



Sarah Koller, BSc

# **Effects of Fines on Paper Properties after Refining**

**MASTER'S THESIS**

to achieve the university degree of

Diplom-Ingenieurin

Master's degree programme: Chemical and Process Engineering

submitted to

**Graz University of Technology**

Supervisors:

Dipl.-Ing. Daniel Mandlez

Assoc.-Prof. Dipl.-Ing. Dr. techn. Ulrich Hirn

Institute of Bioproducts and Paper Technology

Graz University of Technology

Graz, July 2020

# Eidesstattliche Erklärung

Ich erkläre an Eides statt, dass ich die vorliegende Arbeit selbstständig verfasst, andere als die angegebenen Quellen/Hilfsmittel nicht benutzt, und die den benutzten Quellen wörtlich und inhaltlich entnommenen Stellen als solche kenntlich gemacht habe. Das in TUGRAZonline hochgeladene Textdokument ist mit der vorliegenden Masterarbeit identisch.

01.07.2020

Datum

Sarah Koller

Unterschrift

# AFFIDAVIT

I declare that I have authored this thesis independently, that I have not used other than the declared sources/resources, and that I have explicitly indicated all material which has been quoted either literally or by content from the sources used. The text document uploaded to TUGRAZonline is identical to the present master's thesis dissertation.

01.07.2020  
.....

Date

Sarah Koller  
.....

Signature

Die Zukunft gehört denen, die an die  
Wahrhaftigkeit ihrer Träume glauben.

---

ELEANOR ROOSEVELT (1884-1962)  
First Lady der Vereinigten Staaten (1933-1945)



# Danksagung

Ich möchte mich bei allen Personen bedanken, die mich in meinem Studium bis zum Abschluss begleitet haben.

Zuallererst möchte ich mich bei meinem Betreuer Dr. Ulrich Hirn bedanken, der mir diese Arbeit ermöglicht hat. Viele konstruktive Meetings und Inputs formten diese Abschlussarbeit, wie sie schlussendlich geworden ist.

Ein großer Dank gilt meinem Co-Betreuer Dipl.-Ing. Daniel Mandlez, der mich immer mit seinem fachkundigen Wissen unterstützt und mit seiner Begeisterung an der Materie angesteckt hat. Danke, dass du auch nach dem 20. Mal erklären nicht die Geduld mit mir verloren hast.

Danke auch an Dr. Rene Eckhart, der mit seinem umfassenden Fachwissen viel Input zu dieser Arbeit beigetragen hat.

Ein spezieller Dank gilt Heidi und ihren Labormädels. Danke an Bianca, Irmi, Kerstin, Manu und Sarah. Ohne eure tatkräftige Unterstützung bei den Laborarbeiten und der Auswertung wäre nicht alles so reibungslos abgelaufen.

Danke auch an Claudia, Kerstin, Harry und Christian, dass ich immer zu euch kommen konnte, wenn es Probleme aller Art gab.

Danke an alle rund um den APV Activitas Graz und an das gesamte Institut. Die Gemeinschaft und der tolle Umgang miteinander machten alles zu einer schönen Zeit, die ich nicht missen möchte.

Der größte Dank gilt meinen Eltern, die mich während meines gesamten Studiums immer mental und finanziell unterstützt haben. Ohne ihre Unterstützung wäre dieses Studium nicht möglich gewesen. Danke auch an meine Schwester Katrin, die immer an mich geglaubt hat, dass ich dieses Studium schaffen werde.

# Kurzfassung

Das Ziel dieser Masterarbeit ist die Untersuchung der Mahlung und deren Auswirkungen auf Faser- und Papiereigenschaften. Der Schwerpunkt liegt dabei auf dem Festigkeitszuwachs durch den Einfluss der sekundären Feinstoffe, die in einer PFI Mühle und einem Scheibenrefiner generiert wurden. Damit der genaue Einfluss von Feinstoffen analysiert werden kann, wird der Feinstoffanteil mit einem Labordrucksortierer abgetrennt. Zusätzlich wird der Aspekt von Nasspressen untersucht, das auch Einflüsse auf Verdichtung und Festigkeit ausübt. Laborblätter in verschiedenen Konfigurationen wurden hergestellt und anschließend analysiert.

Der lineare Zusammenhang von Dichte und Reißlänge stimmt mit der Literatur überein, wobei sich der Zusammenhang durch Nasspressen verändert. Das Nasspressen hat durchaus positive Effekte auf Verdichtung und Festigkeit, wenn auch diese nicht direkt mit Verdichtungseffekten von Feinstoff und Faserflexibilisierung vergleichbar sind.

Die Hauptaufgabe dieser Arbeit war den Festigkeitsgewinn durch sekundäre Feinstoffe beziehungsweise interner und externer Fibrillierung zu quantifizieren. Die Ergebnisse zeigen, dass im Scheibenrefiner mehr sekundäre Feinstoffe generiert werden und die PFI Mühle mehr Fibrillierung und Flexibilisierung der Faser bewirkt. Die Faserlängenverteilung bestätigt ebenfalls, dass im Refiner viel mehr Faserkürzung auftritt.

Die Qualität der Feinstoffe hängt vom Produktionsprozess ab. Die produzierten Feinstoffe im Scheibenrefiner tragen deutlich mehr zum Reißlängengewinn bei als sekundäre Feinstoffe der PFI Mühle.

# Abstract

The aim of this master thesis is to present the findings of the investigation of refining and its effects on pulp and paper properties. This thesis mainly focuses on the breaking length gain due to effects of secondary fines generated in a PFI-mill and a pilot plant disc refiner. In order to analyze their exact influence, fines were separated from pulp using a lab pressure screen. Additionally, the aspect of wet-pressing was investigated which also affected densification and strengthening behaviour. Handsheets in different configurations were prepared and afterwards analyzed.

The linear correlation between density and breaking length corresponds with literature whereas the correlation is affected by wet-pressing. Wet-pressing had positive effects on densification and strengthening. Nonetheless, it cannot be compared directly concerning densification effects by fines and flexibilization.

The main task of this thesis was to quantify the strengthening gain caused by secondary fines respectively internal and external fibrillation. Results show that the disc refiner generates more secondary fines, while in a PFI-mill more fibrillation and flexibilization of the fiber occurred. The fiber length distribution also confirmed, that in a refiner more fiber shortening occurred.

The quality of the fines depends on the production process, whereas fines from a disc refiner contributed more to breaking length gain than secondary fines from a PFI-mill.

# Table of Contents

<b>1</b>	<b>Introduction</b>	<b>1</b>
1.1	Motivation . . . . .	1
1.2	Overview . . . . .	1
<b>2</b>	<b>Theoretical Background</b>	<b>3</b>
2.1	Fibers . . . . .	3
2.1.1	Material Origin . . . . .	3
2.1.2	Cell Wall Structure . . . . .	3
2.1.3	Chemical Composition . . . . .	4
2.1.4	Types of Fiber . . . . .	5
2.1.5	Pulping . . . . .	6
2.2	Morphology . . . . .	7
2.2.1	Definition of Fines Material . . . . .	7
2.2.2	Characterization of Fines Material . . . . .	7
2.3	Pulp Refining . . . . .	9
2.3.1	Refining Aggregates . . . . .	12
2.3.2	Refining in Laboratory Scale . . . . .	13
2.3.3	Industrial Refining . . . . .	15
2.3.4	Refining Parameters . . . . .	16
2.4	Influence of Refining and Fines on Pulp and Paper Properties . . . . .	20
2.5	Wet-Pressing . . . . .	23
<b>3</b>	<b>Materials and Methods</b>	<b>29</b>
3.1	Fiber Material and Preparation . . . . .	29
3.2	Experimental Design . . . . .	29
3.3	Refining . . . . .	30
3.3.1	PFI-Mill . . . . .	30

3.3.2	Disc Refiner . . . . .	30
3.4	Fines Separation . . . . .	32
3.5	Pulp Analytics . . . . .	32
3.5.1	Consistency and Dry Content . . . . .	32
3.5.2	Fiber Length Distribution . . . . .	33
3.5.3	Dewatering Resistance . . . . .	33
3.5.4	Water Retention Value . . . . .	34
3.5.5	Fines Content with BDDJ . . . . .	34
3.5.6	Microscopy Method . . . . .	34
3.6	Handsheet Preparation . . . . .	35
3.7	Measurement of Handsheet Properties . . . . .	36
3.7.1	General Properties . . . . .	36
3.7.2	Mechanical Properties . . . . .	37
3.7.3	Optical Properties . . . . .	38
<b>4</b>	<b>Results</b>	<b>40</b>
4.1	Specific Impacts by Refining on Pulp and Paper . . . . .	40
4.2	Influence of Fines on Breaking Length . . . . .	42
4.2.1	Evaluation of Gain of Fines on Breaking Length . . . . .	43
4.2.2	Impact of Fines on Breaking Length and Density . . . . .	45
4.3	Further Mechanical Properties . . . . .	48
4.4	Fiber Length Distribution . . . . .	52
4.5	Microscopy . . . . .	54
4.6	Light Scattering . . . . .	55
4.7	Dewatering Resistance . . . . .	55
4.8	Porosity . . . . .	57
<b>5</b>	<b>Conclusion</b>	<b>59</b>
	<b>List of Figures</b>	<b>II</b>
	<b>List of Tables</b>	<b>III</b>
	<b>List of Abbreviations</b>	<b>IV</b>
	<b>Bibliography</b>	<b>V</b>

# Introduction

## 1.1 Motivation

Beating is one of the most important procedures to enhance paper properties. Especially the improvement of fiber-fiber bonding and sheet formation, as well as, improved physical properties of the final product occur because of refining. Besides modification of the fiber itself, such as internal and external fibrillation and flexibilization, another notable process occurs during refining: Secondary fines are generated. In addition to primary fines, which are already available traceable in pulp, secondary fines also have essential functions. They tend to improve strengthening behaviour.

A still unexplored field in the research of secondary fines is the quantification of the effect on tensile strength gain. Therefore, various settings are used to achieve a better understanding of these mechanisms.

## 1.2 Overview

The present thesis deals with the effects of refining on pulp and paper properties and especially focuses on the influence of generated fines, as well as, fibrillation and flexibilization. Additionally, the aspect of wet-pressing will be presented.

The theoretical background discussed in Chapter 2 is subdivided in various sections. First, fibers in general are described, including information on the origin of fibers, cell wall structure, as well as, their composition. Different fiber types and the processing of pulping will

be explained. Furthermore, in the second section, the term "fines" will be introduced and explained. Afterwards, pulp refining will be explained including all proceeding actions. Also common refining aggregates and key figures in refining will be presented. Subsequently, the impacts of fines and wet pressing will be discussed.

In Chapter 3 all examined procedures will be described, including refining with a industrial refiner and a PFI-mill, as well as, the use of the lab pressure screen at Institute of Bioproducts and Paper Technology. Afterwards, handsheets will be prepared and analyzed with different methods. Moreover, all applied analytical methods will be described.

The knowledge and gained results from laboratory experiments will be illustrated and discussed in Chapter 4. The thesis will conclude with a summary of all findings.

## **Theoretical Background**

### **2.1 Fibers**

Fibers are the base material in the paper manufacturing processes. There are also other fiber sources, for example, annual plants and cotton. Depending on the raw material, paper properties vary. As the focus in this thesis lies on fibers gained from wood, only this material is explained in detail. [1] Literature distinguishes between primary and secondary fibers: Whereas primary fibers are made from wood and annual plants, secondary fibers are obtained from waste paper. [1]

#### **2.1.1 Material Origin**

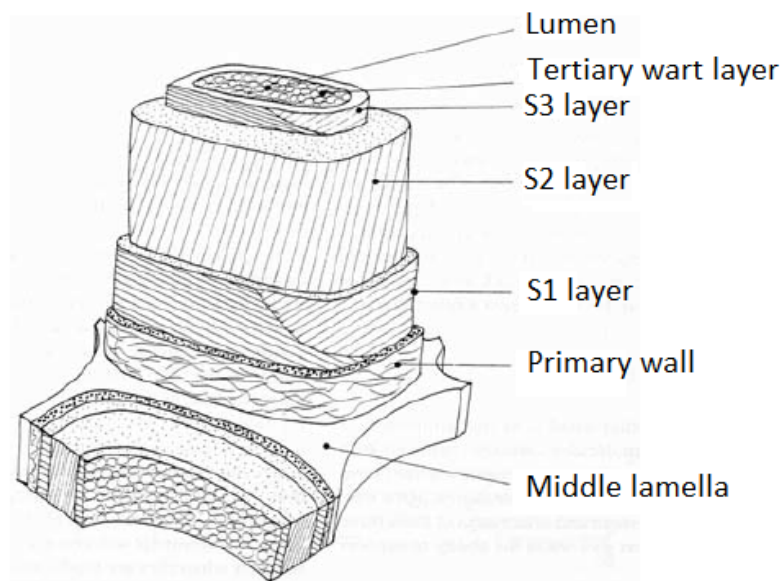
Primary fibers are the main constituent of wood. The structure of a tree trunk consists of three main sections: bark, bast and cambium. The function of the bark is to protect the tree from dangers. The bast provides the tree with nutrients. The cambium is the so-called living part of the trunk. Every year, it generates new outer bast and inner bork by cellular division. [1]

#### **2.1.2 Cell Wall Structure**

The cell wall structure of a tree is illustrated in Figure 2.1. Fibers consist of multilayered cell walls which are arranged around the hollow lumen. In some cases, there is a layer containing lignin "warts", which connects the cell wall to the lumen. This layer is called



tertiary wall layer. The outermost layer of a fiber structure of a softwood is called middle lamella, which is followed by the primary wall and a three-layered secondary wall (S1-S3). The three layers of the secondary wall differ in density and the orientation of the microfibrils. Since the S2 layer has the greatest wall thickness, the orientation of microfibrils is the most significant. The orientation is crucial for the direction of fiber swelling, as well as, the physical properties of the fiber. The fibers are enclosed in a matrix of lignin which are kept together by the middle lamella. [1–4]



**Figure 2.1** Fiber structure of softwood [5]

### 2.1.3 Chemical Composition

The three main chemical constituents of wood are cellulose, lignin and hemicellulose. These components are differently distributed in the fiber wall. Additionally, their composition is different throughout the fiber section. The molecular structure of cellulose is linear, lignin is cross-linked and hemicellulose is branched [6].

Besides the three main constituents, there is an additional small number of biopolymers such as resins, greases and wax. Lignin and hemicellulose are amorphous fillers that act as a kit substance. Figure 2.2 shows that the middle lamella consists mainly of lignin (60 – 80 %). The primary wall is very thin and can therefore be neglected. The secondary

wall S2 generally consists of cellulose and hemicellulose. The percentage of lignin in the S2 layer is just 22 %. [1–3]

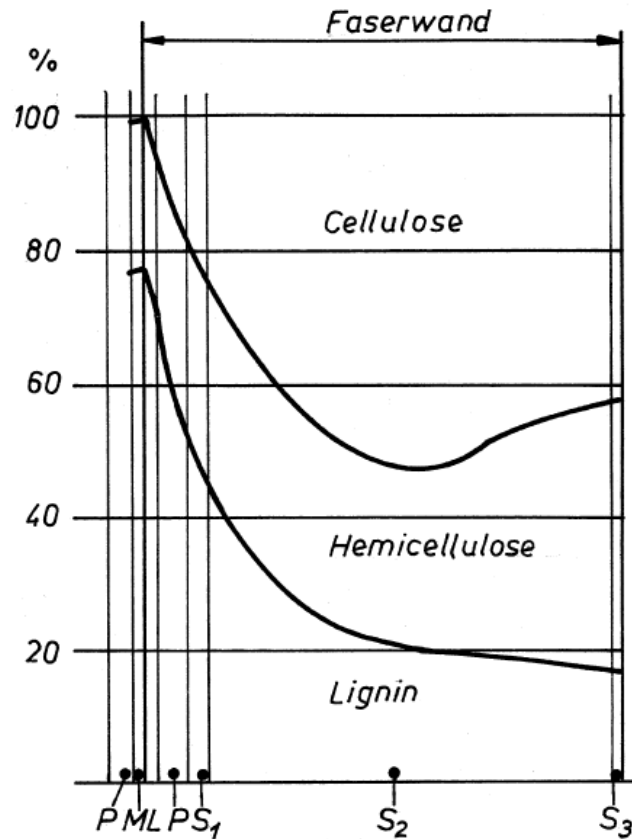


Figure 2.2 Chemical composition of the cell wall layers [7]

#### 2.1.4 Types of Fiber

Due to differences of fiber structures and configurations, wood can be classified as softwood or hardwood. Fibers fulfill various functions which differ in the different kind of woods. In this thesis, an unbleached softwood kraft pulp was investigated.

##### Softwood

Softwood has a simple and homogenous structure and consists of tracheids, wood parenchyma cells and ray parenchyma cells. The greatest part of the structure are tracheids, making up 90 % of softwood. A distinction is made between earlywood and latewood tracheids. Earlywood tracheids transport water and nutrients, while latewood tracheids are important in the papermaking process because of their strengthening properties. The

parenchyma cells transport and store nutrients. Tracheids are oriented in longitudinal direction and have a length of 1.4 - 6.0 mm and a diameter of 20 - 50  $\mu\text{m}$ . Due to their fiber structure, the tracheids are called long fibers. [1, 2]

### **Hardwood**

Unlike softwood, the structure of hardwood is more complex. Hardwood provides a broader variety of different cell types, such as fibers, pores (vessels) and parenchyma cells. However, fibers like libriform cells, sclerenchyma, hard cells and wood cells are responsible for the strength of the tree. Special vessels or pores transport liquid, whereas the parenchyma cells store food supplies.

Although, hardwood fibers are orientated in longitudinal way to the trunk (similar to softwood cells) but they are much shorter than softwood cells. That is the reason why they are called short fibers. The libriform cells amount 40 - 75 % of the wood material. They have a length of 0.4 to 1.6 mm and diameters of 10 to 40  $\mu\text{m}$ . Hardwood fibers are not suitable for papermaking, as their pore diameters (300  $\mu\text{m}$ ) are larger than the short fibers. [1, 2]

### **2.1.5 Pulping**

In section 2.1.4 the structures of important fibers for papermaking were described. It was shown that lignin in wood fulfills the function of a matrix. Revealing and making these fibers accessible is called pulping. There are two types of pulping: mechanical and chemical pulping. In this thesis, mechanical pulping will not be described in detail, as the main focus lies on chemical pulping.

In chemical pulping fibers are liberated from the wood matrix while lignin is dissolved from the middle lamella. The advantage of chemical pulping is, that the fibers are not damaged by mechanical impact. Depending on the used chemicals, the sulfate process or the sulfite process is applied. The product of both processes is called chemical pulp. For this thesis, a sulfate pulp is used. [2]

The sulfate process, also called kraft process, is a prevailing procedure in chemical pulping worldwide. The advantage of the kraft process is, that it can be applied in a wide range of wood species. Additionally, sulfate pulp features a higher strength compared to sulfite pulp. However, a disadvantage of kraft pulp is that it is harder to bleach than sulfite pulp. [2]

The sulfite process was the predominate process until the 1950s before it was replaced with the kraft process. This was due to the fact that new bleaching methods (especially the application of chlorine dioxide) were discovered. Therefore, efficient bleaching of kraft pulp was possible. A fully bleached kraft paper is much stronger than paper made of bleached sulfite pulp. Summarizing, sulfite pulping is not a very common method anymore and is only suitable for trees that are low in resin and low silica, such as spruce and birch. However, it still has advantages over the sulfate process. Sulfite pulp has a higher initial brightness and is easier to bleach. [2]

## 2.2 Morphology

As a consequence of extraction of fibers and their further processing, very small particles are formed. These particles are called fines. There is a distinction between primary and secondary fines. Both of them can be found in the final paper product.

### 2.2.1 Definition of Fines Material

Fines are the smallest components of fibers. Although there is no uniform definition, they are usually specified by their size. According to optical measurement methods, the content of fines in a fiber suspension is determined by particles which have a maximum length of 200  $\mu\text{m}$  (ISO 16065-2) [8]. According to another common definition, fibers are labelled as fines if they are able to pass separation devices which include a metal plate that is equipped with 76  $\mu\text{m}$  pore diameter holes. This metal plate corresponds to a 200 mesh screen [8, 9]. Fines influence final paper properties, depending on whether they originated from mechanical or chemical pulping [10].

### 2.2.2 Characterization of Fines Material

In this section different kind of fines are presented. Due to difference because of their shape and various properties, they are categorized in different groups.

#### Primary Fines

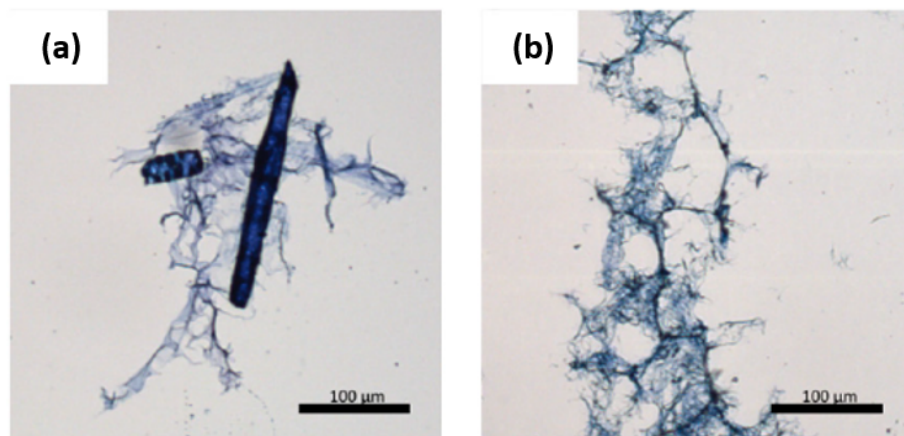
Primary fines can be traced after pulping and bleaching. Fibers which are generated by mechanical pulping are called 'Mehlstoff' ('flour stuff') and 'Schleimstoff' ('slime stuff')

[10]. The proportion of primary fines in mechanical pulp can amount up to 35 % [11]. Because chemical pulp is used in this thesis, mechanical pulp is not further elaborated. Primary fines from chemical pulp reach an average up to 2 % of fiber material. These fines mainly consist of granular material such as ray cells, parenchyma cells, little fragments of primary wall, middle lamella and only a small amount of fibrils [10, 12].

### Secondary Fines

Secondary fines can be traced after mechanical forces such as refining have been applied. They consist of plane shreds of cell wall and fiber fragments such as fibrils. Fibrils are the main components in secondary fines. Due to the fibrillar structure, secondary fines have a higher bonding ability than primary fines [12].

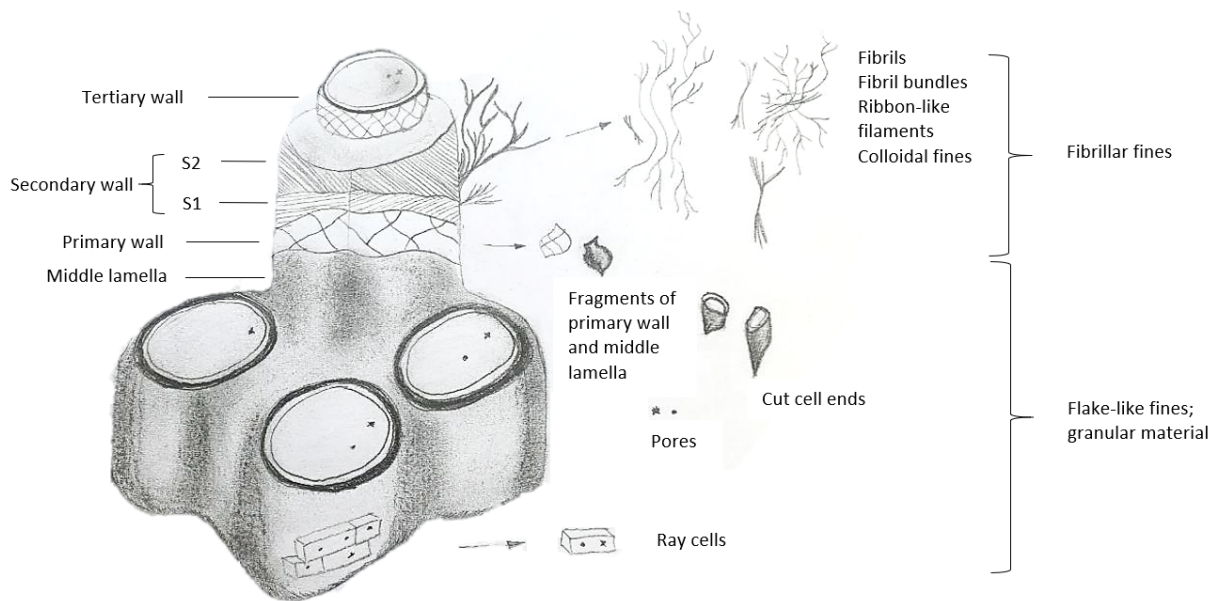
In Figure 2.3 microscopy pictures of primary and secondary fines are shown. The different forms can clearly be seen. While the primary fines consist of granular particles, secondary fines contain fibrillar material.



**Figure 2.3** Microscopy pictures of fines of an UBSK; (a) flake-like fines; (b) fibrillar fines [13]

Both types of fines have different effects on the final paper properties. Whereas primary fines are important for optical properties, secondary fines have a strong influence on strength properties. [12]

Figure 2.4 shows the cell wall structure of fibers which was described in 2.1.2. Furthermore, the difference of fibrillar and flake-like fines are displayed.



**Figure 2.4** Cell wall structure and illustration of fibers and derived fines from these structures; adapted from [10]

## 2.3 Pulp Refining

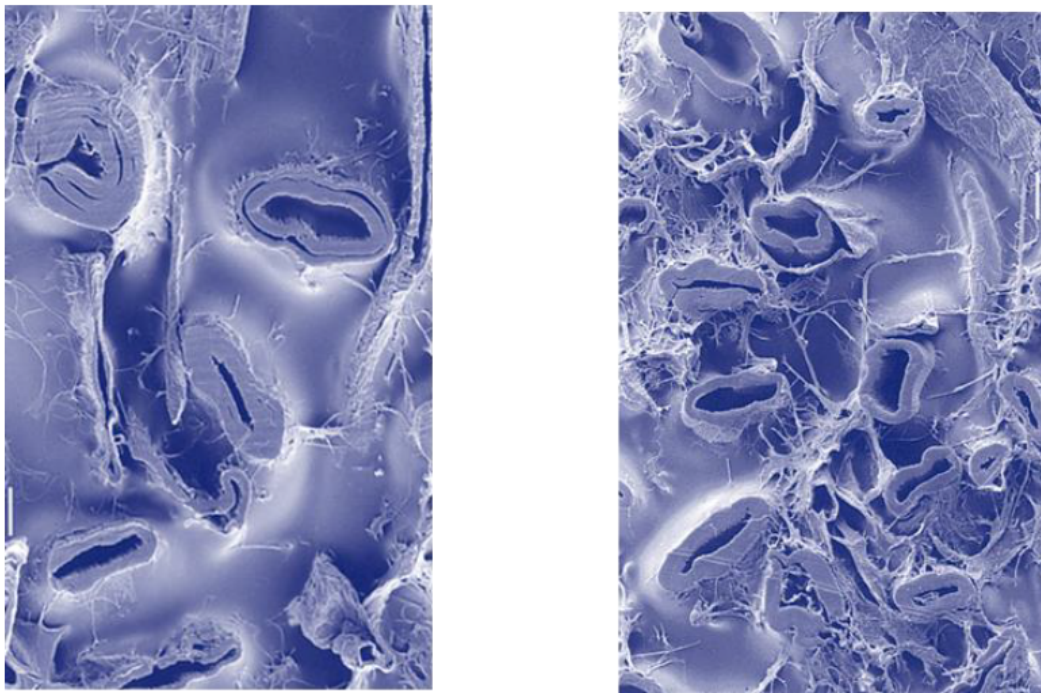
From point of view of process engineering, pulp refining belongs to the most important unit operations. It is a grinding process in which properties of fibers are modified. The purpose of refining is to improve the strength of the fiber network and the quality of the paper surface. Another reason for refining might be to control air permeability or optical properties which could result in an extreme example of transparent paper qualities. In refining, fibers are stressed by mechanical forces between the refining plates. Depending on plate geometry and used process parameters, a certain extent of internal and external fibrillation, as well as, fiber shortening occurs. [14]

### Internal Fibrillation

In internal fibrillation (Figure 2.5 left), delamination of fiber cell wall and swelling of amorphous cell wall parts occur. Therefore, inner bonds between cellulose, hemicellulose and lignin break. Water enters the pores of the cell wall and soft, flexible fibers are formed. Fiber flexibilization has a great influence on physical and optical parameters. Flexible fibers enhance mechanical properties such as tensile strength and lead to denser handsheets. Such dense handsheets have a greater relative bounded area (RBA). [14, 15]

### External Fibrillation

External fibrillation (Figure 2.5 right) means roughening the fiber surface by shear strain during refining. Consequently, fibrils get torn out of the fiber wall. Due to this effect, the relative bonded area increases. Further, tensile strength and Scott Bond strength also rise, which enhance mechanical paper properties. External fibrils which liberate from fibers are defined as secondary fines. [15, 16]



**Figure 2.5** Internal (left) and external (right) fibrillation of fibers after refining [15]

### Fiber Shortening

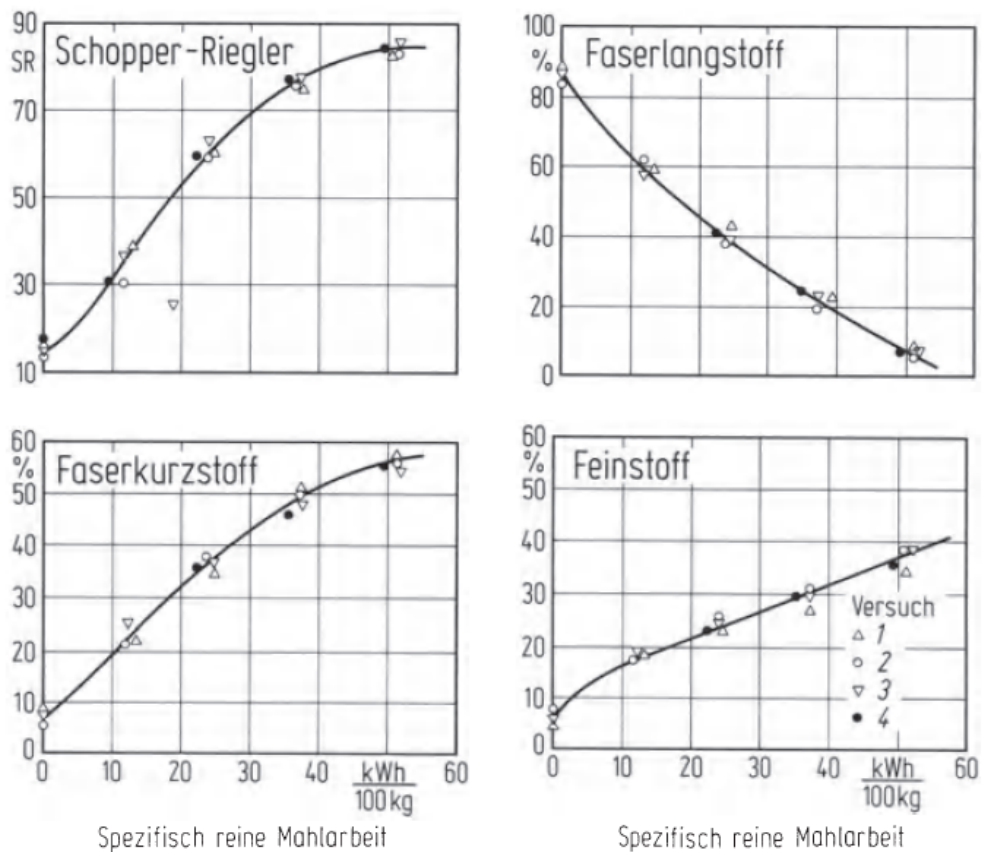
Cutting and shortening of fibers can occur during refining, especially axial tensile strain and shear action are used. This has a positive effect on the paper formation of fibers. Furthermore, shorter fibers are causing reduced flocculation effects. However, if the fiber fragments of the respectively generated fines are very small, they tend to clog pores of paper network and, consequently, hinder dewatering. [15]

### Change of Substance Properties

Figure 2.6 shows the effects of refining on fiber properties plotted on the specific refining energy. Fibers are shortened due to beating. The amount of long fibers ('Faserlangstoff')



sinks to nearly 0 % if beating is executed for a long time (80 - 85 SR). The amount of short fibers ('Faserkurzstoff') and generated fines ('Feinstoff') rises by beating. Furthermore, the dewatering resistance ('Schopper-Riegler') rises with the specific refining energy. On the one hand, this occurs because of fiber flexibilization, and on the other hand, due to generated secondary fines, as well as, shortened fibers. As a result of external fibrillation and detaching of fiber fragments, the fines content ('Feinstoff') starts to increase linearly at a certain point through gaining refining energy. [17]



**Figure 2.6** Fiber properties depending on specific refining energy of an unbleached spruce sulfite pulp [17]

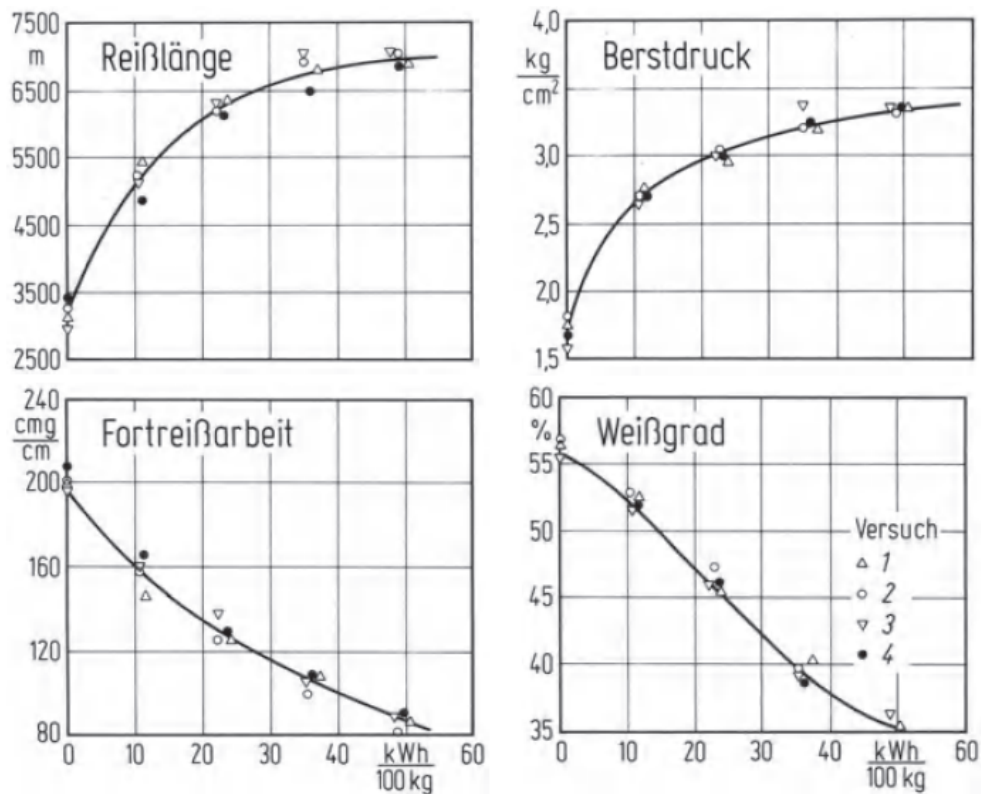
### Change of Paper Properties

As a result of changes in pulp properties, changes in physical properties of paper occur. These changes are shown in Figure 2.7. The breaking length ('Reißlänge') and the bursting strength ('Berstdruck') rise with the specific refining energy increases. Due to internal fibrillation and flexibilization, the strength of the fiber network increase [17]. While the breaking length and the bursting strength rise, the tear growth resistance ('Fortreißarbeit')



decreases rapidly in the beginning because of fiber shortening and decrease of long fiber pulp [17]. This is uncommon because usually tear growth resistance initially increases, after that it decreases.

Furthermore, the degree of brightness ('Weißgrad') is also affected. A higher fines content, as well as, a denser fiber network influence the quantity of bonded area in the sheet of paper. As a result, there is less scattering, which means that more light is transmitted through a sheet of paper and therefore reflected less. [17]



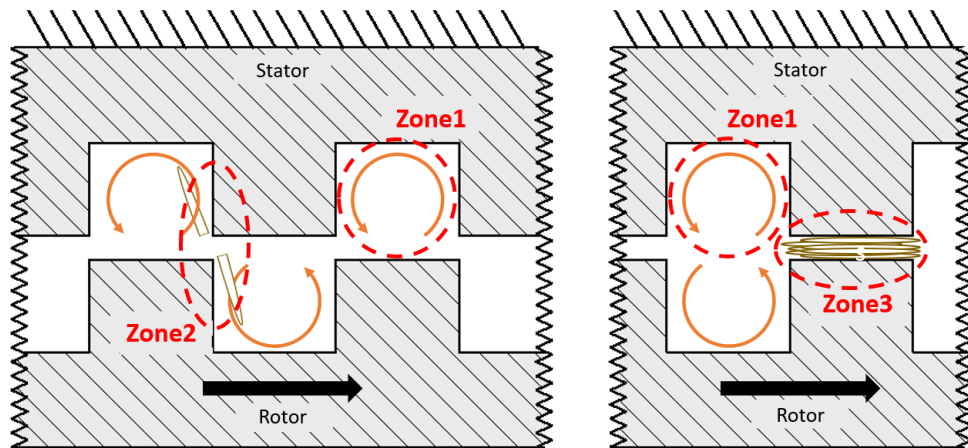
**Figure 2.7** Fiber properties depending on specific refining energy of an unbleached spruce sulfite pulp [17]

### 2.3.1 Refining Aggregates

Modern refining aggregates operate with plates with bars, where one set acts as stator and the other set as rotor. Stator and rotor stand opposing of each other. Blechschmidt [1] described three zones, which are illustrated in Figure 2.8. Zone 1 represents the area of the groove. In this section the transport of the fibers and fines occurs. Fiber networks are split because of the generated turbulences. In this process 40 - 90 % energy demand is required. In zone 2 the edges of the bars come into contact with each other. Due to radial shear strain fiber shortening occurs, fibrillation is rare. As a result, the consistency begins to rise. In

zone 3 the maximum of the consistency increase is reached. Fibrillation of the fiber occurs. Depending on the distance of the bars, destruction of fiber can happen. [1]

In refining aggregates, it is distinguished between laboratory and industrial scale. [1]



**Figure 2.8** Illustration of the operating principle of a refiner [18]

### 2.3.2 Refining in Laboratory Scale

Common refining tools in lab scale are the PFI-mill, the Valley Beater and the Jokro mill. They are used to refine small pulp samples, however their working principles are different from industrial refining. In the present thesis only a PFI-mill was used, therefore, only this mill will be described in detail. The Valley Beater and the Jokro mill will also be explained but merely due to coherency. [19]

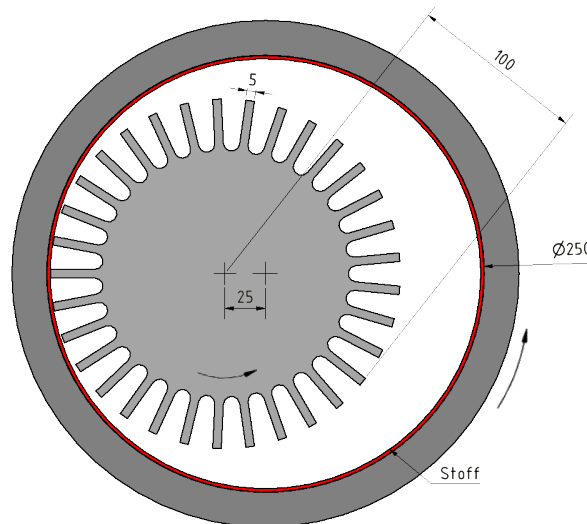
#### PFI-Mill

The PFI-mill is the laboratory refining tool that is most often used. Using this tool, the refining process occurs between the grinding media which is a roll with 33 bars and a rotating disc with a smooth inside wall. Both components rotate in the same direction but at a different peripheral speed. A beating force of 33.3 N/cm guarantees that the pulp is refined under standardized conditions. A sample weight of 30 g with a stock consistency of 10 % is put inside the housing and refined at  $25 \pm 5$  °C [17, 20]. In Figure 2.9 the dimensions of a PFI-mill are illustrated.

Refining with a PFI-mill leads to a better retained fiber length because of a squeezing method while an industrial refiner uses a cutting method [21]. The intensity of impacts of

the PFI-mill was calculated by Welch and Kerekes and was found to make 1.5 - 15 % in a disc or conical refiner. [22]

PFI-beated material results in higher tensile strength and more regular handsheets structures in comparison to the Valley Beater [23]. It is observed that the main effect of PFI-refining is higher internal fibrillation and lower external fibrillation and fiber shortening [21].



**Figure 2.9** Operating mode of the PFI-mill [18]

### Valley Beater

The Valley Beater is a stainless-steel device fixed upon a stainless steel construction. The vessel holds a volume of 23 liters, therefore, it is possible to beat 360 g of pulp within one process. The rolls including the blade have a width of 152 mm and a diameter of 190 – 194 mm. The bed knife is composed of seven 3.2 mm thick stainless steelblades. The bed and bars of the beater are jacketed by a tank cover to ensure safe handling of the apparatus. The refining process starts after fixing a weight of 5.5 kg on the loading arm. The Valley Beater tends to result in higher fiber cutting and fine formation. Since a bigger number of samples is needed, the time for refining takes longer. [19, 24]

### Jokro Mill

The Jokro mill uses the principle of centrifugal force. The mill consists of a horizontal running plate on which six beater housings with grinding rolls inside are placed. The housings revolve like planets around their own axis. The beating process of the pulp takes

place between the inner wall of the grinding vessel and the cylindrical roll. This method enables an extremely constant force application. [25]

In comparison to other beating aggregates, an advantage of the Jokro mill is that just 64 g are needed for four required beating points, whereas the Valley Beater needs 360 g. [17]

### 2.3.3 Industrial Refining

There are different construction types of industrial refiners. They differ mostly in their geometry. The range includes from conical to disc refiners. [1]

Disc refiners, coming in several types of construction, are the most common apparatus in the refining process. Disc refiners are the only type of refiners which can be used in both, the range of low consistency (LC), as well as, in range of high consistency (HC). Other refiner types can only be used in LC range. Low consistency refining means a pulp consistency of 3.5 - 6 %. [14]

#### Disc Refiner

Disc refiners have high flow rate and refining power. The milling material is mechanically treated between two discs. The stock enters the center and passes the grinding disc from the inside to the outside. The peripheral speed of the rotor in disc refiners amounts to  $1500 \text{ min}^{-1}$ . [26, 27]

Modern disc refiners are classified into two types: single disc and double disc refiners. Double disc refiners are more common than single disc refiners. Single disc refiners are used in HC and laboratory refining because of their smaller capacity. [14]

While a single disc refiner has one stationary and one rotating disc, in double disc refiners, the pulp flow is separated through two zones which are formed on each side of the rotating disc between two stationary discs. The discs are equipped with bars made of high-strength steel and various profiles which are compressed hydraulically. The refiner gap has a significant impact on the stock quality. Further, the refiner gap is defined as the distance between the refining discs of the refining aggregate. LC refiners have a refiner gap range of 20 - 100  $\mu\text{m}$ . The gap cannot be set directly, instead it depends on the strain of the set. In order to achieve a constant specific work, the strain is regulated by variable stock consistency and a respectively flow rate. [1, 14]

It is observed that fibers have a less collapsed but a more heavily curved form when using a disc refiner. Furthermore, the fibers show a higher external fibrillation. [28]

### Conical Refiner

In conical refiners the pulp enters the center of the engine through the hollow center shaft. The refining process takes place in its horizontal path. The stock leaves at two outlet pipes. The gap between stator and rotor is adapted by cone-shaped means. Besides, it controls the refining energy. [26]

It is distinguished between flat-angle (20 - 35°) and high-angle (about 60°) conical refiners. Such refiners reach a peripheral speed of 900 - 1020 min<sup>-1</sup>. [27]

### 2.3.4 Refining Parameters

There are various parameters which make it possible to evaluate the refining process. In this section, all relevant parameters are described.

#### Specific Energy Consumption

The specific energy consumption (SEC) in kWh/t represents the transferred power from the throughput of the refiner system to the grinding stock. This is calculated by the effective refining power  $P_{eff}$  in kW and the refiner capacity  $\dot{m}$  in t/h. The relation is shown in Equation (2.1). [29]

$$SEC = \frac{P_{eff}}{\dot{m}} \quad (2.1)$$

$P_{eff}$  cannot be measured directly. Therefore, the refiner is operated with pure water which is declared as no-load power  $P_0$  in kW. In this case, the electric power of the motor  $P_{el}$  in kW is equal to the no-load power. After this step in the process,  $P_{el}$  can be measured at standard operation. The effective refining power can now be calculated by the difference of  $P_{el}$  and  $P_0$  which is shown in Equation (2.2). The electrical losses of the motor are cancelled out because they are equal. [1]

$$P_{eff} = P_{el} - P_0 \quad (2.2)$$

The no-load power must be estimated separately. It consists of two components which are shown in Equation (2.3). The first term  $P_{fric}$  represents the friction loss of a disc refiner which is generated by the law of fluid dynamics. Equation (2.4) shows that the friction loss depends on a constant  $K_d$  which is valid in a wide range of disc diameters. The rotational speed  $n$  and disc diameter  $D$  to the power of three or five have to be considered. The second term  $P_p$  represents the loss by impact of the pump (Equation (2.5)). This impact occurs during the acceleration of the fluid from the inlet to the outlet. The constant  $K_p$  includes the density of the fluid and the gravity constant. Rotational speed and disc diameter increase quadratically. The loss by the pump is depending on the flow rate  $\dot{V}$ . [1, 14, 29]

$$P_0 = P_{fric} + P_p \quad (2.3)$$

$$P_{fric} = K_d \cdot n^3 \cdot D^5 \quad (2.4)$$

$$P_p = K_p \cdot \dot{V} \cdot n^2 \cdot D^2 \quad (2.5)$$

### Specific Edge Load

The most common method to control a mill refiner is the specific edge load (SEL) in  $Ws/m$ . It is a theoretical technical evaluation introduced by Brecht and Sievert [14]. This value represents the load of a bar edge length which is calculated by the effective refining power  $P_{eff}$  related to the cutting speed  $L_s$  in  $km/s$  (Equation (2.6)). [14, 17]

$$SEL = \frac{P_{eff}}{L_s} \quad (2.6)$$

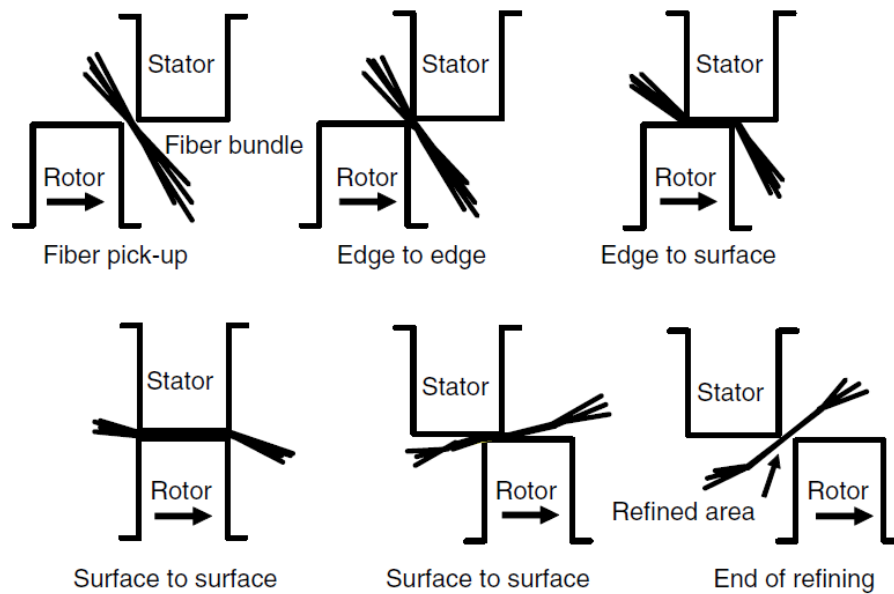
The principle of this theory is that the edge of the set takes the main part of the refining process. The area of the bars is only involved marginally. The higher SEL the more fibers are shortened. SR increases and the refiner gap decreases.  $L_s$  is computed from number of rotor bars  $z_R$  and stator bars  $z_{St}$ , as well as, from length of bars  $l$  and the rotational speed  $n$  (Equation (2.7)). [14]

$$L_s = z_R \cdot z_{St} \cdot \frac{l}{1000} \cdot \frac{n}{60} \quad (2.7)$$

The longer the length of the whole bars, the higher the whole amount of fibrage becomes. This is further resulting in the amount of refining aggregate can be loaded. [14]

### Specific Surface Load

Lumiainen [30] developed the refining theory drawing upon Brecht and Sievert who only included the bar edge length. Therefore, the specific surface load theory additionally includes the bar width and cutting angle. Furthermore, Lumiainen classified the bar-to-bar contact of stator and rotor bar into different phases which are shown in Figure 2.10. The position of rotor and stator bars play an important role for calculation of specific surface load (SSL). After the confrontation of the bar edges of rotor and stator, the edge-to-edge phase is over. It continues with the edge-to-surface phase. For a short period of time, the bar surfaces are standing totally against each other. After this moment, the rotor bar moves on and the trailing edges of rotor and stator bars are separated. If the bar edges are confronted against each other, that is called impact length (IL) in mm. [14, 30]



**Figure 2.10** Different phases of bar-to-bar contact of SSL theory [14]

The impact length depends on the width of rotor bars  $W_R$  in mm, stator bars  $W_{St}$  in mm and the average intersecting angle  $\gamma$ . It is computed from the bar crossing. The calculation of IL is shown in Equation (2.8). [14]

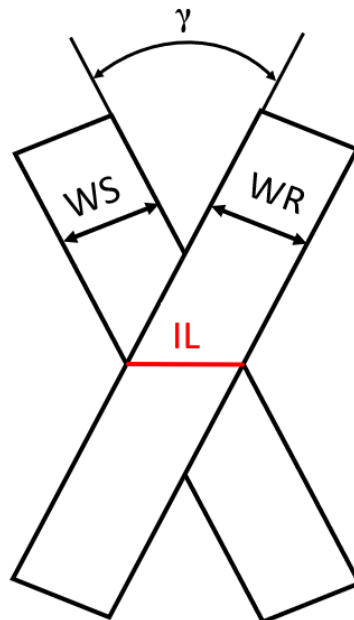
$$IL = \frac{W_R + W_{St}}{2 \cdot \cos(\gamma/2)} \quad (2.8)$$

The impact length increases at broader bars and higher intersecting angles. Figure 2.11 shows an illustration of IL. With the impact length, it is possible to determine the SSL in  $Ws/m^2$  which is shown in Equation (2.9). [14]

$$SSL = \frac{SEL \cdot 1000}{IL} = \frac{P_{eff} \cdot 1000}{L_s \cdot IL} \quad (2.9)$$

The disadvantage of the SSL theory is, that either the bar surface roughness or the bar edge rounding is not considered. The real impact length is affected by the bar edge rounding. Lumiainen also raised the point that the bar surface smoothness also needs to be considered. [14, 30]

A high SSL indicates a high strain of fiber surface which results in a heavy intensity of beating process. The higher the impact length, the longer the residence time amounts between the bars. Thereby, more refining energy is consumed between the bars and less energy is consumed at the bar edges. [14]



**Figure 2.11** Impact length measured from bar crossing, adapted from [14]



## 2.4 Influence of Refining and Fines on Pulp and Paper Properties

As mentioned in section 2.2, fines generated during the refining process which are called secondary fines, affect pulp properties and final paper properties. Moreover, the sheet consolidation changes. Secondary fines feature a more fibrillar characteristic than primary fines. [8] While secondary fines influence strength properties positively, primary fines have a negative impact on strain-to-failure. Nevertheless, they affect optical properties like light scattering positively [12, 31].

The reason for enhanced strengthening properties of secondary fines is the larger hydro-nomic surface, which leads to a higher densification of the paper sheet. Besides the effect on strength properties, the impact of fines on dewatering is very strong [32]. The dewatering resistance is increased because fines feature a higher swelling ability. On the contrary, studys have proven that the air permeability is reduced. The impact of fines on strength properties increases the higher the content of fibrills and the swelling ability become [8].

In general, fines influence sheet properties like higher tensile strength and z-strength. Density also increases if fines are added. In sheets containing fines higher surface area and higher bonded area, as well as, a better stress distribution are found. It is still unclear how fines influence detailed properties of pulp and paper. [8]

Secondary fines have an higher impact on paper properties than chemical pulp primary fines [33]. Dependent on different wood sources and processes in pulping, there are differences found in swelling, specific surface area, and the extractive content regarding strength development [8]. The fractionation of chemical pulp fines shows that these fines fractions have a different effect on tensile strength because of differing chemical and morphological composition [34]. Using different refining aggregates, also changes in quantity and quality have been observed [35].

Many different methods are used to quantify the impact of fines on sheet properties. Whereas the impact of mechanical pulp fines on sheet properties like swelling, fibrillar and fines content is described in detail, the effect of chemical pulp fines on sheet properties cannot be described by neither their origin or their quantity. [8]

Particularly secondary chemical pulp fines have a heterogeneous character concerning morphology and chemical composition. Therefore, Mayr et al. [8] investigated the effect of primary and secondary fines on their size, fibrillar character, and aspect ratio. Handsheets

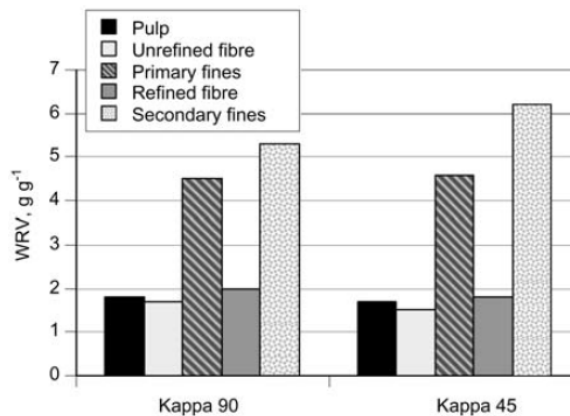
were formed with and without fines in different setups. Softwood bleached kraft pulp, as well as, softwood bleached sulfite pulp were used. An industrial single disc refiner acted as refining aggregate. The content of fines was varied using different refining settings. [8] In general, results show that secondary fines have a more beneficial effect on paper properties than primary fines, which was also proven in literature. The water retention value of fines increases with a higher amount on secondary fines. The microscope method also showed an expected increase of fibrillar material with a higher amount of secondary fines. Additionally, mechanical properties such as tensile index were investigated. The tensile index rose with increasing secondary fines fraction as secondary fines are more fibrillar and therefore have a greater bonding effect than primary fines. These findings were also discussed in literature. The comparison of sulfite and kraft pulp showed that the sulfite pulp reached a lower increase in terms of WRV and tensile index than kraft pulp.

The study of Mayr et al. argues that a more suitable experimental setup would lead to a better understanding of the effect of fines quality on final paper properties. This was not possible to realize with the present setup of standard testing. Furthermore, a direct comparison between the effect of primary and secondary fines cannot be actualized because secondary fines show different properties concerning size, fibrillar character and swelling ability. Nonetheless, it can be revealed that strength properties are affected by fibrillar material and swelling ability. [8]

Htun et al. [36] also tested the influence of primary and secondary fines on paper properties. Two different never-dried UBSK mixtures of pine and spruce were used. The pulps had kappa numbers of 45 and 90 and were refined in an Escher-Wyss conical refiner. The fractionation was executed with a Celleco laboratory filter (100  $\mu\text{m}$  mesh size). Handsheets were formed and analyzed from the following settings:

- original pulp with primary fines
- unrefined fibers without primary fines
- primary fines removed from unrefined pulp
- refined fibers with secondary fines
- secondary fines

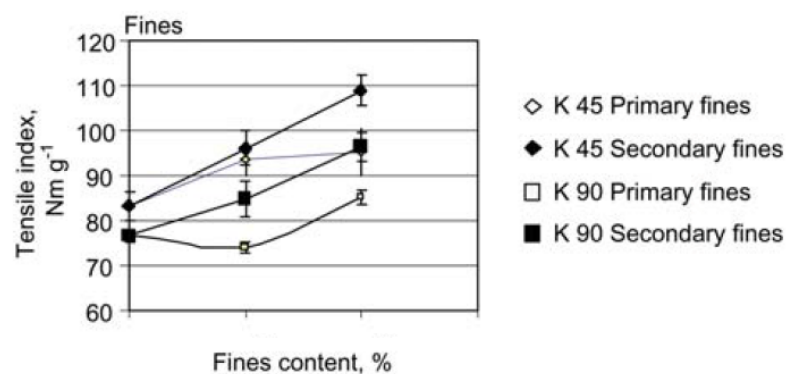
Results show that there are differences between primary and secondary fines. The differences of the swelling degree was measured using the water retention value WRV, which is illustrated in Figure 2.12. Fines have a significantly higher WRV than fibers. The WRV improves with increasing refining because of internal fibrillation, a widening of small internal pores and delaminations. Additionally, secondary fines have a higher water retention value than primary fines. The original pulp and the fiber fractions have similar WRV values.



**Figure 2.12** WRV of the different fractions [36]

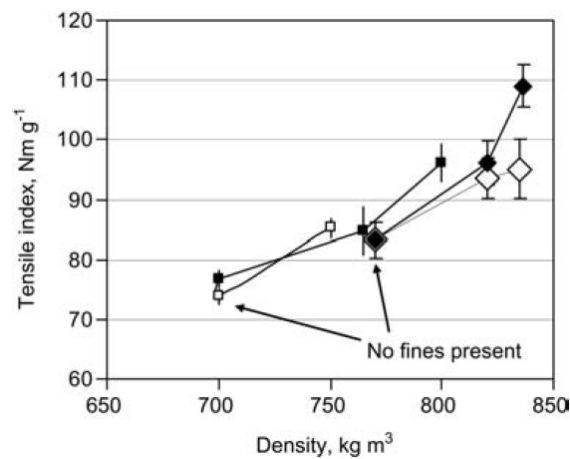
Furthermore, mechanical properties such as the tensile index, the burst index, the tensile energy absorption, and the stretch-to-break were investigated. Since the focus in this thesis lies on tensile index, only this key figure will be displayed and interpreted.

Figure 2.13 shows that the increase of tensile index is related to the fines content. The increase is higher if secondary fines are added. The addition of 10 % secondary fines provides an enhancement of up to 30 %, while primary fines only achieve an improvement of 15 %.



**Figure 2.13** Increase of tensile index if primary or secondary fines are added. Adapted from [36]

In Figure 2.14 the tensile index, depending on given density, is displayed. It becomes obvious that the enhancement of tensile index is caused by the addition of fines, which accompanies an increase in density. There is no clear distinction observed between primary and secondary fines referred to the correlation of tensile index and density. The improvement of paper properties is attributed to the consolidation as a result of greater capillary forces between fiber and fines surfaces. Fines increase the potentiality for fiber-to-fiber contact areas and work as a bridge between fibers.



**Figure 2.14** Tensile index related to density if primary or secondary fines are added [36]

## 2.5 Wet-Pressing

In papermaking processes, wet-pressing leads to a consolidated fiber network and a removal of water from the paper [37]. As a consequence of wet-pressing, fibers are forced into close contact with each other and hydrogen bonding occurs. Due to removal of water, a strengthening of the paper web is established through closer contact of fiber and fiber cell walls. It is further supported by the collapse of chemical pulp fibers [38, 39]. Wet-pressing leads to a denser sheet structure, which has a positive effect on interfiber bonding and also increases the density [37, 39]. There are differences in wet-pressing due to the use of mechanical pulp and chemical pulp. While the density of mechanical pulp only increases a little, chemical pulp presents a comprehensive increase in density [37]. As a result of more contacts between fibers and larger bonded areas, the tensile strength of paper also increases [38].

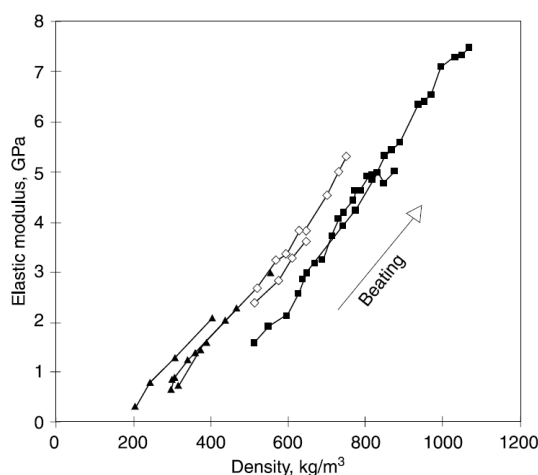
Interfiber-bonding has a crucial effect on sheet strength. In addition to mechanical proper-

ties, optical and electrical properties are also affected by fiber bonds. Processes as refining, pressing and drying influence the structure of interfiber bonds [40]. Drying further activates the fiber network. The swelling ability of pulp fibers also affects this activation of the fiber network. While restrained drying, it was analyzed that mechanical properties of dried paper show a correlation between final drying stress [41]. Otherwise, if strain during drying was applied, drying strain was the crucial variable [42].

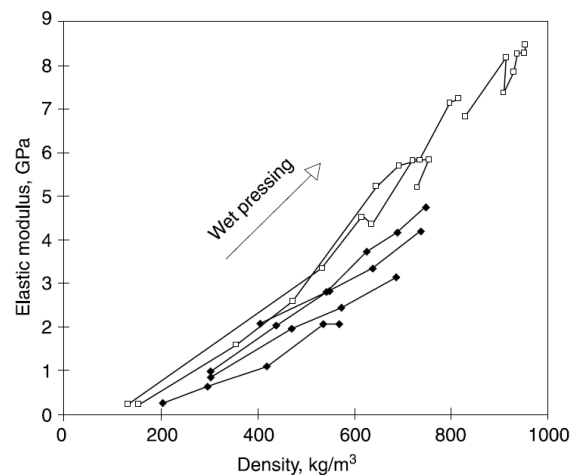
The most important parameters in wet-pressing are the in-plane mechanical properties tensile stiffness, or tensile strength and elastic modulus. The tensile strength states how much a paper can be loaded. The elastic modulus is important for two reasons: Firstly, the elastic modulus controls the small tension of a running web. Secondly, it also controls the bending stiffness, as well as, the structural rigidity of paper. All mechanical properties of paper refer to the bonding degree of fiber network. [43]

Finally, and most importantly, a high E-modulus improves the stress transfer within the sheet, thus inhibiting strain localisation which leads to sheet failure. Therefore, a strong correlation between E-modulus and tensile strength is found in paper.

Elastic modulus and density are influenced by beating, wet-pressing and the mixing of various pulp components. Figure 2.15 displays the case in which the beating degree is varied. Figure 2.16 displays the fact if wet-pressing is the controlled variable.



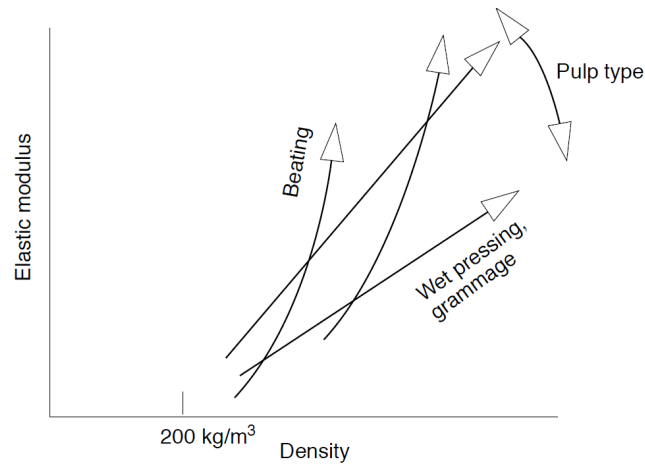
**Figure 2.15** Elastic modulus versus density if beating varies. Each line links the data of one wood species, pulp type and a fixed wet-pressing level. [44]



**Figure 2.16** Elastic modulus versus density if wet-pressing varies. Each line links the data of one wood species, pulp type and a fixed beating level. [44, 45]

Niskanen et al. [46] researched the correlations between elastic modulus and density. The experimental observations are illustrated in Figure 2.17. In their interpretation, the density

increases linearly in dependency on the elastic modulus. Both beating and wet-pressing have influence on the densification. Nonetheless, beating has a stronger positive effect. The plot is not applicable on poorly bonded sheets with a density  $\rho \geq 300 \text{ kg/m}^3$ .



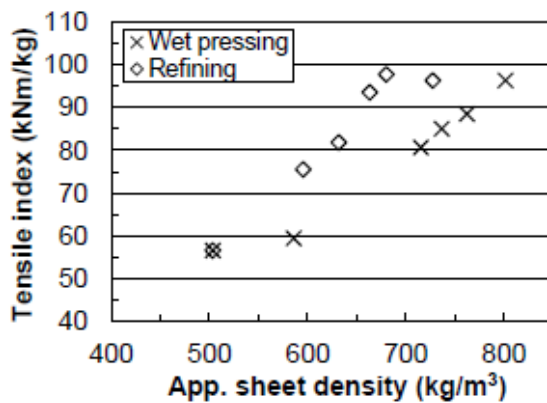
**Figure 2.17** Correlation of density and elastic modulus affected by beating and wet-pressing [43]

Nordström [47] found that mechanical properties such as compression strength, tensile strength and tensile stiffness are affected by densification, refining or wet-pressing. This study provides an insight into the effects of low-consistency refining and wet-pressing. Two different studies are examined using industrial never-dried softwood kraft pulp with kappa numbers of 80 - 90. One study discussed densification with an Escher-Wyss refiner versus wetpressing of non-refined pulp. The other study analyzed the impact of varying wet-pressing pressure (from 400 - 1600 kPa) over the beating curve, using an industrial conical refiner. Free and restrained drying were used. Handsheets were prepared with the grammage of  $140 \text{ g/m}^2$  according to ISO 5269-3.

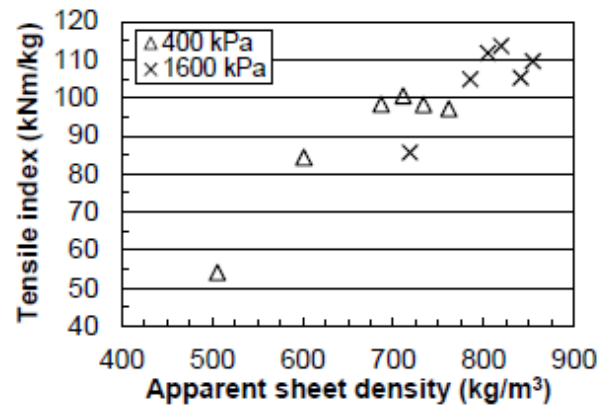
Sheet densification occurred when wet-pressing was confronted with refining by Escher-Wyss. This is illustrated in Figure 2.18. The figure shows the increase of tensile strength by refining and wet-pressing using restrained drying. Wet-pressing is operated at 400 kPa. At high densities, the densification by wet-pressing results in a higher tensile strength compared to refining.

Figure 2.19 shows results of the second study. A beating curve, using an industrial conical refiner, is generated applying two different wet-pressing pressures. The graph demonstrated that the increased wet-pressing pressure causes a shift of the curves to greater densities. Therefore, higher maximum values of tensile strength were achieved.

Considering densities with values of up to approximately  $750 \text{ kg/m}^3$ , higher tensile



**Figure 2.18** Tensile index depending on apparent sheet density in case of restrained drying, including refining or wet-pressing. [47]



**Figure 2.19** Tensile index versus apparent sheet density of industrial refined pulp. Restrained drying is used. [47]

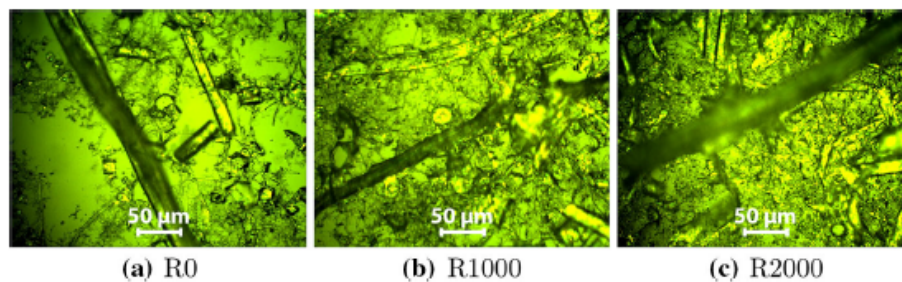
strength for densification by wet-pressing and refining were observed, using restrained drying. This procedure is explained considering the activation effect, as well as, with the effect of a higher bond strength in favor of tensile strength and stiffness. However, fiber curl and fiber shortening increased avoiding further rise in tensile strength with increasing refining. A growth in both of these characteristics (above the maximum of the beating curve) needed an increased wet-pressing pressure and restrained drying. As a result of this effect on properties, the increased wet-pressing pressure allowed an enhanced combination of tensile strength and stiffness, as well as, compression strength for both restrained and free drying. The relevant graphs were included in Nordström's study [47].

Kulachenko et al. [48] also prove that fines influence density, bonding behavior, and tensile strength of sheets in a positive way. Additionally, the effect of wet-pressing was tested to compare it to the impacts of beating. In order to verify their numerical simulation of fiber networks, experimental measurements on handsheets were formed using Rapid-Köthen (ISO 5269-2:2004). A chemithermomechanical pulp (CTMP) was refined using a PFI-mill with 1000 and 2000 revolutions per minute and was compared to unrefined pulp. Before drying, the handsheets were pressed. For comparison, handsheets with and without strength additives were prepared.

It was observed that strength additives only improved strength properties if the pulp was refined before. Furthermore, it was proven that wet-pressing also causes densification. The elastic modulus of handsheets densified by wet-pressing increased linearly with density similar to the densification by refining. Still, there are differences in affecting paper strength. It was observed that densification of handsheets caused by beating led to a higher

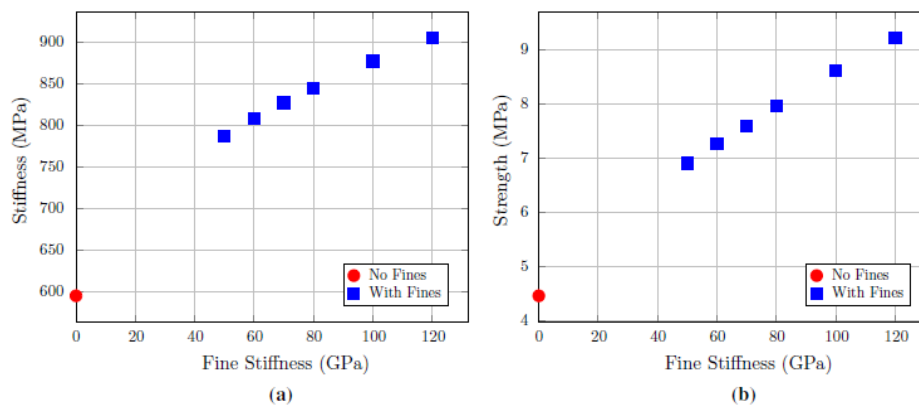
strength at a certain density level. This effect can be traced back to an improved bonding strength and is closely related to the addition of fines. Actually, densification and improved strengthening can be caused by the addition of fines [46]. In fact, it is not easy to differentiate between the effects originated from the increased bonding and strengthening by fines experimentally.

As expected, higher levels of refining lead to improved strength and stiffness. This effects occurred simultaneously with the densification of the handsheets. Both refining and, therefore, an addition of fibrillar material have the same impact on mechanical properties. Microscopy images were used to observe the characteristics of fines. The intention was to compare the shape and the amount of fines from refined and unrefined pulp. The differences of the pulp are illustrated in Figure 2.20. It can be seen that refining increased the percentage of fines and fibrillar material at higher refining levels.



**Figure 2.20** Microscopy images of unbeaten and differently refined pulps [48]

As mentioned before, fines affect strength and stiffness of fiber networks. While the stiffness of fines are dependent on their type, strength is reliant on the bond between fibers and fines. The results of model development with fiber network models are shown in Figure 2.21. It can clearly be seen that fines influence strength properties.



**Figure 2.21** Correlation of elastic modulus of fines and stiffness (a) and strength on networks [48]



Seth and Page [49] observed that strengthening can be improved by wet-pressing but this is not necessary the case. These differences can be seen in Figure 2.22 and Figure 2.23. In both cases, never-dried, unbleached kraft pulp of black spruce was researched. It can be seen that the variation of wet-pressing levels lead to different results. In this case, higher wet-pressing pressures led to higher strenghtening.

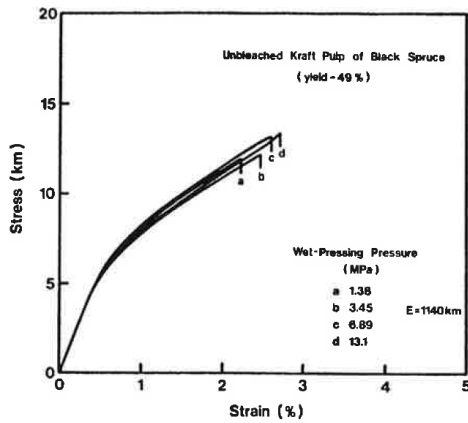


Figure 2.22 Wet-pressing with small effect on strengthening [49]

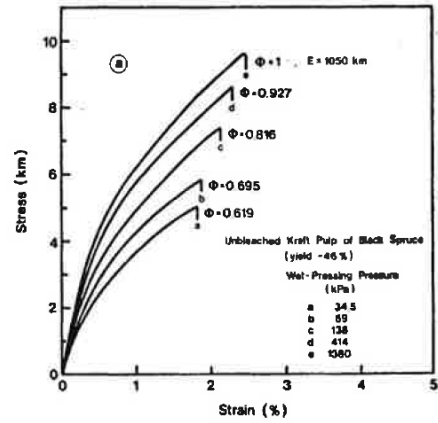


Figure 2.23 Wet-pressing with significant effect on strengthening [49]

In comparison to wet-pressing, beating always improves strengthening behaviour. While in Figure 2.24 a never-dried, unbleached kraft pulp of Douglas fir is tested, a never-dried, unbleached kraft pulp of southern U.S. pine is evaluated in Figure 2.25. In both cases, a significant increase can be observed.

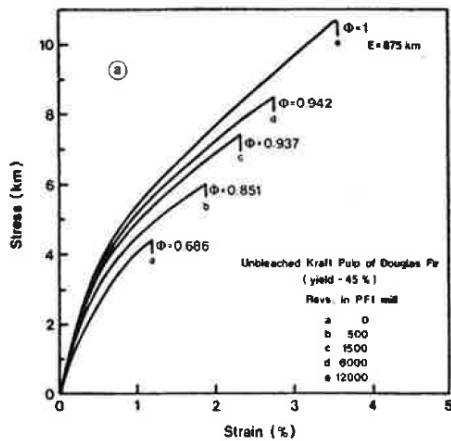


Figure 2.24 Beating effect on strengthening by using a Douglas fir [49]

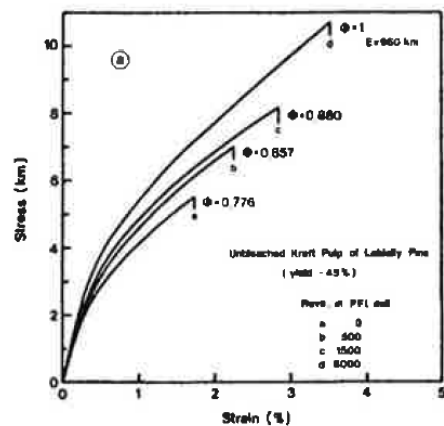


Figure 2.25 Beating effect on strengthening by using a southern U.S. pine [49]

## **Materials and Methods**

This section of the thesis provides an insight into used materials and also to applied analytical and experimental methods. Pulp properties, as well as, physical paper properties are analyzed after preparation of handsheets. Used methods for analysis are explained beginning at section 3.5.

### **3.1 Fiber Material and Preparation**

In this work a once-dried unbleached softwood kraft pulp (UBSK) with a kappa number of 42 was used. The average amount of primary fines was 5 %.

### **3.2 Experimental Design**

In Table 3.1 an overview of the experimental parameters is given. Experiments were performed with and without fines, as well as, with and without wet-pressing. Refining was conducted using a PFI-mill and a pilot plant single disc refiner with varying refining energy. An unrefined pulp was used as a reference. Moreover, a pressure screen was used to remove fines from unrefined and refined pulp. Rapid-Köthen handsheets were prepared and analyzed. By comparing the handsheet properties of the differently refined pulps with and without fines, the effect of fines on the development of paper properties in refining of pulp could be quantified.

**Table 3.1** Overview of experimental design

Abbreviation	Fines	Wet-Pressing	Refining intensity PFI [rotations per minute]	Refining intensity disc refiner [kWh/t]
A	no	no	0, 4000, 7000, 10000	100, 250
B	no	yes	0, 4000, 7000, 10000	100, 250
C	yes	no	0, 4000, 7000, 10000	100, 250
D	yes	yes	0, 4000, 7000, 10000	100, 250

### 3.3 Refining

#### 3.3.1 PFI-Mill

The first refining was carried out with a PFI-mill. Refining with the PFI-mill was performed according to ISO 5264-2. Different refining intensities of 4000, 7000 and 10000 rpm were realized. For each refining trial 30 g of oven-dry (od) pulp was used. Before pulp could be used, pulp was immersed in deionized water for 4 hours. After swelling, the pulp had to be treated with a L&W Pulp disintegrator 10 minutes before refining.

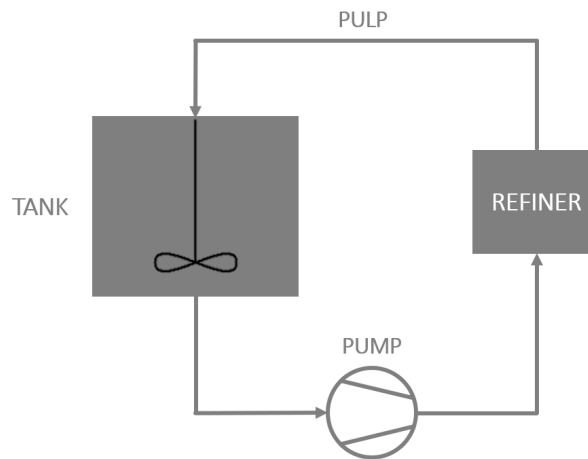
#### 3.3.2 Disc Refiner

For comparison purpose, another refining aggregate was used. A 12-inch single disc refiner in pilot scale was used. Two different refining intensities were performed: 100 kWh/t and 250 kWh/t. The process was run with 62 kg od pulp  $m_{od}$  with a consistency  $C$  of 3.9 %. Before refining, the pulp was deflaked for 15 minutes with open refining gap. In Figure 3.1 the principle of the disc refiner is shown. The process was operated in closed loop operation between the stirred vessel and the refiner.

In a first attempt, 10 % of the vessel was used for sampling. (Equation (3.1)). The remaining pulp  $m_{pulp}$  in kg was used for beating.

$$m_{pulp} = m_{od} - 10\% \cdot m_{od} \quad (3.1)$$

Using the refiner capacity  $\dot{m}$  in kg/s and the amount of  $m_{pulp}$ , it was possible to calculate the cycle time  $t_{cycle}$  in min (Equation (3.2)).



**Figure 3.1** Process scheme of the disc refiner

$$t_{cycle}[min] = \frac{m_{pulp}[kg]}{\dot{m} \cdot \frac{1}{3.6 \cdot 60}[kg/min]} \quad (3.2)$$

Sampling was done at defined time steps. With a calculated  $t_{cycle}$  of 7.5 min and specific refining energy of 22.5 kWh/t, it was achievable to determine sample-taking for both configurations 100 kWh/t and 250 kWh/t (see Table 3.2).

**Table 3.2** Determination of sampling

kWh/t	min
22.5	7.5
45	15
100	28.8
250	78.8

In Table 3.3 all relevant parameters (given and calculated) of the disc refiner are displayed.

**Table 3.3** Given and calculated parameters of disc refiner

Parameters	Unit	Values
$P_{eff}$	kW	10
$\dot{V}$	l/min	190
C	%	3.9
$\dot{m}$	t/h	0.4446
$m_{pulp}$	kg	55.8
SEC	kWh/t	22.5
$L_s$	km/s	33.8
SEL	Ws/m	0.3
IL	m	0.003
SSL	Ws/m <sup>2</sup>	98.62

### 3.4 Fines Separation

For fractionation of fines from fibers, unrefined and refined pulps were separated using a laboratory scale pressure screen, which was built within the FLIPPR<sup>2</sup> on the Institute of Bioproducts and Paper Technology. It was equipped with a screen, implemented as a plate with 150  $\mu\text{m}$  diameter holes. In Figure 3.2, the principle of the pressure screen is shown.

The pulp suspension was fed with 20 l/min and separated at 1 % dry content using the pressure screen. Material which was able to pass the screen was defined as fines fraction and was discarded. Additionally, a dilution flow was supplied to the pressure screen which was varied dependent on the accept. The accept flow rate amounted up to 60 %.

Since the removal of all the fines material was not realizable in a single step, the pulp suspension was recirculated until the remaining fines content was below 1 %. This was measured with the BDDJ method which is explained in section 3.5.5. The termination criterion was the turbidity of the accept. Approximately 20 runs were needed to achieve this result. If the residual fines content below 1 % was not reached, it was recirculated again. After the circulation, the water was separated from the pulp without fines using a centrifuge.

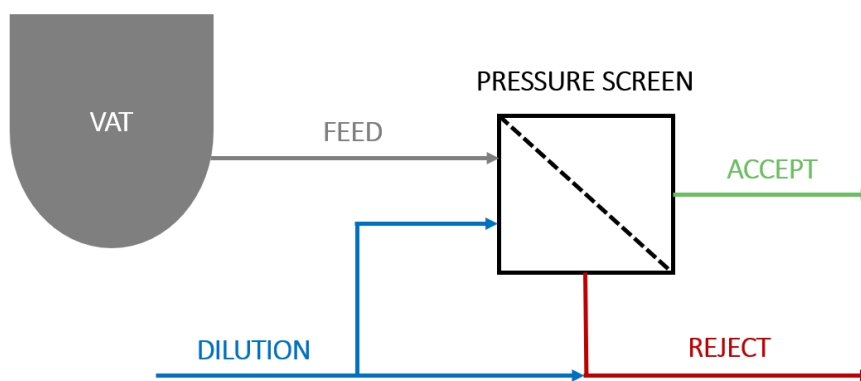


Figure 3.2 Process scheme of laboratory pressure screen

### 3.5 Pulp Analytics

#### 3.5.1 Consistency and Dry Content

While the consistency was determined according to EN 4119, the dry content was determined by using DIN EN 20638. In both applications, the ratio of the wet mass  $m_w$  in g and

the dried mass  $m_d$  in g, resulted in the dry content or the consistency, respectively. [1] The calculation is shown in Equation (3.3).

$$DC = \frac{m_d}{m_w} \quad (3.3)$$

### 3.5.2 Fiber Length Distribution

The fiber length distribution was determined using a L&W Fiber Tester<sup>+</sup> (Figure 3.3). For the determination, an amount of 0.1 g pulp was diluted in 300 ml deionized water. Images were taken by the device to identify parameters such as the length and width of fibers, as well as, the presence of other particles.



**Figure 3.3** L&W Fiber Tester<sup>+</sup> [18]

In order to determine the fiber length distribution, three measurements of each data point were examined. The device measures a minimum number of 5000 fibers. All information about the fiber length distribution were length-weighted according to Equation (3.4). While the term  $n_i$  means the number of fibers of class  $i$ , the term  $l_i$  represents the fiber length of class  $i$ .

$$L_L = \frac{\sum n_i \cdot l_i^2}{\sum n_i \cdot l_i} \quad (3.4)$$

### 3.5.3 Dewatering Resistance

The drainability was determined using the Schopper-Riegler (SR) method (EN ISO 5267-1). SR was calculated with the difference between 1000 ml and the amount of running out

liquid  $z$  divided by 10. It was proved that the higher the SR values, the poorer was the drainability of the pulp. The range of SR covers values from 14 to 90 °SR. Before executing, the pulp was disintegrated as well. [17]

$$SR = \frac{1000ml - z}{10} [^{\circ}SR] \quad (3.5)$$

### 3.5.4 Water Retention Value

The water retention value (WRV) is a measurement using a centrifugation method based on the standard ISO (23714:2014). It reveals the degree of swelling of pulp. Before conducting the experiment, the pulp must be disintegrated. After the usage of centrifugal forces was defined under specific conditions retained water in a fiber pad was determined. Therefore, the wet mass  $m_w$  in g and the oven-dried mass  $m_d$  in g of the same sample were used to determine WRV. The calculation of WRV is shown in Equation (3.6).

$$WRV = \frac{m_w - m_d}{m_w} \cdot 100[\%] \quad (3.6)$$

### 3.5.5 Fines Content with BDDJ

A Britt Dynamic Drainage Jar (BDDJ) according to SCAN-CM 66-05 was used to determine the fines content of the unrefined and the refined pulp. Before executing, the pulp was treated in a L&W Pulp disintegrator. Afterwards, 5 g pulp and 5 l deionized water were mixed and washed out using a 200  $\mu$ m mesh screen. As a result, a fiber-filter cake remained. Both fibers and fines in the filtrate were vacuumed, dried and weighed in. The fines content was calculated with the Equation (3.7).

$$FC = \frac{m_{fines}}{m_{fines} + m_{fibers}} \cdot 100[\%] \quad (3.7)$$

### 3.5.6 Microscopy Method

To see the effects of refining, unrefined and refined pulps were reviewed using transmitted light microscopy introduced by Mayr et al. Firstly, 0.01 g crude tall oil was mixed with deionized water (5 g) in a test tube. The compounds were emulsified at a temperature of

80°C in an ultrasonic bath for 30 minutes. In another test tube a 0.01 % pulp suspension was prepared. The 0.06 g tall oil and water emulsion was added to 5 g of the pulp suspension and homogenized through powerful shaking. Three droplets of this pulp suspension were positioned on a microscope slide (76x26 mm), fixed in place with a cover glass (60x24 mm) and dried on a hot plate. A standard transmission light microscope (Leica 301-371.010), equipped with a conventional CCD camera (Jai AM-200GE/AB-200GE) and an automatized stage control (Märzhauser Multicontrol 2000), were applied for mapping the samples. 700-800 images were automatically captured per microscope slide. The results showed 1600x1200 pixels per image, an image area of 1380x1035  $\mu\text{m}^2$  and a resolution of 0.86  $\mu\text{mm}/\text{pixel}$ . The stage control and the camera were operated with ImageJ.

### 3.6 Handsheet Preparation

Handsheets of 80 g/m<sup>2</sup> were prepared on a Rapid-Köthen handsheet former (Figure 3.4) using white water recirculation (ISO 5269-3). Before preparation, the pulp was disintegrated. Handsheets which were formed with Rapid-Köthen featured an area of 0.0317m<sup>2</sup>. To ensure a stable fines content, the first four sheets were discarded [15]. Handsheets were formed with two different methods: with and without wet-pressing.



**Figure 3.4** Rapid-Köthen Handsheet former equipped with a white water recirculation system [15]

#### Wet-Pressing

The handsheets were directly wet-pressed after preparation. The wet-pressing was examined under the following conditions: The handsheets were positioned between the two



pressing plates. Additionally, there were two press felts cut into the size of specimen to absorb the excess water during the process. The handsheets were pressed for 120 seconds at 150 bar. Using the hydraulic area of the cylinder  $A_c$  in  $m^2$  and the pressure  $p$  in bar made it possible to calculate the force of the cylinder  $F_c$  in N acting on the pressing plate (Equation (3.8)).

$$F_c = p \cdot A_c \quad (3.8)$$

Now it was feasible to calculate the distributed load  $s$  in  $kN/m^2$ , acting on the area of the handsheets  $A_h$  in  $m^2$ .

$$s = \frac{F_c}{A_h} \quad (3.9)$$

Table 3.4 shows the calculated force acting on cylinder and the distributed load that acts on the handsheets.

**Table 3.4** Calculated parameters of wet-pressing

Parameters	Unit	Values
$F_c$	kN	95.43
$s$	$kN/m^2$	3010.28

## 3.7 Measurement of Handsheet Properties

After a storage for at least 24 hours in a climate room of 23 °C and with 50 % relative humidity, the handsheets were tested.

### 3.7.1 General Properties

#### Grammage

The grammage in  $g/m^2$  (Equation (3.10)) is defined according to DIN EN ISO 536, as the ratio of the mass  $m$  of the paper related to the area  $A$  of the handsheet. As mentioned before, the area of handsheets which are formed with Rapid-Köthen average to  $0.0317 m^2$ . The grammage is one of the most relevant properties of paper.

$$\textit{Grammage} = \frac{m}{A} \quad (3.10)$$

### Thickness

Besides grammage, the thickness  $d$  in  $\mu\text{m}$  is also a fundamental key component in paper characteristics. The sheets were tested according to EN ISO 534. For each handsheet, three positions were measured.

### Density

The density  $\rho$  in  $\text{g}/\text{cm}^3$  was calculated using the grammage and the sheet thickness according to Equation (3.11).

$$\rho = \frac{\textit{Grammage}}{d} \quad (3.11)$$

## 3.7.2 Mechanical Properties

### Air Permeability by Gurley

The air permeability by Gurley was measured according to ISO 5636-5. During testing, an in-oil swimming cylinder with a defined mass pushes air through a fixed paper sample. In dependence of the air permeability of the paper, the cylinder sinks downwards. The results of testing show the time and length of the path of the cylinder. The unit is measured in Gurley seconds which is the time required to push a certain amount of air in ml through the paper sample.

### Roughness by Bendtsen

The roughness by Bendtsen was measured according to DIN 53108. The ring-shaped gauging head rests on the sample with its tare weight. The flow rate of the air in  $\text{ml}/\text{min}$  is the result of the measurement. It is pressed out of the holes between the paper surface and the ring of the gauging head. Considering rougher surfaces, more air can evade, and thus leads to a higher flow rate.

## Tensile Strength

The tensile strength of a paper is determined by the strength of fiber-fiber-bonds and the strength of single fibers in strongly bound sheets. Fiber connections fail because of externally applied forces which are transferred from fiber to fiber by shear forces.

The tensile test, according to DIN EN ISO 1924-2, provides results concerning breaking strength, breaking strain, and E-modulus. Using breaking strength, other relevant parameters such as tensile index and breaking length can be calculated. It must be ensured that the free clamping length of the test strip is sufficiently large enough to measure. Due to the heterogeneity of the paper, the longer the length of the test strip is, the lower the tensile strength. Furthermore, the tensile testing speed has also influence on measured tensile strength because of viscoelastic behavior.

## Z-Strength

The measurement of z-strength is basically a tensile test. In internal bond tests (z-tensile test), the bond strength of layers among each other are tested according to TAPPI T541. In this test, the strength of the paper in thickness direction is evaluated. The sample is fixed with double-sided adhesive tape. The measured value is tensile strength, which is related to sample area. The result is the tensile strain. [50]

### 3.7.3 Optical Properties

#### Opacity

Opacity is the opaqueness of a paper. According to DIN 53146 the reflexion of a single-sheet over a defined black standard  $R_0$  and on a pack  $R_\infty$  are measured. The calculation of opacity is shown in Equation (3.12). [51]

$$Opacity = \frac{R_0}{R_\infty} \cdot 100[\%] \quad (3.12)$$

The Kubelka-Munk theory is based on the assumption that in a homogenous sheet of paper with an amount of random spreaded particles, light is scattered and absorbed. For simplification, rays of light are recieved as one-dimensional. [51]

**Light Scattering and Absorption Coefficient**

The light scattering coefficient  $S$  in  $\text{m}^2/\text{kg}$  and absorption coefficient  $K$  in  $\text{m}^2/\text{kg}$  are strongly dependent on the papermaking conditions. These include the origin of pulp, beating, as well as, the influence of filler. By means of  $R_0$  and  $R_\infty$  it is possible to calculate  $S$  in Equation (3.13), as well as,  $K$  from Equation (3.14). [51]

$$S = \frac{1}{\text{Grammage}} \cdot \frac{1}{\frac{1}{R_\infty} - R_\infty} \cdot \ln \left( \frac{1 - R_0 \cdot R_\infty}{1 - \frac{R_0}{R_\infty}} \right) \quad (3.13)$$

$$K = \frac{(1 - R_\infty)^2}{2 \cdot R_\infty} \cdot S \quad (3.14)$$

## Results

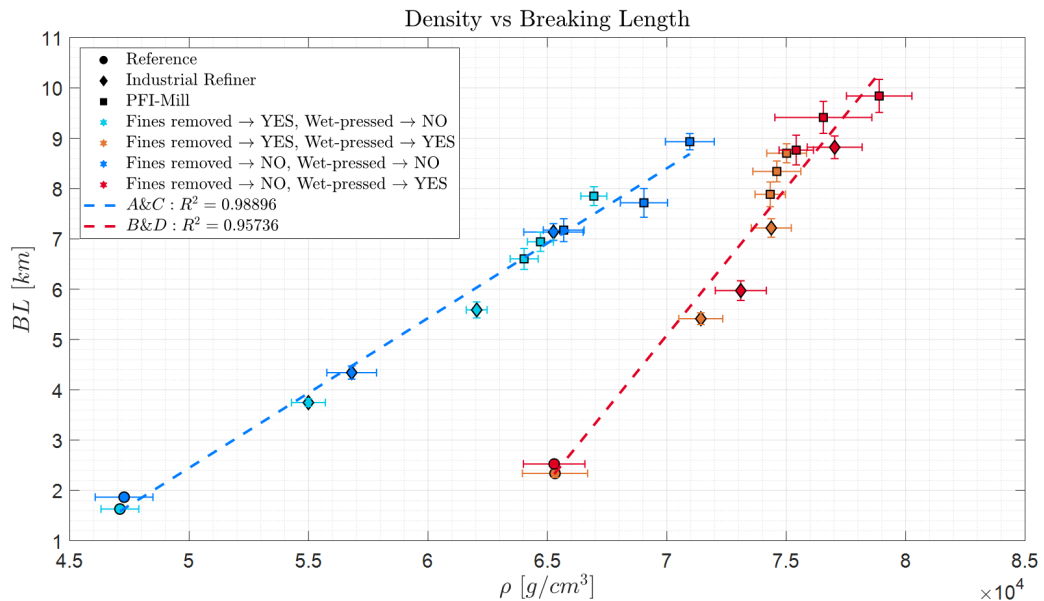
In the following part the results of the experiments will be presented and discussed. The results will be presented in 8 sections. In the first section, the intention of this thesis investigating the influences of fines and modifications of fibers on pulp and paper will be presented. Besides that, the aspect of wet-pressing will be demonstrated. Both refining aggregates will be compared and differences in regard to strengthening properties such as breaking length will be influenced by secondary fines produced during beating process will be shown. Furthermore, results will be compared to findings from literature. Besides mechanical properties, also optical properties will be examined.

### 4.1 Specific Impacts by Refining on Pulp and Paper

Figure 4.1 shows the clear correlation between density and breaking length. This connection is often discussed in literature [8, 48]. In both cases it can be seen that densification by refining or refining with wet-pressing is necessary to achieve higher breaking length. Observing both setups, a distinctive trend was identified, regarding beating (light blue and dark blue colouring) and beating with wet-pressing (orange and red colouring). Both configurations beating, as well as, beating with wet-pressing, showed a steady increase in breaking length.

It was noticeable that the slope of beating with wet-pressing was much steeper than beating only. Therefore, densification by beating resulted in a different outcome than densification by beating with wet-pressing. Therefore, it can be concluded that in wet-pressing other

interactions must occur due to densification. Due to that, these mechanisms have to be considered separately. Although pore volume was decreasing, it seems that not too much fiber-fiber bonding area was created. With reference to the roughness (Figure 4.14) it can be seen, that densification by wet-pressing actually generated density and not smoothness. The roughness will be further discussed in section 4.8.



**Figure 4.1** Correlation of density and breaking length; dark blue: pulp including fines; light blue: pulp without fines; red: wet-pressed pulp including fines; orange: wet-pressed pulp without fines

In summary it can be stated that both beating and beating with wet-pressing generate higher density and breaking length. Nonetheless, densification by wet-pressing leads to different results because of other interactions. Wet-pressing has a positive effect on the strengthening behaviour but the precise way of how wet-pressing exactly affects densification has not become apparent and will require further research.

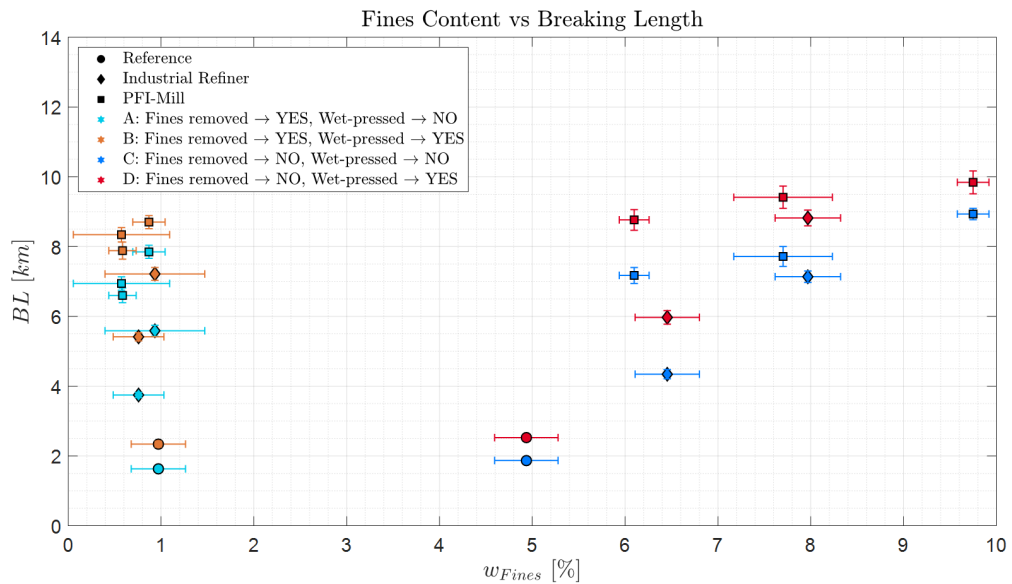
Comparing these results to literature [47] it could be seen that the trend of wet-pressing and beating can be compared to the findings in Figure 2.18. Beating reached higher tensile values faster, while wet-pressing featured a higher tensile strength at higher densities.

Different factors like primary and secondary fines, absence of fines, internal and external fibrillation, as well as, flexibilization have to be considered beside wet-pressing due to densification. All of these aspects influence densification to a certain percentage. In the next section, all aspects will be examined and it will be discussed how they influence pulp and paper properties.

## 4.2 Influence of Fines on Breaking Length

In this section, the influence of various beating intensities respectively resulting fines content on breaking length is shown. Figure 4.2 illustrates the correlation of the fines content  $w_{\text{fines}}$  in % and the breaking length (BL) in km of all experimental settings. Data points without fines (light blue colouring) and without wet-pressing (orange colouring) were created to see the actual effect of fines and wet-pressing. Fines separation was examined using a lab scale pressure screen. It became apparent that fines contribute to the strengthening behaviour which was raised in literature [8, 36]. In addition, wet-pressing noticeably increases breaking length which was stated in literature [37–39].

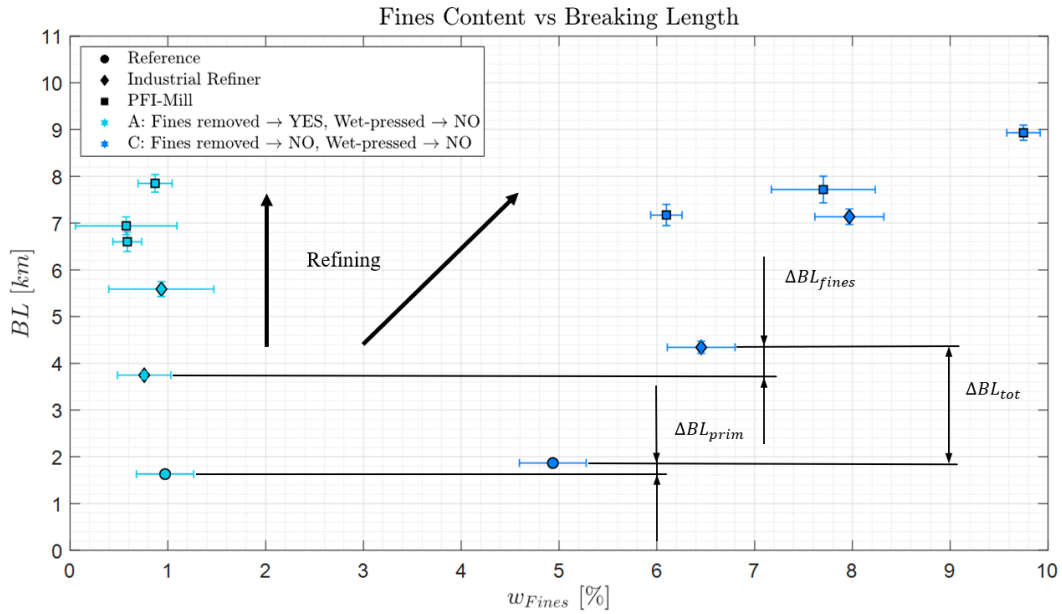
Comparing both diagrams (Figure 4.2 and Figure 4.3), it could be seen that wet-pressing contributed to a higher breaking length. That can be explained because of the fact that wet-pressing leads to a denser fiber network and sheet structure which in turn leads to higher strength.



**Figure 4.2** Correlation of fines content and breaking length of all samples; dark blue: pulp including fines; light blue: pulp without fines; red: wet-pressed pulp including fines; orange: wet-pressed pulp without fines

For simplification Figure 4.3 (samples without wet-pressing) will be applied to explain the following equations, which are used to determine the gain induced by secondary fines. Of course, the calculations are also valid for wet-pressing. Using the reference pulp, the calculation of the breaking length gain caused by primary fines  $\Delta BL_{\text{prim}}$  in km is shown in Equation (4.1). Equation (4.2) refers to the total gain of breaking length  $\Delta BL_{\text{tot}}$  in km of

each refined sample. Using the difference of refined samples including fines and refined samples without fines  $\Delta BL_{fines}$  in km, the gain caused by fines is calculated according to Equation (4.3). Furthermore, the achieved breaking length gain by secondary fines that is generated during refining  $\Delta BL \text{ Gain}_{sec}$  in % was calculated using Equation (4.4).



**Figure 4.3** Correlation of fines content and breaking length of not-pressed samples; dark blue: pulp including fines; light blue: pulp without fines

$$\Delta BL_{prim} = BL_{ref,withfines} - BL_{ref,withoutfines} \quad (4.1)$$

$$\Delta BL_{tot} = BL_{beating,withfines} - BL_{ref,withfines} \quad (4.2)$$

$$\Delta BL_{fines} = BL_{beating,withfines} - BL_{beating,withoutfines} \quad (4.3)$$

$$\Delta BL \text{ Gain}_{sec} = \frac{\Delta BL_{fines} - \Delta BL_{prim}}{\Delta BL_{tot}} \cdot 100 [\%] \quad (4.4)$$

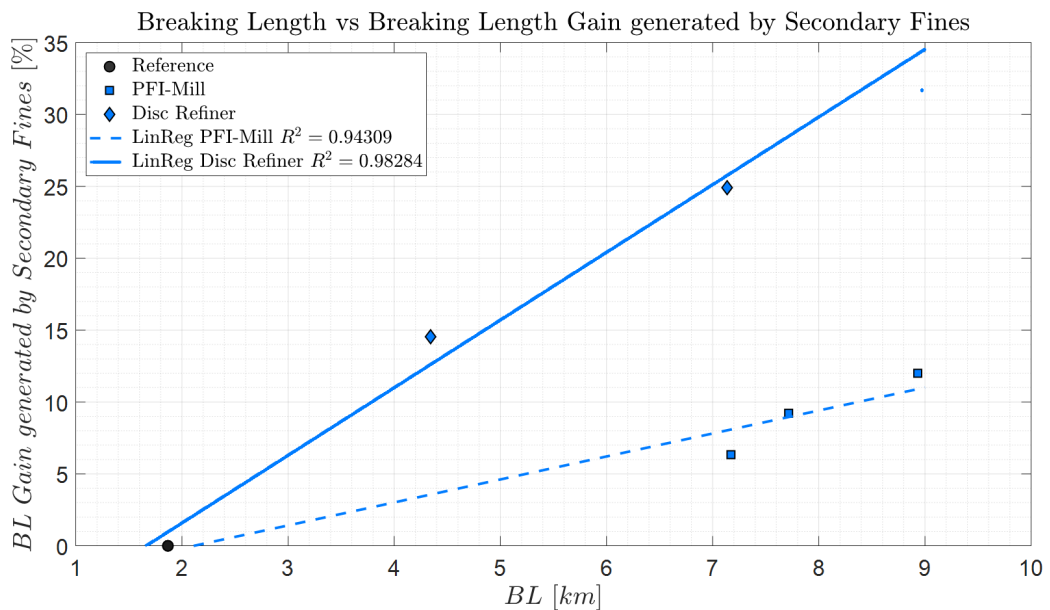
#### 4.2.1 Evaluation of Gain of Fines on Breaking Length

In this section the effects of fines on the breaking length will be discussed. Figure 4.4 and Figure 4.5 show the breaking length gain caused by secondary fines generated during



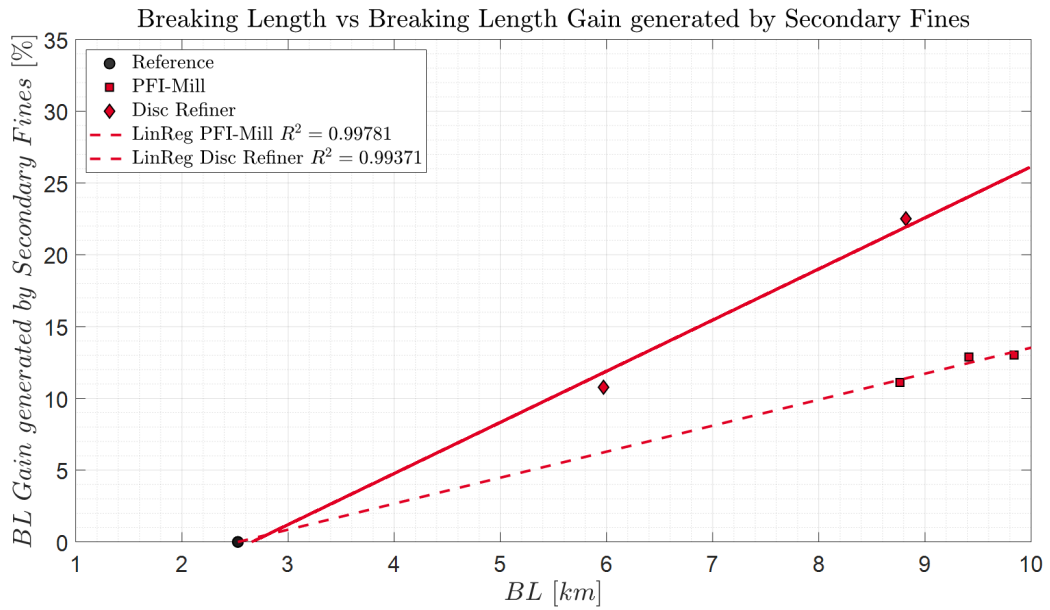
the refining process. While Figure 4.4 represents the not-pressed pulp (blue), Figure 4.5 represents the wet-pressed pulp (red). Additionally, linear regressions are generated to show the process of the PFI-mill and the disc refiner in a more clear way. The PFI-mill is illustrated as a broken line while the disc refiner is illustrated as a solid line.

Figure 4.4 shows that approximately 6 to 25 % of breaking length gain is reached using secondary fines. The rest of the strength increase is generated due to internal and external fibrillation. The increase of the disc refiner is noticeably steeper than of the PFI-mill. Examining 250 kWh/t in the disc refiner, about 25 % of strength increase, is due to fines production. The rest contributes to internal and external fibrillation which leads to flexibilization in turn. In contrast, the amount of flexibilization and fibrillation after 10000 rpm in the PFI-mill is nearly 90 %. These results are in good accordance to results published in literature stating that the PFI-mill is known to feature higher internal fibrillation and flexibilization than disc refiners [28]. Therefore, the present results suggest that fines contribute less to strengthening gain in case of the PFI-mill.



**Figure 4.4** Gain breaking length generated by secondary fines of not-pressed samples

Examining wet-pressing (Figure 4.5), secondary fines contribute 11 to 23 % in breaking length gain. It could be seen that the combination of refining with the PFI-mill and wet-pressing leads to higher breaking length than the maximum breaking length without wet-pressing. It was also observed that the gain from secondary fines created by the disc refiner decreased using wet-pressing. Furthermore, it was noticed that the straight line of the PFI-mill approached the disc refiner straight line using wet-pressing.



**Figure 4.5** Gain breaking length generated by secondary fines of wet-pressed samples

It became apparent in both cases that higher refining intensity leads to higher amount of secondary fines but they get produced in a higher extent in a disc refiner. This correlates with literature [21, 28]. In case of wet-pressing, secondary fines generated in the disc refiner contributed less to strength than in the case of beating only. As mentioned before, the PFI-mill features internal fibrillation especially in comparison to the disc refiner that features more fiber shortening and external fibrillation.

#### 4.2.2 Impact of Fines on Breaking Length and Density

In the following passage, the total fines content, including primary and secondary fines, will be considered to analyze the impact on breaking length  $BL_{Impact_{fines}}$  in  $km/\%$ . Therefore, the relation of fines content with fines  $w_{with\ fines}$  in % and without fines  $w_{without\ fines}$  in %, as well as, the relation of breaking length with fines  $BL_{with\ fines}$  in km and without fines  $BL_{without\ fines}$  in km. Figure 4.3 will be used to calculate the slope between corresponding datapoints of same refining intensity with and without fines (Equation 4.5).

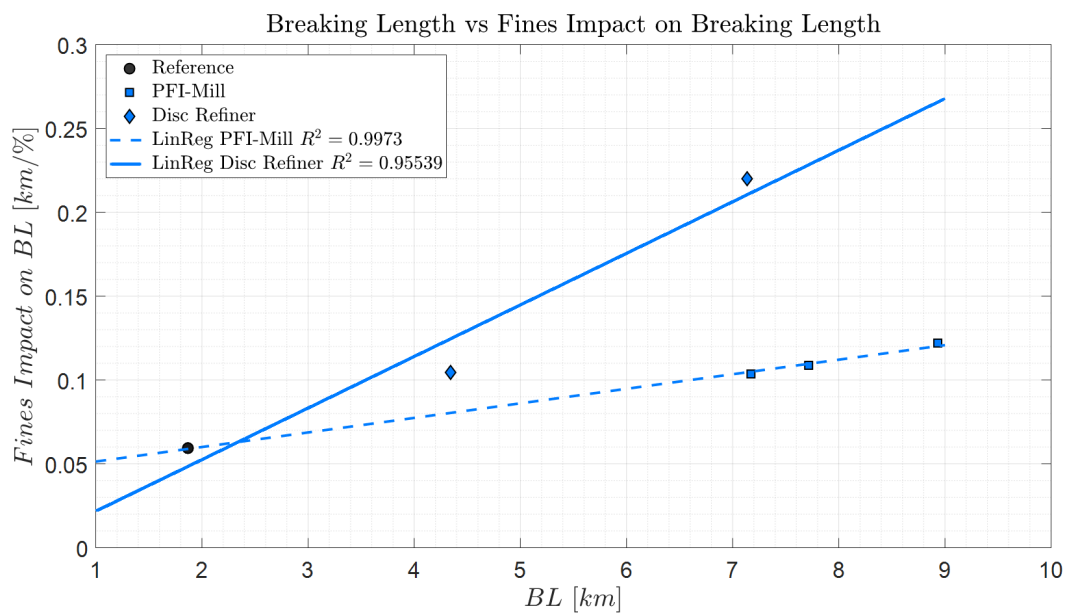
$$BL_{Impact_{fines}} = \frac{BL_{with\ fines} - BL_{without\ fines}}{w_{with\ fines} - w_{without\ fines}} [km/\%] \quad (4.5)$$

The impact on breaking length leads to a rise of breaking length per weight percentage fines in pulp. Figure 4.6 and Figure 4.7 show the fines' impact on breaking length. It can

be seen that the fines' impact influences the tensile properties for an increased breaking length. This observation applies to both refining aggregates.

In both cases, the increase of breaking length might be explained by the improvement of sheet density and the structure of pores. Samples with a lower tensile strength feature a more bulky structure including larger pores. Therefore, fines may not be able to close these pores. In other cases, concerning denser sheets, fines are capable to close smaller voids. The influence on RBA may be greater in case of already denser sheets which also influence tensile strength to a greater extent.

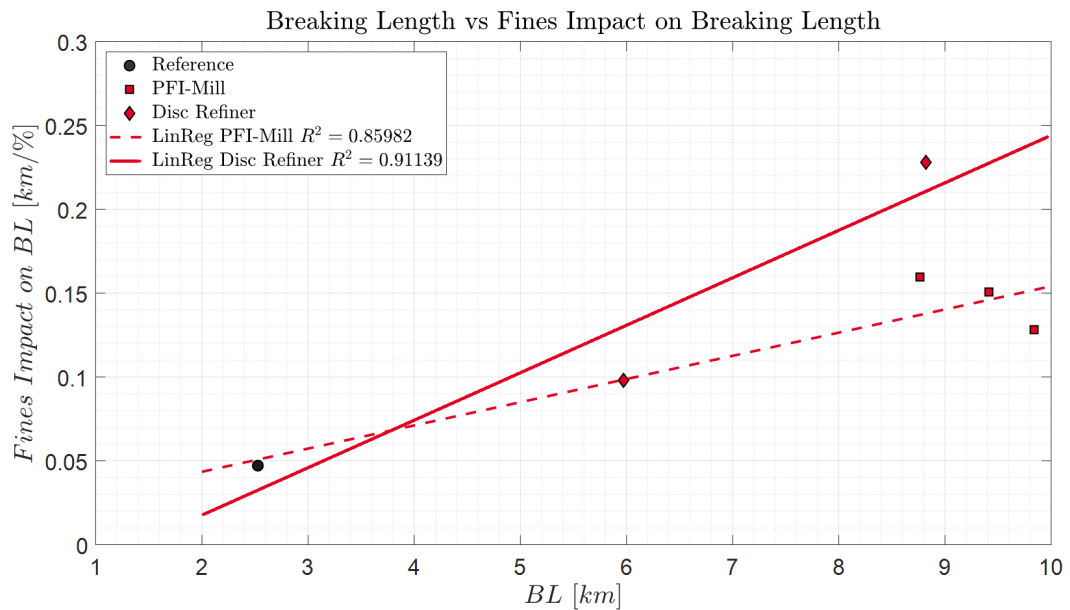
Observing not-pressed samples in Figure 4.6, the increase of disc refiner is distinctly higher than of the PFI-mill. Regarding 250 kWh/t in the disc refiner, up to 220 m of additional breaking length are created by an additional weight percent of fines. Looking at the PFI-mill, just 120 m of breaking length per weight percent of fines were reached using 10000 rpm intensity, because high density had already been generated through flexibilization.



**Figure 4.6** Impact of fines on breaking length of not-pressed samples

Considering wet-pressing in Figure 4.7, the increase of the disc refiner regression was relatively similar to the disc refiner regression without wet-pressing. In the opposite, the increase of the PFI-mill regression including wet-pressing was much steeper and approached the disc refiner straight line again. Therefore, wet-pressing must interact with other mechanisms. It can be seen in the case of the PFI-mill that the impact of fines decreases with higher beating intensity. While the disc refiner reaches approximately 230 m of breaking

length per weight percent, the PFI-mill just reaches up to 160 m of breaking length per weight percent with sinking tendency.



**Figure 4.7** Impact of fines on breaking length of wet-pressed samples

It can be concluded that the quality of generated fines of the disc refiner and the PFI-mill is different. Both plots show that the same amount of fines leads to various impact on each kilometer breaking length. The impact of secondary fines generated in a disc refiner on breaking length is much stronger than the impact of secondary fines produced in a PFI-mill. Therefore, secondary fines from a disc refiner contributes more to breaking length while fibrillation and flexibilization occur more often while beating with a PFI-mill.

Additionally, the fines impact on breaking length is plotted over density for both configurations which is illustrated in Figure 4.8 and Figure 4.9. Comparing both plots, it can be seen that the effect of fines is decreased by wet-pressing in case of industrial refining. Using a PFI-mill, the effect of fines by wet-pressing is higher. The PFI-mill straight line also increases after wet-pressing and reaches the disc refiner straight line.

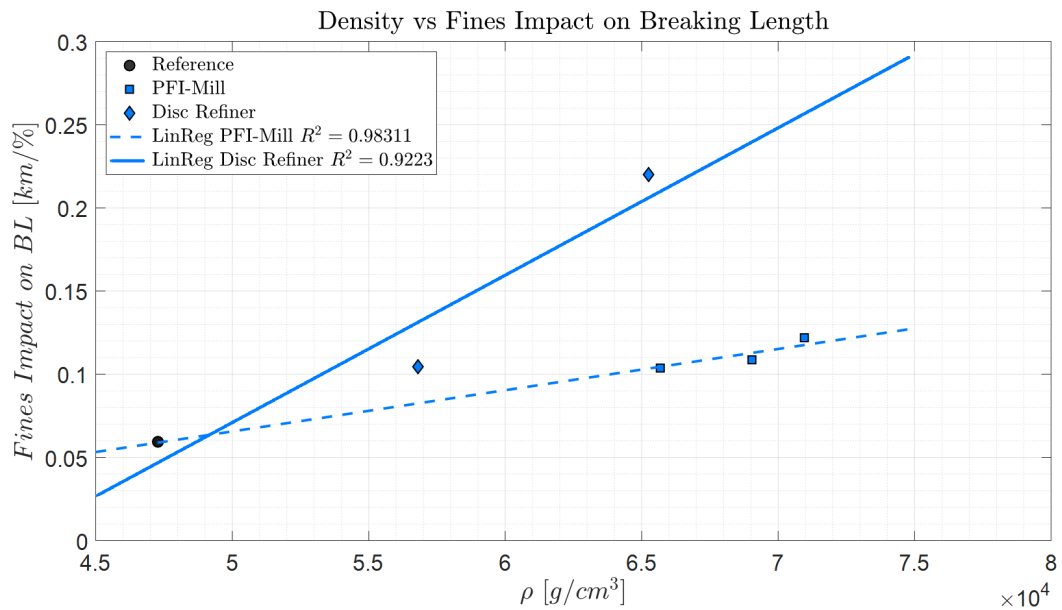


Figure 4.8 Impact of fines on density of not-pressed samples

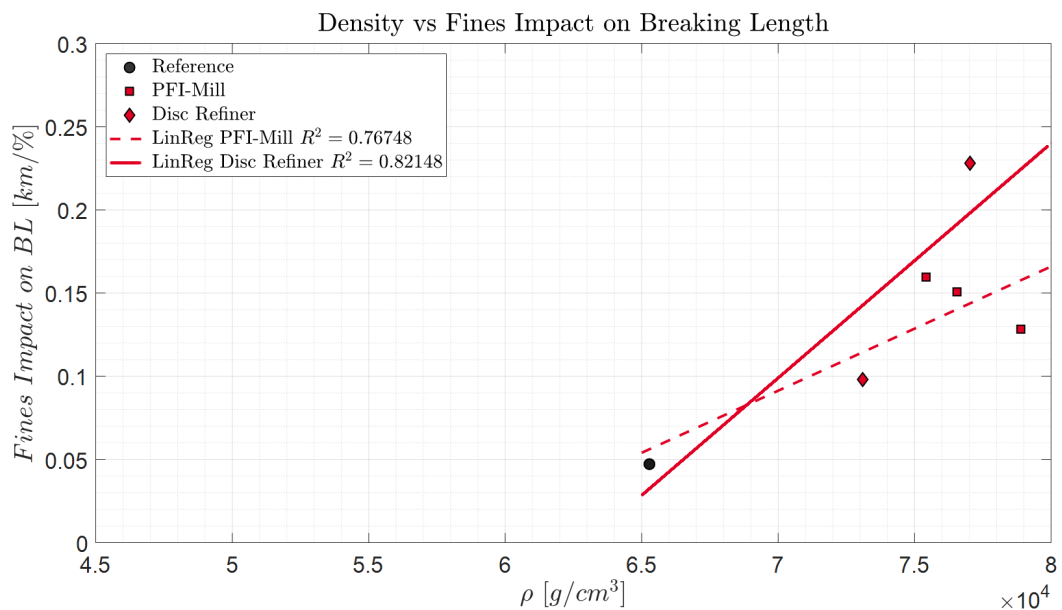


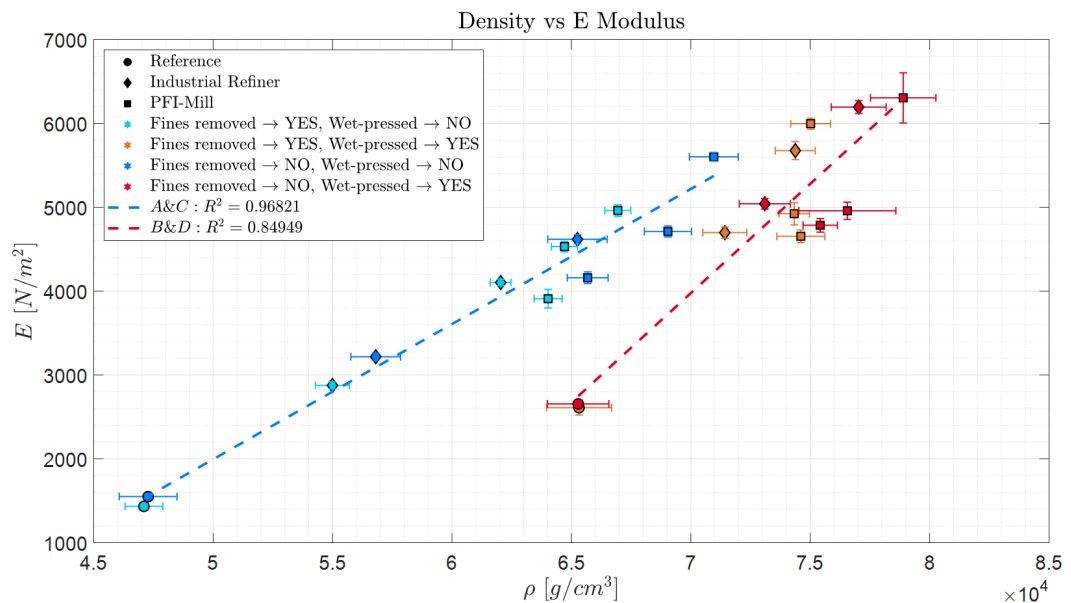
Figure 4.9 Impact of fines on density of wet-pressed samples

### 4.3 Further Mechanical Properties

Literature [51] shows that the correlation of elastic modulus and density reflects changes in RBA. At a fixed grammage, elastic modulus and density depend on wet-pressing and beating. The correlation of density and elastic modulus is shown in Figure 4.10. It can be seen that the slopes of both, beating and beating with wetpressing, are higher than in literature.

Regarding beating, the trend is relatively linear and the correlation between density and E-modulus is appropriate. However, a closer look reveals that the correlation in case of wet-pressed samples is lower than compared to without wet-pressing. Looking at both straight lines, the disc refiner datapoints are rather located above the straight lines, whereas the PFI-mill datapoints are rather located below the straight lines. Consequently, the PFI-mill tends to lower elastic modulus at certain density levels in comparison to the disc refiner. A reason for that might be that fiber properties directly influence this behaviour. Due to different beating aggregates, the fibers are differently strained.

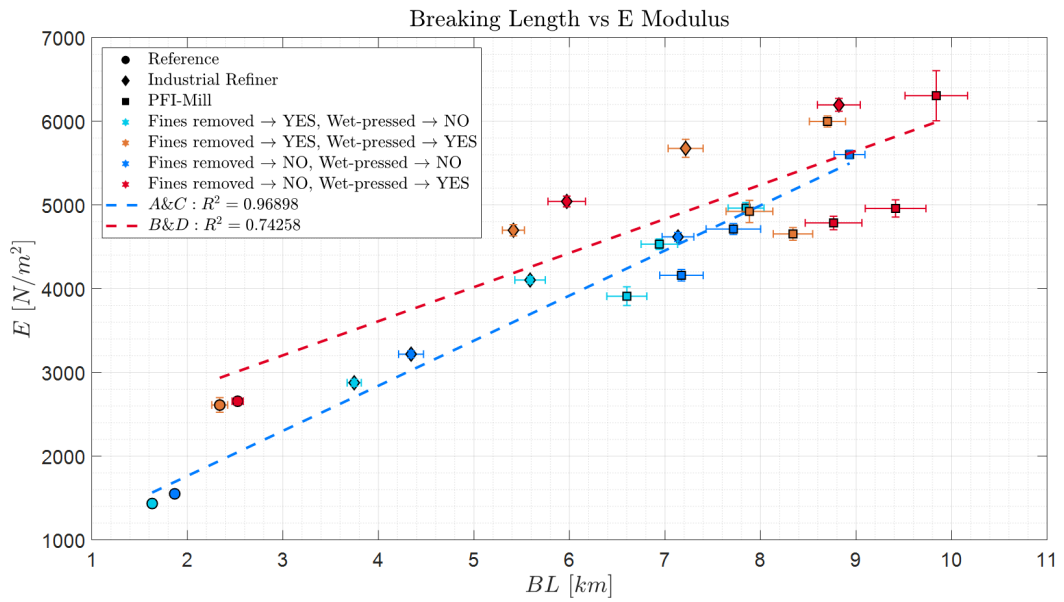
Considering the combination of beating and wet-pressing, as expected, at higher densities, the elastic modulus is higher due to densification after wet-pressing. It was observed that the increase at higher densities is steeper. Comparing the present result with findings from literature [44–46] it can be seen that there is no linear correlation given in wet-pressing. Both configurations create two straight lines which can intersect if the pulp endures higher beating.



**Figure 4.10** Correlation of density and E-modulus of all samples

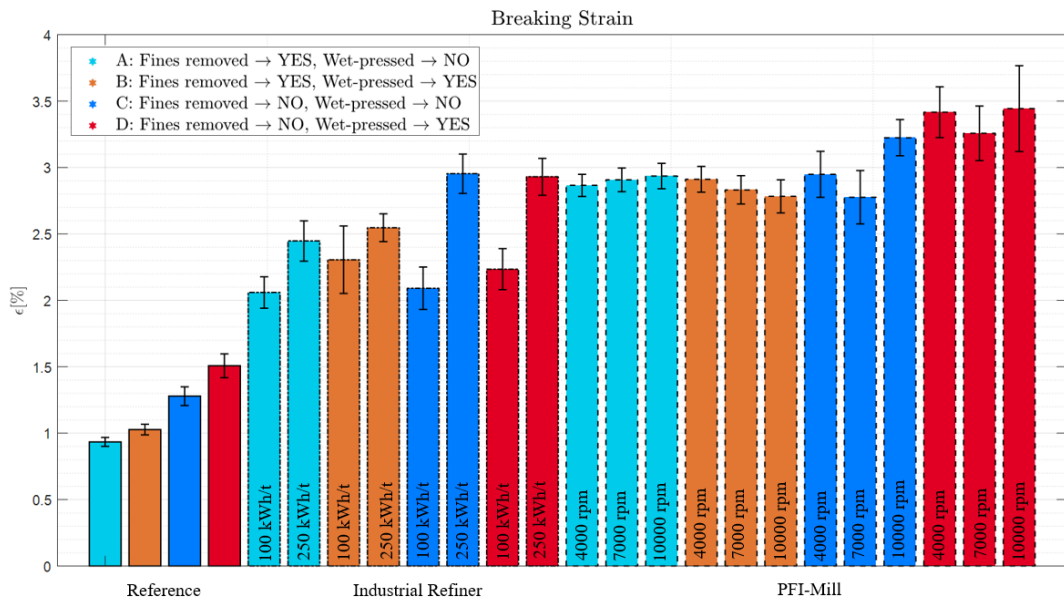
In Figure 4.11 breaking length and elastic modulus are displayed. The well established correlation between E-modulus, representing the networks ability for stress transfer, and tensile strength is applicable to the PFI-refined pulps. In the case of the industrially refined pulps, equal E-modulus may lead to strong differences in the tensile strength, indicating that other mechanisms than stress transfer might become more relevant for network failure.

Figure 4.12 shows the breaking strain of all configurations. It is clearly evident that break-



**Figure 4.11** Correlation of E-modulus and breaking length of all samples

ing strain increases with higher beating intensities. The PFI-mill achieves higher elongation values than disc refiner. As a result, samples beaten with a PFI-mill tend to elongate more than in disc refiner. These findings correspond to results from elastic modulus. The higher the breaking strain the lower the elastic modulus.



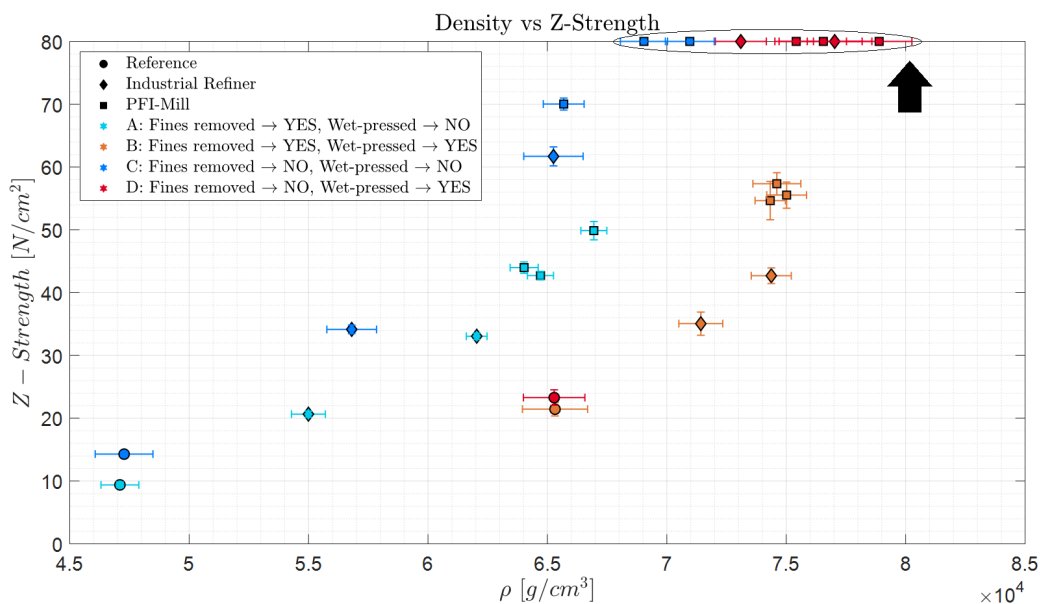
**Figure 4.12** Breaking strain values of all samples

In Figure 4.13 the z-strength is plotted over density. Comparing both configurations, wet-pressing reaches significantly higher density values. At the same density level ( $6.5 \cdot 10^4 \text{ g/cm}^3$ ) various z-strengths are present. As a result, wet-pressing contributes to z-strength.

Configuration "B" beaten with the PFI-mill shows that at a certain density level higher beating cannot reach higher results in z-strength anymore. Comparing the disc refiner and the PFI-mill samples, the PFI-mill generates more z-strength. A reason might be that during beating with a PFI-mill more fibrillation and fiber flexibilization develop.

The plot shows that not all samples could be measured using the existent tools. A reason might be that samples are too compressed to analyze due to higher beating intensities and increasing fines content. In these cases, it was not possible to detach the double-sided tape from the samples. Therefore, the z-strength of not measurable samples was presumed to be  $80 \text{ N/cm}^2$ . That was done to see the trend of density. The real z-strength is unknown but might be much higher. These samples are circled and marked with an arrow.

From these findings, we can conclude that an increase in paper density does not necessarily increase the z-strength, particularly, if it is obtained by wet pressing. The type of refining process plays an important role here. Interestingly, industrial refining, which leads to a stronger external fibrillation, is showing lower z-strength at equivalent density. This was unexpected as external fibrillation is known to be beneficial for fiber-fiber bonding.



**Figure 4.13** Correlation of density and z-strength of all samples

Figure 4.14 shows the correlation of roughness and density of all configurations. It is apparent, that wet-pressing does not increase smoothness, on the contrary it decreases. Density increases using wet-pressing. As already mentioned, actual densification is generated, not smoothness.



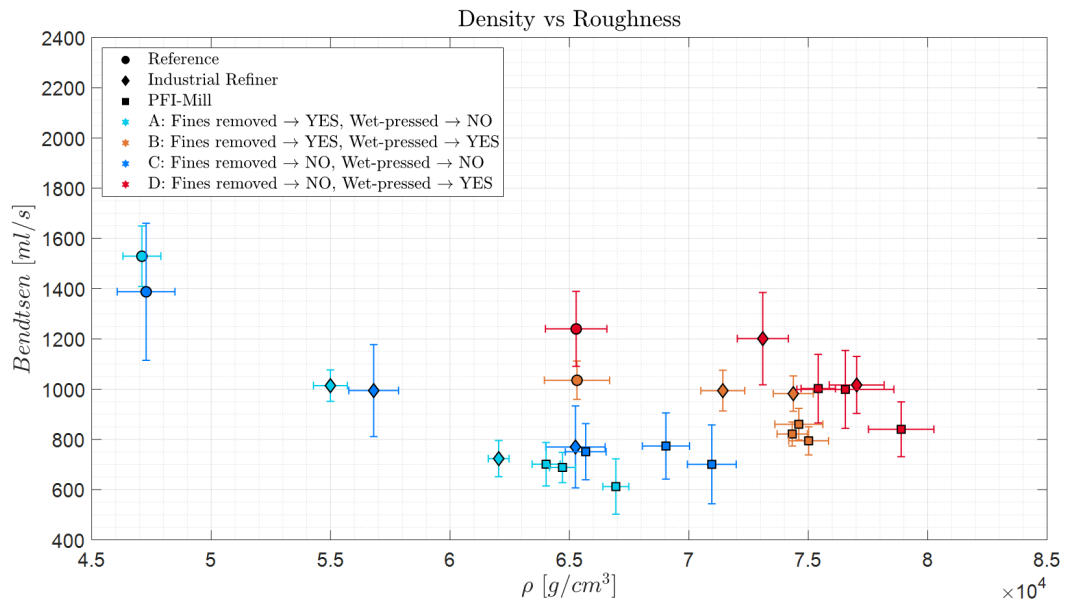


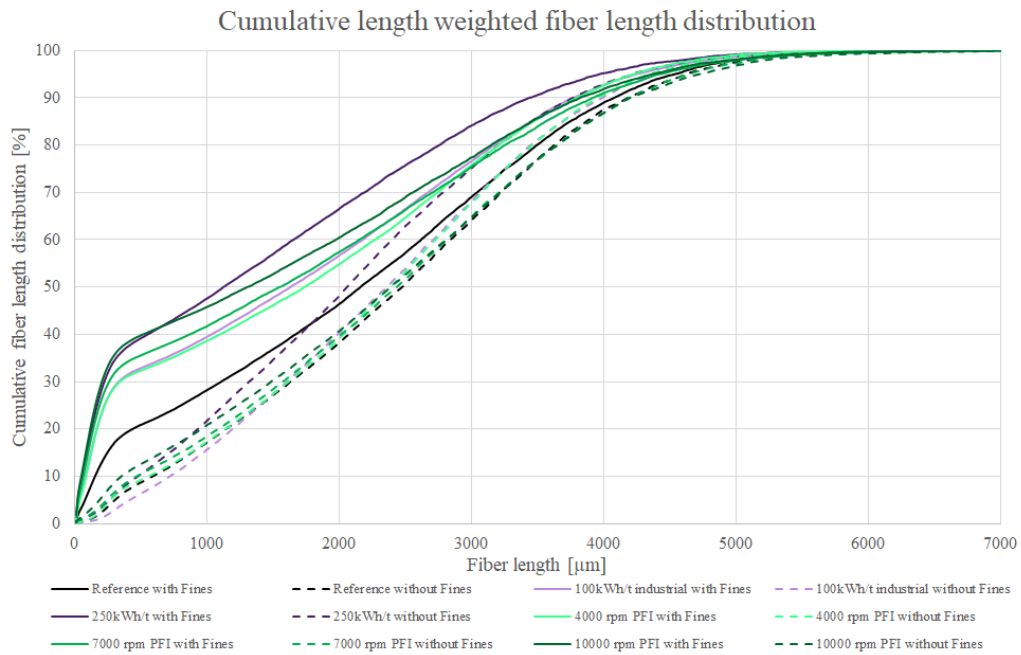
Figure 4.14 Roughness plotted over density of all samples

#### 4.4 Fiber Length Distribution

In Figure 4.15 the fiber length distribution of reference and beaten pulp with and without fines is shown. For simplification, reference pulp is characterized in black, pulp beaten with the industrial refiner in purple and pulp beaten with the PFI-mill is portrayed in green. The intenser the color, the higher the beating intensity is displayed. Pulp including fines is shown as a solid line, pulp without fines is represented as a broken line.

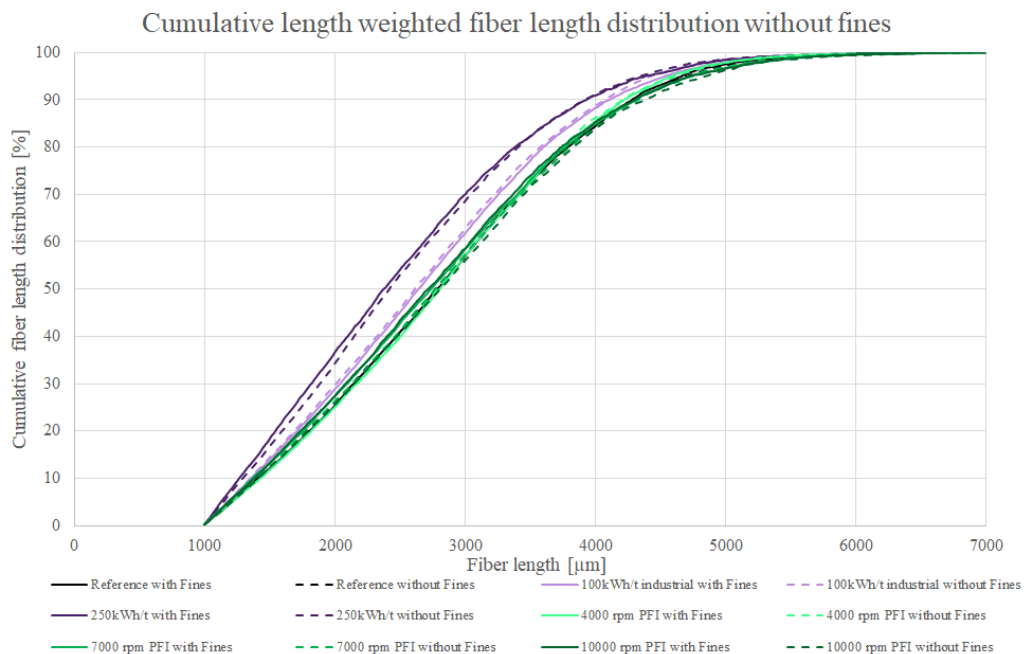
The distribution was measured with the L&W Fiber Tester<sup>+</sup>. This plot was used to understand processes better during beating at different intensities. It can be seen that especially in disc refiner at 250 kWh/t most fiber shortening occurs when many little fibers and secondary fines are produced. The figure displays that approximately at 800  $\mu\text{m}$  fiber shortening happens. Observing 10000 rpm of the PFI-mill, fiber shortening does not occur in that intensity compared to the disc refiner. It is also observed that a disc refiner at 100 kWh/t generates more fines than beating at 4000 and 7000 rpm with the PFI-mill. Therefore, the thesis that in a disc refiner more fines are generated and more fiber shortening occurs than in a PFI-mill can be confirmed [28].

Additionally, the fiber length distribution is observed from another perspective which is illustrated in Figure 4.16. In this case, fines and fiber fragments up to 1000  $\mu\text{m}$  are neglected to see the actual fiber shortening. The most fiber shortening can clearly be seen at 250



**Figure 4.15** Fiber Length Distribution measured with L&W Fiber Tester<sup>+</sup>

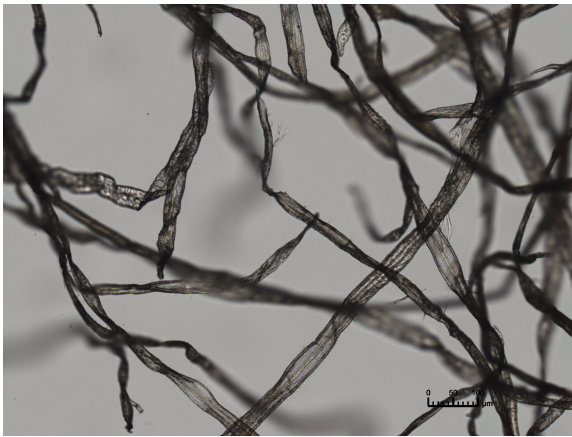
kWh/t of the disc refiner. In other words, all PFI-curves overlay nearly exactly at the same point. Therefore, the thesis that in a disc refiner fiber shortening happens and in a PFI-mill rather occurs flexibilization is proven again.



**Figure 4.16** Fiber Length Distribution without fines measured with L&W Fiber Tester<sup>+</sup>

## 4.5 Microscopy

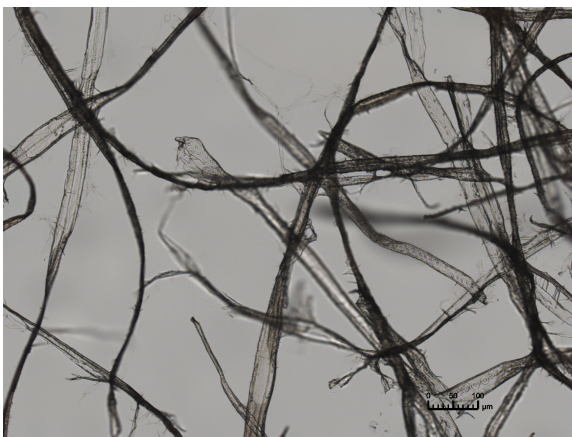
In the following microscopical images, pulp with and without fines are displayed. Reference pulp is compared to 10000 rpm beaten pulp by the PFI-mill. Comparing the reference pulp with and without fines, fiber fragments or fines can clearly be seen in Figure 4.18. After using the pressure screen, no fines can be found in Figure 4.17. Looking at Figure 4.19 and Figure 4.20, fibrillation by beating is evident. Furthermore, fines and fiber fragments after beating can clearly be made out. This amount is significantly higher due to high refining intensity. It is also evident that fibers are obviously kinked and the fiber wall is broken up.



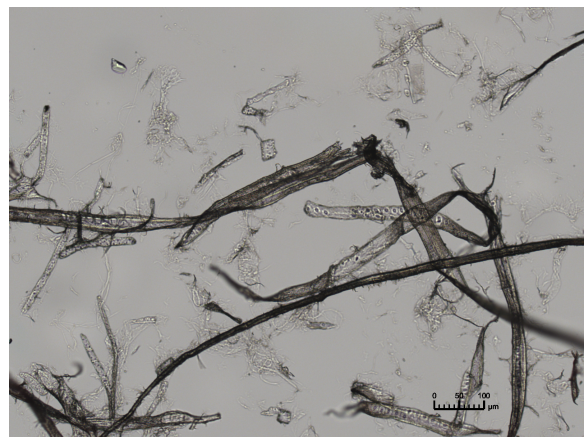
**Figure 4.17** Microscopy image of reference pulp without fines



**Figure 4.18** Microscopy image of reference pulp with fines



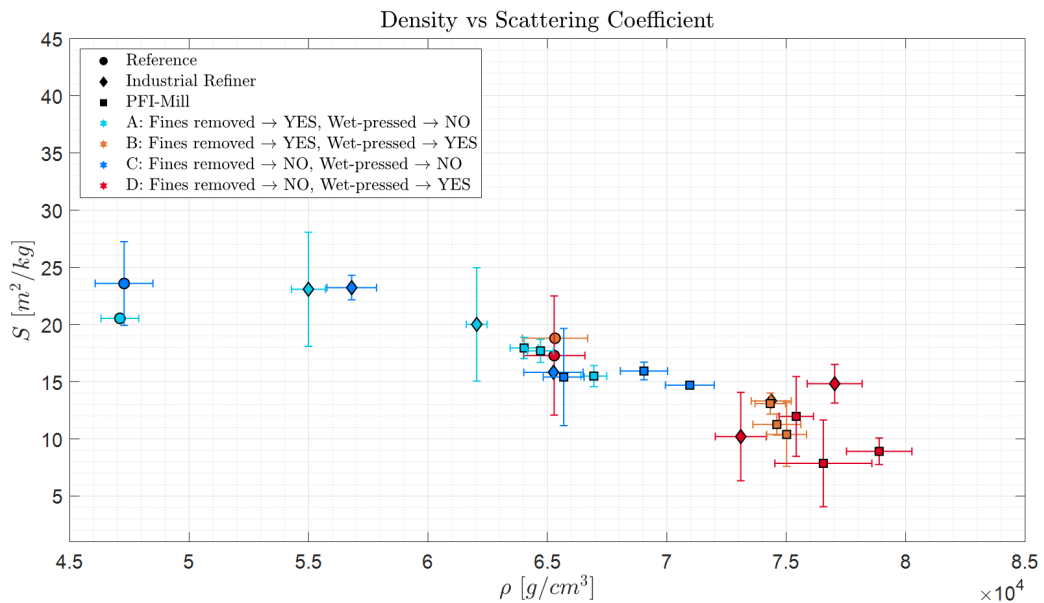
**Figure 4.19** Microscopy image of 10 000 rpm pulp using PFI-mill without fines



**Figure 4.20** Microscopy image of 10 000 rpm pulp using PFI-mill with fines

## 4.6 Light Scattering

In Figure 4.21 the light scattering coefficient  $S$  over density is plotted. The big confidence intervals might be explained because it was calculated using three parameters (Equation 3.13) with a certain variance each. Therefore, error propagation leads in very pessimistic calculated variance for the parameter  $S$ . As stated in literature [51], the light scattering coefficient decreases because of the reduction of free surface due to beating and wet-pressing. In case of wet-pressing, light scattering is even further decreased. It was also observed that beating with the PFI-mill generates less light scattering than with the disc refiner. It was found that in case of wet-pressing, the correlation between density and the light scattering coefficient stays linear. Therefore, it seems that wet-pressing leads to densification due to air removal from the fiber network. Densification as a result of wet-pressing generates additional RBA, but not in the same extent as fiber flexibilization and fines.

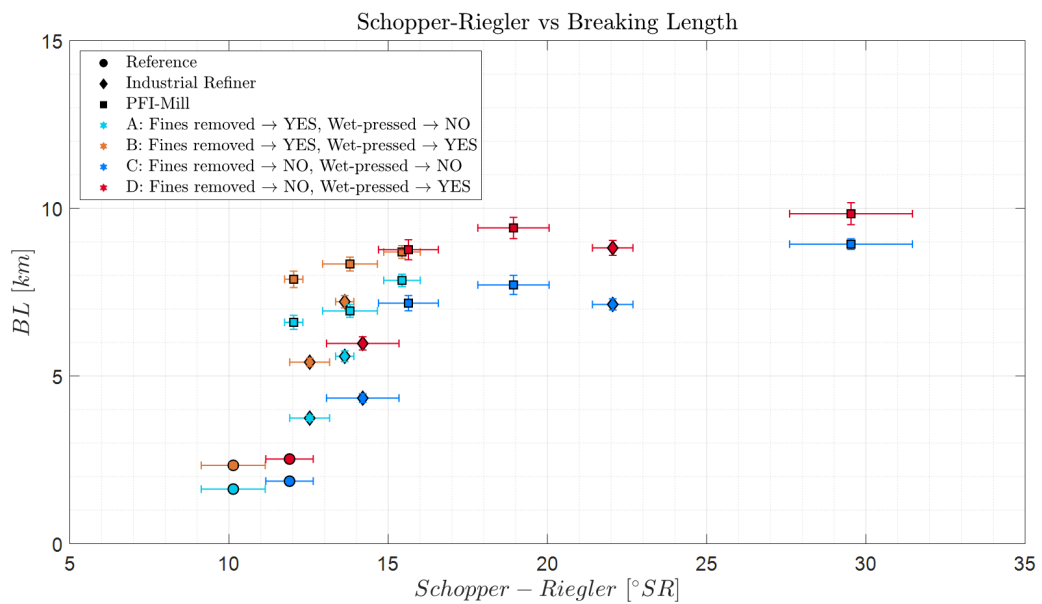


**Figure 4.21** Correlation of light scattering coefficient and density of all samples

## 4.7 Dewatering Resistance

In Figure 4.22, Schopper-Riegler over breaking length of all settings are plotted. It can be seen that the development of the disc refiner proceeded lower than of the PFI-mill. Also, the disc refiner reached higher Schopper-Riegler values at lower breaking length. A reason might be because in disc refiners more secondary fines are produced. It is obvious

that fines contribute to strengthening behaviour. Due to fines content, also dewatering resistance increases because of a "fines mat", which is formed by the produced fines. Comparing not-pressed and wetpressed samples, it becomes apparent that the curve is shifted upwards. Schopper-Riegler values are nearly the same, but the breaking length is slightly increased. It can be concluded that disc refiners reach a different strength potentials than PFI-mills which represent the optimum of ideal strength. Nonetheless, Schopper-Riegler is inappropriate to predict the strength increase due to refining.



**Figure 4.22** Correlation of Schopper-Riegler and breaking length of all samples

The correlation of Schopper-Riegler and fines content is shown in Figure 4.23. In this plot, the theory of increasing fines content is leading to higher dewatering resistance is confirmed. It can be seen that Schopper-Riegler rises higher because of higher fibrillation and flexibilization by PFI-mill. Despite higher fiber length, the PFI-mill features higher Schopper-Riegler values.

In Figure 4.24 the correlation of the water retention value and Schopper-Riegler is examined. The reference pulp and the 10000 rpm pulp refined by the PFI-mill, both with and without fines are compared. It is apparent that the WRV increases with higher Schopper-Riegler, due to higher fines content by beating. Pores in beaten fibers become more clogged due to the increased amount of fines. As a result, pores can absorb more fines and fiber fragments. Therefore, the dewatering resistance increases.



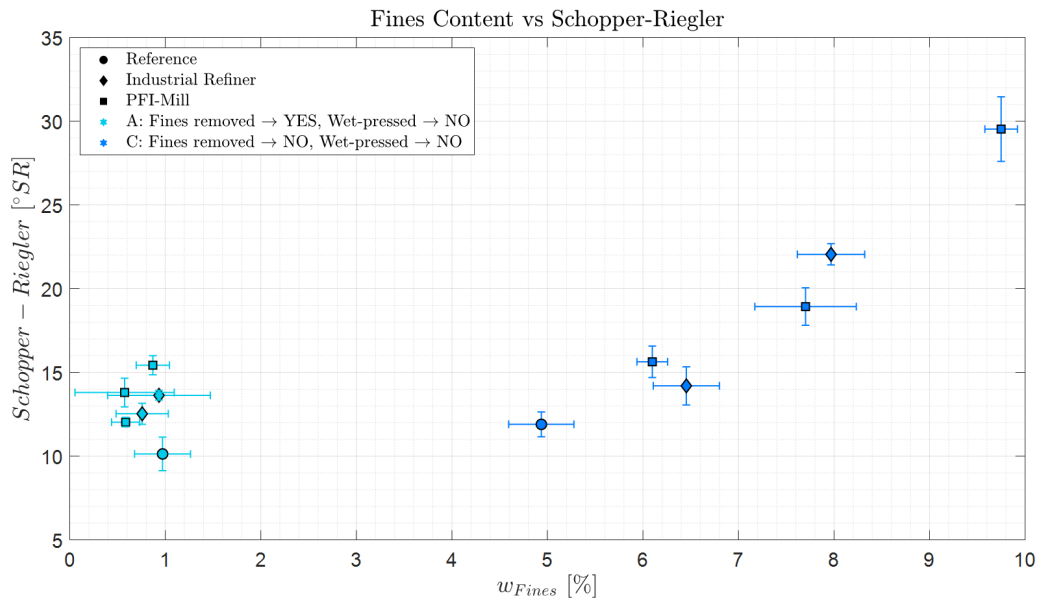


Figure 4.23 Correlation of fines content and Schopper-Riegler

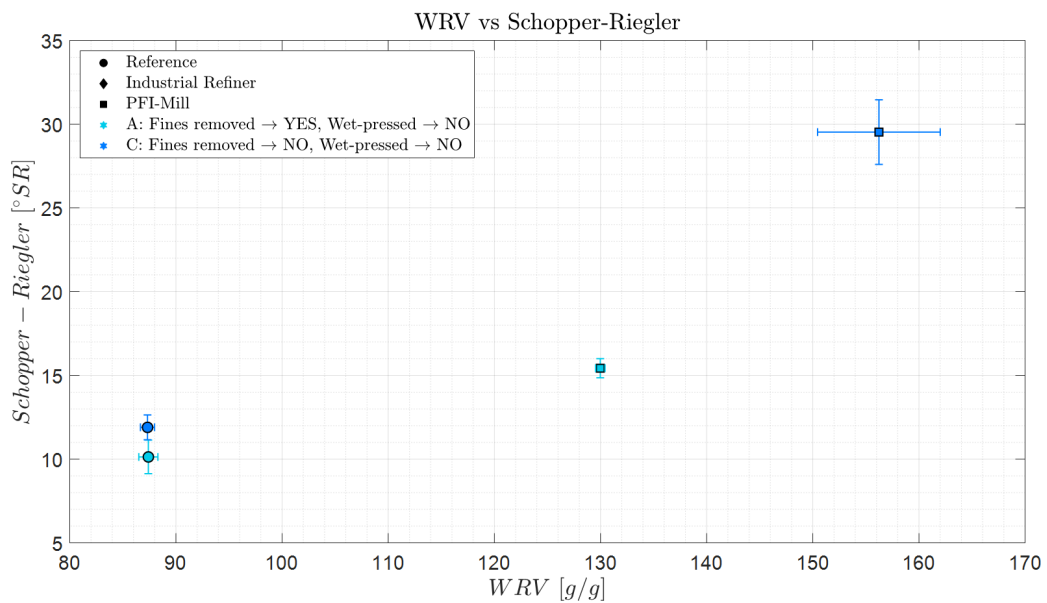
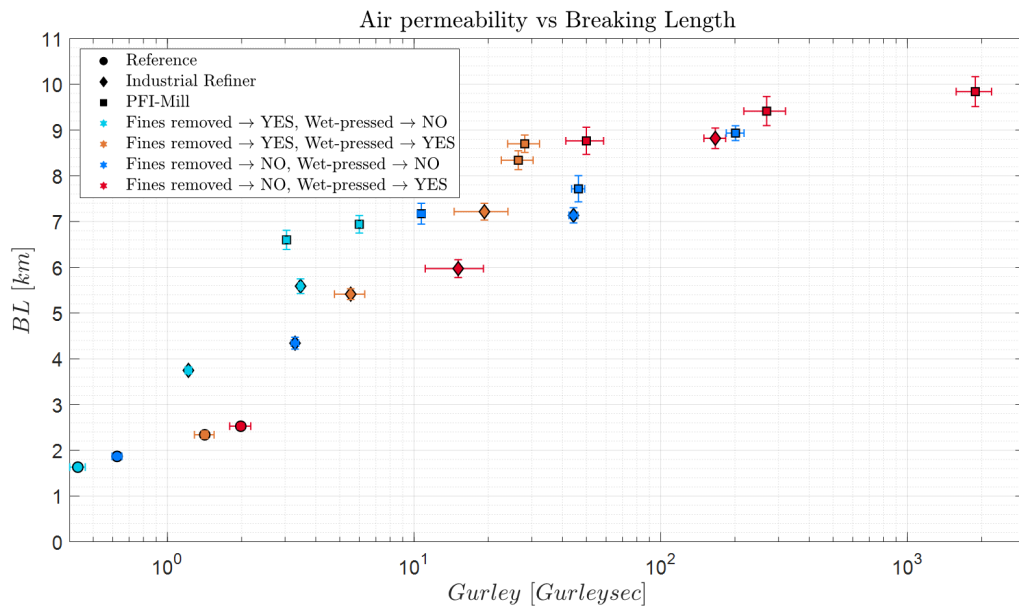


Figure 4.24 Correlation of WRV and Schopper-Riegler of reference pulp and 10000 rpm PFI pulp

## 4.8 Porosity

In Figure 4.25 the correlation of air permeability and breaking length is illustrated. It was noticed that the PFI-mill reaches higher breaking length, than disc refiner, at equivalent air resistance (Gurley). By removing fines, the air permeability rises drastically, while tensile properties are not harmed in a high extent. Therefore, the breaking length increases massively at a certain level of air permeability, just by removing fines. However, it needs

to be taken into account that the maximum tensile strength is limited in absence of fines material. This can be traced in wet-pressed and not wet-pressed samples. In case of high refining intensities, it is shown that wet-pressing impairs the air permeability at a very high extent.



**Figure 4.25** Correlation of air permeability and breaking length of all samples

## Conclusion

In this master thesis, the effects of refining on pulp and paper properties were investigated. The focus lay on the effect of secondary fines, which were generated in a PFI-mill and an industrial disc refiner in pilot scale. In order to research the exact impact of fines, fines were separated using a lab pressure screen. Additionally, wet-pressing was applied to evaluate the effects on densification.

For this purpose handsheets were prepared and analyzed. The results showed significant differences in the strengthening behaviour between different configurations.

First, the correlation of breaking length and density as discussed in literature, showed differences in wet-pressed paper compared to samples which were not wet-pressed. For each of these two configurations, the correlation was strongly linear. However, it was shown through the differences in slope and absolute values, that the wet-pressing induced densification does not cause the same increase of tensile strength, compared to internal and external fibrillation of fibers and fines material. The assumption was that densification by wet-pressing was not creating more relative bonded area, compared to other processes that cause a higher density. This theory was confirmed due to the light scattering measurements, as wet-pressing showed that the phase boundaries were barely reduced. Besides the differences resulting from wet-pressing, the correlation of breaking length and density was not affected by the refining aggregate.

The main aim of this thesis was to quantify the gain on breaking length by either secondary fines and internal and external fibrillation due to refining. It could be shown that the impact of secondary fines on strength gain is up to 25 % depending on the used aggregate and



beating intensity. While the PFI-mill generates more internal fibrillation and flexibilization, the disc refiner tended to produce more secondary fines. Therefore, the effect of fines was approximately four times higher in the case of a disc refiner, compared to the PFI-mill. In addition, the fiber length distribution confirmed that in a disc refiner fiber shortening and fines production occurred while in the PFI-mill flexibilization was rather prevalent.

The quality of generated fines are also different, depending on the refining aggregate. Secondary fines produced in a PFI-mill generated less breaking length at a certain fines content compared to the disc refiner. It could also be observed that in a PFI-mill the fiber network was already too dense that the impact of fines decreased.

The dewatering resistance, in terms of Schopper-Riegler measurements, increased with increasing fines content. However, this measurement made no statement about the strengthening behaviour or the degree of beating.

# List of Figures

2.1	Fiber structure of softwood . . . . .	4
2.2	Chemical composition of cell wall . . . . .	5
2.3	Microscopy pictures of different fines . . . . .	8
2.4	Cell wall structure . . . . .	9
2.5	Illustration of internal fibrillation (left) and external fibrillation (right) after refining . . . . .	10
2.6	Change of pulp properties . . . . .	11
2.7	Change of paper properties . . . . .	12
2.8	Operating mode of refiner . . . . .	13
2.9	Operating mode of PFI-Mill . . . . .	14
2.10	Different phases of bar-to-bar contact of SSL theory . . . . .	18
2.11	Illustration of impact length . . . . .	19
2.12	WRV of the different fractions . . . . .	22
2.13	Correlation of tensile index and fines content . . . . .	22
2.14	Correlation of tensile index and density including fines . . . . .	23
2.15	Correlation of elastic modulus and density using varied beating levels . . . . .	24
2.16	Correlation of elastic modulus and density using varied wet-pressing levels . . . . .	24
2.17	Correlation of E-modulus and density in case of beating and wet-pressing . . . . .	25
2.18	Comparison of refining and wet-pressing illustrated with correlation of tensile index and density . . . . .	26
2.19	Correlation of tensile index and density using wet-pressing . . . . .	26
2.20	Microscopy images of unbeaten and beaten pulp . . . . .	27
2.21	Correlation of E-modulus and stiffness . . . . .	27
2.22	Wet-pressing with small effect on strengthening . . . . .	28
2.23	Wet-pressing with significant effect on strengthening . . . . .	28
2.24	Beating effect on strengthening . . . . .	28
2.25	Beating effect on strengthening . . . . .	28

3.1	Scheme of the disc refiner . . . . .	31
3.2	Scheme of pressure screen . . . . .	32
3.3	L&W Fiber Tester <sup>+</sup> . . . . .	33
3.4	Illustration of Rapid-Köthen Handsheet former . . . . .	35
4.1	Correlation of density and breaking length of all samples . . . . .	41
4.2	Correlation of fines content and breaking length of all samples . . . . .	42
4.3	Correlation of fines content and breaking length of not-pressed samples . . . . .	43
4.4	Gain breaking length generated by secondary fines of not-pressed samples . . . . .	44
4.5	Gain breaking length generated by secondary fines of wet-pressed samples . . . . .	45
4.6	Impact of fines on breaking length of not-pressed samples . . . . .	46
4.7	Impact of fines on breaking length of wet-pressed samples . . . . .	47
4.8	Impact of fines on density of not-pressed samples . . . . .	48
4.9	Impact of fines on density of wet-pressed samples . . . . .	48
4.10	Correlation of density and E-Modulus of all samples . . . . .	49
4.11	Correlation of E-modulus and breaking length of all samples . . . . .	50
4.12	Breaking strain values of all samples . . . . .	50
4.13	Correlation of density and z-strength of all samples . . . . .	51
4.14	Roughness plotted over density of all samples . . . . .	52
4.15	Fiber Length Distribution measured with L&W Fiber Tester <sup>+</sup> . . . . .	53
4.16	Fiber Length Distribution without fines measured with L&W Fiber Tester <sup>+</sup> . . . . .	53
4.17	Microscopy image of reference pulp without fines . . . . .	54
4.18	Microscopy image of reference pulp with fines . . . . .	54
4.19	Microscopy image of 10000 rpm pulp using PFI without fines . . . . .	54
4.20	Microscopy image of 10000 rpm pulp using PFI with fines . . . . .	54
4.21	Correlation of light scattering coefficient and density of all samples . . . . .	55
4.22	Correlation of Schopper-Riegler and breaking length of all samples . . . . .	56
4.23	Correlation of fines content and Schopper-Riegler . . . . .	57
4.24	Correlation of WRV and Schopper-Riegler of reference pulp and 10000 rpm PFI pulp . . . . .	57
4.25	Correlation of air permeability and breaking length of all samples . . . . .	58

# List of Tables

3.1	Experimental design . . . . .	30
3.2	Determination of sampling . . . . .	31
3.3	Refiner parameters . . . . .	31
3.4	Wet-pressing parameters . . . . .	36

# List of Abbreviations

**BDDJ** Britt Dynamic Drainage Jar

**BL** breaking length

**HC** high consistency

**IL** impact length

**LC** low consistency

**od** ovoidry

**RBA** relative bounded area

**SEC** specific energy consumption

**SEL** specific edge load

**SSL** specific surface load

**UBSK** unbleached softwood kraft pulp

**WRV** water retention value

# Bibliography

- [1] Jürgen Blechschmidt. *Taschenbuch der Papiertechnik*. Carl Hanser Verlag GmbH & Co. KG, 2 edition, oct 2013. ISBN: 978-3-446-43802-6.
- [2] Stefan Willför, Raimo Alén, Jan van Dam, Zhiming Liu, and Miia Tahminen. *Chemical Pulping Part1, Fibre Chemistry and Technology*, chapter Raw materials, pages 12–187. Number 6 (Part 1) in *Papermaking Science and Technology*. Paper Engineers' Association/Paperi ja Puu Oy, 2. edition, 2009. ISBN: 978-952-5216-41-7.
- [3] Herbert Sixta. *Handbook of Pulp*, volume 1. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2006. ISBN: 978-3-527-30999-3.
- [4] Marianne Harders-Steinhäuser. *Faseratlas zur mikroskopischen Untersuchung von Zellstoffen und Papieren*. G(ü)ntter-Staib Verlag, 1974.
- [5] Sebastian Baum et al. *Holzkunde II*. ETH Zürich, 2001.
- [6] E. Gruber. *Pflanzenaufschluss (Grundlagen der Zellstoffherstellung)*, chapter 5, page 7. E. Gruber, 2012.
- [7] Lennart Salmén, Mikael Lucander, Esko Harkonen, and Jan Sundholm. *Mechanical Pulping*, chapter Fundamentals of mechanical pulping, pages 36–67. Number 5 in *Papermaking Science and Technology*. Paper Engineers' Association/Paperi ja Puu Oy, 2. edition, 2009. ISBN: 978-952-5216-35-6.
- [8] A. Thaller M. Mayr, R. Eckhart. Characterization of fines quality and their independent effect on sheet properties. *Transactions of the 16Th Fundamental Research Symposium Held in Oxford: September 2017*, page pages 299–322, 2017.
- [9] Leena Paavilainen. Importance of particle size - fibre length and fines - for the characterization of softwood kraft pulp. *Paper and Timber* 72, 72(5):516–526, 1990.
- [10] Nora Odabas, Ute Henniges, Antje Potthast, and Thomas Rosenau. Cellulosic fines: Properties and effects. *Progress in Materials Science*, 83:574–594, oct 2016.
- [11] E. Retulainen, P. Moss, and K. Nieminen. Effect of fines on the properties of fibre networks. In *10th Fundamental Research Symposium, Oxford*, pages 727–769, 1993.
- [12] W. Bauer M. Mayr, R. Eckhart. Improved microscopy method for morphological char-

- acterisation of pulp fines. *Nordic Pulp & Paper Research Journal Vol 32 no 2, 2017, 2017.*
- [13] Spirk S. Reishofer D. Jagiello L. A. Schmiedt R. Colson J. Zankel A. Bauer W. Fischer W., Mayr M. Pulp fines characterization, sheet formation, and comparison to microfibrillated cellulose. *MDPI*, 2017.
- [14] Kari Koskenhely. *Papermaking Part1, Stock Preparation and Wet End*, chapter Refining of chemical pulp fibres, pages 92–139. Number 8 in Papermaking Science and Technology. Paper Engineers' Association/Paperi ja Puu Oy, 2. edition, 2007. ISBN: 978-952-5216-25-7.
- [15] Rafael Giner Tovar. *Fractionated refining and sulphonation as a tool to reduce the energy consumption during refining*. PhD thesis, Technical University of Graz, Institute of Paper-, Pulp- and Fibertechnology, 2016.
- [16] T. Kang and H. Paulapuro. Effect of External Fibrillation on Paper Strength. *Pulp and Paper Canada*, 107(8):51–54, 2006.
- [17] Otmar Töppel. *Physikalisch-technologische Prüfung*. Number 3 in Prüfung von Papier Pappe Zellstoff und Holzstoff. Springer Berlin Heidelberg, 1993. ISBN: 3-540-55896-9.
- [18] Mandlez Daniel. *Fraktionierte Mahlung zur Optimierung der Papiereigenschaften und des Energieverbrauches*. Master Thesis at Graz University of Technology - Institute of Pulp-, Paper- and Fibertechnology, 2017.
- [19] Salim Newaz Kazia Hooman Yarmanda Ahmad Badarudina Mohammad Reza Safaeib Mohd Nashrul Mohd Zubira Samira Gharehkhania, Emad Sadeghinezhada. Basic effects of pulp refining on fiber properties. 2014.
- [20] Hamjern Maskin. *PFI Laboratory Mill*. Hamjern Maskin.
- [21] Richard J. Kerekes. Characterization refining action in PFI mills. *TAPPI Journal*, 4(3):9–14, mar 2005.
- [22] Kerekes R.J. Welch, L.V.: Characterization of the pfi mill by the c-factor. *JPPS Appita* 47(5), pages 387–390, 1994.
- [23] Hauan S. Arlov, A.P. Beating at high consistencies in the pfi mill. pages 267–277, 1965.
- [24] Xell. *Laboratory Beater »Valley«*.
- [25] FRANK-PTI GMBH. *Jokro-Mill*. FRANK-PTI GMBH.
- [26] Herbert Holik. *Handbook of Paper and Board*. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2006. ISBN: 3-527-30997-7.
- [27] Casimir Katz Lothar Göttching. *Papier Lexikon, R–Z*. Euwid Verlag, 1999.

- [28] M.L.O. Park Song Wong Yasamura, Patrícia Kaji D’Almeida. Refining actions in pfi mill and in industrial disc refiners. *O Papel (Brazil)*, 2008.
- [29] William Herbert and P.G. Marsh. Mechanics and Fluid Dynamics of a Disk Refiner. *TAPPI Journal*, 51(5):235–239, May 1968.
- [30] Lumiainen J. A new approach to the critical factors effecting refining intensity and refining result in low-consistency refining. *Papermakers Conference, TAPPI Press*, VII:269–278, April 1990.
- [31] A. de Ruvo M. Htun. The implication of the fines fraction for the properties of bleached kraft sheet. *Svensk Papperstid*, 81:507–510, 1978.
- [32] Kibblewhite R.P. Interrelations between pulp refining treatments, fibre and fines quality, and pulp freeness. *Pap. Puu*, 57:519–526, 1975.
- [33] Rene Eckhart Wolfgang Bauer Rafael Giner Tovar, Wolfgang J. Fischer. White water recirculation method as a means to evaluate the influence of fines on the properties of handsheets. *BioResources*, 10(4):7242–7251, 2015.
- [34] Kaarina Fagerholm Hannu Paulapuro Elias Retulainen, Kari Luukko. Papermaking quality of fines from different pulps - the effect of size, shape and chemical composition. *Appita Journal* 55(6), pages 457–460,467, 2002.
- [35] Hanna Lindqvist, Kristian Salminen, Janne Kataja-aho, Elias Retulainen, Pedro Fardim, and Anna Sundberg. The effect of fibre properties, fines content and surfactant addition on dewatering, wet and dry web properties. *Nordic Pulp and Paper Research Journal*, 27(01):104–111, mar 2012.
- [36] Myat Htun Marie Bäckström, Marie-Claude Kolar. Characterisation of fines from unbleached kraft pulps and their impact on sheet properties. *Holzforschung*, 62:546–552, 2008.
- [37] Z Szikla. On the basic mechanisms of wet pressing. *PSC Communication 31, Oy Keskuslaboratorio – Centrallaboratorium Ab, Espoo,Finland.*, 1992.
- [38] Sparker-D.G. Poirier N.A. Pikulik, I.I. and R.H. Crotogino. Dewatering and consolidation of wet webs. *81st PAPTAC Annual Meeting, Montreal, Canada, Jan 31-Feb 3, Preprints A, Canadian Pulp and Paper Association, Montreal, Canada*, pages pp. A123–A136, 1995.
- [39] H. Paulapuro. Wet pressing – present understanding and future challenges. *The Science of Papermaking Vol. 1, 12th Fundamental Research Symposium, Oxford, UK, Sept. 17-21, The Pulp and Paper Fundamental Research Society, Bury, UK.*, pages pp. 639–678., 2001.



- [40] E. Retulainen. The role of fibre bonding in paper properties,. *Laboratory of Paper Technology, Reports, Series A 7, Helsinki University of Technology, Otaniemi*, 1997.
- [41] M. Htun. The influence of drying strategies on the mechanical properties of paper. *Doctoral Thesis, The Royal Institute of Technology, KTH, Stockholm, Sweden*, 1980.
- [42] P. Mäkelä. Effect of drying conditions on the tensile properties of paper. *Advances in Pulp and Paper Science Research, Oxford 2009, Trans. XIVth Fund. Res. Symp. Oxford, 2009, (S. J. I'Anson, ed.)*, page 1079–1094.
- [43] Alava and Niskanen. *Paper Physics*, chapter 5, pages 182–229. Finnish Paper Engineers' Association/ Paperi ja Ouu Oy, 2008.
- [44] J. T. Gray T. Tajima, Y. Hirabayashi J. M. Uprichard. *Japan Wood Res. Soc. 22(12)689(1968); Appita 26(1):39(1972)*.
- [45] C. P. Donofrio S. D. Alexander R. Marton P. Luner, A. E. U. Kärnö. *Tappi 44(6):409(1961) Tappi 51(6)283(1968)*.
- [46] Kaarlo Niskanen Jari Sirviö, Tiina Pöhler. A simple physical model for tensile stiffness of paper based on fiber activation. *Conference: Progress in Paper Physics Seminar, Finland, 2008*.
- [47] Bengt Nordström. Densification by wet pressing versus refining of neverdried high-yield softwood kraft pulp – effects on compression strength, tensile stiffness, and tensile strength strength. *PAPER PHYSICS, Nordic Pulp & Paper Research Journal Vol 31 no (3) 2016*, pages 422–431, 2016.
- [48] A. Kulachenko H. R. Motamedian, A. E. Halilovic. Mechanisms of strength and stiffness improvement of paper after pfi refining with a focus on the effect of fines. *Cellulose*, page 26:4099–4124, 2019.
- [49] R.S. Seth; D.H. Page. The stress strain curve of paper. *The Role of Fundamental Research in Paper Making, Trans. VIIIth Fund. Res. Symp. Cambridge*, pages 421–452, 1981.
- [50] Zwick Roell. *Prüfmaschinen und Prüfsysteme für Papier, Pappe und Tissues*.
- [51] Nils Pauler. *Paper Optics*. 2008.