and thus their effects on paper properties. While classification into different types of fines and their impact on paper properties is widely accepted, only a few studies deal with the morphological characterization of fines (Luukko 1999; Retulainen et al. 2002; Yin et al. 2013) in more detail. A review by Hyll (2015) summarizes the methods for size and shape characterization of fillers and fines. He found that no available method is capable of determining both size and shape of fines quantitatively.

Methods concerning morphological characterization can be roughly separated in gravimetrical and optical methods. A rather different method being neither gravimetrical nor optical is the electrical sensing zone method, which was applied for pulp fines by Ferreira et al. (2000). The changes in electrical conductance when a particle suspended in a conductive fluid passes a small gap are measured and size distributions are obtained.

Gravimetrical methods using sieving techniques, e.g. Bauer McNett, classify particles also according to their size. This technique is limited in resolution based on the number of screens and has other restrictions as well. Whether a particle contributes to one or another class is not only dependent on particle size but also on shape, flexibility and swellability of the particle.

When it comes to optical methods one has to consider that all optical methods are relative methods, as particle properties like surface roughness, refractive index, size, shape and color influence the optical response. Optical methods can be distinguished into non-imaging and imaging methods. Non–imaging methods are based on different interactions of particles and light such as e.g. attenuation, scattering or reflectance. In comparison to imaging methods, they can operate over broader size ranges and have higher resolution. Especially the crill technique has to be mentioned in the field of the optical non - imaging methods as it is the only commercially available technique addressing the measurement of small fines, beyond the detection limit of optical imaging systems (Williamson and Back 2014). The crill

Nordic Pulp & Paper Research Journal Vol 32 no 2, 2017 --- DOI 10.3183/NPPRJ-2017-32-02-p244-252

measurement is based on the optical response of a suspension illuminated with different wavelengths of light. While the IR source roughly detects only fibers the UV light source gives additionally response to smaller particles as fibrillar fines. The ratio between the response given by the UV light source and the response from the IR light source is the so called 'crill value' (Osong et al. 2014). Still, information about size and shape cannot be obtained.

Optical imaging methods allows combining information about size and shape, measuring the properties of each single particle. Due to the highly heterogeneous nature of fines, these methods are considered advantageous over non-imaging approaches.

Flow microscopy is already widely used in pulp and paper industry. Fiber analyzers equipped with a flow cell were especially developed for morphological fiber characterization. Fiber analyzers from different manufacturers work all based on a similar principle. They are equipped with a transparent flow cell and images of the flowing suspension of particles are captured based on transmitted light microscopy. Resolution is the main limiting factor when it comes to fines. With the development of optical imaging technology today's fiber analyzers are capable to evaluate fines down to the single digit micrometer scale. Nevertheless, imaging is not only an issue of size. The contrast has to be high enough to recognize particles and separate them from the background (Hyll 2016). For highly swollen particles (like fibrillar fines) this contrast is often too low for such systems especially when the objects to be measured are out of focus. Even when these swollen fines can be detected, dimensions are oversized. A method presented recently uses an image stream flow cytometer, detecting particles simultaneously in different illumination modes: brightfield, darkfield and fluorescence (Hyll 2016). The different response of the particles to the illumination modes allowed to distinguish between fillers and fines and imaging enables the measurement of size and shape. This method, although higher in resolution and better in contrast, still shows limitations in resolving highly swollen fines, as the refractive index of such particles is close to water, resulting in a still too low contrast for detection. Another approach to analyze fines suspended in water with a static microscope was introduced by Hafrén et al. (2014), where the identification and analysis of fines was based on the intrinsic auto fluorescence of the lignin contained in the fines. This method works well for lignin rich mechanical pulp fines, but cannot be applied to bleached chemical pulp fines.

Fines also can be analyzed in dry state using static microscopy. Luukko et al. (1997) developed an imaging method to distinguish flake-like and fibrillar material based on their difference in gray level. Imaging was done with a conventional light microscope in the bright field mode. Luukko (1999) found a linear relationship between tensile index and fibrillar content of sheets made of 100% fines. Although evaluation of length for fibrillar fines and area for flake–like fines was implemented in Luukko's method, in most publications based on this method, only the fibrillar content was used for fines characterization while size and shape was not considered (Krogerus, et al. 2002; Mosbye 2003; Taipale et al. 2011; Yin, et al. 2013). Retulainen et al. (2002) characterized size and shape of fines, but did not distinguish between flake–like and fibrillar material. In both methods from Luukko and Retulainen samples were stained with methylene blue to achieve a high contrast necessary for the detection of fibrillar fines. Methylene blue sorption however depends on the anionic group content of fines (Fardim and Holmbom 2003) and thus pulp fines from different origins might not be directly comparable. As already mentioned fibrillar and flake–like fines are not only different in their morphology, but also in their chemical composition and thus their influence on paper properties. Size and shape of fibrillar fines were never investigated quantitatively and thus it remains unclear how these parameters affect paper properties. This paper describes a method that allows a detailed characterization of pulp fines by combining quantitative information on size and shape (aspect ratio) with the information on the character of fines (fibrillar fines, flake–like fines), with minimized impact of contrast issues.

Materials and Methods

Pulp samples and fines separation

In this study four different unrefined pulps and one pulp at four different refining intensities were evaluated (see *Table 1*). These pulps were fractionated at 1% dry content with a lab-scale pressure screen. The pressure screen was equipped with a perforated plate (hole diameter 100 µm). The material passing this plate was defined as the fine fraction. A comparison between the fraction generated by the pressure screen and the fraction generated with the BDDJ method, using a 76 µm screen (SCAN-CM 66:05) is shown in the appendix (*Fig A1*). A fines suspension with approximately 0.001% dry matter, was obtained after fractionation and the fines were allowed to settle three days in 60 l barrels. The supernatant was removed and a dry content of approximately 1% was achieved. The removed water does not show visual turbidity. Eventual colloidal particles not affecting turbidity are not considered, as such particles would neither be recognized by the applied methods.

Table 1 - Pulp description and abbreviations for fine fractions.

Pulp description	Abbreviation
unbleached softwood kraft	UBSK
bleached softwood kraft	BSK
bleached sulfite HW/SW 20/80	BSSU
pressurized ground wood	PGW
bleached sulfite HW/SW 10/90 unrefined	SU - 0
bleached sulfite HW/SW 10/90 refined 90kWh/t	SU - 90
bleached sulfite HW/SW 10/90 refined 110kWh/t	SU - 110
bleached sulfite HW/SW 10/90 refined 130kWh/t	SU - 130

Nordic Pulp & Paper Research Journal Vol 32 no 2, 2017 --- DOI 10.3183/NPPRJ-2017-32-02-p244-252

Static (light) microscopy

Staining procedure

Samples were stained with methylene blue (CAS-Nr.: 122965-43-9) in suspension to enhance the contrast of fines relative to the background (Luukko, et al. 1997). Depending on the pulp type, adsorption of methylene blue varied and the results for the different pulps were not comparable. Most probably the differences are related to the differences in their chemical nature affecting the charge content (methylene blue adsorption was used as a fast determination method for fibre charge (Fardim and Holmbom 2003)). Also for fibrillar and flake–like material of the same pulp sample coloring is different (e.g. for bleached softwood kraft fines, see *Fig 1a*). To overcome this limitation, trials to minimize these differences in dye adsorption were conducted. In a first stage various dyes, addition of salt (NaCl) and variations in pH were tested. None of these adjustments resulted in a uniform coloring of the samples and therefore they are not discussed further in this article. In flotation trials using fines, we found out that dosing of crude tall oil, obtained from kraft process (Zellstoff Pöls AG, EC Number: 931-433-1) prior to staining improves dye adsorption independently from the pulp or fines type (*Fig 1b*).

The component of the crude tall oil actually responsible for the enhanced dye adsorption, could not be identified. Observation under the microscope showed that methylene blue is attracted by the tall oil droplets in the tall oil – water emulsion, probably by carboxyl groups of fatty acids, contained in the tall oil. During the drying process, water evaporates and tall oil droplets adhere to the fines and form a film on the fines surface. For the preparation of a tall oil emulsion 0.01 g commercially available crude tall oil was mixed with 5 g deionized water in a test tube. The mixture was emulsified at 80°C in an ultrasonic bath for 30 min. A 0.01% fines suspension was prepared in another test tube. 0.06 g tall oil - water emulsion was added to 5 g of the fines suspension and homogenized by vigorous shaking. 0.1 g methylene blue (1 wt% in water) was added and homogenized again.

Sample preparation and image acquisition

Three droplets of the prepared fines suspension were placed on a microscope slide (76x26 mm), fixed with a cover glass (60x24 mm) and dried on a heating plate. Given that the tall oil emulsion and dye is already prepared sample preparation will take approximately one hour and drying on the heat plate 30 min. A conventional transmission light microscope (Leica 301-371.010) equipped with a standard CCD camera (Jai AM-200GE/AB-200GE) and an automated stage control (Märzhäuser Multicontrol 2000) was used. Automated capturing of 700-800 single images per microscope slide (1600x1200 pixels per image; image area: 1380x1035 μm^2; resolution 0.86 µm/pixel), will last approximately 30 min. The camera and the stage control were operated by the open source software ImageJ.

Several exemplary images of fibrillar fines are shown in *Fig 2a-d*. Due to the tall oil addition before dyeing, also small fibrillar fines are visible. Fibrillar fines are usually discussed as elongated particles having a high aspect ratio. Only very rarely they are described as aggregates or networks (Cheng et al. 2007), Our measurements showed that, fibrillar fines from chemical pulps form connected networks (*Fig 2a–c*) rather than singular fibrils as is the case for PGW fines (*Fig 2d*). These networks of chemical pulp fines tend to have a "backbone", which is a thick fibril bundle (in this article referred to as macrofibrillar backbone or macrofibrils). Smaller fibrils or fibril bundles are partly detached from that backbone, but still connected. The structure can be compared to externally fibrillated fibers, although the structure of fibrillar fines is more branched and branches are longer in relation to the backbone. Further, some of the attached fibrils can again form a macro fibrillar structure. In these examples, bleached softwood kraft fines (BSK) form the largest fibrillar networks, with a high share of micro fibrils. Bleached softwood sulfite fines (BSSU) form smaller networks, which are less branched, but also show a high share of micro fibrils. Bleached hardwood kraft fines (BHK) show a similar network structure than BSSU fines, but have a lower share of micro fibrils. Due to the sample preparation, the fibrillar structures are rather fixed between the microscope slide and the cover glass and microfibrils adhere also to the glass surface, by capillary forces. Nevertheless it cannot be excluded that during the drying process some microfibrils condense with the backbone and may affect the morphology of fibrillar fines. However in the microscopic images (*Fig 2*) the backbone is visibly surrounded by microfibrils, which allows the assumption that this effect is a minor one.

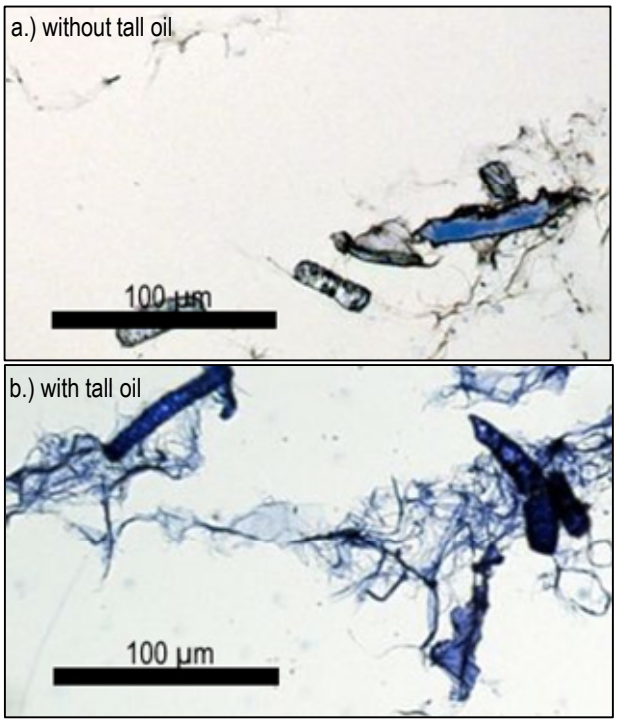

Fig 1 - BSK primary fines stained with methylene blue: a) without addition of tall oil; b) with addition of tall oil

Nordic Pulp & Paper Research Journal Vol 32 no 2, 2017 --- DOI 10.3183/NPPRJ-2017-32-02-p244-252

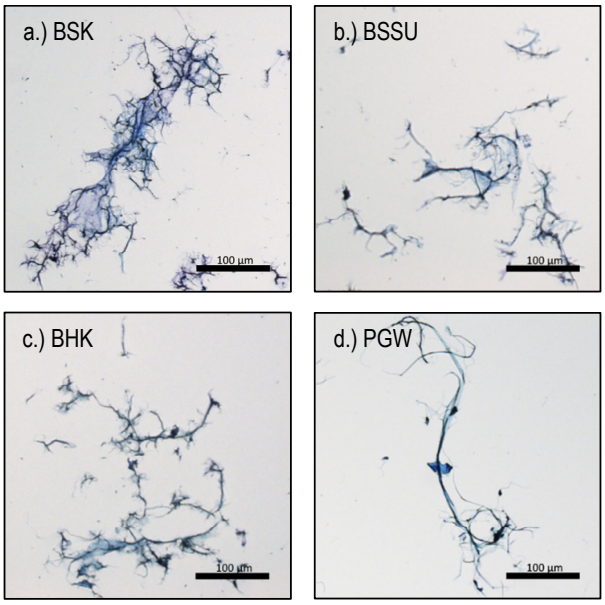

Fig 2 - Fibrillar fines from refined bleached chemical pulps (a) BSK, b) BSSU, c) BHK) and fines from mechanical pulp d) PGW

Image processing and calculation of size and shape parameters

Given these observations, it is evident that it is not straightforward to describe the morphology of fibrillar fines on a similar basis than for fibers, where length, width, aspect ratio or the external macro fibrillation of the fibers are determined. An image analysis routine was developed using MATLAB, with the aim to classify and quantify regions of different morphology. For better visualization only a detail of the 1380x1035 µm^2 microscope image, corresponding to 10% of this image size is shown. The RGB images (see *Fig 2a*) are transferred into grayscale images selecting the red channel of the RGB image, which shows the highest contrast between background and particle (see *Fig 3a*).

As a first step in image processing background correction was implemented to overcome illumination differences between the center and the border areas of the grayscale images. Although the effect of uneven contrast was reduced by background correction and an improved staining procedure, an eventual variation in contrast and particle size due to the material and the sampling procedure may lead to differences in detection applying a global thresholding algorithm. Local thresholding is less sensitive to such variations, but usually needs much longer run time. Lee et al. (1990) compared six different global thresholding techniques and concluded that Otsu's method (Otsu 1975) shows good performance considering such variations. The separation gray tone value (threshold) is defined in Otsu`s method as the value where the intra–class variance of the gray tone values in the histogram (frequency distribution of gray tone values) is at a minimum.

In this image processing routine for thresholding of microscope images the function "multithresh" of the Image Processing Toolbox in MATLAB applying Otsu's method, for multilevel thresholding was used. The obtained threshold values separate the histogram of the grayscale microscope image in three regions (see Appendix, *Fig A2*). The regions correspond to gray tone values for the background, for flake–like material and for fibrillar material, allowing a separation of these different classes. Thereby three images were obtained; the background image, the image containing flake–like and the image containing fibrillar material. For better visualization these three separated images are merged (see *Fig 3b*). The black region represents the background, the magenta region the fibrillar material and the turquoise region the flake-like material. The material classified as flake-like material comprise of ray cells and parenchyma cells but also contains the macrofibrillar backbone of fibrillar fines, when applying the described thresholding procedure.

The resolution sets the limit for the assignment of gray tone values in transition areas (fibrillar/background; flake-like/background; fibrillar/flake-like), as a pixel in these regions represents an average of gray tone values corresponding to the one and the other region. Therefore the outermost pixels of all detected regions - these transition areas – are discarded applying the operation "imerode" in MATLAB. The size of small singular fibrils as well as flake-like particles will be overestimated for similar reasons, and above of that such small particles are hard to assess visually, whether these particles are flake-like, fibrillar or just impurities (e.g. dust, filler). Therefore it was decided to not consider objects smaller than 40 pixels. After applying these criteria every separate segment is considered a distinct particle (see *Fig 4a*). The skeleton (connected one pixel line) of these particles is obtained, applying the operation 'skel' in MATLAB (see *Fig 4b*).

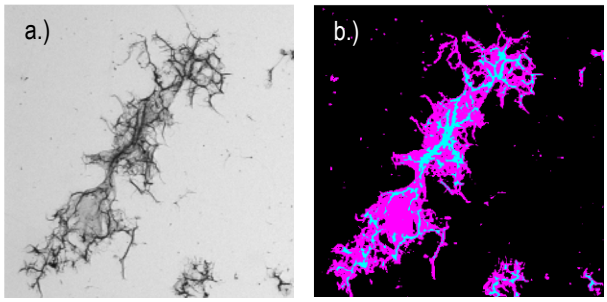

Fig 3 - Fibrillar BSK fines; a.) gray scale image; b.) threshold image obtained applying Otsu's method: background (black); fibrillar material (magenta), flake-like material (turquoise)

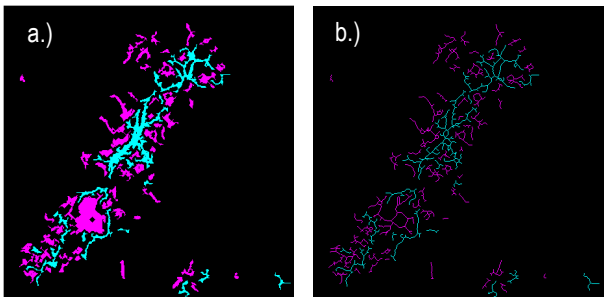

Fig 4 - Fibrillar material (magenta) and flake-like material (turquoise) after image processing a.) image after applying criterions for transition regions and objects smaller than 40 pixels; b.) skeleton of image a.)

The area of each segment (A_i) after image processing (see *Fig 4a*) is transferred to µm² units, by multiplying the counted pixels of the segment, with the area of one pixel (0.86x0.86 µm²). The pixels comprising the skeleton of each segment (see *Fig 4b*) are counted and transferred to µm units by a multiplication with the length of one pixel (0.86 µm) thus representing the particle ´length´. It can be seen that the fibrillar segments contain a large number of fibrils appearing as a kind of crowd, which makes their detection possible in the first place at this rather 'low' resolution. Thereby it is possible to get a measure for their size. The crowded appearance does of course not allow an exact measure for each fibril based on area and skeleton but gives a relative and significant number to describe differences between fibrillar structures of different fines varieties quantitatively. Exemplarily area and skeleton length of five flake-like and fibrillar segments of the particle in *Fig 4* are shown in the appendix (*Fig A3*).

Particle size of flake-like and fibrillar particles were determined based on circle equivalent diameter (CED). The CED is defined as the diameter of a circle with the same area as the projection area (A_i) of the image taken from the microscope slide (see *Eq 1*). Mean particle size was area weighted (q2) and determined according to *Eq 2*. Particle size distribution was determined according to *Eq 3* and *Eq 4*. x_k is the class mean of a class k, with class width 10 µm (Eq 3). y_k is the relative frequency of the squared CED of class *k*, calculated by the sum of CED² in class *k* divided by the sum of CED² contained in the sample (*Eq 4*). With the measurement of CED information regarding particle size is obtained, but length and with dimensions are neglected. The particle length (L_i) was estimated by the particles skeleton, reducing the particle to a connected one pixel line (see *Fig 4*). Dividing the particle area (A_i) through this 'length' (L_i), particle 'width' (W_i) was determined (*Eq 5*). Particle shape was assessed by the aspect ratio (AR_i), which was calculated dividing the estimated 'length' by the 'width' (*Eq 6*). Mean AR was number weighted (q0) and determined according to *Eq 7*. Similar to the fines content measured by a flow cell analyzer the fibrillar content in a fines fraction measured by the microscopy method was calculated. This fibrillar content (Fibril Area) was measured by the sum of the areas of fibrillar material (A_{fibril}) divided by the sum of the areas of fibrillar material (A_{fibril}) and flake-like material (A_{flake}) (*Eq 8*) of all images taken from one microscope slide.

Flow microscopy

Results from the microscopy method were compared to results of an L&W Fiber Tester$^+$ (FT$^+$). Resolution of the FT$^+$ images was determined to be 3.3 µm / pixel based on images captured with the vessel cell software (additional software capturing single particles together with information on particle length and width). Approximately 0.05 g dry matter of fines suspension was weighed in the sample beaker and suspended in 200 ml of deionized water. Analysis of 100000 particles at applied concentration took approximately 15 min. The raw data for particle length (l_i) and width (w_i), obtained from the FT$^+$, were exported to MATLAB. The particle area (A_i) was calculated assuming a rectangular particle shape (see *Eq 9*). CED was determined according to *Eq 1*. Mean particle size was area weighted (q2) and determined according to *Eq 2*. Particle size distribution was determined according to *Eq 3* and *Eq 4*, the same way as for the microscopy method.

$$CED_i = \sqrt{\frac{4 * A_i}{\pi}} \quad [1]$$

$$\overline{CED_{q2}} = \frac{\sum_{i=1}^{n} CED_i^3}{\sum_{i=1}^{n} CED_i^2} \quad [2]$$

$$x_k = \overline{CED_k} = \frac{1}{2} * \left(CED_{k+1} - CED_k\right) \quad [3]$$

$$y_k = \frac{\sum_{i=k}^{k+1} CED_i^2}{\sum_{i=1}^{n} CED_i^2} * 100 \quad [4]$$

$$W_i = \frac{A_i}{L_i} \quad [5]$$

$$AR_i = \frac{L_i}{W_i} \quad [6]$$

$$\overline{AR_{qo}} = \frac{\sum_{i=1}^{n} AR_i}{\sum_{i=1}^{n} 1} \quad [7]$$

$$Fibril \quad Area = \frac{\sum_{i=1}^{n} A_{fibril,i}}{\sum_{i=1}^{n} A_{fibril,i} + \sum_{i=1}^{n} A_{flake,i}} \quad [8]$$

$$A_i = l_i * w_i \quad [9]$$

Results

Comparison of static microscopy with flow analysis

Size distributions of fines from different unrefined pulp sources obtained by the new microscopy method were compared to the results of the L&W Fiber Tester$^+$ (FT$^+$) (*Fig 6*). In *Fig 6a*, the CED-size distribution of fibrillar fines and in *Fig 6b* the CED-size distribution of flake–like fines obtained by the microscopy method are shown. The fines fraction evaluated using the FT$^+$ is shown in *Fig 6c*. Although the FT$^+$ size distribution should include fibrillar and flake–like fines, it resembles the microscopy distribution including only flake–like fines (*Fig 6b*). This is even more evident plotting these size distributions in

Nordic Pulp & Paper Research Journal Vol 32 no 2, 2017 --- DOI 10.3183/NPPRJ-2017-32-02-p244-252

one diagram (see *Fig 7*).The microscopy distribution of fibrillar fines, show particles in a size range, in principle large enough to be measured by the FT⁺ (*Fig 6a*). Still, due to the high swelling of fibrillar fines suspended in water, the contrast between particles and background is insufficient for detection of fibrillar fines with the FT⁺ (see *Fig 5*).

Detection and size measurement using flow analysis seems to be affected by the color of fines. Size distributions of unbleached softwood kraft fines (UBSK) and bleached softwood kraft fines (BSK), measured by the FT⁺ show a similarity in shape, but have different mean values (*Fig 6c*). UBSK fines appeared darker and thus the contrast is higher than for BSK fines, yielding more regions distinctly differentiable from the background. Considering additionally a fixed threshold value, regions appearing lighter in the BSK sample, may be assigned to the background, whereas the same regions appearing darker in the UBSK samples are assigned to the particle leading to an over estimation of the size of UBSK fines compared to BSK fines, by the FT⁺. In the microscopy method these differences were eliminated by the sample preparation procedure and dynamic thresholding giving comparable mean values for UBSK and BSK flake-like fines (*Fig 6b-c*). Apart from these differences, size distributions of flake-like fines obtained by the microscopy method and the FT⁺ are in a similar size range and show similar trends. Therefore it is legitimate to consider that flake–like fines do not swell much.

When comparing the size distributions for flake-like fines (*Fig 6b-c*) with the one for the fibrillar fines (*Fig 6a*) of these four primary fines samples, considerable differences are detected that paint a different picture than the distributions for the flake-like fines do. This underlines the importance of detection and differentiation between flake–like and fibrillar material in the description of fines, which can only be achieved using the microscopy method as flow analyzers fail to detect a large number of fibrillar fines (*see Fig 5*).

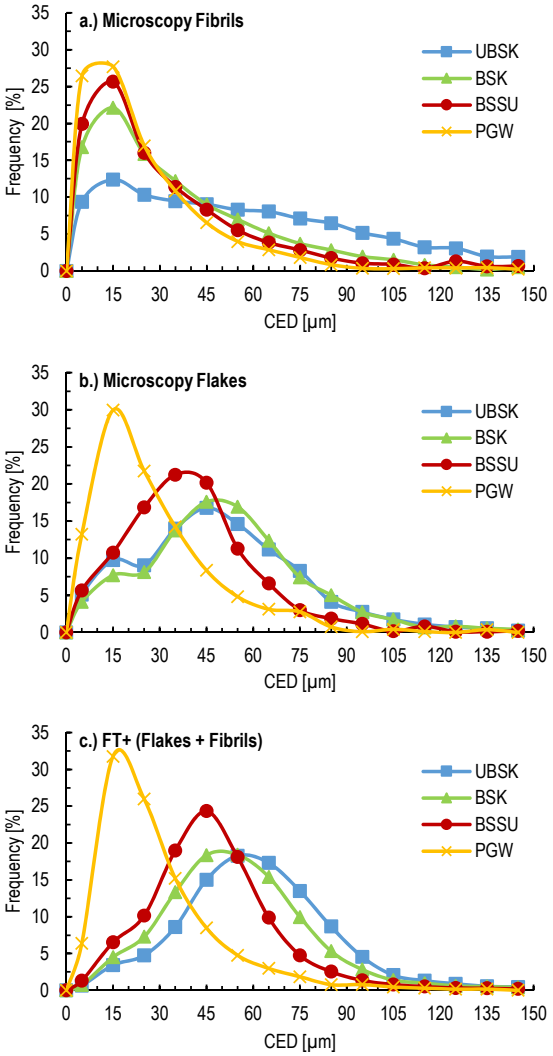

Fig 6 - Circle equivalent diameter (CED) size distribution of four different types of primary fines: a.) Microscopy method Fibrils; b.) Microscopy method Flakes; c.) Fiber Tester⁺ (FT⁺) Flakes and Fibrils

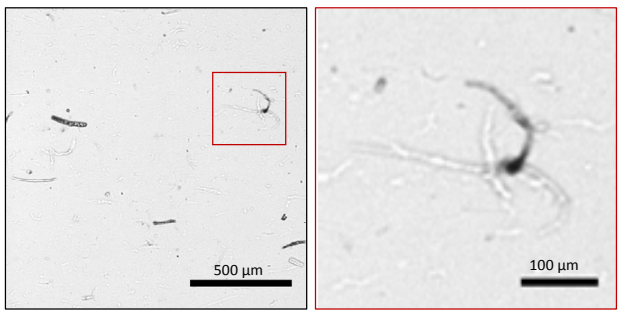

Fig 5 - Image section of BSK fines captured with the FT⁺. Flake-like material (ray cells, parenchyma cells) can be detected (left). Detection of highly swollen fibrillar fines insufficient (image section (right)).

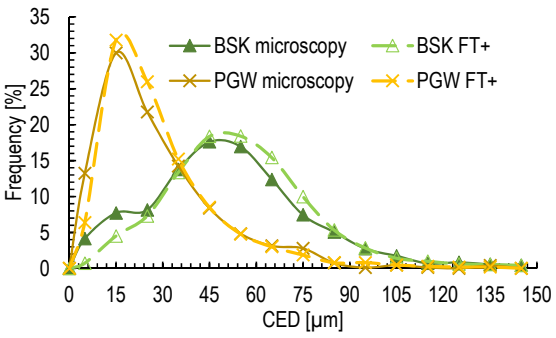

Fig 7 - Comparison of size distributions for flake-like material obtained by the microscopy method (full line) with size distributions obtained by the FT⁺ (dashed line) for BSK fines (triangle) and PGW fines (cross).

Nordic Pulp & Paper Research Journal Vol 32 no 2, 2017 --- DOI 10.3183/NPPRJ-2017-32-02-p244-252

Evaluation of refined pulp

Bleached sulfite pulp (SU) was refined in an industrial disk refiner at refining energies from 0 to 130 kWh/t and the obtained fines quality was evaluated using the microscopy method. Three replicates were made for each sample and the results are shown in *Table 2*. The circle equivalent diameter (CED) and the aspect ratio (AR) of fibrillar fines from refined pulps is significantly higher compared to unrefined pulps. Fibrillar fines from unrefined samples are less branched and form smaller networks. For the refined samples CED remains constant over the applied refining energies, while AR increases further with higher specific energy input. This indicates that networks did not grow larger when applying higher refining energies, but that micro fibrillation increased. The fibril area, increases with refining as mainly fibrillar fines are produced. Only small changes were observed in the properties of the flake-like material. CED decreases slightly between the unrefined sample (SU – 0) and the refined samples. As already mentioned the macrofibrillar backbone or dense fibril bundles of secondary fines are also part of the flake-like material and responsible for the decrease in CED. Aspect ratio for flake–like material increased slightly for the refined samples, because these dense fibril bundles have a higher AR compared to the fines before refining. For fibrillar as well as flake-like fines the major difference in the values was observed between unrefined and refined samples; the influence of refining intensities on the results was far less pronounced. These data show a clear difference in morphology of unrefined and refined pulp fines respectively between primary and secondary fines. Morphology of fibrillar primary fines differs significantly from secondary fines and also the quality of secondary fines changes with higher specific refining energy input.

Discussion

The proposed microscopy method and the measured parameters explain morphological characteristics of fines especially fibrillar fines in more detail than conventional fiber analyzers. In order to detect fibrillar fines not only resolution is a limiting factor for a conventional flow cell analyzer, which today can analyze particles down to a few micrometers. Especially the low contrast due to extensive swelling reduces the detectability of fibrillar fines for the analyzers as is demonstrated by our results showing that predominantly flake-like fine material and dense fibril bundles are detected. These dense fibril bundles are assigned to the flake–like material based on their grey level, in the microscopy method. Thus the size distribution of the flow analyzes resembles the size distribution for flake–like material analyzed with the microscopy method. (*Fig 6,7*). The structure of the networks of fibrillar fines became detectable due to the dyeing procedure and the microscopy method allows a quantification of fibrillar material in addition to the flake-like material.

Initially the resulting color was dependent on pulp quality but with the addition of tall oil the dyeing of different types of fines became more uniform allowing a comparison of fine fractions independently from the pulp type. Differences in contrast between unbleached and bleached fines, leading to differences in size measurement with flow cell analyzers are eliminated by the uniform coloration using the modified dyeing procedure.

The structure of fibrillar fines was found to be a branched network of fibrils of different sizes, which cannot be simply, described using length and width dimensions. Parameters as CED, derived from the particle area, and AR, calculated using the skeleton and the area of such a network, were determined to better describe fibrillar fines morphology. Considering the complexity of the fines fractions including micro- and macrofibrillar structures it also appears inaccurate to measure particle size using indirect optical methods, such as DLS, due to the likely differences in optical behavior and shape affecting the result. Because of their heterogeneous network structures also a gravimetrical classification, e.g. sieving, would not lead to a meaningful classification with respect to fines properties. Fibrillar networks of fines can have a size of up to some 100 µm in one dimension while microfibrils are much smaller. Although analysis with high resolution imaging methods such as SEM and AFM would lead to a more accurate size measurement of microfibrils, the true fibrillar structure cannot be captured, because of the small measurement area. Also statistically significant values are not that easy to obtain with these high-resolution methods. Because of limited resolution, microfibrillar networks can appear as a continuum in the microscopy method, which influences the determination of area and aspect ratio. Nevertheless, the results from the refining trials with sulfite pulps indicate that fines morphology at different refining energies can be adequately described with the microscopy method. Aspect ratio and fibrillar network size increased already at low energy input in refining and increased further at higher refining energies, forming thinner fibrils. Thus, the detection of microfibrillar structures seems to be accurate enough to describe the development of fines properties during refining. Of course further research is needed in

Table 2 - Fibril area, equivalent diameter and aspect ratio of sulfite pulp at different refining levels

Refining energy		SU	-0	-90	-110	-130
Fibril area	[%]	AV	52.1	72.0	78.0	79.5
		CI 95	1.1	2.2	0.9	1.6
Circle - equivalent diameter (CED)						
Flake	[µm]	AV	43.8	37.5	36.3	38.7
		CI 95	0.6	1.4	0.6	1.4
Fibril	[µm]	AV	41.0	52.9	52.9	52.0
		CI 95	1.3	1.4	1.2	3.2
Aspect ratio (AR)						
Flake	[-]	AV	8.4	10.5	10.0	11.6
		CI 95	0.1	0.4	0.2	0.3
Fibril	[-]	AV	21.7	29.0	29.6	31.0
		CI 95	0.2	0.2	0.1	0.4

order to validate the microscopy method e.g. against high resolution methods such as SEM or AFM. A limitation of the microscopy method resulting from image processing routine is that fibrillar structures are separated, at transition areas, by the thresholding procedure. And of course there is also the limitation due to the maximum resolution of light microscopy. Additionally the need for a tedious and complex manual sampling procedure may lead to a certain operator-effect when applying this technique.

Conclusions

Similar methods for quantitative determination of fines morphology using optical microscopy were already introduced by Luukko et al. (1997) and Retulainen et al. (2002). The main idea of Luukko's method was to classify fines into fibrillar and flake–like material. Retulainen on the other hand described fines by their size and shape. The method introduced in this article combines both, a classification in fibrillar and flake–like material and a determination of size and shape. Influences of optical properties of the fines on their detection, especially for fibrillar fines, were eliminated using an adapted dyeing procedure, which allows a quantitative comparison of fines from different pulp sources. As also small fibrils show enough contrast the structure of fibrillar fines network can be evaluated and new insights into the morphology of the fines fraction of pulps become possible. The advantages of the method are the possibility of a quantitative evaluation, the good repeatability and the possibility to describe shape and size independently from differences in the optical properties due to the adapted dyeing procedure.

However there is a need to automate sample preparation in order to be less operator dependent and time consuming. Image analytical routines for a more detailed description of the complex fibrillar networks could also be developed further if sampling is more uniform and the size and composition of fibrillar networks itself allows a deduction of structural information in terms of single fines particles.

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Appendix

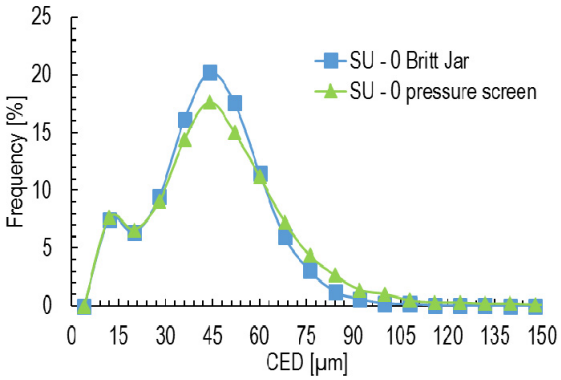


Fig A1 - Size distributions of unrefined sulfite pulp (SU – 0) pulp fractionated with the Britt Jar method (76 µm) and with a lab – scale pressure screen (100 µm)

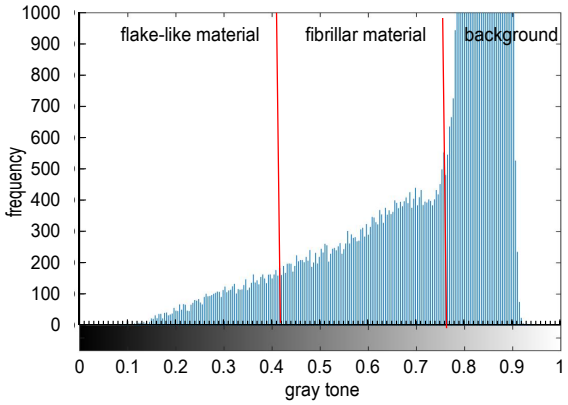
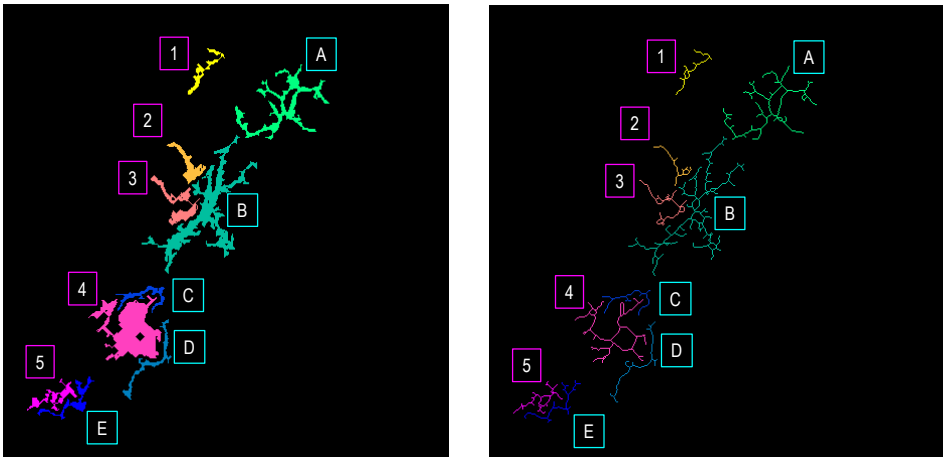


Fig A2 - Histogram of gray scale image (see Figure 3); red vertical lines show the threshold gray values, applying Otsu's method, dividing the histogram into regions correspond to background, fibrillar material and flake – like material



fibrillar material		
	area [µm²]	length [µm]
1	193,9	76,7
2	280,1	69,0
3	388,6	119,8
4	1602,0	263,8
5	260,8	105,2

flake-like		
	area [µm²]	length [µm]
A	934,0	328,4
B	1693,4	494,8
C	276,4	111,2
D	217,0	82,8
E	260,1	102,6

Fig A3 - Illustration of five exemplary fibrillar and flake-like fragments a.) particle area, b.) particle skeleton; c.) values for particle area and length of these segments.

II

Mayr, Melanie, Eckhart Rene, Winter Heribert and Bauer Wolfgang (2017). “A Novel Approach to Determining the Contribution of the Fiber and Fines Fraction to the Water Retention Value (WRV) of Chemical and Mechanical Pulps.” Cellulose 24 (7): 3029-36 doi:10.1007/s10570-017-1298-6.

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ORIGINAL PAPER

A novel approach to determining the contribution of the fiber and fines fraction to the water retention value (WRV) of chemical and mechanical pulps

Melanie Mayr · Rene Eckhart · Heribert Winter · Wolfgang Bauer

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Abstract The swelling behavior of pulp fibers has a significant influence on process and product properties. The water uptake of fibers is controlled by a different mechanism. While fiber charge is a driving factor for swelling, the swelling is hindered by the solid structure of the fiber wall. In the case of the fines fraction of pulps, this structure is broken to some extent and the fines are able to swell two to three times more compared to fibers. Thus fines are an important factor regarding the swelling behavior and water retention of pulps, although, at least for chemical pulp, their mass fraction is only between 4 and 15%. For this reason, it is of interest to investigate not just the swelling behavior of pulps, but also of the fiber and fines fractions separately. Swelling is often characterized using the water retention value (WRV) based on a centrifugation technique. WRV measurement is a standardized method for the measurement of the amount of water retained in a given pulp sample. For fine cellulosic materials the standardized procedure cannot be performed. Thus, various modifications of the standard method have been applied by different groups for the evaluation of these materials. Due to these modifications the values obtained cannot be related to the standardized method. In this work a novel approach to determining the WRV of the fines fraction in a given pulp based on the standard procedure will be presented. This allows a quantitative investigation of the contribution of the fibers and fines fraction to the WRV of any given pulp sample.

Keywords Water retention value · Swelling · Fibers · Fines · Refining

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Introduction

The swelling tendencies of pulps have an important impact on sheet consolidation and interfiber bonding. (Chen et al. 2013; Hii et al. 2012; Koskenhely et al. 2005). As swelling is influenced by structural changes and pulp chemistry, the effect of different pulp treatments can be monitored by its characterization and thus swelling yields important information regarding, e.g., dewaterability on the paper machine or strength development after sheet consolidation. The swelling behavior influenced by the pulping process and yield (Andreasson et al. 2003; Forsstrom et al. 2005; Stone and Scallan 1967), by drying and rewetting (Stone et al. 1968; Wang 2006) and by refining (Bäckström and Haimnar 2010; Laivins and Scallan 1996) have been documented. Further, swelling is influenced by enzymatic treatment (Gil et al. 2009; Stock et al. 1995), by chemical modification

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(Chen et al. 2013; Racz and Borsa 1997; Scallan 1983; Zhao et al. 2016) or by addition of cationic polymers (Aarne et al. 2012; Strom and Kunnas 1991). Swelling depends to a certain extent, also, on charge density. The more carboxylic groups, the higher the swelling potential. The effect of anionic groups can be explained based on the Donnan theory (Rasanen et al. 2001; Scallan 1983). The anionic groups located in the cell are balanced by positively charged counterions. If there are more ions in the fiber wall than in the surrounding liquid, an osmotic pressure difference arises. This pressure difference is balanced by the fiber wall absorbing water and thus 'diluting' the charges within the fiber wall. Based on this fundamental effect it is obvious that a change in swelling can result from pH, conductivity of the water phase, the types of counterions of the carboxylic groups and addition of chemical additives (Scallan 1983; Scallan and Grignon 1979; Stone et al. 1968; Strom and Kunnas 1991). The final degree of swelling of a pulp fiber is limited by the structure of the fiber wall, which hinders the unlimited dilatation of the fiber. Stone and Scallan (1967), therefore, defined different regions of a fiber, whose water holding capacity obviously is affected by the fiber morphology. The accessible volume and therefore the water holding capacity of these regions change due to chemical, mechanical or thermal action.

Several methods for the measurement of swelling and related properties are reported in the literature. These include water evaporation (Stone and Scallan 1967), thermoporosity measurement (Wang et al. 2003), nuclear magnetic resonance (NMR) (Forsstrom et al. 2005; Hui et al. 2009; Maloney et al. 1997) and inverse size exclusion chromatography (ISEC) (Berthold and Salmén 1997). The two most common methods, however, are the fiber saturation point (FSP) and the water retention value (WRV).

In FSP measurement, a weighed quantity of wet pulp of known moisture content is immersed in a dilute aqueous solution of a high molecular weight dextran polymer (approximately 1wt% in water). The polymer molecules are larger in size than the pores and therefore cannot enter the cell wall. Thus water contained in the pores will lead to a change in the polymer concentration. The FSP, which can be seen as the amount of water in the cell wall, is then determined based on Stone and Scallan (1967). As swelling also depends on the surrounding liquid, it is advantageous that this measurement is performed in aqueous solution, without any structural changes to the fibers, which are constantly in a wet state. Thus it is considered the most direct measurement of fiber swelling (Maloney et al. 1999). Nevertheless, a high measurement uncertainty compared to other methods has to be accepted, as changes in polymer concentrations are quite small. The accessibility of dextran to the fiber lumen might also depend on the fiber damage. Dextran molecules may have difficulties approaching a fiber when its surface is highly fibrillated and water entrapped between these fibrils and the fiber surface could then be considered as inaccessible (Stone et al. 1968).

WRV measurement has a quite different principle. The WRV is a centrifugation technique, determining the water retained in a fiber pad after the application of centrifugal forces under defined conditions. It is an indirect method influenced by sample mass, centrifugation force and time, and therefore has to be performed under defined conditions specified by the standard (ISO 23714:2014). Nevertheless, a good correlation of FSP and WRV for different types of pulps was observed up to certain values (Scallan and Carles 1972), after which the WRV fell below the FSP. To reach this level of swelling the fibers have to be highly fibrillated. It was assumed that the more swollen a fiber is, the more sensitive it will be against compression, forcing out the water during centrifugation (Scallan and Carles 1972). On the other hand, one might argue that the FSP obtains higher values, as water molecules trapped between highly swollen fibrils and the fiber surface become inaccessible as mentioned before (Stone et al. 1968). In another study it was shown that WRV also differs from FSP for less swollen pulps. It was concluded that water retained between the fibers and water removed from the cell wall in centrifugation are responsible for these differences (Maloney et al. 1999). The influence of drying and rewetting on swelling was found to be higher for WRV than for FSP (Forsstrom et al. 2005), and the correlation of WRV and FSP is affected by different refining strategies for various types of pulps (Hui et al. 2009). It can be concluded that measurement of pulp fiber swelling is not a straightforward task and that the method, as well as the morphology and origin of the pulp sample, have to be considered. Depending on the method used, different aspects of swelling are evaluated.

As mentioned before, both charge and structural properties of fibers affect swelling. For example, carboxymethylation of unbleached hardwood kraft pulp (UBHK) leading to a 280 µeq/g higher total fiber charge resulted in an increased WRV of 1.4 g water per g fiber (Chen et al. 2013), while the fiber morphology remained almost unchanged. Refining, on the other hand, has little effect on the fiber total charge (Horvath and Lindström 2007), but generates fines (particles passing a 200 mesh screen), or more precisely, secondary fines (Krogerus et al. 2002). Primary and secondary fines are usually both present in a refined pulp. Bäckström et al. (2008) removed primary fines prior to refining and found differences in WRV between unbleached kraft secondary fines and the corresponding fibers to be 4.2 g water per g fiber. As secondary fines are parts of the fiber wall torn out by the refining treatment, this change in swelling can be assumed to be mainly caused by structural changes. Several other studies also reported that fines after refining, which include primary and secondary fines, swell two to three times more than fibers, i.e. fines hold up to three times more water than fibers (Laivins and Scallan 1996). Although there are these obvious differences, the impact of the swelling of fines on paper properties was rarely discussed. Fines were often neglected from such investigations, because it is a tedious task using the common methods to separate fines in a high enough quantity to measure swelling. Swelling of fines can be determined by the FSP method directly, but a high amount of fines is required and the FSP method is also quite a time consuming procedure. For WRV measurement, a fiber pad first needs to be formed by filtration, which is not practicable in the case of the high dewatering resistance of fines. Thus several modifications of the method were made to be able to measure the WRV of pulp fines or other fine cellulosic materials. The mass of the sample was reduced in almost all modifications, centrifugation was replaced by other methods to remove excess water, membranes were implemented to be able to hold back the fine material and centrifugation time and force were varied. It was shown that each of these modifications had an influence on the results (Cheng et al. 2010; Scallan and Carles 1972). Due to these modifications the values obtained for the fines fraction cannot be related to the standardized method anymore, and the contribution of fibers and the corresponding fines fraction on the WRV of a given pulp sample cannot be directly determined. An approach to measure the WRV of micro and nanofibrillated fine fractions on the basis of the standard procedure was presented by Rantanen et al. (2015). With this method, however, only the WRV of the fines fraction can be determined, neglecting the WRV of the fiber fraction, which would be important for papermaking pulps. In this work a novel approach to determining the WRV of the fiber and the fines fraction based on the standard procedure is presented.

Materials and methods

Pulp samples and sample preparation

In this study various industrial chemical and mechanical pulp samples from different process steps (bleaching, refining) were chosen for the validation of the novel approach (see Table 1). The gravimetric fines content of these pulps was determined by the Britt Dynamic Drainage Jar method (BDDJ, SCAN-CM 66:05). The WRV of these pulps was determined according to the standard method (ISO 23714:2014). A fiber pad formed by filtration has to have a dry mass of the pad of 2.5 g. This fiber pad was centrifuged (centrifugation time: 30 min, centrifugation force: 3000 g) and the pad was weighed after centrifugation (m_{wet}), dried and weighed again (m_{dry}). The water retention value is calculated according to Eq. 1.

Table 1 List of pulps and treatments

Nr.	Pulp	Treatment
P1	Pressurized ground wood 1	Unbleached
P2	Pressurized ground wood 1	Bleached
P3	Softwood kraft pulp 1	Unbleached, unrefined
P4	Softwood kraft pulp 2	Unbleached, unrefined
P5	Softwood kraft pulp 2	Bleached, unrefined
P6	Softwood kraft pulp 3	Bleached, unrefined
P7	Softwood kraft pulp 3	Bleached, refined
P8	Hardwood kraft pulp 1	Bleached, unrefined
P9	Hardwood kraft pulp 1	Bleached, refined
P10	Softwood sulfite pulp 1	Unbleached, unrefined
P11	Softwood sulfite pulp 1	Bleached, unrefined
P12	Softwood sulfite pulp 1	Bleached, refined

$$\mathrm{WRV}\left[\frac{\mathrm{g}}{\mathrm{g}}\right] = \frac{m_{\mathrm{wet}}}{m_{\mathrm{dry}}} - 1 \quad (1)$$

In order to obtain a sufficient amount of the fines fraction and a pure fiber fraction, the pulps were fractionated at 1% solids content using a laboratory-scale pressure screen. The pressure screen was equipped with a perforated plate (hole diameter 100 µm). The material passing through this plate was defined as the fines fraction. The pulp was recirculated through the pressure screen until the remaining volumetric fines content measured with a commercial flow cell based fiber analyzer (L&W Fibertester^{+}) was lower than 0.5%. This pulp fraction was defined as the fiber fraction.

Determination of WRV by the novel method

The fiber and fines fractions obtained using the abovementioned screening procedure were recombined to obtain three blends per pulp sample containing proportions of fines between 5 and 15% for chemical pulps and between 15 and 30% for mechanical pulps. The WRV of all these blends was determined in duplicate according to the standard (ISO 23714:2014).

Each component (fibers and fines) is considered to have an intrinsic water retention capacity. Based on the knowledge that fines show a higher WRV than the fibers, it is expected that WRV increases linearly when the fines content is increased, as depicted in Fig. 1.

The linear equation (Eq. 2) obtained from this relation was solved according to the two boundary conditions $w_{\mathrm{Fines}} = 0\%$ (100% fibers) and $w_{\mathrm{Fines}} = 100\%$ to determine the WRV of fibers (WRVFiber, Eq. 3) and the WRV of fines (WRVFines, Eq. 4), respectively. $\mathrm{WRV}_{\mathrm{Pulp}}$ was calculated using Eq. 5 based on the values for $\mathrm{WRV}_{\mathrm{Fines}}$, $\mathrm{WRV}_{\mathrm{Fiber}}$ and the gravimetric fines content (w_{Fines}, see Table 1) measured for the original pulp. The contribution of fibers and fines to $\mathrm{WRV}_{\mathrm{Pulp}}$ was also determined by this approach .

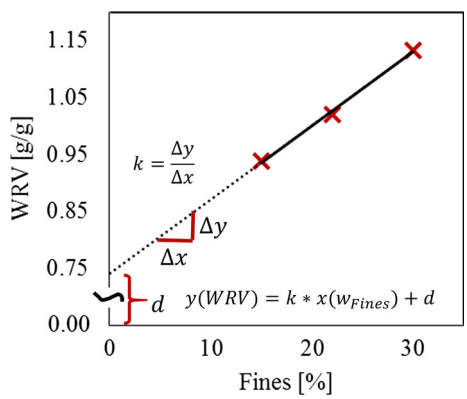

Fig. 1 Linear development of WRV of pulp blends in dependency of the fines content of these blends

$$\mathrm{WRV} = k * w_{\mathrm{Fines}}[\%] + d \quad (2)$$

$$w_{\mathrm{Fines}} = 0\% \rightarrow \mathrm{WRV} = d \triangleq \mathrm{WRV}_{\mathrm{Fiber}} \quad (3)$$

$$w_{\mathrm{Fines}} = 100\% \rightarrow \mathrm{WRV}_{\mathrm{Pulp}} = k * 100 + d \triangleq \mathrm{WRV}_{\mathrm{Fines}} \quad (4)$$

$$\mathrm{WRV}_{\mathrm{Pulp}} = \mathrm{WRV}_{\mathrm{Fiber}} * (1 - w_{\mathrm{fines}}) + \mathrm{WRV}_{\mathrm{Fines}} * w_{\mathrm{fines}} \quad (5)$$

Results

Validation of the novel approach

For the validation of the novel approach, the WRV of the pulps were measured directly by the standard method and additionally calculated according to Eq. 5 using the approach described above (see Table 2). To allow a comparison of calculated and measured WRV values, it is of importance that the fine fraction obtained by pressure screening is similar to the fine fraction obtained with a BDDJ (SCAN-CM 66:05). Size distributions of the fraction generated by the pressure screen and the fraction generated with the BDDJ, show a similar size range (see "Appendix"). Thus, similar fractions are obtained by both methods, allowing the determination of $\mathrm{WRV}_{\mathrm{Pulp}}$ based on the fines content obtained by the BDDJ method.

The values obtained by the calculation were correlated with the measured values of the pulps (see Fig. 2). A coefficient of determination R^2 of 0.985 demonstrated the validity of the novel approach.

The WRV is not only a material property, but also depends on structural properties (structure of the pad, Maloney et al. 1999). The influence of structural properties becomes evident as the values for pure fibers ($\mathrm{WRV}_{\mathrm{Fiber}}$) measured directly were higher compared to the calculated ones, applying the novel approach (Table 2). The difference was even higher for unrefined pulp samples than for refined pulp (Table 2). As

Table 2 Gravimetric fines content (SCAN-CM 66:05) of pulp samples (see Table 1) and WRV (ISO 23714:2014) measured directly from these pulps

Nr.	Fines content (%)	WRV (g/g) standard		WRV (g/g) novel approach (calculated values Eqs. 3–5)		
		Fiber	Pulp (measured)	Fiber	Fines	Pulp
P1	33.1	0.825	1.202	0.755	2.045	1.182
P2	33.5	0.824	1.139	0.741	2.041	1.176
P3	2.7	1.275	1.276	1.203	3.233	1.257
P4	3.4	1.124	1.160	1.119	2.489	1.166
P5	4.3	1.090	1.083	1.035	2.585	1.101
P6	4.9	0.805	0.812	0.734	2.754	0.832
P7	7.7	1.061	1.226	1.046	3.366	1.224
P8	9.8	0.812	0.877	0.738	2.138	0.874
P9	10.8	0.924	1.099	0.896	2.666	1.086
P10	4.8	1.219	1.184	1.172	2.242	1.223
P11	4.4	1.103	1.086	1.048	2.348	1.105
P12	11.5	1.178	1.324	1.154	2.914	1.357

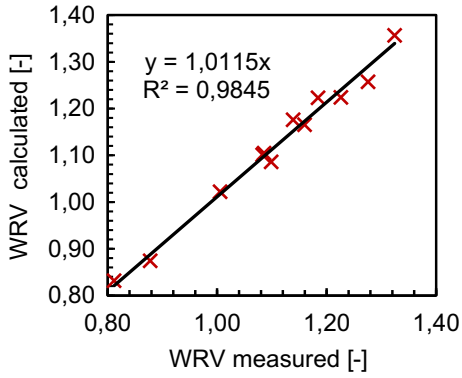

Fig. 2 WRV of pulps given in Table 2; Correlation between values measured directly using the standard procedure (*x*-axis) and calculated values (Eq. 5) based on the novel approach (*y*-axis)

an example for a mechanical pulp (P2) as well as for a chemical pulp (P5), WRV values measured for blends with different fines content and for the pure fiber fraction are presented in Fig. 3, illustrating the deviation of WRV_{Fiber} from the linear relationship between fines content and WRV. This behavior might be explained by structural changes of the pulp pad due to capillary forces introduced by fines and external fibrils of fibers. Capillary forces lead to a higher densification of the pad similar to the effect fines have on sheet consolidation (Sirviö and Nurminen 2004). This structural impact may also be present when the novel approach is used based on blends with different fines contents, but at least it follows a linear trend.

In the validation trials presented above, fibers were always mixed with the originally corresponding fines fraction. To validate the stability and structural impact of different fiber and fines morphology on WRV applying the novel approach, the fiber and fines fractions of two morphologically and chemically different pulps, pressurized groundwood (PGW, Table 2—P1) and unbleached softwood kraft (UBSK, Table 2—P3), were recombined. UBSK fibers and PGW fibers were combined with three levels of their own fines again (Trial A and Trial B), as there was a certain time period, between the above discussed validation (Table 2) and this experiment, possibly leading to changes in pulp quality. USBK fibers were additionally combined with three levels of PGW fines (Trial C) and vice versa (PGW fibers with UBSK fines (Trial D)). WRV_{Fiber} and WRV_{Fines} were determined for all four trials using Eqs. 3, 4 and are listed in Table 3. WRV_{Fiber} obtained by mixing the fibers with the corresponding fines and by mixing it with fines from the other pulp led to similar results. For WRV_{Fines} the differences were slightly larger, presumably because of greater differences in fines morphology influencing the water removal during centrifugation. Still, the variations in the WRV results are within the measurement uncertainty given in the standard. Thus, the novel approach is also applicable in determining WRV_{Fiber} or WRV_{Fines} without the necessity for the fiber and the fines fraction to come from the same original pulp. This approach could also be useful in the

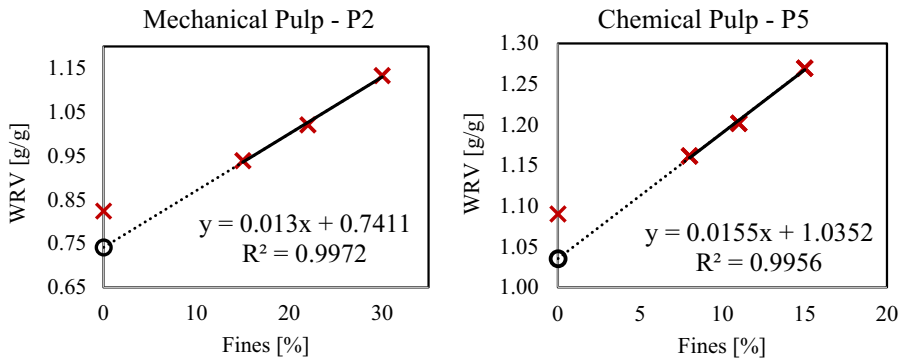

Fig. 3 WRV values for mechanical pulp (P2) and chemical pulp (P5), measured for blends with different fines content and for the pure fiber fraction (x) and WRV_{Fiber} calculated by the novel approach (o)

Table 3 Determination of WRV fibers and fines from UBSK and PGW pulps. Determination for fiber and corresponding fines fraction (A, B) and for combinations of different pulp fibers and fines (C, D)

Trial	WRV (g/g)			
	UBSK		PGW	
	Fiber	Fines	Fiber	Fines
A	1.26	3.16		
B			0.76	1.75
C	1.24			1.55
D		3.46	0.80	

determination of the WRV of other cellulosic fine materials, such as micro- or nanofibrillated celluloses.

Application example

To underline the value of this novel method, we present an exemplary application regarding the development of WRV with refining. The unrefined bleached softwood kraft pulp (BSK) (Table 2—P5) was refined using an industrial, single disk refiner and the corresponding refined BSK pulp (Table 2—P6) was obtained. Table 4 lists the mass fractions for fibers, primary and secondary fines of the unrefined and refined BSK pulp. Unrefined pulp consists only of fibers and primary fines. The percentage of primary fines is assumed to remain constant after refining, and all additionally created fines during refining are classified as secondary fines and assumed to originate only from the fibers. Thus the amount of fibers decreases and the total amount of fines increases after refining, while the amount of primary fines remains constant.

In Fig. 4a the WRV of the unrefined and refined BSK fibers (WRV_{Fiber}) and fines (WRV_{Fines}) is shown. With refining, WRV_{Fiber} increases due to internal and external fibrillation of the fibers. WRV_{Fines} increases because of the production of secondary fines, which usually swell more than primary fines (Bäckström et al. 2008). In Fig. 3b the mass fractions of fibers and fines contained in the pulp are also taken into account (see Eq. 5) and show WRV_{Pulp} , including the contribution of fibers and fines to WRV_{Pulp}. As fibers are the dominant mass fraction in unrefined and refined BSK pulp, WRV_{Fiber} is the major contributor to WRV_{Pulp}. Yet despite their low mass fraction, fines have quite a significant influence on WRV_{Pulp} because of their much higher WRV. With refining, the contribution of

Table 4 Mass fractions of components present in unrefined and refined BSK pulp

	Mass fractions (%)	
	BSK (unrefined)	BSK (refined)
Fiber	95.1	92.3
Primary fines	4.9	4.9
Secondary fines	0.0	2.8

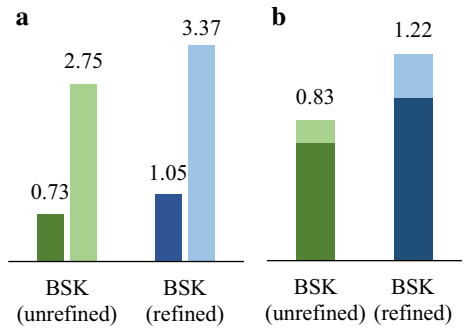

Fig. 4 **a** WRV_{Fiber} (*dark bars*) and WRV_{Fines} (*light bars*) of unrefined and refined BSK pulp; **b** WRV_{Pulp} of unrefined and refined BSK pulp and the contribution of fibers (*dark bars*) and fines (*light bars*) calculated according to Eq. 5

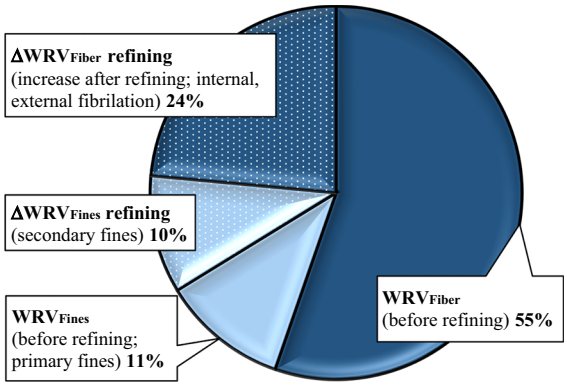

Fig. 5 Contribution of fibers (*dark areas*, 79%) and fines (*light areas*, 21%) to the WRV of refined BSK pulp and increase of WRV of fibers (*dotted dark area*, 24%) and WRV of fines (*dotted light area*, 10%) due to refining

the fines fraction increases, not only due to an increase of WRV_{Fines} (Fig. 4a), but also by the higher mass fraction of fines after refining (Table 4). In the refined BSK pulp the fibers contribute 79% and the fines of 21% to WRV_{Pulp}. While the overall increase of WRV_{Pulp} due to refining can of course be determined using the standard WRV method, the novel method provides additional information by distinguishing the effect refining has on fibers and fines (see Fig. 5). For the example of the BSK pulp, refining increased the WRV of fibers as a result of internal and external fibrillation by 24% and the WRV of the fines by 10% by the production of secondary fines.

Conclusion

Nearly all processes in pulping and stock preparation, such as bleaching, drying or refining, influence the amount of water retained in a pulp measured by the WRV. The simple method presented allows separate determination of the WRV of pulp fibers and fines. The contribution of fibers and fines to the water holding behavior of a given pulp can thus be calculated using the standardized WRV measurement procedure. This is seen as an advantage over alternative methods to determine the WRV of cellulosic fines, which require modifications to the standard procedure and therefore are not directly comparable. WRV_{Pulp} derived from the novel approach is comparable to values measured by the standardized procedure, which underlines the validity of the method.

As it is not necessary to blend fibers and fines from the same origin to obtain values for the contribution of fibers and fines to the WRV, this method might also be useful in the determination of the WRV contribution of other cellulosic fine materials, such as MFC or NFC.

The example of the development of WRV with refining underlines the value of the novel approach. While the overall increase of the WRV of a pulp can be measured using the standardized procedure, the novel approach, in addition, allows us to differentiate between WRV_{Fiber} and WRV_{Fines}, and thus the contribution of each fraction to the water holding behavior. This valuable information allows a more targeted process and product optimization.

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Appendix

Comparison of BDDJ and pressure screen

See Fig. 6.

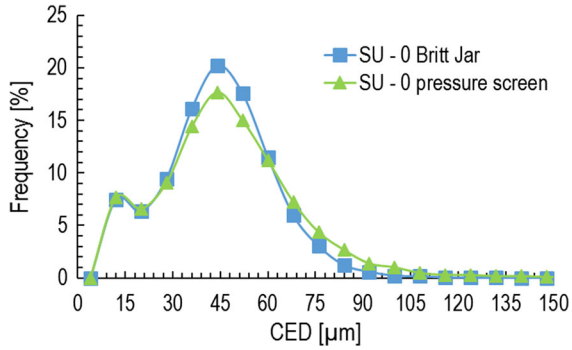

Fig. 6 Size distributions (Fibertester^{+}) of the fines fraction of bleached unrefined softwood sulfite pulp 1 (SU – 0) fractionated with the Britt Jar method (hole diameter 76 µm) and with a lab—scale pressure screen (hole diameter 100 µm)

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CHARACTERIZATION OF FINES QUALITY AND THEIR INDEPENDENT EFFECT ON SHEET PROPERTIES

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ABSTRACT

It is widely accepted that pulp fines (particles passing a 200 mesh screen) largely affect pulp properties, sheet consolidation and the final paper properties. Especially fines produced during refining - so called secondary fines – showing a more fibrillar character compared to primary fines already present after the pulping process, have a positive effect on strength properties. Although this is common knowledge within the paper physics community, it is still largely unclear which detailed properties of fines influence pulp and paper properties to what extent. As fines show some similarity to MFC, this question is also of interest regarding the use of MFC as an additive in papermaking. We apply established and new methods for fines characterization, such as the secondary fines content, the swelling ability and data on fibrillation and fibrillary material together with a suitable experimental setup to isolate the technological impact of fines in the final product. Thus we are able to evaluate the technological effect of fines with different characteristics in terms of the above mentioned properties. Our results clearly show that categorizing primary and secondary fines is not sufficient when it comes to their technological impact and only in depth analysis of the fines present in a given pulp allows to understand their effect on paper properties.

INTRODUCTION

Pulp fines are most commonly defined according to their size as all particles in a papermaking furnish passing a 200 mesh screen (76 µm hole diameter; SCAN-CM 66:05). Fines definition based on commercially available fibre analyzers is different by categorizing particles smaller than 200 µm in length as fines (ISO 16065-2). Besides these two standard classifications authors have also used other definitions and methods in their work. Therefore, whenever fines are addressed in literature, one has to keep in mind that the respective definitions may vary and direct comparison may be difficult.

In addition to the size definition chemical pulp fines are further distinguished in primary and secondary fines according to their origin. Primary fines are those fines present after the pulping and bleaching process mainly consisting of ray cells, parenchyma cells, fragments of the middle lamella and only a small portion of fibrils. Secondary fines contain fibrillated and lamellar material originating from the fibre wall, as a result of mechanical forces acting on a fibre during beating [1]. When it comes to mechanical pulp fines, Brecht and Klemm [2] classify flour stuff (granular or powdery fiber pieces, cells) and slime stuff (mucilage material) according to their morphology.

Another category used in literature when referring to the fine fibre fraction is crill, defined as the part of cellulosic material that does not necessarily become entangled in the plug of fibres during

plug flow [3, 4]. Based on its definition the crill of chemical pulps consists mainly of slender fibrillar particles. For PGW crill includes both flour stuff and slime stuff.

Luukko et.al. [5] introduced the terms flake-like (non-fibrillar) and fibrillar material which are applied for mechanical as well as for chemical pulp fines [1, 6, 7]. Flake-like material contains fibre wall fragments, thick lamellae, and ray and parenchyma cells whereas fibrillar material contains fibrils and thin lamellae as well as fibrils that are attached, for example, to a fibre wall fragment.

Prior to characterization fines have to be separated from the fibre fraction which is performed mainly using the Britt dynamic drainage Jar [1, 8] or the Bauer McNett classifier [9–11]. Fines fractions were further separated into subfractions based on screening techniques [8, 12, 13], tube flow fractionation [14, 15] and sedimentation [13, 16].

Chemical composition was analyzed by several groups, e.g. [10, 13, 17–22] showing among other differences, that fines have higher lignin and extractives content compared to the fibre fraction [10, 19]. The higher lignin content is most prominently attributed to primary fines but also to secondary fines originating mainly from the outermost fibre wall [10]. Charge and charge related measurements like zetapotential [8, 23], total charge by conductometric titration [24], total and surface charge by polyelectrolyte titration [25–27] and methylene blue adsorption [22, 28] have been applied. Specific surface area was estimated by settling techniques [16, 29, 30], turbidity or transmittance measurements [31, 32] and Congo red adsorption [17].

Morphological characterization is mainly performed applying optical imaging using commercially available flow cells and optical microscopy but also using techniques based on fractionation and measurement of specific surface area which were already introduced. Other non – imaging but optical methods include the crill measurement (based on the difference in the signal under UV- and IR illumination) [33] and dynamic and static light scattering [34]. A quite rarely used non-optical technique is the electric sensing zone method [35]. These methods allow the evaluation/characterization of a certain part of the fines fraction (e.g. crill) and/or yield the corresponding size distributions. In addition to the information on content and size, imaging methods allow the evaluation of particle shape. Still, the flow cell analyzers are mainly used for the determination of fines content but not for further characterization of this fraction related to insufficient detectability of fines in aqueous media due to their transparency [36]. High resolution microscopy was mainly applied for qualitative characterization of fines and visualization of the effects of these on paper structure, e.g. [37–39]. Static light microscopy was used qualitatively and quantitatively for content size and shape characterization by several authors, e.g. [9, 19]. The most frequently cited and used method was introduced by Luukoo and coworkers [5], first applied on mechanical pulp fines but later on also used to characterize chemical pulp fines. This method uses staining prior to evaluation and distinguishes flake-like and fibrillar material based on grey level differentiation. Flake like material appears darker than fibrillar material and thus can be separated by an image processing routine. Size of flake like material, length of fibrillar material and fibrillar content can be determined.

The swelling characteristics representing the ability of the material to absorb or retain water was measured using size exclusion determining the fibre saturation point [40], or a variety of modifications of WRV measurements [10, 17, 42–44].

Due to their similarity in character methods for fines characterization are also applied for MFC or methods used for MFC might be also suitable for fines [44].

Fines in general are known to affect sheet properties [2, 3, 9, 10, 19, 46–48]. They increase tensile strength and z-strength, which is attributed to the high surface area and conformability yielding a high bonded area and better stress distribution in sheets containing fines [49–51]. Between two bonding fibres a bonding layer was identified [51] only existing in refined chemical pulps.. When secondary fines are present this layer's thickness increases, while it is reduced when the fines are removed. Macrofibrils (thick bundles of microfibrils) form a network structure and microfibrils seem to fill the space between the macrofibrils. It is suggested that the microfibrils are the ones predominately contributing to bond strength. Besides, secondary fines were found to cover the surface of fibres, as they are attracted to the fibres by capillary forces thereby also covering the edges of the fibre bonds. It is also suggested that fines have more effect on bonding than external fibrils still connected to the fibres [49, 53]. Together with tensile strength, density is also increased by the addition of fines. On the one hand fines pull the fibres closer together by capillary forces which are more pronounced for thin fibrillar fines, on the other hand they fill the voids within the network structure. Air permeability is reduced for similar reasons and the dewatering resistance is increased [46]. Dewatering resistance is increased even further because of the high swelling ability of fines [53]. Light scattering was found to be improved by mechanical pulp fines, but reduced for chemical pulp fines as more interfaces are created by the stiffer mechanical pulp fines whereas they are reduced by the flexible, fibrillar chemical pulp fines.

Differences in quality of mechanical pulp fines were discussed in detail and quantified based on the fibrillar content and the swelling of the fines [5, 9, 24, 46, 54]. The higher the fibrillar content and the swelling ability the higher the impact on strength properties. Connections were also drawn to size and shape of the material, but these parameters seem play a minor role in paper property development for mechanical pulps [9, 54]. When it comes to chemical pulps primary fines have a lower impact on paper properties than secondary fines [55], again attributed to the higher swelling ability of secondary fines [10]. Differences in swelling, extractive content and specific surface area of fines from different wood sources and pulping processes were found to be related to strength development of sheets [17, 19, 40]. Sub fractionation of chemical pulp fines shows that the impact of these fractions on tensile strength is differing probably depending on morphology and chemical composition [19]. Changes in quality and quantity were observed when using different refining aggregates [47, 56]. It was also found that that particle size of secondary fines is larger and number of fines lower in late wood than in early wood related to the lower S2 fibril angle and fiber wall thickness of latewood fibers promoting a cutting action [48].

As listed above a wide range of methods was applied resulting in different conclusions regarding the effect of fines quality and quantity on sheet properties. While for mechanical pulp fines the parameters fibrillar content, swelling and fines content seem to describe quite effectively their impact on sheet properties, the parameters finally determining sheet properties for chemical pulp fines are not that clear. To relate fines properties to product properties various research groups used different approaches. Sheets were formed with and without fines, allowing no clear differentiation between quality and quantity as variations in fines content in a sheet also imply a variation of the fibre content. When it comes to secondary fines most of studies used laboratory refining, where only the duration of the refining treatment is changed but not the intensity and thus merely the

quantity of secondary fines is influenced but not their quality. If different aggregates were used, only differences in size and quantity of the produced fines were discussed. As especially secondary chemical pulp fines are of a heterogeneous nature, the morphology of fines cannot be described by size only. Variations in paper properties achieved by the addition of fines from different wood sources are not related to a distinct characteristic, as the character of these fines is different on a wider range. Additionally one has to consider potential variations in fines content due to differences in fines retention in the standard sheet forming process.

In this work we will first present two improved methods dealing with the characterization of the swellability (WRV) and the morphology of chemical pulp fines. These two methods are then applied to describe differences in fines quality, relevant in terms of their impact on paper properties. Fines were produced from two different pulps using an industrial disk refiner. In order to achieve differences in fines quality of a certain pulp, refiner settings were varied. These fines are added to different fibre qualities in sheet forming based on a trial matrix. The experimental setup thus allows to separate the impact of a given fines fraction on sheet properties.

EXPERIMENTAL SETUP

Samples:

Softwood bleached kraft pulp (SBK) and softwood bleached sulfite pulp (SBSU) were refined in an industrial single disk refiner at five different refiner settings varying flow rate and refiner pressure. The refiner was operated in a range, relevant for production, leading to different settings for SBK and SBSU pulp. Details regarding the refiner settings are not given in this paper as the intention is mainly to evaluate the effect of secondary fines of a different character on paper properties. The detailed refiner settings are given in [57].

Samples were taken from the unrefined pulps as well as from the five different refiner settings for each pulp. Corresponding samples were taken within the time frame of five hours to minimize the impact of variation in pulp quality.

Methods:

Pulp characterization and fractionation:

The drainability according to the Schopper-Riegler (SR) method (ISO 5267-1:1999), the gravimetrical fines content determined by the Britt Dynamic Drainage Jar (SCAN-CM 66:05) and the fibril perimeter determined by a L&W Fiber Tester^{+} (FT^{+}), were evaluated on all pulp samples.

The unrefined and refined pulp samples were fractionated using a lab-scale pressure screen [58]. The pressure screen was equipped with a perforated plate (hole diameter 100 µm). The material passing through this plate was defined as the fines fraction and collected in a separate tank. The pulp was recirculated until the remaining volumetric fines content (measured with a L&W Fiber Tester^{+}) was below 0.5%. This fraction was defined as the fibre fraction. The fines were allowed to settle for three days, before the supernatant was removed and approximately 1% solids content was reached. Fibres were centrifuged to approximately 30% consistency.

Fines characterization:

Secondary fines content:

The secondary fines content of a given sample was determined based on the fines content of the unrefined pulp and the fines content of the refined pulps (measured using the BrittJar method SCAN-CM 66:05), assuming that primary fines are not changed during refining.

Water retention value (WRV):

Measuring the WRV according to the standard procedure (ISO 23714) requires the formation of a pad of defined mass by filtration. Due to blocking of pores of the filtering element and the high dewatering resistance of fines this approach is not feasible for the pure fines fraction. The method applied in this work allows the use of the standard procedure also for fine material, without modification of the experimental conditions. Samples with a defined fines content (5, 10, 15 %) are prepared and WRV is measured according to the standard (ISO 23714). WRV increase linearly with the fines content. Based on the results linear regression (Eq. 1) allows the determination of the WRV of fines (WRV_{Fines}), inserting a fines content of w_{Fines} = 100 % (Eq.2) [59].

$$WRV = k * w_{Fines}[\%] + d \quad (1)$$

$$w_{Fines} = 100\% \rightarrow WRV_{Fines} = k * 100 + d \quad (2)$$

Microscope method – Determination of Fibril Area:

The method applied in this work is based on the method proposed by Luukko et al. [5] Luukko's method was mainly designed for mechanical pulp fines. The segmentation process was discussed for these fines, giving a clear picture which particle corresponds to flake – like and which to fibrillar material. As can be seen in Figure 1 (first row) mechanical and chemical pulp fines are highly different in their morphology. Staining of fines is important for contrast enhancement allowing a complete detection of the fines material, especially microfibrillar fines. For chemical pulp fines the dye adsorption varies between different wood sources and different morphological entities (raycells, parenchymacells, fibrillar fines) within the sample. Most probably the differences are related to the differences in their chemical nature affecting the charge content (methyleneblue adsorption was used as a fast determination method for fibre charge [28]). We found that addition of tall oil levelled out these differences and gives uniform coloration independent from chemical composition (see Appendix 1).

The microscope method determining the morphology of fines consists of three parts; sample preparation, image acquisition and image processing.

A 0.01% fines suspension was prepared in a test tube. A tall oil - water emulsion was prepared by adding 0.01 g commercially available crude tall oil to 5 g deionized water and the mixture was emulsified at 80°C in an ultrasonic bath for 30 minutes. 0,06 g of this emulsion was added to 5 g of the fines suspension and homogenized by vigorous shaking. 0.1 g methylene blue solution (1 wt.% in water) was added and homogenized again.

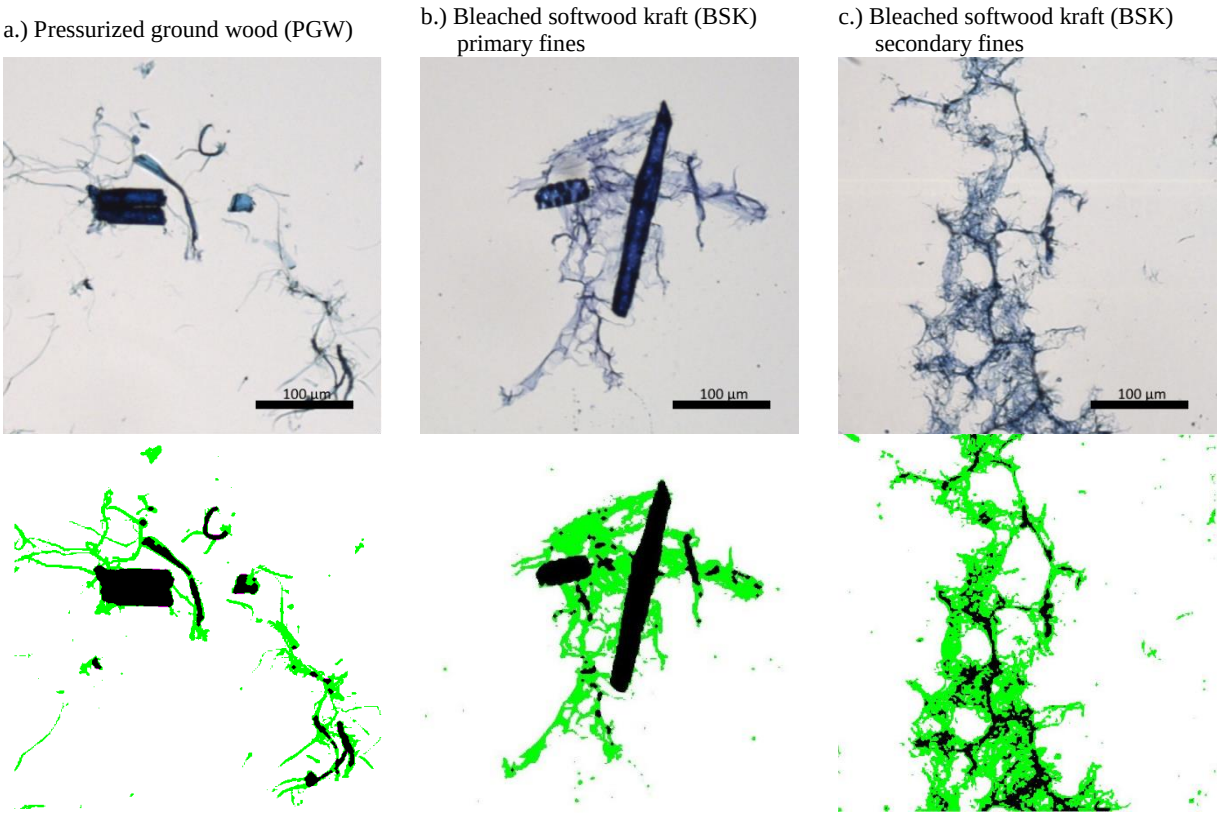

Figure 1: Microscopic images of PGW fines (a), BSK primary fines (b), BSK secondary fines (c) of fines (first row) and segmentation of these images into flake –like materal and fibrillar material (second row). Black (dark) areas correspond to flake-like fines (ray cells, parenchyma cells, fibre fragments, macrofibrillar backbone); green (light) areas correspond to fibrillar material (fine fibrils or micro fibrils)

Three droplets of the prepared fines suspension were placed on a microscope slide (76 x 26 mm), fixed with a cover glass (60 x 24 mm) and dried on a heating plate. A conventional transmission light microscope (Leica 301-371.010) equipped with a standard CCD camera (Jai AM-200GE/AB-200GE) and an automated stage control (Märzhäuser Multicontrol 2000), operated by the open source software ImageJ was used for automated capturing of 700-800 single images per microscope slide (1600x1200 pixels per image; image area: 1380x1035 µm^2). An image analysis routine was programmed on the basis of Luukko's method in MATLAB. OTSU thresholding (standard routine implemented in MATLAB) was applied for multilevel thresholding, distinguishing between fibrillar material and flake–like material based on grey level differences.

In Figure 1 (second row) an example of a segmentation result for PGW fines, BSK primary fines and BSK secondary fines is shown. Lighter areas are classified as fibrillar material, consisting of microfibrillar fines, whereas darker areas are classified as flake-like material. Flake-like material contains ray cells, parenchyma cells but also the macrofibrillar backbone of fibrillar secondary fines. Particle size and shape of the detected segments is determined as follows. The pixels of each segment are transferred into µm² unit representing the segment area (A_i). After that the segments undergo a skeletonizing process and the pixels comprising the skeleton are counted and transferred to µm units. The length of the skeleton is used to approximate particle 'length' (L_i).

As a size parameter for flake-like and fibrillar segments the circle equivalent diameter (CED_i) is determined for each single particle with Area (A_i) (Eq. 3). Based on this parameter the area weighted mean size ($\overline{CED_{q2}}$, Eq. 4) is determined. The width (W_i) for segments is determined by dividing the Area (A_i) by the skeleton approximated length (L_i, Eq. 5). The aspect ratio (AR_i) is defined as the length (L_i) divided by width (W_i, Eq. 6). Mean aspect ratio ($\overline{AR_{qo}}$) was determined according to Eq. 7.

The Fibril Area is defined as the sum of the areas of fibrillar material (A_{fibril}) divided by the sum of the areas of fibrillar material (A_{fibril}) and flake-like material (A_{flake}, Eq. 8) of all images taken from one microscope slide. Thus Fibril Area gives the microfribrillar fines content of a fines fraction, the CED for flake-like and fibrillar material, express the size of these fragments connected after segmentation and the aspect ratio corresponds to the slenderness and branching of these segments. [60]

$$CED_i = \sqrt{\frac{4 * A_i}{\pi}} \tag{3}$$

$$\overline{CED_{q2}} = \frac{\sum_{i=1}^{n} CED_i^3}{\sum_{i=1}^{n} CED_i^2} \tag{4}$$

$$W_i = \frac{A_i}{L_i} \tag{5}$$

$$AR_i = \frac{L_i}{W_i} \tag{6}$$

$$\overline{AR_{qo}} = \frac{\sum_{i=1}^{n} AR_i}{\sum_{i=1}^{n} 1} \tag{7}$$

$$Fibril \quad Area = \frac{\sum_{i=1}^{n} A_{fibril,i}}{\sum_{i=1}^{n} A_{fibril,i} + \sum_{i=1}^{n} A_{flake,i}} \tag{8}$$

Recombination of fibres and fines fractions:

A first, rather simple trial setup was used to illustrate the effect of secondary fines quantity on fines characteristics and paper properties (Table 1). Samples of unrefined and refined pulp were taken from an industrial disk refiner during production without choosing defined refiner settings. Different ratios of primary fines (SBSU uref/SBK uref) and fines after refining (SBSU ref/SBK ref) were blended and added to the sulfite fibres obtained from the same refined pulp in a constant ratio of 91% fibres and 9 % total fines with varying ratio of primary and

secondary fines (Table 1). Thus six blends containing SBK (VS_1:3) and SBSU fines (VE_1:3) with different secondary fines content were established.

A more complex trial setup was developed to look into the effect of secondary fines quality (Table 2). Refined pulp samples were produced by changing refiner settings and separated into fines and fibre fractions as described in the beginning of this chapter. These fractions are then applied based on a sample matrix including ten different fines fractions from refined SBK (HS_1:5) and SBSU pulp (HE_1:5) and 4 different fibre fractions, SBK (HS_3,5) and SBSU (HE_3,5), also originating from these refined pulps. 9% of each fines fraction was blended with 91% of each fibre fraction yielding forty sample points. In this setup quality as well as quantity of secondary fines is changing as in industrial refining not only the quality of produced secondary fines is influenced but also the quantity. The influence of fines quantity on paper properties is however reduced, as a constant amount of 9% fines was added and the impact can be related to the characteristics measured from the pure fines fraction. Only the grey coloured combinations in Table 2 were actually prepared and tested due to time reasons.

	Fiber fr.	Fines fractions			
	SBSU ref	SBSU uref	SBSU ref	SBK uref	SBK ref
VS_1	91			4	5
VS_2	91			2	7
VS_3	91			0	9
VE_1	91	4	5		
VE_2	91	2	7		
VE_3	91	0	9		

Table 1: Trial setup for evaluation of the influence of secondary fines quantity: Primary and secondary fines were blended in different ratios; 91% sulfite fibres were blended with 9% BSK fines (green) increasing secondary fines content in the order of VS_1 to VS_3 and with 9% sulfite fines (yellow) increasing secondary fines content in the order of VE_1 to VE_3; reverence point (red coloured line)

			Fines fractions									
			HS_1	HS_2	HS_3	HS_4	HS_5	HE_1	HE_2	HE_3	HE_4	HE_5
			y1	y2	y3	y4	y5	y6	y7	y8	y9	y10
Fibre fractions	HS_3	x1										
	HS_5	x2										
	HE_3	x3										
	HE_5	x4										

Table 2: Trial setup for the evaluation of the influence of secondary fines quality and quantity: Fines quality was influenced by applying different refiner settings. Blends including 10 different fines qualities, five BSK fines qualities (HS_1:5, $y_{1:5}$ green) and five SBSU fines qualities (HE_1:5, $y_{6:10}$ yellow) and four different fibre qualities, two BSK fibre qualities (HS_3,5, $x_{1:2,}$ green) and two SBSU fibre qualities (HS_3,5, $x_{3:4,}$ yellow). Forty combinations containing 9% fines and 91% fibres of these different qualities are obtained; prepared and measured combinations (grey coloured fields); reference point (red coloured field).

Sheet preparation:

Handsheets of 60 g/m² were prepared on a Rapid – Köthen sheet former (ISO 5269-2:2004) using white water recirculation [45, 55] in order to obtain comparable retention of fines in the sheets. The first five sheets were discarded until stable fines content in the sheets was achieved. Eight sheets were formed and wet pressed (150 bar, 90 sec) between two blotting papers, directly after sheet formation. Wet pressing was performed to limit the influence of capillary forces and their effects on sheet consolidation. It was found in pre-trials that the influence of fines on some sheet properties (e.g. light scattering, tear strength), became more pronounced after wet pressing.

Pulp and sheet testing:

Water retention value (WRV;ISO 23714:2014) and drainability Schopper-Riegler (SR: ISO 5267-1:1999) were measured for the pulp blends. Density (ISO 534:2011), Bendtsen air permeability (ISO 5636-3:2013), tensile index (EN ISO 1924-2), z-strength (Scott Bond, ISO 15754:2009) and tear strength (ISO 1974:2012), were measured for the paper sheets.

Data processing:

Data processing was applied to minimize the impact of random variation on sheet properties. To give an example: Blending fibre quality x_1 and fines quality y_1 might affect sheet formation differently than blending fibre quality x_2 and fines quality y_1. If the effect is purely related to the fines quality and thus apparent in all sets prepared with fines quality y_1 independent from the fibre type, this effect will be also visible after data processing. If the effect is only evident in one single data point it is considered random variation, which will be evened out by the data processing routine described below.

The first row $(x_{i=1})$ was taken as a basis and the mean difference $\left(\overline{\Delta x_{i,j}}\right)$ between the row $(x_{i=1})$, and the rows $(x_{j=1:4})$ was calculated applying Eq. 9 (see Figure 2). The same routine was applied with the other rows $(x_{i=2:4})$ taken as a basis.

In a second step the mean differences $\left(\overline{\Delta x_{i,j}}\right)$ were added to the first row $(x_{i=1})$ and the matrix $X_{i=1}$ was calculated (Eq. 10). Applied also for the other basis rows $(x_{i=2:4})$, four 4x10 matrices $X_{i=1:4}$ were calculated.

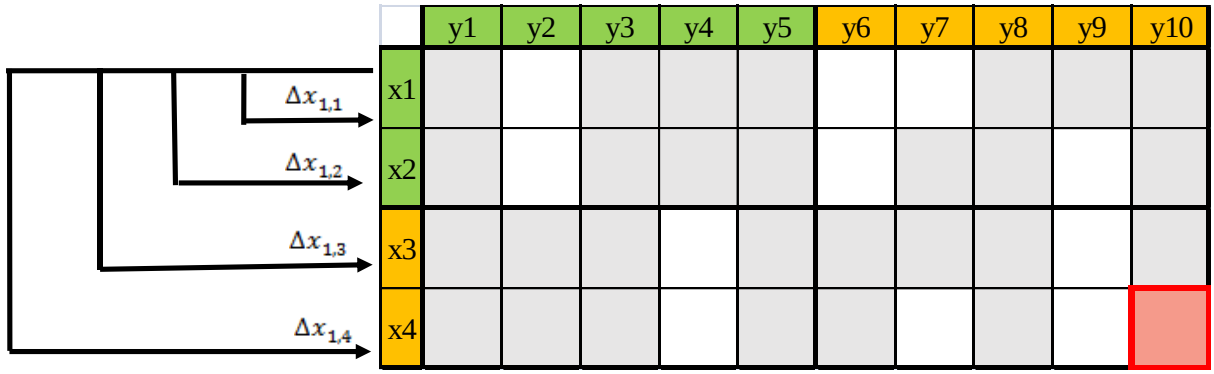

Figure 2: Data processing; determination of differences between basis row $(x_{i=1})$ and the rows $(x_{j=1:4})$

The same routine was applied in the other direction, thus taking columns $(y_{k=1:10})$ as basis and determining the mean differences $\left(\overline{\Delta y_{k,l}}\right)$ (Eq. 11), adding these differences to columns $(y_{k=1:10})$ ten 4x10 matrices $Y_{i=1:10}$ were generated (Eq. 12). The average matrix was calculated from the 14 matrices and represents the processed data matrix $(\overline{XY})$ (Eq. 13). This operation allows also the interpolation of sample points which were not measured. This interpolation gets more uncertain when only one data point is measured in a row or a column, thus column y_9 (Figure 2) will be not considered in the discussion.

$$\overline{\Delta x_{i,j}} = \frac{\sum_{n=1}^{10} x_i, y_n - x_j, y_n}{\sum_{n=1}^{10} 1} \quad (9)$$

$$X_{i=1:4} = x_{i,j} + \overline{\Delta x_{i,j}} \quad (10)$$

$$\overline{\Delta y_{k,l}} = \frac{\sum_{m=1}^{4} x_m, y_k - x_m, y_l}{\sum_{m=1}^{4} 1} \quad (11)$$

$$Y_{k=1:10} = y_k + \overline{\Delta y_{k,l}} \quad (12)$$

$$\overline{XY} = \frac{\sum_{i=1}^{4} X_i + \sum_{k=1}^{10} Y_k}{\sum_{i=1}^{4} 1 + \sum_{k=1}^{10} 1} \quad (13)$$

Presentation of data:

In the data matrix a reference point is set (marked red in **Table 1** and **Fehler! Verweisquelle konnte nicht gefunden werden.**) and mean differences to that reference point are calculated. The data is presented as is shown in Figure 3 (secondary fines quantity) and Figure 5 to Figure 10 (fines quality) respectively. The reference point is set to 1 and the relative difference to that point represents the difference arising due to changes in fines quality. The averaged measured value of this reference point is added in the diagram as a number (in red text).

RESULTS:

Variation of secondary fines quantity at equal quality:

As is discussed by several authors [55, 60], secondary fines show a more beneficial influence when it comes to paper properties compared to primary fines. This topic will be addressed in the first trial series (see **Table 1**) to show the capabilities of the applied methods for evaluation of fines characteristics and their effect on paper properties in a simple setup. Therefore the effect of the quantity of secondary fines on tensile index and fines characteristics is investigated. Different quantities of secondary fines were achieved by blending primary fines with fines from pulp after refining in different ratios (see **Table 1**). Thus a variation in secondary fines content of constant quality was achieved (Figure 3 a).

Looking at the fines characteristics with the above described methods it is evident that the water retention value (WRV) of fines as well as the Fibril Area measured by the microscope method rises continuously with increasing quantity of secondary fines (Figure 3 b,c). This reflects the expected higher swelling ability and more fibrillar character of secondary fines. When evaluating their impact on sheet properties it has to be pointed out that the fines content in the sheets was held constant at 9 %, varying only the ratio between primary and secondary fines. The influence of fibres on sheet properties was held constant by blending these fines always with the same fibres.

Tensile index showed an increase with increasing amount of secondary fines as those fibrillar secondary fines are more bondable than the ray and parenchyma cells containing primary fines. This is in accordance with the findings in the literature.

That sulfite pulp achieves lower strength properties compared to kraft pulp is well known, but here it is shown that this is also the case for the isolated behavior of the corresponding fines fraction. Although the secondary fines content is higher in the blend for sulfite pulp (Figure 3 a) fibril area is comparable and WRV is even lower compared to kraft fines, related to the lower tensile index achieved for the sulfite fines [40].

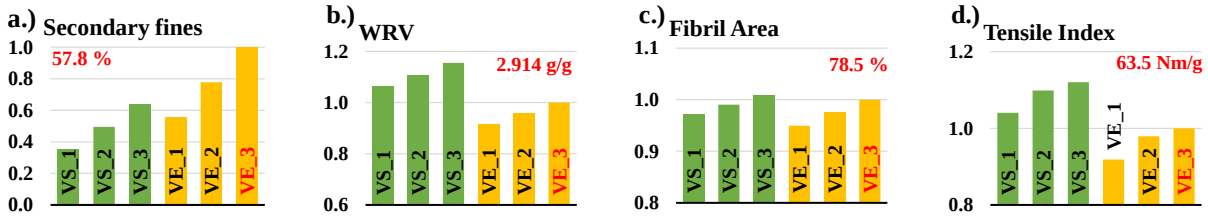

Figure 3: **Trial setup for evaluation of the influence of secondary fines quantity:** fines properties: a) share of secondary fines in the fines fraction containing primary and secondary fines; b.) WRV of fines, c.) Fibril Area determined by the microscope method, d.) Tensile Index measured from sheets with 91% fibre (of same quality) and 9% fines with varying quantity of secondary fines; reference value given in red

Variation of secondary fines quality and quantity:

Characterization of pulps:

Pulps obtained by the variation of refiner settings in terms of flow rate and refiner pressure were characterized prior to fractionation. Due to these refining variations different quantities of secondary fines were produced resulting in a change of the total fines content in the refined pulp samples (Figure 4 a). Also variations in the fibril perimeter determined by the FT^{+}, representing external fibrillation of the fibres, are measured (Figure 4 b). Although fines production and external fibrillation is related, the trends are not directly comparable (Figure 4 a,b). The SR represents a sum parameter not differentiating between fibre properties and fines properties (Figure 4 c). Still, when it comes to paper properties work in literature shows that external fibrillation has less effect than secondary fines content most probably due to the higher freedom of fines moving to any possible position within a network [48, 51, 52]. In this respect it is also of interest to separate the impact of fines from the impact of fibres on pulp and paper properties.

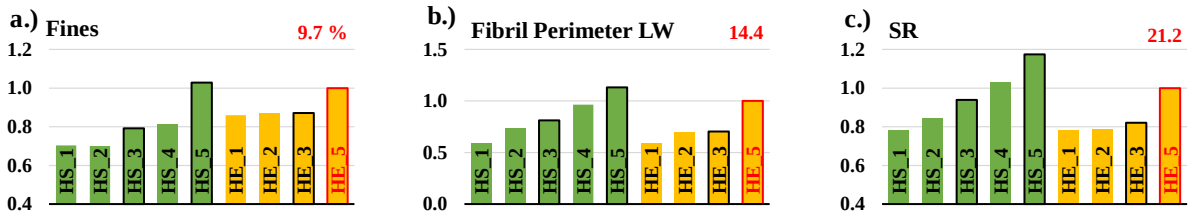

Figure 4: Characterization of pulps obtained by variations of refiner settings; a.) fines content after refining, b.) fibril perimeter, c. SR; reference value given in red

Characterization of fines quality:

Fines quality was characterized from the separated fines fractions with the methods described above yielding WRV representing swelling ability and the Fibril Area, representing quantity of microfibrillar fines (Figure 5 b,c). As only secondary fines are produced during refining, the quantity of secondary fines of the separated fines fraction (Figure 5 a) will change according to the change in total fines content of the pulp (Figure 4 a). Sample HS_2 possessing one of the lowest secondary fines contents in the provided samples shows the highest WRV and Fibril Area (Figure 5 b,c) which is totally different to the trial series above where secondary fines content showed clearly the same trend as WRV and Fibril Area. This underlines that not only quantity of secondary fines is of interest when it comes to the properties of fines, but to a considerable extent also the fines quality. These big differences in fines quality could not have been observed when refining pulp in a lab device (e.g. in the PFI mill), as only the duration of the treatment is changed but not the intensity of the impact on the fibres which is achieved in industrial refining when changing the specific edge load and specific energy consumption. WRV correlated well with the measurement of Fibril Area for BSK fines (HS_1:5) but not for sulfite fines (HE_1:5). Especially in sample HE_5 the low Fibril Area is in contrast to the high WRV, indicating that Fibril Area and WRV are not measuring the same property, although this would be assumed considering results from the trial series on the quantity of secondary fines. An explanation will be given below based on the in depth morphological characterization of the fines networks.

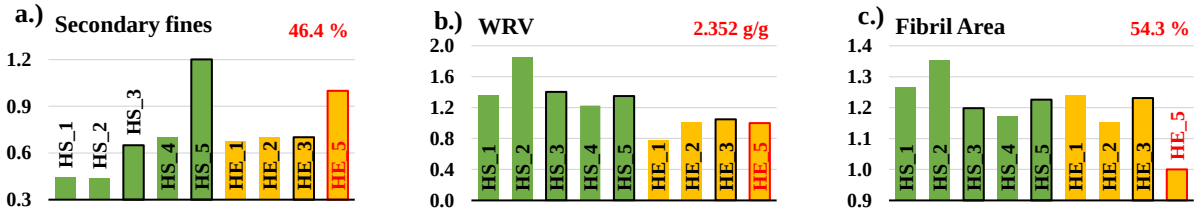

Figure 5: **Trial setup for evaluation of the influence of secondary fines quality and quantity:** Characterization of separated fines fractions of fines obtained by the variation of refiner settings; a.) secondary fines content; b.) WRV; c.) Fibril Area; reference value given in red

Figure 6 shows parameters obtained by the microscope method additional to the Fibril Area. The first row shows parameters of the flake like material, the second row parameters of the fibrillar material. The circle equivalent diameter (CED) describes the average size of a connected fragment after segmentation, representing the area of the fragment. The aspect ratio (AR) describes the slenderness and/or the branching of the segment. Fibril Area (Figure 5c) is related to the size of flakes (CED flakes) and fibrils (CED fibril). For BSK fines at similar secondary fines content a decrease in flake size is accompanied by a decrease in fibril size (HS_1 -> HS_2) or vice verca (HS_3 -> HS_4). This indicates the size of secondary fines networks – comprised of flake - like and fibrillar segments – as is exemplarily shown in Figure 7 (first row). The size of flake like material in sulfite fines remain rather constant for HE_1,2,5 while fibril size decreases, leading to a reduction in fibril area. This change of morphology representing the change in the size ratio between flake like and fibrillar segments is illustrated in Figure 7 (second row). Therefore the WRV does not reflect Fibril Area as it is the case for kraft fines, because the high secondary fines

content in HE_5 shows a high proportion of flake like segments yielding a low Fibril Area. Still, the high proportion of macrofibrillar backbones in the secondary fines networks has a higher WRV compared to ray or parenchyma cells contained in primary fines.

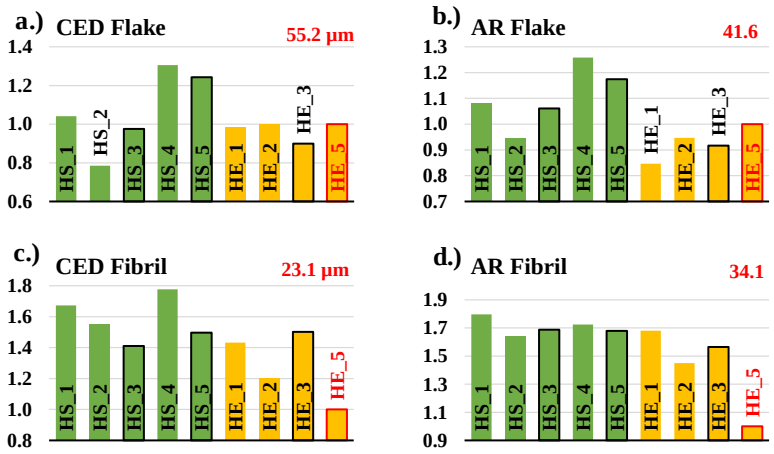

Figure 6: Parameters obtained by the microscope method in addition to the Fibril Area; size of segments expressed by the CED of flake – like (a) and fibrillar material (c); aspect ratio (AR) indicating slenderness and branching of segments for flake-like (b) and fibrillar material (d); reference value given in red

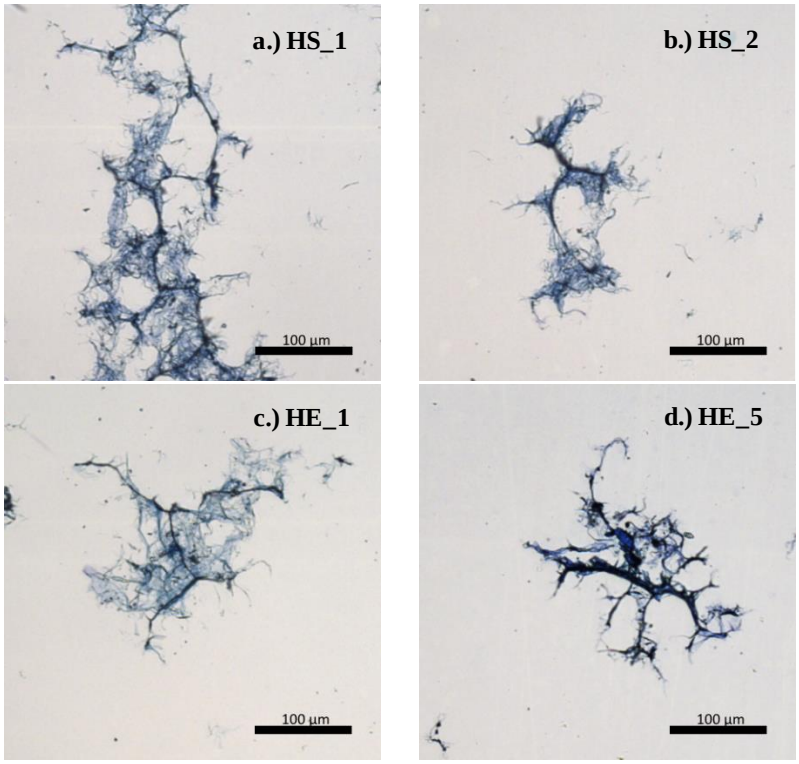

Figure 7: Microscope images demonstrating the differences in fines morphology determined by the parameters obtained from these images; Size of fines networks (a, b); Ratio between fibrillar and flake - like material of the fines network (c,d).

Impact of fines quality on pulp and sheet properties:

The above discussed results of fines and pulp characterization will now be related to pulp and sheet properties measured on the blends of 9% fines and 91% fibres (see **Fehler! Verweisquelle konnte nicht gefunden werden.**) based on the results after data processing.

The WRV of the different fines fractions derived from the results after data processing (Figure 8 a) correlates well with the WRV measured directly on these fines fractions (Figure 5 b). The differences between these two values represent the difference in the amount of fines addressed. In the directly measured values the variation represents 100% fines whereas in the processed results the variation represents the impact of 9% fines in a blend with the fibre fraction. Keeping that in mind not only the trend but also the absolute values match quite well. This high correlation between directly measured and extracted data confirms that the trial setup and the data processing routine yield correct and reliable results for the impact of the different fines fractions.

SR shows the same trend as the WRV (Figure 8 a-b), indicating that the impact of the fines fraction on the SR is directly related to the volume change of fines due to swelling.

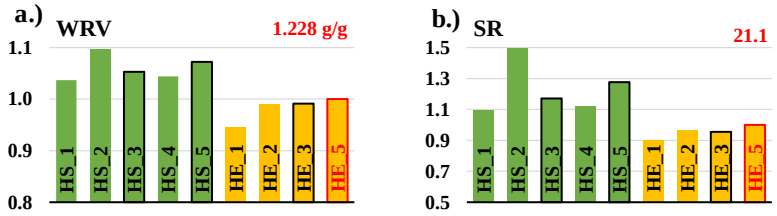

Figure 8: Impact of variation of fines quality on a.) WRV and b.) SR of blends containing 9% fines and 91% fibres; reference value given in red

The apparent sheet density (Figure 9 a) of the wet pressed sheets is also affected by the fines quality. For example when comparing HS_1 and HS_2, containing a comparable quantity of secondary kraft fines, sheet density is higher for HS_2. This fines fraction also shows a higher WRV and fibril area and may be capable of filling up voids more easily due to the more fine fibrillar character. Considering the trend in sheet density for sulfite fines, sheet density seems to be to a greater extend affected by the fibril area (microfibrillar fines), than by the WRV, as in this case WRV does increase while fibril area decreases together with decreasing density .

Air permeability (Figure 91 b) shows a large difference between BSK and sulfite fines quality with sulfite fines obtaining higher air permeability at similar sheet density. That BSK fines show a lower air permeability is most probably also related to the higher swelling of these fines qualities (HS_2 showing the highest WRV and Fibril Area also exhibits the lowest air permeability). Apart from that a correlation between fines characteristics and air permeability is not obvious but porosity will most probably be affected by sheet density, fibril area, WRV and the secondary fines content to different extents that cannot be separated and quantified based on this data.

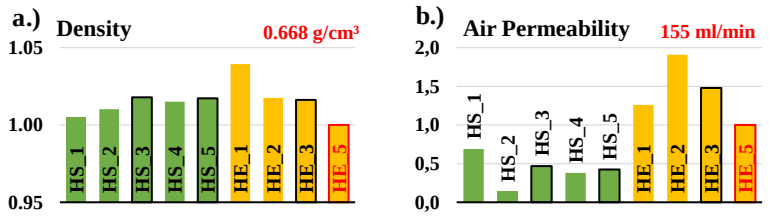

Figure 9: Impact of variation of fines quality on a.) sheet density and b.) air permeability of blends containing 9% fines and 91% fibres; reference value given in red

Scott Bond (Figure 10 b) is especially for BSK fines highly consistent with the development of fibril area. Also Nanko and Ohsawa [51] considered the microfibrillar fines predominantly responsible for bonding in refined chemical pulps. The high variation in sulfite fines qualities in terms of flake-like and fibrillar character does not allow to link Scott Bond development directly to Fibril Area. Nevertheless the difference in Scott Bond between HE_2 and HE_3, showing similar secondary fines content, WRV and sheet density, is most probably related to the difference in Fibril Area. Tensile index (Figure 10 a) develop somewhat different from Scott Bond. In addition to the Fibril Area (microfibrillar fines), secondary fines content (macrofibrillar backbone + microfibrillar fines) seems to affect this parameter. For example HS_1 and HS_2 with the lowest secondary fines content achieve lower tensile index in relation to Scott Bond. HS_5 on the other hand with the highest secondary fines content shows the highest tensile index, but not the highest Scott Bond, which was achieved for the sample HS_2 with the highest Fibril Area. The secondary fines content implies the quantity of macrofibrillar backbones of fines, influencing tensile index, were the sheet is loaded in plane during measurement to a higher extent than Scott Bond, applying the load out of plane as there might be an orientation of such structures predominantly in plane. This would be reasonable considering SEM images of fines stretching between voids and covering the surface of fibres [37].

That this backbone contributes to tensile index is also evident in the higher difference between SBSU and BSK fines when it comes to tensile strength, compared to Scott Bond. Sulfite fibres and fines are widely accepted to show considerably different character than kraft fibres and fines especially when it comes to tensile properties [40, 61, 62] which is also shown in the appendix for the 91% fibre fraction of sulfite and kraft pulps (Appendix 2). Thus the macrofibrillar backbone consisting of oriented microfibrils might have similar characteristics than a fibre.

Also tear strength (Figure 10 c) is influenced by fines quality. Fines were found to decrease tear strength due to their higher bonding ability compared to fibres [45, 48]. This is evident from HS_2 fines with the lowest tear strength at highest Scott Bond. Additionally tear strength shows a similar trend than the AR of flakes for both kraft and sulfite fines (Figure 6 b). The AR is a measure for the slenderness but also for branching of the macrofibrillar backbone. A higher AR indicates a higher total backbone length seeming to give higher tear strength.

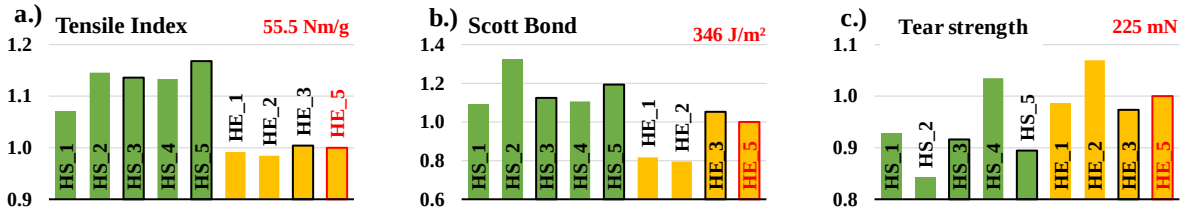

Figure 10 Impact of variation of fines quality on strength properties, a.) tensile index and b.) Scott Bond c.) tear strength,of blends containing 9% fines and 91% fibres; reference value given in red

CONCLUSION:

Chemical pulp fines are highly heterogeneous in terms of morphology and chemical composition and their impact on sheet properties cannot simply be described by their quantity or by their origin. In this setup fines quality was varied by applying different refiner settings thus affecting fines morphology in terms of size, aspect ratio and fibrillar character. As all fines varieties were produced from two different pulps, a discussion of the influence of different pulp chemistry is not possible, which of course is also important for bond formation and thus strength properties. The measured differences in quality are only described in terms of morphology and swelling ability determined based on methods implemented especially for this task.

This study shows that such an in depth fines characterisation together with a suitable experimental setup allows a better understanding of the impact of fines quality on paper properties, which is usually superimposed by the impact of the fibre fraction and the quantity of fines. Such insights are not possible with standard testing and without a setup to separate the impact of the fines fraction from that of the fibre fraction.

Based on the presented results it is obvious that a differentiation in primary and secondary fines usually applied to address fines characteristics is not sufficient as secondary fines can show quite different properties in terms of fibrillar character, size and swelling ability. Depending on the sheet property one or more fines characteristics are descriptive. Strength properties for example are highly related to fine fibrillar material and the respective swelling ability of the material.

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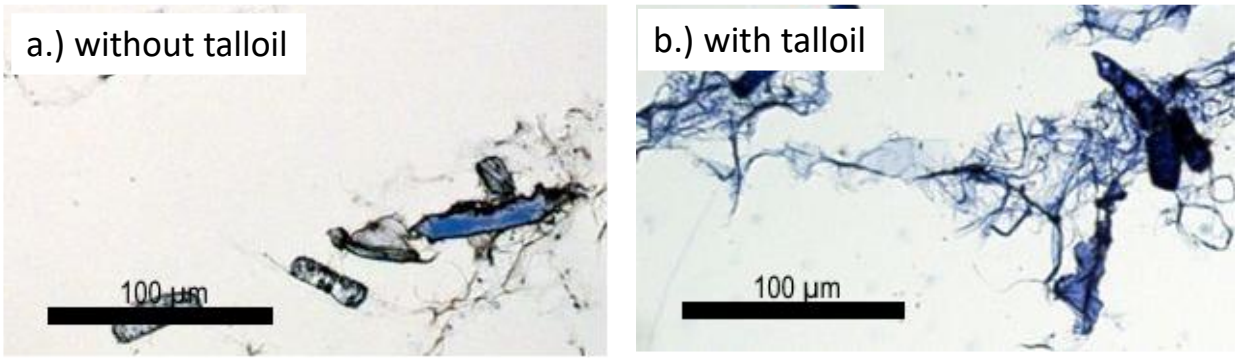
APPENDIX:



Appendix 1: Sample preparation microscope method, staining of BSK primary fines a.) without talloil, b.) with talloil

Appendix 2: Development of strength properties as a result of changing fibre quality, a.) Tensíle Index, b.) Scott Bond

IV

Mayr, Melanie, Odabas Nora, Eckhart Rene, Henniges Ute, and Bauer Wolfgang (2017) "Cationization of Lignocellulose as a Means to Enhance Paper Strength Properties." BioResources 12 (4): 9338–47. doi:10.15376/biores.12.4.9338-9347.

Cationization of Lignocellulose as a Means to Enhance Paper Strength Properties

Melanie Mayr,[a,*] Nora Odabas,[b] Rene Eckhart,[a] Ute Henniges,[b] and Wolfgang Bauer [a]

Chemical modification by attaching functional groups to lignocellulosic pulp fibers might be a strategy for improving the pulp, and thereby, paper properties. Several studies have described positive effects on paper strength properties for handsheets prepared from cationic-modified pulp or pulp fractions. This study addressed whether these effects are related to the cationic groups, *e.g.*, by increasing electrostatic attraction and thus paper strength, or rather side effects of the chemical modification process, *e.g.*, fiber flexibilization. To eliminate or at least minimize these side effects, only the fines fraction, which was already highly flexible, was cationized. While the addition of cationized fines affected various pulp and paper properties, most notably drainage time, no difference in strength properties was observed when comparing the addition of cationic or unmodified fines to different pulps or fractions thereof.

Keywords: Chemical modification; Cationization; Pulp; Fines; Paper properties

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INTRODUCTION

While the requirements for many paper properties (*e.g.*, smoothness, bulk, and porosity) can vary depending on the application, high paper strength is a focus for almost all paper grades. A certain level of strength is important for good runnability in the paper machine and in further converting steps, as well as for the end use of the given product. For many paper products, the issue might not be enhancing strength, but rather keeping the required strength properties while reducing raw material costs by reducing basis weight, increasing the content of mineral fillers, or using less expensive pulps. Thus, paper strength is a topic of many studies applying different strategies, such as physical modification (*e.g.*, refining and fractionation), enzyme treatment, and the addition of chemical additives in the wet end (so-called wet and dry strength agents), as well as in surface sizing. Chemical modification of the pulp or of fractions thereof, such as TEMPO (2,2,6,6-tetramethylpiperidinyloxyl) oxidation, grafting fibers with carboxymethylcellulose (CMC), and cationization are also means to improve strength properties (Prado and Matulewicz 2014; Zhao *et al.* 2016), but they are rarely applied in industrial practice.

Cationization of pulp refers to the attachment of cationic functionalities onto lignocellulosic fibers. Similar to the effects of soluble cationic polyelectrolytes, cationization of lignocellulose leads to electrostatic interactions in the suspension, which are apparent during the forming process as improved retention (Käufer and Krause 1984a). In addition to hydrogen bonding, Coulomb, London dispersion, and Van der Waals forces

are responsible for interfiber bonding (Lindström *et al.* 2005; Hirn and Schennach 2015). Cationization may also increase strength properties through its impact on these effects.

Several scientific studies have dealt with the cationization of lignocellulosic pulps or fractions thereof. Krause *et al.* (1981) cationized bleached sulfite pulp. Handsheets of the unrefined pulp showed an increase in breaking length, with a higher degree of substitution (DS), *i.e.*, a higher cationic charge content (Käufer and Krause 1984b). Refining this cationized sulfite pulp in a Jokro mill showed a lower beating resistance, indicated by the lower drainability expressed in Schopper Riegler (SR value) compared with the unmodified pulp after a given treatment. Breaking length was improved for the cationized pulp compared with the unmodified pulp at the same energy input in refining, as well as at the same SR value (Käufer and Krause 1984b). The lower beating resistance was explained by a "spacer effect" (Gruber 2002) introduced with the cationic charges. Cationic groups are chemically bound to the cellulose molecules not only on the surface, but also in the bulk. It is not possible to form intermolecular hydrogen bonds in close proximity to charged groups because of steric hindrance. Thus, the cationic group acts as a spacer between cellulose chains.

In a study on cationized thermo mechanical pulp (TMP), the increase in breaking length was reported to be 24%, and internal bond strength (Scott bond) increased by 60% (Montplaisir *et al.* 2006). In another study, only the long-fiber fraction of the TMP pulp was cationized. Tensile index increased only up to a certain level of cationization, at which point it decreased, although apparent sheet density further increased. The decrease in breaking length was explained by the degradation of cellulose chains at very high cationic charge densities (Ma *et al.* 2010). Contrary to the effects reported for pulps or long-fiber fractions, a recent study comparing the addition of cationized microfibrillated cellulose (MFC) and unmodified MFC as papermaking additives found no significant difference in tensile index for either material (Gao *et al.* 2016).

Most studies have provided no explanation for the positive effect of cationized pulp, fibers, and fiber fractions on strength properties. Gruber (2002) mentioned two possible mechanisms for the improvement. In the first mechanism, cationic groups act as a spacer in the fiber wall, thereby making the fiber more flexible. Thus, conformability and sheet consolidation are improved. In the second mechanism, electrostatic interactions may bring fibers into closer contact and thus, enhance strength properties. Increased fiber flexibility, along with the possibly related increased swelling ability, can also be introduced by other means, such as refining, TEMPO oxidation, or surface grafting with CMC (Zhao *et al.* 2016), and thus, is not exclusively related to cationic groups.

Bringing fibers into closer contact because of cationic-anionic charge interactions is a mechanism directly related to the cationic functional groups, and the results will vary depending on whether soluble polymers are added to the fiber suspension or the cellulosic fibers themselves are cationized. Soluble cationic polymers linking the cellulose fibers may increase the distance between these fibers, while cationic groups directly attached to the cellulose might decrease the distance and bring the molecules into closer contact.

Whether Coulomb forces have an influence on interfiber bonding has not been investigated for cationic pulp fibers, but it has been investigated for soluble dry strength agents. Zhang *et al.* (2000) examined whether the cationicity of soluble dry strength agents had an effect on interfiber bonding. Their results showed that tensile index remained constant when the DS increased, and therefore concluded that there was no such effect on interfiber bonding. Pelton and Hong (2002) performed a similar study, impregnating newsprint with polyvinylamine with varying DS and came to the same conclusion, also

summarized in a review (Pelton 2004), that the charge of soluble dry strength agents affects the amount of polymer adsorbed onto the fiber, but has no effect on interfiber bonding.

This study investigated whether cationic groups chemically bound to lignocellulosic fiber fractions contribute to interfiber bonding, and thus paper strength, or whether the reported strength enhancement is instead related to side effects such as fiber flexibilization, not an exclusive property of cationic functionalities themselves. To eliminate or at least minimize the simultaneous effect of fiber flexibilization caused by the spacer effect, only the already highly flexible fines fraction (particles passing a screen with 100 µm hole diameter) was cationized and added to the unmodified pulp or fractions thereof. Fines show a higher surface area than fibers. Assuming that only surfaces participate in bonding, any effect on strength should be even more pronounced for modified fines. To exclude the effect of improved retention because of the cationic charges, white water recirculation (Giner-Tovar *et al.* 2015) was used to guarantee comparable retention of unmodified and modified fines. Consumption of the cationized fines by the unmodified fines, as well as differences in adsorption or flocculation, were addressed by adding the cationized fines to refined pulp (unmodified fines present), refined pulp with the fines washed out (no fines present), and unrefined fibers (also fines-free).

EXPERIMENTAL

Fractionation

Industrially bleached hardwood (refined and unrefined) and unrefined bleached softwood kraft pulp were fractionated. The fiber and fines fractions were produced with a lab-scale pressure screen at 1% consistency (Jagiello 2017). The pressure screen was equipped with a perforated plate (100 µm hole diameter). The material passing through the plate was defined as the fines fraction. The pulp was recirculated until the remaining volumetric fines content (measured with an L&W Fibertester^{+}, Lorentzen & Wettre, Stockholm, Sweden) was less than 0.5%. This fraction was defined as the fiber fraction. The highly diluted fines suspension was stored in large barrels to allow settling of the material. After 3 to 4 d, the supernatant was removed to obtain a fines suspension of approximately 1% consistency. The fiber fraction was filtrated to a consistency of 30%. The fractions obtained from the different pulps are summarized in Table 1.

Table 1. Pulps and Fractions Thereof, Abbreviations Used in this Study

Pulp	Fraction	Abbreviation
Unrefined bleached softwood kraft (spruce)	Fines	BSK_{fines} ($cBSK_{fines}$)
Unrefined bleached hardwood kraft (eucalyptus)	Fibers	BHK_{fibers}
Refined bleached hardwood kraft (eucalyptus)	Fibers	$rBHK_{fibers}$
	Fines	$rBHK_{fines}$

Chemical Modification (Cationization)

Prior to cationization of the BSK_{fines}, acidic washing was conducted. The pH of the fines suspension, as achieved after pressure screening (approximately 1% consistency), was adjusted to a pH of 1 by adding HCl (4 N). After 1 h, the fines were filtered off and washed with deionized water until neutral. Then, 10 g (dry weight) of the fines and 22.2

mL of NaOH (4.5 N) were supplemented with deionized water to achieve a solids content of 1% fines and a concentration of 0.1 N NaOH in the reaction volume. After 30 min, 36 mL of 2,3 epoxypropyltrimethylammonium chloride (EPTMAC; Sigma-Aldrich, technical grade, 21.6% water, 90% purity of dry substance) were added to the stirred reaction volume. After 15 h at 40 °C, the reaction was stopped by adding enough HCl (4 N) to decrease the pH to approximately 1. The suspension was then filtered through a fine cloth in a Büchner funnel, and the solid material was washed with water until neutral. These cationized fines ($cBSK_{fines}$, Table 1) were again brought to 1% consistency. Further experimental details are published in Odabas (2016).

Degree of Substitution

The DS was determined by conductometric titration using a system by Metrohm (Herisau, Switzerland). An amount of the fines suspension corresponding to 100 mg of the dry sample was diluted to 50 mL prior to titration. During titration, 50 µL of a 10 mM aqueous silver nitrate solution were added every 10 s (Odabas 2016). Triplicate measurements were performed. From the equivalence point (EP) (mL) and the dry mass of the titrated aliquot m_{dry} (mg), the DS was calculated, taking into consideration the concentration of the silver nitrate solution c_{AgNO3} (mmol mL^{-1}), the molar mass of one AGU (MM_{AGU} = 162 g mol^{-1}), and also the molar mass of the functional group (MM_{FG} = 152 g mol^{-1}), as described by Eq. 1,

$$DS = \frac{EP \,.\, c_{AgNO3} \,.\, MM_{AGU}}{m_{dry} - EP \,.\, c_{AgNO3} \,.\, MM_{FG}} \quad (1)$$

Sample Preparation

The fractions produced by pressure screening and cationization (Table 1) were blended as shown in Table 2 in order to obtain combinations with 5% unmodified BSK fines (Reference A-D), as well as combinations with 5% cationized BSK fines (A-D). The BSK fines were used because they showed a high water-holding capacity (more details: Mayr *et al*. 2017), and thus, they were considered to show a high conformability even before cationic modification. These fines were added to hardwood (BHK) pulp and fractions instead of the corresponding BSK fractions in order to minimize the effect of inferior sheet formation and thus, lower the variation in tensile measurement. The cationic fines were added to the refined pulp (refined fibers and fines), refined fibers (refined pulp without fines), and unrefined fibers (without fines), to see whether there were any differences depending on the addition of the cationized fines to unmodified fines (present in refined pulp), external fibrils still connected to the fibers (present in refined fibers with fines washed out), or plain fibers (unrefined fibers with fines washed out). For the combination with the refined pulp, the influence of mixing order was also evaluated by adding cationized fines ($cBSK_{fines}$) both to the refined pulp with unmodified fines present, and to the refined fibers (without fines) with subsequent addition of unmodified fines ($rBHK_{fines}$). In both cases, the composition of the final blend was the same, but any effects resulting from electrostatic interaction between the modified and unmodified fines dependent on the sequence of their addition should have become visible. To ensure a homogeneous distribution of fines, the suspension was mixed for 5 min with a kitchen blender with a flat rotating disk (1200 rpm, diameter 36 mm) directly after the addition of each fraction.

Table 2. Mass Proportion of Fractions in Blends and the Corresponding Mixing Order

		Composition (%)					
		$rBHK_{fibers}$	BHK_{fibers}	$rBHK_{fines}$	BSK_{fines}	$cBSK_{fines}$	Mixing Order
Refined Pulp	Ref. AB	86		9	5		$rBHK_{fibers}$+$rBHK_{fines}$+BSK_{fines}
	A	86		9		5	$rBHK_{fibers}$+$rBHK_{fines}$+**$cBSK_{fines}$**
	B	86		9		5	$rBHK_{fibers}$+**$cBSK_{fines}$** +$rBHK_{fines}$
Refined Fiber	Ref. C	95			5		$rBHK_{fibers}$+BSK_{fines}
	C	95				5	$rBHK_{fibers}$+**$cBSK_{fines}$**
Unrefined fiber	Ref. D		95		5		BHK_{fibers}+BSK_{fines}
	D		95			5	BHK_{fibers}+**$cBSK_{fines}$**

Sheet Preparation of Pulp and Paper for Testing

Drainability (ISO 5267-1 (1999), SR Tester, Gockel & CO) and zeta potential (Mütek SZP – 04, BTG Instruments) were measured directly on the blended samples. Handsheets of 60 g/m² were prepared (ISO 5269-2 (2004), Rapid-Köthen sheet former, FRANK-PTI) using white water recirculation. Following a method implemented by Giner-Tovar *et al.* (2015), the first five handsheets were discarded to ensure a stable and defined content of fines, independent of the given retention, being different for unmodified and cationic fines. For each fiber blend, eight handsheets were formed, and density (ISO 534 (2011)), tensile index, and elongation at break (ISO 1924-2 (2008), Tensile Tester, FRANK-PTI) were measured. Formation index was determined recording weight maps, captured in a Formex Betaformation Box (Science Imaging Scandinavia AB, Saltsjö-boo, Sweden), and subsequently scanned in a Fujifilm BAS 1800-II scanner (Fujifilm, Tokyo, Japan). An internal routine was applied on the weight maps to calculate a formation index, taking into consideration the intensity and size of the flocs.

RESULTS AND DISCUSSION

Whether cationic charges themselves led to increased paper strength was addressed by attempting to reduce side effects concerning the structural changes cationizing the fines fraction instead of the fibers. The pulp and sheet properties of the blends with cationized fines (A-D) were compared to their references (Ref. A-D), representing blends with the same amount of unmodified fines (Figs. 1, 3, and 4).

Differences in the consumption of the cationized fines by the unmodified fines, which may lead to changes in the pulp and paper properties, were considered by adding the cationized fines to refined pulp containing unmodified fines and external fibrils (black bars), to refined fibers containing only external fibrils still attached to the fibers (striped bars), and to unrefined fibers (dotted bars).

The chemical modification resulted in fines with a positive charge, *i.e.*, "cationized" fines with a DS of 0.034. Adding 5% of these fines to negatively charged pulp or fibers led, as expected, to a lower zeta potential (Fig. 1a). The effect on zeta potential was more

pronounced when adding cationic fines to the unrefined fibers (D), as fewer negative surface charges were available compared to the blends where unmodified fines (A, B) or refined fibers (C), having a higher surface area, were also present.

Electrostatic attraction between the positively charged fines and the negatively charged fibers or unmodified fines present in the pulp led to a reduction of drainage time (Fig. 1b) for all of the blends.

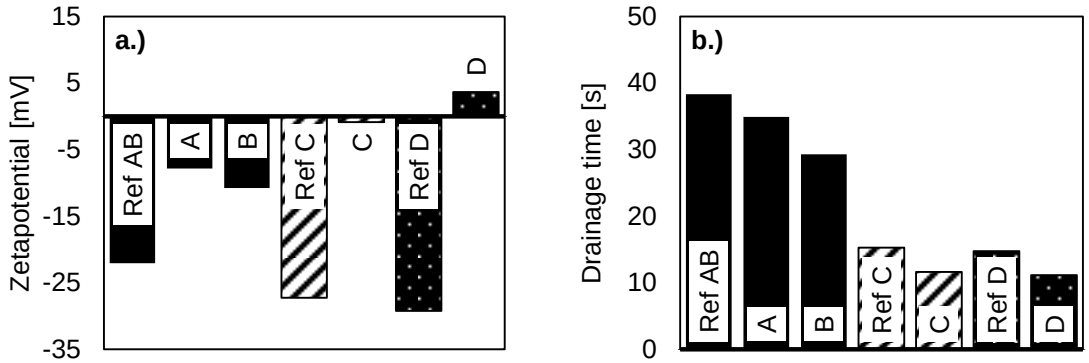

Fig. 1. Pulp properties: zeta potential (a) and drainage time (b); References (Ref. A-D) contained unmodified fines and (A-D) replacement of unmodified fines by cationic fines; black bars: fines were added to refined pulp (fibers + fines); striped bars: fines were added to refined fibers (fines removed); dotted bars: fines were added to unrefined fibers.

A combination of a certain flocculation of the fines material and an attachment thereof to the fiber surfaces was likely responsible for this decrease. This phenomenon is illustrated schematically in Fig. 2. Typically, both fines and fibers are negatively charged. Because of electrostatic repulsion, the fines would be quite uniformly distributed around the fibers (Fig. 2a). By replacing part of these unmodified fines with cationic-modified fines (Fig. 2b), the opposite charges are attracted, and therefore, cationic fines flocculate with unmodified fines and attach to the fibers (Fig. 2c). Less space is required and the fines no longer tend to plug the pores of the fiber mat, thereby reducing drainage time.

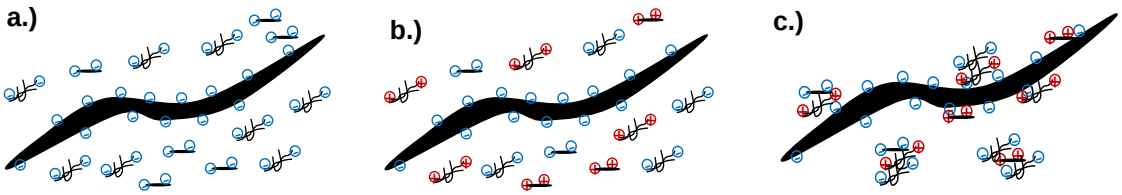

Fig. 2. Illustration of pulp suspension containing fibers and (a) unmodified fines; (b) replacement of unmodified fines by cationic fines and (c) its effect on flocculation, leading to lower dewatering resistance

The blend in which the cationic fines were added prior to the unmodified fines (trial point B) showed a faster drainage time than the blend in which the cationic fines were added after the unmodified fines (trial point A), although both blends were comprised of the same components (Table 2). In the case of trial point B, a higher proportion of cationic fines adhered to the fibers, as no other negative charges were available. The unmodified fines added afterwards then adhered to the fiber surface. In trial point A, the cationic fines could adhere to both the unmodified fines and fibers. Flocculated fines presumptively had

a higher potential to hinder dewatering, as they could fill up the pores of the formed fiber mat more easily than fines adhered to the fiber surface. The fact that these differences in flocculation were apparent, even after the application of high shear forces (1200 rpm) during sample preparation, indicates a strong adhesion and high shear resistance of the formed flocs.

Sheet density and formation index were not affected by the cationized fines addition in most of the blends (Fig. 3). An exception was sample C, where the decrease in density corresponded to an increase in formation index, indicating inferior sheet formation. This blend of fines-free, externally fibrillated fibers and cationic fines might have induced enhanced floc formation at positions of high external fibrillation because of the higher surface area available for electrostatic interaction with the cationized fines.

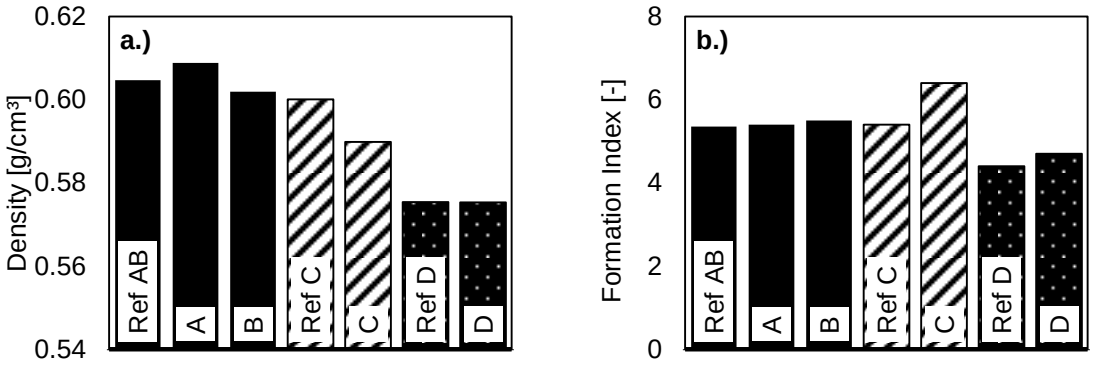

Fig. 3. Paper structural properties: apparent density (a) and formation index (b); for coding see Fig. 1.

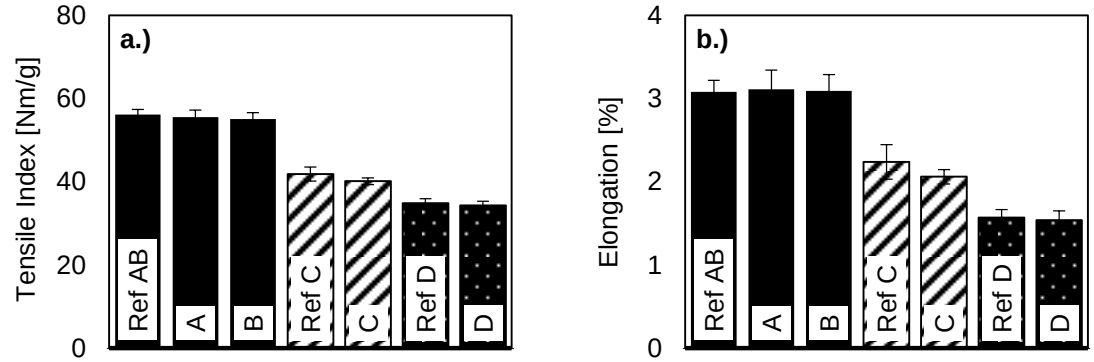

Fig. 4. Paper mechanical properties: tensile index (a) and elongation (b); for coding see Fig. 1.

Overall, blends including cationic fines showed noticeably different behavior compared to the reference samples, influencing zeta potential, drainage time, and flocculation, as the result of the interaction of cationic groups with anionic-charged pulp components. However, no effects on tensile index or elongation at break were observed (Fig. 4), regardless of whether the cationic fines were added to pulp containing unmodified fines, refined fibers, or unrefined fibers. One might argue that soluble cationic dry strength agents, *e.g.*, cationic starch, improve strength properties. Pelton (2004) investigated this effect and found that it was not cationicity itself that was responsible for the strength enhancement, but rather the hydrophilic character of the soluble dry strength agent. He concluded that the electrically charged groups were mainly responsible for retention, but

not for strength development. In the case of soluble dry strength agents, the sheets containing them are typically compared to sheets without dry strength agents. In these experiments, the reference sheets contained the same amount of fines as the sheets with the modified fines. Considering the different setup, effects similar to the addition of soluble dry strength agents were also visible in a higher strength when an additional 9% fines (trial setup A-B compared to setup C) was added.

Similar to the cationic fines, an experiment adding cationic MFC (Gao *et al.* 2016) also gained no improvement in tensile strength. These observations do not support the findings for cationic pulps or fibers, where obviously improved strength properties were reported.

It seems reasonable to argue that the improvement in paper strength properties observed by other authors as the result of cationization of pulp or fibers was related to the spacer effect (Gruber 2002), increasing fiber flexibility and thereby conformability. Similar effects were also observed in a study by Zhao *et al.* (2016) in which the carboxyl group content of mechanical pulp fibers was increased. This treatment resulted in higher fiber flexibility and thus, improved strength properties. The scheme of a fiber cross-section and the outermost fiber wall of both unmodified (Fig. 5a) and cationized fibers (Fig. 5b) illustrate the proposed effect of cationic charges acting as a spacer in the fiber wall, and thereby improving paper strength. Negative charges are already present in the fiber wall and on the surface of unthreaded fibers (Fig. 5a). In the direct proximity of these charges, hydrogen bonding is hindered. The light areas of the illustration of the outermost fiber wall indicate regions that are loosely bound because of charged groups. Upon increasing the content of charged groups by cationization, the fiber wall may become more delaminated and thus, the fiber more flexible. This spacing would also take place on the fiber surface, increasing the loosely bound region of the outermost fiber wall and enhancing conformability.

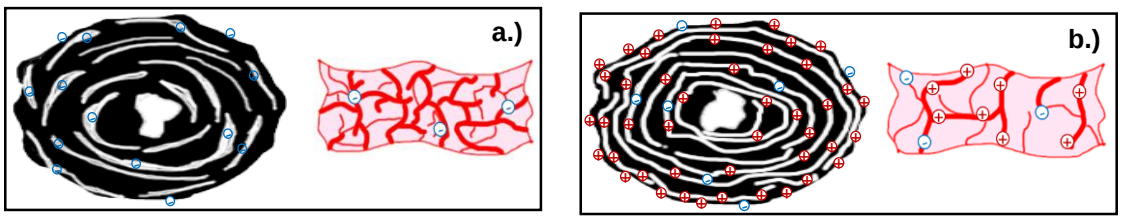

Fig. 5. Illustration of fiber cross-section and the possible effect of charges on the topology of the outermost fiber wall; tightly bound areas (dark red), loosely bound areas (light red); unmodified fibers negatively charged (a), and cationized fibers (b), proposed effect of cationic charges acting as a spacer in the fiber wall.

In addition to fiber flexibilization and the resulting improved sheet consolidation, cationic groups also promote retention. The associated strength improvement comparing sheets from cationic pulp (fibers + fines) with sheets from untreated pulp might also be related to improved fines retention, especially for mechanical pulps showing a high proportion of fines (Montplaisir *et al.* 2006).

Although cationic groups do not improve strength properties intrinsically, strength improvement is possible with cationizing fibers due to flexibilization of the fiber without mechanical treatment. Taking into consideration the other positive effects of cationization, such as improved runnability and cleanliness of the system, improved filler and fines retention, improved drainage, reduced beating-resistance because of the spacer effect, and

even improved internal sizing adding only small amounts of cationic fibers (Krause *et al.* 1981; Gruber 2002), cationization of fibers might nevertheless be an interesting option for upgrading fibers and stock compositions.

CONCLUSIONS

1. Sheets containing cationic fines showed differences in zeta potential, flocculation behavior, and drainage time, compared to sheets containing the same amount of unmodified fines, revealing the activity of cationic groups.
2. Nevertheless, cationic fines did not have a significant effect on paper strength improvement, which is in accordance to the findings concerning cationic polyelectrolytes.
3. Therefore, it might not be the cationic groups *per se*, but rather the increased fiber flexibility that is responsible for the strength-enhancing effect seen in several studies on cationic pulp and pulp fibers.

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