Matti Törmänen

IMPROVED ANALYSIS OF TUBE FLOW FRACTIONATION DATA FOR MEASUREMENTS IN THE PULP AND PAPER INDUSTRY
ACTA UNIVERSITATIS OULUENSIS
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IMPROVED ANALYSIS OF TUBE FLOW FRACTIONATION DATA FOR MEASUREMENTS IN THE PULP AND PAPER INDUSTRY

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Abstract

Economic and environmental considerations are increasingly driving pulp and paper processes towards energy and material savings through more energy-efficient systems and increased material recycling. Wood fibers are a major renewable bio-resource from which not only paper and board but also many new products, such as biofuels, biopolymers and biocomposites, can be produced using various production processes. Both traditional and new wood-based processes require increasingly accurate and easy-to-use measurement methods.

Tube flow fractionation is an efficient treatment method for qualitatively dividing a measured sample into different parts. Fractionation occurs as a sample of limited volume proceeds in a long tube filled with water. Due to the turbulence caused by the walls of the tube, the larger particles travel faster than smaller particles and reach the end of the tube earlier and are thus measurable in time as their own fractions.

In this study, an improved analysis method of fractionation data for pulp sample suspension measurements, DFA (Dynamic Fractional Analysis), was invented and implemented. The functionality of the DFA method was studied in consistency measurements and in monitoring the particle changes produced by pulp refining and grinding processes.

By combining tube flow fractionation and optical measurements with DFA, the fibrous index and size index distributions are formed in a completely new way. This significantly reduces the measurement error introduced by water temperature, flow rate and sample consistency to previously known analysis method.

The advantages of the DFA in consistency analysis include easy and reliable calibration and the possibility of fractional consistency measurements. The progress of refining or grinding can be described by the fiber and size index distributions and the key figures formed from them. The quality indices and their distributions follow reliably the fragmentation of particles up to the size class of micro- and nanofibrillated cellulose.

The developed DFA method makes it possible to simplify the structure of the fractionation system and also improves the reliability of the obtained measurements. The usability of tube flow fractionation is thus improved, and its potential application range expands from the current research-focused applications towards process measurements.

Keywords: nanocellulose, optical measurement, pulp consistency, pulp grinding, tube flow fractionation
Törmänen, Matti, Putkivirtausfraktiointia hyödyntävien mittausten parannettu data-analyysimenetelmä.
Oulun yliopiston tutkijakoulu; Oulun yliopisto, Tieto- ja sähköteknikan tiedekunta
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Oulun yliopisto, PL 8000, 90014 Oulun yliopisto

Tiivistelmä

Putkivirtausfraktiointi on tehokas mittauksen esikäsittelymenetelmä näytteen jakamiseksi laadullisesti eri osiin. Fraktioituminen tapahtuu, kun tilavuudeltaan rajallinen näyte etenee pitkässä vesitäytteisessä putkessa. Putken seinämien aiheuttaman turbulenssin vuoksi suuret partikkelit kulkevat nopeammin kuin pienemmät saavuttaa putken pään aikaisemmin ja ovat siten aikaerotteisesti mitattavissa omina fraktioinaan.

Tässä tutkimuksessa luotiin parannettu fraktioitujen massasuspensioiden mittaustietojen analyysimenetelmä, DFA (Dynamic Fractional Analysis). Menetelmän toimivuutta tutkittiin selluja- ja paperiteollisuuden näytteiden sakeusmittauksissa sekä jauhatuksen etenemisen seurannassa.

Putkivirtausfraktioinnin, optisten mittausten ja DFA-menetelmän yhdistelmällä voidaan muodostaa näytteen ominaisuuksia kuvaavia kuitumaisuusindeksi- ja kokoindeksijaakaumia uudella tavalla. Tämä vähentää merkittävästi veden lämpötilan, virtausnopeuden ja näytteen sakeuden tuotamaan mittausvirhettiä aiemmin tunnettuun analyysimenetelmään verrattuna.


Kehitetty DFA-menetelmä yksinkertaistaa fraktiointisysteemin rakennetta ja parantaa saatavien mittausten luotettavuutta. Näin ollen putkivirtausfraktioinmin käytettävyys paranee ja potentiaalinen sovellusalue laajentuu nykyisistä tutkimuspainotteisista sovelluksista prosessimmittauksiin.

Asiaskanat: nanoselluloosaa, optiset mittaukset, paperimassan jauhatus, putkivirtausfraktiointi, sakeusmittaus
Acknowledgements

This work summarizes my journey in the field of optical measurement technology for paper and pulp materials, a journey that begun in 1997 when I started research work in the Measurement and Sensor Laboratory of the University of Oulu (later CEMIS-Oulu) in Kajaani and continued at the Optoelectronics and Measurement Techniques Laboratory in Oulu. Ever since then this experience of university research has greatly benefited my work in the development of industrial measuring devices.

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My gratitude goes to my parents Terttu and Teuvo for being there in the spirit and for the appreciation of self-development that I have learned from you.

Finally, I am grateful for my beloved wife Anni-Inkeri and sons Tuomas and Sakari for your patience and support during this process.

Livo, October 2021

Matti Törmänen
**List of abbreviations and symbols**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>BNC</td>
<td>Bacterial nanocellulose</td>
</tr>
<tr>
<td>CNC</td>
<td>Cellulose nanocrystal</td>
</tr>
<tr>
<td>CSF</td>
<td>Canadian standard freeness</td>
</tr>
<tr>
<td>Cs</td>
<td>Consistency</td>
</tr>
<tr>
<td>Cs-%</td>
<td>Consistency percentage</td>
</tr>
<tr>
<td>DCS</td>
<td>Dissolved colloidal substances</td>
</tr>
<tr>
<td>DFA</td>
<td>Dynamic fractional analysis</td>
</tr>
<tr>
<td>DIP</td>
<td>De-inked pulp</td>
</tr>
<tr>
<td>Euca</td>
<td>Eucalyptus</td>
</tr>
<tr>
<td>FBA</td>
<td>Flow based analysis</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field emission scanning electron microscope</td>
</tr>
<tr>
<td>Fi</td>
<td>Fibrous index</td>
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<tr>
<td>FR</td>
<td>Fraction</td>
</tr>
<tr>
<td>GCC</td>
<td>Ground calcium carbonate</td>
</tr>
<tr>
<td>GW</td>
<td>Ground wood</td>
</tr>
<tr>
<td>HCHL</td>
<td>High consistency high load</td>
</tr>
<tr>
<td>HW</td>
<td>Hardwood</td>
</tr>
<tr>
<td>IUPAC</td>
<td>International Union of Pure and Applied Chemistry</td>
</tr>
<tr>
<td>ISO</td>
<td>International Organization for Standardization</td>
</tr>
<tr>
<td>LC</td>
<td>Low consistency</td>
</tr>
<tr>
<td>LCHL</td>
<td>Low consistency high load</td>
</tr>
<tr>
<td>LED</td>
<td>Light emitting diode</td>
</tr>
<tr>
<td>LF</td>
<td>Long fiber fraction</td>
</tr>
<tr>
<td>MFC</td>
<td>Microfibrillated cellulose</td>
</tr>
<tr>
<td>NFC</td>
<td>Nanofibrillated cellulose</td>
</tr>
<tr>
<td>NIR</td>
<td>Near infrared</td>
</tr>
<tr>
<td>PGW</td>
<td>Pressurized ground wood</td>
</tr>
<tr>
<td>P200</td>
<td>Fraction passing a 200 mesh wire</td>
</tr>
<tr>
<td>P48</td>
<td>Fraction passing a 48 mesh wire</td>
</tr>
<tr>
<td>R48</td>
<td>Fraction rejected by 48 mesh wire</td>
</tr>
<tr>
<td>SCAN</td>
<td>Scandinavian Pulp, Paper and Board Testing Committee</td>
</tr>
<tr>
<td>SEC</td>
<td>Specific energy consumption</td>
</tr>
<tr>
<td>SF</td>
<td>Short fiber fraction</td>
</tr>
<tr>
<td>SGW</td>
<td>Stone ground wood</td>
</tr>
<tr>
<td>SI</td>
<td>Size index</td>
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</table>
SR  Schopper-Riegler
°SR  Schopper-Riegler unit
TAPPI  Technical Association of the Pulp and Paper Industry
TMP  Thermomechanical pulp
TMP AR  Thermomechanical pulp after reject refining
TMP BR  Thermomechanical pulp before reject refining
Vis  Visible
WRV  Water retention value

\( A \)  Geometrical cross section area of particle
\( a \)  Albedo
\( C_1 \)  Gain
\( C_2 \)  Exponent
\( D \)  Tube diameter
\( e \)  Euler’s number / Napier’s constant
\( I \)  Intensity
\( I_{\text{Detector}1} \)  Intensity measured by detector 1
\( I_{\text{Detector}2} \)  Intensity measured by detector 2
\( I_{\text{Sample}} \)  Intensity through sample
\( I_{\text{Water}} \)  Intensity through pure water
\( I_0 \)  Original intensity
\( L \)  Optical pathlength
\( L_c(l) \)  Length-weighted average fiber length
\( s \)  Travel distance in medium
\( T \)  Penetrating probability
\( V \)  Flow rate
\( Q_a \)  Absorption efficiency
\( Q_s \)  Scattering efficiency

\( \mu \)  Viscosity
\( \mu_a \)  Absorption coefficient
\( \mu_b \)  Balanced concentration coefficient
\( \mu_{DP} \)  Depolarized light amount
\( \mu_{ext} \)  Extinction coefficient
\( \mu_s \)  Scattering coefficient
\( \rho \)  Medium density
\( \rho_a \)  Number of absorbing particles in volume
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>$\rho_s$</td>
<td>Number of scattering particles in volume</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Standard deviation</td>
</tr>
<tr>
<td>$\sigma_a$</td>
<td>Absorption cross-section</td>
</tr>
<tr>
<td>$\sigma_{ext}$</td>
<td>Extinction cross-section</td>
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<td>$\sigma_s$</td>
<td>Scattering cross-section</td>
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1 Introduction

In the never-ending chain of development, it sometimes happens that looking at things from a whole new perspective leads to a significant leap to the next level. Let this work be an example of how finding a small missing link in an existing solution can open entirely new possibilities and prospects.

Measurements are vital for process control and product quality characterization. The measurements of the pulp and paper industry, the subject of this study, typically deal with particle suspensions in which various organic and inorganic solid particles are present in a liquid matrix.

The quality properties of the resulting paper or board are dependent on the properties of these particles, and therefore the particles are modified in order to produce the desired quality. The diversity of the particles makes the characterization of the pulp particularly important, and this study aims to answer for its part to this need for advanced characterization methods. In this work, the data obtained by a combination of tube flow fractionation and optical measurement is processed in a novel way for a more robust and comprehensive analysis.

1.1 Overview and motivation

The pulp and paper industry has played an important role both in the Finnish economics and globally during the last century. Especially board and tissue as conventional products are still expanding, and new applications of wood materials will further increase the importance of the forest industry.

Environmentally friendly industry and renewable bio-resources to substitute the petrochemical and mineral resources are increasingly important to the humankind. Environmental and economic aspects drive the conventional pulp and paper processes increasingly towards energy and material conservation through more energy efficient systems and increased material recycling. Continuously tightening environmental norms demand waste load minimization. These reasons necessitate continuous research and development in process control, including pulp and paper process measurements.

Wood is a major renewable bio-resource that can be used in various bio-processes to obtain many necessary products, such as paper, biofuels, biopolymers and biocomposites. These products will be usable in numerous industrial, environmental and medical applications. Cellulose-based materials could have industrial use in construction and concrete structures; as a functional element in
paints, rubber, ceramics, thermosets and thermoplastics; in barriers, foils, films and coatings; in displays, panels and insulation; in packaging, housings and extrusion profiles; in adhesives; in food industry and health care; in membranes, and aerogels (Chinga-Carrasco, 2013; Henriksson, Berglund, Isaksson, Lindström & Nishino, 2008; Liebner et al., 2010).

As these numerous new application areas and processes develop alongside traditional production processes, measurements will play an important role in process control and product quality characterization. All these factors together mean that currently known measurement techniques must be continuously improved and new, more efficient methods developed.

At the present and in the future, there is a continuing need for more selective measurements of multicomponent industrial raw materials. Selectivity in this context means that the measurement system response is independent of changes in non-actual measurands.

In a forest industry mill the wood material goes through complicated bioprocesses, which include the transport of energy and mass, before the end products are obtained. Traditionally, wood blocks are used as the raw material of a pulp suspension containing wood fibers, fiber fragments, fine particles or fibrils, colloidal substances, and dissolved chemical material. Usually some artificial additives are added to the suspension to control the quality of the produced paper.

When all these components are mixed in varying amounts in a sample, selective measurement is hard to achieve. Especially for optical measurement methods alone this kind of mixture is very challenging because the different components have their specific responses.

Measurement selectivity has been enhanced by the simultaneous use of several different physical methods, for example a combination of ultrasound and optical measurements (Törmänen, Niemi, Löfqvist & Myllylä, 2006) or using photoacoustic methods (Zhao, Törmänen & Myllylä, 2006, 2010).

Measurement selectivity can be significantly increased by using tube flow fractionation which enables real separation of the different particle types. Fractionation occurs as a sample of limited volume proceeds in a long tube filled with water. As the particles progress, the smaller ones remain near the wall of the tube in a slowly advancing turbulent flow, while the larger particles progress in a faster, more laminar flow in the center of the tube. Thus, large particles reach the measurement at the end of the tube faster than smaller ones, whereby sets of particles of different quality can be measured separately in time. Tube flow
fractionation serves in the measurement system as a pre-treatment method for the pulp sample. The actual measurement is made by optical methods.

Tube flow fractionation has been identified decades ago as a functional and efficient phenomenon which can be exploited to characterize pulp samples, and a lot of significant research and development has been done on it. This study provides a new improved solution for the interpretation of measurement data obtained from the fractionated sample.

In the previously known method of fractional analysis, the material quantity is measured while the quality of the material is a static, flow-based factor. This method of analysis is abbreviated in this work as FBA (Flow Based Analysis). Due to the static flow moment-based quality assay, FBA requires a well-stabilized sample consistency, water temperature and flow velocity. Any deviations in these factors may cause even significant errors in the measurement result obtained.

The new insight brought by this work is that quality can be measured simultaneously with quantity, thus achieving a dynamic way of analyzing. This new method of analysis is called DFA (Dynamic Fractional Analysis). The dynamic analysis brings many advantages to both the applicability of the measurement method and the structure of the fractionation system.

This thesis work aims to answer for its part to this need for improved ways of measurement. In the future, the novel combination of fractionation and different measurement technologies will result in a completely new generation of measurement products. Using these measurements will lead to a wider business potential by enabling more effective industrial processes and reduced environmental emissions.

1.2 Aim of the thesis

The aim of this thesis was to answer the following questions:

1. How will Dynamic Fractional Analysis method (DFA) improve the tube flow fractionation analysis compared to Flow Based Analysis (FBA) method?
2. How does DFA improve the known consistency measurements?
3. How can the distributions produced by DFA be utilized in refining or grinding measurements?
1.3 Contributions to the thesis

The scientific core of the work is the development of a new dynamic fractional analysis (DFA) algorithm, entirely contributed by the author. The fractionating measurement devices used in the work were manufactured by Valmet Automation Inc. A large quantity of different and differently processed samples were needed in the algorithm development work. In addition to the author, also other persons participated in the sample processing, reference measurements and fractionator measurements.

Samples validating the performance of the developed method for consistency measurement in chapter 5 were measured between years 2002 and 2014. With regard to these, the author's contribution is the re-analysis of the recorded measurements by using the developed algorithm. The consistency calibration system and all consistency related calibrations in this work were also done by the author.

The production of samples for the nanofibrillated and nanocrystalline material tests in chapter 7 was done by the University of Oulu, Fiber and particle engineering laboratory, and also the reference measurements of the samples were performed there. Fractional measurements of these sample sets were performed by laboratory personnel under the supervision of the author.

The preparation and reference analysis of the microfibrillated sample series described in chapter 8 have been performed in Åbo Akademi’s Laboratory of Fibre and Cellulose Technology. Fractionator measurements of these sample sets were also performed by laboratory personnel under the supervision of the author.

The author's main contribution has been generating a new algorithm based on measurement data for analyzing the fractional measurement results, comparing the performance of the new algorithm to the previously known method, processing and analysis of the measurement data, and reporting the results.

1.4 Outline of thesis

The structure of the thesis is described in Fig. 1. After the introduction, the book is constructed of an introduction, a description of the developed analysis method and its applications, followed by discussion and conclusion.

Chapter 1 outlines the structure of the thesis. It includes an overview and motivation, objectives of the thesis and author’s contribution to the thesis. In the background chapter 2 the main paper pulp components and related measurements
are generally examined, and the interaction of optical radiation and paper pulp components is discussed specifically with regard to measurement. Chapter 3 concerns the mechanism of tube flow fractionation and state of the art. In chapter 4 the new dynamic fractional analysis (DFA) method for fractionated sample is revealed. The performance of the DFA and previously known analysis method are compared in chapter 5. Chapters 6 to 8 deal with applications that will be enabled by using tube flow fractionation combined with the new DFA method. Discussion and interpretation are presented in chapter 9, and conclusions and future work suggestions in chapter 10.

Fig. 1. Structure of thesis.
The principle of the analysis method presented in this work is suited for a very wide range of applications. In this thesis only a few application areas are discussed by way of example. The usability of the method in other application areas is considered in the discussion chapter.
2 Background

As this work deals with an applied measurement technique, we first need to explore both the application area and the basics of the measurement technology. This chapter introduces the components of pulp and their processing, as well as the basic concepts of optical measurement.

Section 2.1 provides an overview of the production of wood-based pulp, section 2.2 the modification of the fiber properties by refining, section 2.3 the components forming the suspension and the properties of the pulp, as well as a short review of pulp measurement and characterization in section 2.4.

Section 2.5 presents the key optical parameters in suspension measurement. Section 2.6 describes the measurement system used in the studies of this thesis and the associated measurement quantities.

2.1 Pulp manufacturing

Pulp manufacturing is the step where solid wood material is converted into a wet slurry. This step is preceded by wood treatment and related steps, such as debarking and possibly chipping.

The target in pulp manufacturing is to loosen the fibers of the raw material into separate particles, and generally to accomplish this defibering with minimal fiber breakage. This separation is achieved by dissolving the lignin between the fibers using a suitable combination of chemicals, water, elevated temperature and mechanical force. Traditionally, two main processes have been used: chemical and mechanical pulping.

In fully chemical pulping the raw material is cooked at a high temperature and pressure under the effect of chemicals. Thus the lignin will dissolve into the cooking liquor, and fibers will easily detach as whole from each other. Chemical pulping causes the fibers to come off very intact.

However, part of the fiber material will dissolve in the liquor, thus decreasing the yield of process. Typically, the yield of chemical cooking is 50%, often even less, whereas the yield of mechanical pulping is more than 90%.

In the mechanical pulping process, inter-fiber bonds will soften due to the temperature caused by mechanical stress, and fiber removal happens because of friction and shear forces. The important variables affecting the mechanical pulping process are temperature, pressure and the moisture of wood. There are two main mechanical pulping processes. Thermo Mechanical Pulp (TMP) is formed when
Wood chips are refined between rotor and stator plates. Ground wood (GW) is manufactured by pushing the logs against a rotating grindstone.

Wood pulp is very inhomogeneous in nature. Variations can arise already from the raw material (Giertz, 1977; Hartler, 1986; Rudie, 1995; Tyrväinen, 1995):

- early / latewood content
- wood species (birch, pine, spruce, eucalyptus, etc.)
- basic density
- moisture content
- fiber properties (length, width, cell wall thickness, microfibril angle, etc.)
- content of heartwood and sapwood
- content of mature and juvenile wood
- content of compression wood
- knotwood content
- defects (decay)
- chemical composition of wood (lignin, extractives)
- effect of wood procurement, storing and handling (bark content, chip quality)
- effect of impurities (sand, dirt, etc.)

Big variations are also caused by numerous process-related factors, such as:

- process type
- processing time, temperature, pressure
- condition of process components (refiners, grinding stones, etc.)
- chemicals (cooking, bleaching)
- pumping
- storing
- added material (fillers, pigments, coaters, retention aids, etc.)

All variations due to process and raw material produce a continuum of particle sizes. Conventionally pulp particle size distributions have been characterized with a Bauer-McNett instrument which uses wire screens of different mesh sizes.

2.2 Pulp refining

Pulp refining refers to the mechanical treatment of fibers during papermaking. Due to their chemical and physical structure, chemical pulp fibers as such are not suitable to produce paper or board, as their adherence to each other will be weak and the produced sheet material will be poor and unevenly formed.
In low consistency (LC) refining, mechanical and hydraulic forces are repeatedly exerted on fibers, which breaks their internal and external structure. LC refining is applied on 2 to 6 Cs-%. Metallic bars in the stator - rotor refining system cause the necessary refining forces on the fiber material. The mechanically treated fibers have a high specific surface area which will form strong bonds between the fibers, and the increased fiber flexibility gives a smooth sheet surface.

The refining energy is illustrated by specific energy consumption (SEC), the unit of which is the amount of energy relative to the dry weight of fibers in kWh/t. The more energy is used, the more morphologically treated the fibers will become. The energy consumption is affected by many factors, such as the gap between refiner stator and rotor, the condition of the blades, pulp material, pulp consistency, and the residence time of pulp in the refiner (Smook, 1992).

### 2.3 Pulp suspension components

Pulp suspension contains a very wide variety of particles: long and short wood fibers, fines particles, or fibrils, and dissolved and colloidal chemical substances. The term suspension according to International Union of Pure and Applied Chemistry (IUPAC) means a liquid in which solid particles are dispersed, and colloidal suspension is a suspension “in which the size of the particles lies in the colloidal range” (Everett, 1972, p. 606). The colloidal particle range is defined as the range where the smallest dimension of particles is roughly between 1 nm and 1 µm (Everett, 1972, p. 605).

#### Fibers

Wood is structured of tiny cells or fibers attached to each other. The quality of wood, and the quality of pulp and paper products made from wood, is greatly influenced by cell morphology, for example the cell length and width as well as cell wall thickness.

The shape of the fibers, especially long fibers, is often irregular, multi-branched, and flexible, and therefore above a certain consistency the fibers will easily aggregate together to form flocs in the pulp suspensions.

Most wood fibers are elongated tracheids, fibrous cells, which form the majority of wood material. Tracheid fibers typically have a hollow center and intricately layered walls with closed ends. The cross section of a softwood tracheid is schematically shown in Fig. 2 a). The clearest difference between the layers is in
the orientation of microfibrils. Microfibrils are cellulosic elementary fibril bundles and their combination forms macrofibrils, in other words fibrils. The longitudinal circulation angle of fibrils is called the fibril angle.

Fig. 2. Tracheid fiber structure in a) and classification of fines in b). The tracheid fiber has a hollow center and intricately layered walls with closed ends. Fines can be divided into fibrillar fines and flake-like fines based on their origin (Redrawn from Odabas, Henniges, Potthas, & Rosenau, 2016 and Rundlöf, 2002).
Softwood tracheids typically range in length from 1 mm to 6 mm, whereas in hardwood they are considerably shorter, less than 2 mm long. The width of a tracheid is roughly about a hundredth of its length.

Ray cells are specialized cells that carry water and nutrients between tracheids in the radial direction of wood. Water and nutrients are transferred through the pores in the fiber walls. Ray cells are smaller in size and smaller in number than tracheids.

Fines

During the pulp manufacturing, as fibers are detached from wood matrix, smaller fines particles are also generated. Because of their large surface area, fines improve bonding between fibers. In paper, most of the fines surface is bonded to fibers when the paper dries. In chemical pulps the amount of fines is lower than in mechanical pulps.

Fines are commonly defined as the fraction that passes through 200 or 100 mesh wire of the Bauer-McNett or similar device. The median size of fines is a few micrometers. The largest fines particles are fiber fragments, the smallest are fibrils or parts of fibrils whose size may be well below 1 μm (Retulainen, Niskanen & Nielsen, 1998).

Fig. 2 b) illustrates the morphological classification of the fines. Flake-like fines and granular material consist of ray and parenchyma cells, pores, and broken pieces of fiber. Fibrillar fines are fibrils or fibril bundles peeled from the walls of the inner layers of the fibers (Odabas et al., 2016).

Usually the fines content of mechanical pulps is 20–40% by weight, in chemical pulps less than 10%. The generation of fines in mechanical pulping or refining occurs at the expense of fiber damage. The share of long, intact fibers can be less than 20% by weight in GW mechanical pulp and nearly 40% in TMP. In a chemical pulp, the long fiber fraction may be as high as 90% (Retulainen et al., 1998).

Fines consist of cellulose, hemicelluloses, lignin, and extractives in approximately the same proportions as the other fiber fractions. In chemical pulps the hemicellulose content of fines is higher than in the fiber fraction (Htun & de Ruvo, 1978). Since the fines of mechanical pulps originate partly from the lignin-rich middle lamella and primary wall of fibers, their lignin content is higher than in the fiber fractions (Chang, Sinkey & Yan, 1979). The fines content in mechanical pulps grows in the order TMP>PGW>SGW when compared at the same freeness.
Fines have a very large specific surface area because of their small particle size. Refining increases the surface area further. The characteristic length of fines particles increases when refining energy increases.

In chemical pulp, the specific surface area of primary fines is 4–5 m²/g and that of secondary fines 10–20 m²/g. Mechanical pulp fines have a specific surface area of 7–8 m²/g. A typical value for fibers is 1 m²/g (Retulainen et al., 1998). The values of specific surface area depend on the measurement method and therefore only indicate relative differences (Heikkurinen & Hattula, 1993; Hirvonen et al., 1996).

**MFC and NFC**

The 21st century has brought increased interest in micro- and nano-sized cellulosic materials. This interest is caused by the variety of applications for nanofibrillated material due to its unique properties: the specific surface area of nanofibrillated cellulosics has been estimated to be rather large, around 100–200 m²/g (Lavoine, 2012), and their aspect ratio is high, in the range 100–150 (Siró, 2010).

The internal structure of wood fibers consists of nanoscale elementary fibrils that form macrofibrils, which are part of the cell wall and thus form the whole cellulosic fibers. The fibrils are attached to each other with strong hydrogen bonds and weak van der Waals forces (Thomas, 2020). The manufacture of fibrillated material focuses on the release of these bonds, which is in principle very energy intensive.

There has been variability in the terms describing micro- and nanofibrillated cellulosic material, but they can be divided into three main categories:

- mechanically produced micro-/nanofibrillated cellulose MFC/NFC
- bacterial nanocellulose BNC, produced by biotechnological synthesis (Klemm, 2021)
- cellulose nanocrystals CNC, produced by acid hydrolysis (Thomas, 2020)

The principles of NFC and CNC production methods are shown in Fig. 3. Micro- and nanofibrillated cellulose can be produced by different mechanical processing equipment: grinders, homogenizers or microfluidizers (Klemm, 2011; Lavoine, 2012; Siró, 2010). When the target is to produce mainly MFC, also LC refining can be used (Jahangir, 2020).

The cellulose nanocrystals manufacturing process may have a fiber pre-opening mechanical step at the beginning, followed by the actual acid hydrolysis. The acid hydrolysis removes amorphous regions between the crystalline fibril
parts. The end result contains crystals, acid and material that still needs to be cleaned and separated (Lavoine, 2012).

**Fig. 3. The principles of NFC and CNC production methods.** The mechanical treatment generates the NFC, acid hydrolysis removes the amorphous regions between crystalline regions generating CNC (Particle dimensions from Moon, Martini, Nairn, Simonsen & Youngblood, 2011).

There is no clear boundary between microfibrillated and nanofibrillated cellulose materials. Nanofibrillated material is typically more of a mono-dispersion whereas microfibrillated material has a wider particle size distribution, often also including nanomaterials.

There are several potential applications for fibrillated cellulose nanomaterials and new applications are constantly being explored. Examples of the applications currently under research include:

- strength enhancement additives in packages, light-weight composites and textiles (Chen, 2017; Gan, 2020; Mazhari Mousavi, 2018)
- food industry and food-contact packaging (Andrade, 2015; Gicquel, 2017; Hemmati, 2018; Pereira, 2017)
- as porous and absorbent materials for various purposes, such as water purification (Cruz-Tato, 2017; Karim, 2016; Liu, 2016; Sirviö, 2016)
- life sciences and medical applications, e.g. implants, wound dressings and drug delivery systems (Li, 2016; Mohan, 2020; Prakash Menon, 2017; Qiao, 2015; Wang, 2016)
- fuel cells (Xu, 2018)

Nano-sized particles are invisible to normal light microscopes, so particle analyses are typically performed by electron microscopy. This is a very time-consuming method, and new high-performance measurements for nanomaterials are therefore needed.

**Fillers**

Fillers have traditionally been used to promote the optical properties of paper, made possible because the fillers’ brightness and light scattering coefficient are higher than those of the fiber network. These ideas still apply, but today it is a fact that some chemical pulp types can be produced at brightness levels equal to fillers. Moreover, some mechanical pulps have almost the same scattering efficiency as traditional fillers. In this situation, specialty pigments are required to further improve brightness and light scattering (Krogerus, 1999).

Natural ground calcium carbonate (GCC) from limestone and precipitated calcium carbonate (PCC) obtained synthetically by calcination have quite narrow size distributions: their mean diameters are 0.8 to 1.2 µm and aspect ratios 1 to 1.5, whereas natural kaolin clay has a mean diameter 2 to 5 µm and aspect ratio of 4 to 30 (Hubbe & Gill, 2016, p. 2898). The mean diameter of natural talc is the widest of the commonly used fillers, being 1 to 20 µm and the aspect ratio 5 to 20 (Hubbe & Gill, 2016, p. 2898).

In most cases, fillers and pigments are inert, water-insoluble substances or materials. Calcium carbonate is an important exception: even though it is very sparingly soluble in alkaline conditions, it effectively buffers the pH of the aqueous system to a slightly alkaline range. In an acid medium the calcium carbonate decomposes and gives rise to dissolution of calcium and carbonate ions into the water phase and saturation by carbon dioxide.
Water

In the papermaking process, water can be regarded as one of the principal raw materials. It is used as a transport medium and solvent for raw materials and chemicals.

The aqueous phase in a paper machine system contains a wide range of different substances with different characteristics and behavior. In the aqueous system of a paper machine, there are solid particles, dissolved and dispersed colloidal substances, and gaseous substances, as well as micro-organisms. Thus, since the composition of the water-based liquid is very complex and it can contain many different components, it is virtually impossible to describe in an exact way all the interactions between the components or to predict their influence on the papermaking process.

Of the different pulp types used in papermaking, mechanical pulps bring the largest part of dissolved colloidal substances (DCS) to the white water. In the defibration of mechanical pulps, 2–5 kg/ton of the wood material is dissolved or dispersed into the water phase (Holmberg, 1999).

2.4 Pulp measurement and characterization

Pulp measurement and characterization gives valuable information throughout the pulping process, from the earliest stages where fibers are originally co-attached to the final stage: paper, board, or other cellulose product. Measurements are important on one hand for process control, on the other hand for the characterization of the final product. In industrial production, optimizing the use of raw materials and resources is very important for cost-effectiveness.

The quality of the final product must exceed the minimum requirements, but there is usually no economical compensation for excess quality. The more precisely the process can be controlled, the smaller a margin can be left to the minimum quality requirements. In this case, in addition to cost-effectiveness, product quality variations remain small.

Pulp properties can be determined using various methods to measure the individual fiber or particle properties, pulp suspension properties, or dried hand sheet properties. Characterization is determined by numerous laboratory standards maintained by several organizations, like the Technical Association of the Pulp and Paper Industry (TAPPI), International Organization for Standardization (ISO), and Scandinavian Pulp, Paper and Board Testing Committee (SCAN).
Pulp characterization could be at least roughly divided into quantity or quality determination. Ideally, a quantity measurement produces the same result regardless of qualitative variations of the measured objects, and on the other hand the quality measurement results should be independent of quantity. The quantity-like properties, as consistencies or concentrations, are properties describing the pulp slurry, not the fibers, particles or hand sheet. The quality-like properties indicate certain properties of the pulp slurry derived from the properties or existence of individual particles.

Real-time process measurements can rarely be performed by a method fully compliant with laboratory standards, which makes them indirect measurement methods. An indirect method uses the measurement of a physical quantity which, through calibration, is made to correspond to a determination made in a laboratory. In indirect measurement methods the measured quantity is affected by many process and raw material variables which makes process measurements very challenging.

Pulp slurry measurement arrangements can be roughly divided into three different categories as shown in Fig. 4. These arrangements describe the most typical situation in processes where pulp is transported in process pipes. In some cases, the measurement is made from an open channel flow or an open or closed tank. For example white water measurements at the wet end of a paper machine are usually made using a sample taken from the white water tray.
Fig. 4. Pulp slurry process measurement arrangements can be divided into three categories. In in-line method a) the measurement is done straight from the flowing pulp. On-line type measurement b) uses a side flow sampled from the process flow. c) Measurements that execute sample preparation before analysis are called off-line measurements.

In the context of this work, in-line means measurement that is done straight from the flowing pulp inside the process pipe or from a corresponding position. The measurement where a sample is separated from the process to a side flow is called on-line measurement.

In-line and on-line type measurements typically produce an instantaneous real-time measurement from the process. The measurement that needs sample preparation before analysis is called off-line measurement. These limitations in the definitions are of course not exact, and there are situations where it is not always possible to determine precisely whether a measurement is of the in-line, on-line or off-line type.
Consistency

Consistency, defined as the amount of solid material relative to the total amount, is one of the most important control parameters in pulp and paper manufacture. Consistency influences especially the process performance and control. The operation of many sub-processes requires a controlled consistency.

The total consistency of pulp is defined as the mass percentage of all dry material in a given pulp sample. In laboratory standard methods ISO 4119 (Internal Organization for Standardization, 1994) and TAPPI T240 (Technical Association of the Pulp and Paper Industry, 2019), a known amount of pulp sample is taken and most of the water is filtered away through a paper filter. The dry material rejected by the filter is then dried in an oven. Sample consistency is defined as the ratio of dried material mass to the total sample mass and expressed as Cs-% when TAPPI standard is used. When ISO standard is used, the consistency is defined as the ratio of dried material mass to the total sample volume and expressed as g/l.

Today, there are several commercially available methods to measure total consistency in-line. These methods are mainly based on the attenuation and scattering of optical radiation, the attenuation and retardation of microwaves, or changes in the viscosity of the flowing pulp. In all these methods, calibration is recognized as the key to accurate consistency measurements (Tornberg, 1999). On-line type consistency measurements are mainly realized by optical methods. There is also an off-line type analyzer that conforms to the laboratory standard. In it, a sample of known volume is dried and weighed. The results obtained by this method correspond exactly to the results of the standard method, but the response time is not sufficient for most consistency adjustment needs.

Consistency applications can roughly be split into three ranges: Low, medium, and high consistencies. The low consistency (0–1 Cs-%) sensing needs are in the wet end of a paper machine: sorting, disc screen, and wastewater. The medium consistency range (1–6 Cs-%) is used in both paper and pulp mills, being obviously the most widely needed control range. The high consistency range (8–15 Cs-%) is typically used in the pulp mill blow line, or in the bleach plant.

Total consistency is understood as the sum of partial component consistencies (fiber, filler and fines consistency). These consistencies are here classified as quantity properties, quantifying the amount of a given component in relation to the total water amount.
**Filler or fines content**

Filler content describes the relative amount of inorganic material in the total dry matter and is usually expressed as a percentage. In laboratory analyses, the organic material in the dried pulp sample is burned in an oven and the mass of the remaining ash is compared with the mass of the original pulp sample. The standards defining filler content are ISO 1762 (Internal Organization for Standardization, 2019) and TAPPI T211 (Technical Association of the Pulp and Paper Industry, 2016), where the combustion of organic material is carried out at a temperature of 525 °C.

Correspondingly, fines content describes the relative amount of fines in the total dry matter and calculated in the traditional way, is calculated as the proportion of the Bauer-McNett P200 fraction in the total dry matter. Modern measurement methods based on microscopy and image processing determine the amount of fines based on the dimensions of the particles.

The visible change in pulp property is that the larger the filler or fines content, the more homogeneous and evenly flowing the pulp will be. In the case of optical measurement, radiation does not penetrate deep into the pulp sample, and therefore the optical measurement signal of a homogeneous and uniformly flowing pulp sample is less noisy than for a non-homogeneous sample.

**Drainability**

Pulp suspension properties are commonly determined by means of drainage measurement; other terms referring to the same phenomenon are drainability, dewaterability, freeness or filtration resistance (Kalliokoski, 2011). Drainage measures how fast water is removed from a pulp suspension. Drainage is affected by numerous processes, such as fiber property changes through refining, the mixtures of different fiber types, and the fines and filler material. Two main methods are used for drainage measurements: Canadian Standard Freeness (CSF) for mechanical pulps and Schopper-Riegler (SR) for chemical pulps.


Even though drainability correlates with other pulp properties such as fines content or shives content, this parameter gives only limited information of the fiber
properties and paper quality. An increase in fines content will strongly improve surface smoothness and light scattering.

2.5 Optical parameters

Optical parameters are used to describe the properties of either individual particles or a set of particles in a suspension. The basic parameters related to photon propagation in transilluminated optical systems are presented in this section.

The main physical phenomena utilized in the optical measurements of pulp processes are absorption, scattering, and de-polarization. Absorption decreases the propagating light intensity and it occurs in all measurable materials. In addition to variable absorption, pulp and paper industry samples are very rarely free of scattering. Scattering is very sensitive to changes in the particle and matrix medium characteristics, thus causing great challenges, but when properly understood, it also presents opportunities for optical measurements.

Absorption is an event where radiation energy excites the energy of molecules or atoms on a higher level. In absorption, the exciting radiation frequency corresponds to quantized energy band differences due to Planck's law of radiation. The absorbed energy will often turn into a temperature rise of the absorbing medium.

Scattering happens when electromagnetic radiation meets an elastically bonded, charged particle that sets on the vibration mode according to the electric field. Unlike in absorption, the electric field frequency in scattering normally does not correspond to the particle energy band difference. Thus, the effects of scattering are spectrally more gently sloping than those of absorption.

The scattering phenomenon can be divided based on wavelength or on the size and shape of the scattering particles. Scattering is generally independent of direction but dependent on particle shape, orientation, and the direction of the plane of polarization (Bohren & Huffman, 1983; Malacara, 1988).

The absorption cross-section of particles $\sigma_a$ defines the cross-dimensional area where the particle absorbs radiation. This area can be smaller or wider than the particle's geometrical dimensions (Bohren & Huffman, 1983). Absorption cross-section is defined as

$$\sigma_a = Q_a A,$$  \hspace{1cm} (1)
where dimensionless $Q_a$ is absorption efficiency and $A$ is the geometrical cross section area of particle. Fig. 5 presents absorption cross-section and total area schematically.

**Fig. 5.** Absorption cross-section $\sigma_a$ defines the cross-dimensional area where particle absorbs the radiation. The absorption cross section may be different from the geometric cross section area $A$ of the particle.

Absorption coefficient $\mu_a$ is a parameter describing the absorption property of the medium formed by the particles and the material between them, and it is defined as

$$\mu_a = \rho_a \sigma_a,$$

(2)

where $\rho_a$ is the number of absorbing particles in volume. Absorption coefficient expresses the probability for a photon to become absorbed during propagation of a unit distance.

Correspondingly, a particle's scattering cross section $\sigma_s$ is the area in which the photons encounter a scattering effect. Scattering cross section is defined as

$$\sigma_s = Q_s A,$$

(3)

where dimensionless $Q_s$ is scattering efficiency and $A$ is the geometrical area of particle. In Fig. 6 the scattering cross-section and total area are presented schematically.
Scattering coefficient $\mu_s$ is a parameter describing the scattering property of the medium formed by the particles and the material between them, and it is defined as

$$\mu_s = \rho_s \sigma_s,$$  

where $\rho_s$ is the number of scattering particles in volume. Scattering coefficient expresses the probability of photon direction change during unit distance propagation.

In most cases, especially in pulp process samples, both absorption and scattering take place. Extinction is a term combining both of these. Another term for extinction is optical attenuation. Extinction cross-section $\sigma_{ext}$ is the sum of absorption and scattering cross sections:

$$\sigma_{ext} = \sigma_a + \sigma_s.$$  

In the same way, absorption and scattering coefficients can be combined into extinction coefficient $\mu_{ext}$ of

$$\mu_{ext} = \mu_a + \mu_s.$$  

When particle size in relation to wavelength decreases, absorption cross section increases relatively more than scattering cross section (Bohren & Huffman, 1983). When the travel distance in medium is $s$, the dimensionless penetrating probability $T$ influenced by scattering and absorption can be defined as
The ratio of scattering and extinction is defined as albedo or reflectivity, $a$. When albedo is calculated using cross-sections, it indicates the reflectivity of a single scattering event:

$$ a = \frac{\sigma_s}{\sigma_{ext}}, \quad (8) $$

and when albedo is calculated using the scattering and extinction coefficients, it indicates the reflectivity of the whole medium as

$$ a = \frac{\mu_s}{\mu_{ext}}. \quad (9) $$

**Water absorption**

Because water is the most important medium in papermaking processes, a brief overview of water absorption is appropriate. The absorption coefficient spectrum of pure water from 400 nm to 1200 nm is shown in Fig. 7 (Segelstein, 1971). As seen in the spectrum, water absorption decreases from the infrared wavelength region to the visible region. The absorption coefficient difference in Vis–NIR region is more than three decades, which must be addressed in optical measurements.

![Water absorption coefficient spectrum](image)

Fig. 7. Water absorption coefficient spectrum in the visible and near infrared wavelength regions.
The waters in the wet pulps on a paper machine are relatively pure, at least compared to chemical cooking liquors which contain wood lignin and hemicellulose components in addition to cooking chemicals. Some amounts of wood components and other possible impurities are of course also dissolved in the pulps of the paper process, and this should be evaluated and considered in optical measurements.

2.6 Optical measurement system used in this work

The optical measurement in the fractionator system used in this work is based on continuous measurement of material flowing through a cuvette. The measurement module is similar to the one used in the Valmet RM3 retention measurement system. The principle of the measurement module is presented in Fig. 8. The light sources are light emitting diodes (LED) working in the visible and near-infrared wavelengths. The beams of two LEDs are superimposed in the same optical path by a 50/50 beam splitter. These light beams are directed through the sample in a windowed cuvette. For the sake of clarity of presentation not all light rays have been drawn, only those that were used in signal detection.

![Fig. 8. Transmission and depolarization measurement module consist of two separately pulsed LED light sources whose light beams are superimposed by using a beam splitter, and a corresponding detection system where half of the beams are directed onto detectors 1 and 2 by a beam splitter. The light beam of the visible wavelength LED is polarized by a polarizer that is at 90° rotation relative to the analyzer in detector 2.](image-url)
Extinction measurements of both wavelengths are measured by detector 1. In addition, depolarization is measured using both detectors 1 and 2 on separate branches. The dark values of both detectors are subtracted.

**Extinction coefficient**

The extinction coefficient, also called attenuation coefficient, describes the quantity of attenuation in the intensity of light traveling in a medium, observed in the original radiation direction. As mentioned in the previous section, the attenuation of light is affected by two mechanisms: light absorption and scattering. Absorption refers to the absorption of light energy into matter, while in this context scattering is understood as the change in the direction of light when it encounters solid matter in a fluid.

In a pulp slurry, attenuation is caused mainly by light scattering which is proportional to the amount of particles; an example of this effect is shown in Fig. 9. Part of the light is deflected from its original direction by wood fibers and other particles on the light path, resulting in a decrease in the light intensity at the detector. This phenomenon is the basis of attenuation-based consistency measurement. When consistency is higher, there are more scattering particles on the light path and thus the intensity decreases more.

![Fig. 9. Attenuation of light intensity caused by absorption and scattering. a) Pure water causes extinction due to absorption. b) When particles appear in the water causing a low consistency, weak scattering occurs due to particles shading the light beam. c) A higher consistency causes more scattering as more particles are in the light beam.](image)

The intensity decreases exponentially in relation to extinction and pathlength due to Lambert-Beer’s law of

\[ I = I_0 e^{-\left(\mu_a + \mu_s\right)L} = I_0 e^{-\mu_{ext}L}, \]  

(10)
where $I$ is intensity, $I_0$ is the original intensity, $\mu_{\text{ext}}$ is extinction coefficient and $L$ is the optical path length. When the optical path length is increased, the change in extinction causes a larger intensity variation, which means improved sensitivity.

The schematic example in Fig. 9 illustrates a single scattering situation where the scattering coefficient is so low that only very little of the scattered light reaches the measurement detector. In such a single scattering situation, the scattering coefficient is directly proportional to the number of particles in the sample volume.

The degree of extinction is calculated as the relation between the intensities of the measurement and the reference measurement. Based on Eq. 10, the extinction coefficient is calculated by equation

$$\mu_{\text{ext}} = -\ln \left( \frac{I}{I_0} \right).$$

(11)

This equation describes the attenuation of intensity with relation to path length. Often in different applications, the reference intensity $I_0$ is the intensity measured through clean air. However, in the case of a flow-through cuvette, the most practical way to reference intensity is by a reference measurement with a pure water-filled cuvette. This is described by the equation:

$$\mu_{\text{ext}} = -\ln \left( \frac{I_{\text{sample}}}{I_{\text{water}}} \right),$$

(12)

where $I_{\text{sample}}$ is intensity measured through a cuvette filled with sample, $I_{\text{water}}$ is intensity measured through a water filled cuvette, and $L$ is the optical path length determined by the thickness of the cuvette. Thus the zero value of the extinction coefficient corresponds to the pure water absorption coefficient at a given wavelength.

The attenuation coefficient starts from zero in the water reference, and it may also be considered primarily linear in relation to consistency, but this linearity increasingly disappears towards higher consistencies.

The non-linear response of the attenuation coefficient is caused by multiple scattering. When the particle density increases with increasing consistency, some of the diverged light is redirected back to its original direction and thus the increase in attenuation in relation to consistency begins to decrease. The principle of the multiple scattering effect is schematically shown in Fig. 10.
The transition from the single scattering range to the multiple scattering range greatly complicates the theoretical review of light propagation and the determination of optical properties of turbid medium. In this multiple scattering range, for example, diffusion approximation (Farrell, 1992) or Monte Carlo simulations (Wang, 1995; Wilson & Adam, 1983) are used instead of Lambert-Beer's law. These methods are typically used in biomedical material characterization (Jacques, 2013), but are also applicable to the measurement and characterization of wood fiber suspensions (Juttula, Törmänen, Mäkynen, 2020; Keränen, Mäkynen, Prahl & Törmänen, 2009).

However, the measurements of this thesis remain in the linear single-scattering region due to dilution in tube flow fractionation. The linearity related aspects are important to consider in the quality index calculations that will be introduced in chapter 4.

**Depolarization**

The polarization of light describes the directional dependence of the amplitude of the electric field of optical radiation in a plane perpendicular to the direction of propagation of the wave. As the electric field oscillates in only one direction, the light is linearly fully polarized.

Birefringence is a property of the material where the refractive index varies depending on the viewing angle. Linear polarization can be utilized in measurements of birefringent materials such as cellulosic fibers (Pethrick, 2007).
Depolarization measurement describes the reversal of linear polarization of light when it encounters the crystalline parts of cellulose in wood fibers. In depolarization measurements with the system shown in Fig. 8, the parameter of depolarized light, $\mu_{DP}$ is calculated as

$$\mu_{DP} = \frac{I_{\text{Detector}2}}{I_{\text{Detector}1}},$$

where $I_{\text{Detector}1}$ is intensity measured by detector 1 in Fig. 8 and $I_{\text{Detector}2}$ is correspondingly intensity measured by detector 2. The measurement values are divided in order to correct the effect of attenuation on the depolarized light. In principle, depolarization measurement response usually begins from zero because water does not cause depolarization.
3 Tube flow fractionation

This chapter discusses the history, principle, and current state of tube flow fractionation. The tube flow fractionation is an effective phenomenon by which sample particles with different flow resistance properties can be separated from each other. Section 3.1 will explain the background of tube flow fractionation, section 3.2 concerns the principle of the fractionation system and the current state of fractionation analysis is discussed in section 3.3.

3.1 Background of tube flow fractionation

The phenomenon has been known for several decades and applied mainly for research purposes. This limitation to research use only is mainly due to the complex system requirements for tube flow control. Tube flow fractionation is based on the cross-sectional flow rate gradient that is caused by the flow resistance of the tube wall: the flow rate in the middle of the tube is higher than in the edge areas next to the wall. Centrifugal forces caused by turbulence force the smallest particles near the tube walls while other particles stay in the quicker flow in the middle of the tube. Larger particles are more likely to be swept away by the quicker flow in the middle of the tube and will thus be the first to arrive at the end of the tube, because the particles in the middle flow will pass by the more slowly travelling particles in the edge areas (Krogerus, Fagerholm & Löytynoja, 2003; Olgård, 1970; Pascal & Silvy, 1991; Pascal & Silvy, 1993). Thus tube flow fractionation enables sorting particles into various size classes and the sample fractions can also be guided to separate containers if necessary, based on the flow at different moments of time (Laitinen, Kemppainen, Stoor & Niinimäki, 2011).

A fractionator device is based on this tube flow fractionation principle. It utilizes an optical measurement module to measure the sample fractions flowing spatially separately. Due to spatial separation, sample fractions arrive to measurement at different moments, thus enabling fractional measurement. Based on the currently used calculation method, the optical measurement signals can be calibrated into Bauer-McNett distributions (Laitinen, 2011).

Earlier fractionator measurements are sensitive to temperature and flow rate variations, which increases the inaccuracy of the measurement results.
3.2 Principle of fractionation system

The fractionation system basically consists of three parts: the sample dosing system, the fractionation tube, and the measurement module. The system schematic is shown in Fig. 11. Typically, the fractionating tube is several tens of meters long, its diameter from millimeters to centimeters. The flow-through type measurement module used implements the optical sensing. After measurement the sample flow can be collected or led to the drain.

Fractionating measurement takes place in three steps: sample dosing, sample separation and sample measurement. In sample dosing, a constant volume sample is dispensed into the beginning of the water-filled hose reel. When a water valve is opened, the constant water flow begins to push the sample through the tube coil. As the sample passes through the tube, it is fractionated so that the long fibers and large particles reach the measurement first and the particles coming later decrease in size. The water flow is precisely standardized for temperature and flow rate so as to ensure reproducible fractionation.

The principle of fractionation is shown in Fig. 12. The initial sample is a heterogeneous mixture consisting of many different particles, as seen in Fig. 12 a). The interface between the sample in the tube and the water on both sides is sharp at this point and the sample is like a plug in a tube.
As the sample propagates, long fibers seek the rapid flow in the center of the tube while smaller particles progress in the turbulent area at the edges of the tube. In the example of Fig. 12, the volume of the original sample is 200 ml. As seen in Fig. 12 b), the first fiber particles arrive at 17 liters, and at a volume flow of 19.4 liters there are still plenty of fines particles. Thus the sample particles originally in a volume of 200 ml are distributed over a volume of more than 2.4 liters during the flow propagation.

From the measurement point of view, the spatial distribution in the tube is shown as a temporal change of the measurement object.

Fig. 12. Principle of fractionation. a) The initially dosed sample is a heterogeneous mixture consisting of many different particles. b) After fractionation, the particles in the sample are distributed over a long distance and arranged according to size. The largest particles, such as fibers, reach the measurement first and the particles coming later decrease in size.
Flow conditions affect the Reynolds number according to the equation

\[ Re = \frac{\rho V D}{\mu}, \]  

where \( \rho \) is medium density, \( V \) is flow rate, \( D \) is tube diameter and \( \mu \) is medium viscosity. The working Reynolds number scale for tube flow fractionation is rather large, being 1000–10 000 (Laitinen, 2011). Temperature affects the Reynolds number through medium density and medium viscosity. When the temperature is above +4 °C both the density and viscosity of water decrease towards higher temperatures, the relative reduction of viscosity being typically bigger than that of density. For this reason, an increase in temperature will also increase the Reynolds number of the water flow: when water temperature increases from 10 °C to 40 °C the Reynolds number will double. More generally, a temperature change that causes a change in the Reynolds number of the water flow may result in a failed or inaccurate fraction measurement, as seen in section 3.3.

In addition, the Reynolds number will also be higher when the flow rate or tube diameter increases. Thus, if the fractionation time is shortened by using a quicker flow while keeping the Reynolds number constant, the increase in flow rate can be compensated by decreasing the diameter of the tube or by using colder water.

Previous studies (Krogerus et al., 2003) have indicated that the phenomenon fractionates sample particles primarily according to particle length: fiber bundles and long fibers come first, after them the fiber length decreases as the fractionation progresses and fines arrives at the end.

Empirical studies into the effects of the other dimensions of organic particles on fractionation time have shown that fiber length is not the only explanatory factor, as particle width and thickness also affect the propagation time (Laitinen, 2011; Laitinen et al., 2011). Based on this result a multilinear regression model was produced that seeks to also predict the effect of other dimensions, not only length, on the particle arrival time in fractionation. Particle length was still seen as the most significant factor influencing arrival time, but its effect did not progress linearly over the entire length scale: the shorter the particles, the stronger the effect of length on the time of arrival. For the other dimensions, the change was almost linear.

### 3.3 Flow based fraction analysis

The long-established method of fraction analysis is based on observing the changes in a measurement signal at successive, known moments of total flow. In this work
this method is called flow based analysis, FBA. Fig. 13 shows an example of how fibrous material and fines are separated in tube flow fractionation measurement, and the fraction limit used in the flow based analysis is also shown.

The measurement signal in this example is the extinction coefficient at visible wavelength. The fractionated particle images in Fig. 12 correspond to the results of the measurement in Fig. 13.

In Fig. 13, the $x$-axis depicts the cumulative amount of water flow from the moment the sample begins to propagate in the tube. As shown, the first sample particles reach the measurement at a flow rate of about 16 500 milliliters, at which point the first particles in the sample start to elevate the extinction coefficient from zero. As described in section 2.6, zero extinction value corresponds to the absorption value of pure water.

![Graph showing extinction signal as a function of flow](image)

**Fig. 13.** An example of the extinction signal of sample containing fibers and fines as a function of flow. Fibers arrive before the 18.4-liter fraction limit and fines after this.

Extinction reaches local maximum readings at about 18 100 ml and 19 000 ml, which shows that the sample consists of roughly two differently fractionated sets of particles: fibers and fines. In fact, even in the beginning, in the flow range of 17 000 ml to 17 500 ml, there is a third set of particles composed of the coarsest fibers. These sets of particles with different fractionation properties overlap, which can be seen from the fact that the extinction does not return to zero, i.e. the reading indicating pure water between the subsets of sample.
For fraction analysis, equivalent total flow value limits are set and the different fractions are divided into their own calculatory classes based on these limit values. In the measurement example shown in Fig. 13, two different fractions are separated at a fraction limit set at 18 400 ml. Particles before the limit value are classified as fibers in fraction A, after the limit as fines in fraction B. More than two separate fractions can also be used to analyze the sample, but for the sake of simplicity only two fractions are described in this example.

The total amount of materials in the sample is estimated as the total integrated area covered by the signal. This area can be calculated as the total sum of the signal values during the measurement sequence as

\[
\mu_{\text{ext,Total}} = \sum_{i=15 \, 500 \, ml}^{22 \, 000 \, ml} \mu_{\text{ext}} (Q_i) \Delta Q,
\]

where \(\Delta Q\) is the differential value of flow in fractionation. The measurement is sampled every 1.85 ml, which corresponds the value of \(\Delta Q\).

Correspondingly, the fractional amount of material can be estimated by the sum of the flow values belonging to the partial fractions. The amount of material belonging to fraction A is calculated as the sum of the signal values before the flow reading 18 400 ml and the amount of material belonging to fraction B as the sum of the signals coming after it, respectively, by equations:

\[
\mu_{\text{ext,fractionA}} = \sum_{i=15 \, 500 \, ml}^{18 \, 400 \, ml} \mu_{\text{ext}} (Q_i) \Delta Q
\]

and

\[
\mu_{\text{ext,fractionB}} = \sum_{i=18 \, 400 \, ml}^{22 \, 000 \, ml} \mu_{\text{ext}} (Q_i) \Delta Q.
\]

In the example of Fig. 13, the relative amount of fraction-wise material in the total sample is 24.4% for fraction A and 75.6% for fraction B. Here it is necessary to consider that the response of the optical signal, in this case extinction coefficient, depends on the properties of the sample, such as the size and shape distribution of the particles. Fines have a relatively stronger effect on extinction than fibers due to the high scattering, but on the other hand fibers produce a stronger depolarization effect than fines. This difference in the responses can be compensated by combining measurement methods based on different physical phenomena (Laitinen, 2011).
new way for balancing the different responses is presented in section 4.3 of this thesis.

In this flow-based analysis method, the flow moment describes the properties of the particles being measured. Such a method based on flow moment is effective and usable, but it requires an accurately controlled and stable flow during the separation and measurement. However, flow control is challenging particularly in long-term use of the measurement system. Besides flow rate also other factors, such as the temperature and viscosity of the fractionation fluid and the properties of the tube wall, will further influence the fractionation occurring during the flow. Changes in these variables cause error in the fractionation calculation.

An example of how such an error can arise is shown in Fig. 14. In this case an error of about 1% occurs in the sample flow, meaning that the sample enters 150 ml before the correct arrival time. Such a situation may result for example from problems with the flow or temperature control. In this error situation, if the fraction limit separating the fines and fibers is not changed, there will be error in the determination of the fraction proportions. This disturbance in the flow situation would cause the fines content (Fraction A) to erroneously increase from 24.4% to 29.1%, which means an error of more than 4.5 percentage points in the measured fraction determinations.

Fig. 14. An example of the effect of a 1% error in the sample flow. The sample enters the 150 ml mark before the correct arrival time causing an error of more than 4.5 percentage points in the measured fraction determinations.
Such large errors rarely occur in practice if the control systems work, but even small errors can be significant when an accurate determination is needed. Technical defects in the components of the control system can, of course, cause an error in the measurement. This thesis presents an analysis method by which the flow and temperature control requirements can be significantly reduced.
4 Dynamic fractional analysis method

This chapter of the thesis describes a new dynamic fractional analysis (DFA) method that does not require information of the fluid flow, unlike the flow-based analysis (FBA) method described in section 3.3. In addition to basic quantity-indicating signals like extinction and de-polarization, the DFA method utilizes their interrelation that describes the qualitative fibrous property of the sample. A patent application has been published for the method (Törmänen, 2021).

This quality depicting fibrous index is presented in section 4.1. Section 4.2 describes a variable balancing the response differences between fines and fibrous material that can be used to measure the amounts of solids. The actual DFA method and the resulting fibrous index distribution are described in section 4.3. Size index, which provides the support variable for the fibrous index or is useful on its own, is presented in section 4.4, and finally section 4.5 presents the key figures to be calculated from the fibrous index distribution.

4.1 Fibrous index

In fiber suspension measurements a new term, fibrous index \((FI)\), is defined and used as the ratio between the depolarization and extinction coefficient signals. This ratio depicts how fibrous the sample is, and here it is referred to as

\[
FI = \frac{\mu_{DP}}{\mu_{ext}}, \tag{18}
\]

where \(\mu_{DP}\) is the amount of depolarized light and \(\mu_{ext}\) is the extinction coefficient, both defined in section 2.6. The elements of fibrous index are normally measured together at the same wavelengths.

The usefulness of the index is based on the selective response of the signals in the case of different elements of sample. Pure and unbroken fibers produce a strong depolarization signal in relation to the extinction signal, thus keeping the fibrous index high. Fines and fillers will produce the opposite, causing a low fibrous index.

The fibrous index and its source variables extinction and depolarization are shown as a function of flow in Fig. 15. The pulp sample is the same as in the examples in chapter 3. As can be seen from Fig. 15 a), when the fibers come first in the sample the depolarization reading is at first many times stronger than the extinction at the corresponding point. The order of intensity of the signals changes
as the sample proceeds from fibers to fines at a flow point of approximately 18 600 ml.

The fibrous index obtained in the signal division is shown in Fig. 15 b). Readings at flow moments when extinction and depolarization are zero or very close to it are not shown. When the signals are close to zero, there is strong noise in the fibrous index; on the other hand, this indicates that there is no significantly measurable sample material at that moment, and thus it is ignored as negligible.

The numerical value of the index directly indicates the fibrous property of that sample point: higher fibrous index value corresponds to more purely fibrous sample. Towards the fines fraction the fibrous index decreases to about 1, and the extinction and depolarization signal values are at the same numerical level. A low fibrous index value thus indicates that the sample is on average highly non-fibrous, like fines or fillers at that moment of flow.

Fig. 15. a) Signals $\mu_{\text{DP}}$ and $\mu_{\text{ext}}$, and b) new fibrous index variable (calculated as a ratio of signals $\mu_{\text{DP}}$ and $\mu_{\text{ext}}$) as a function of flow. In the fiber fraction the fibrous index is high, in fines fraction low, thus indicating the qualitative properties of sample.
Noise at the beginning of the fiber fraction is typical in optical measurements. The first fibrous material consists of coarse, partly still inseparable fibers, “shives”. The relatively large size and high opacity of such particles, combined with their small number, will leave the flowing sample spatially inhomogeneous. A single large particle can cause the measurement signal to become high, while the moment when there is no particle in the measurement produces a very low extinction or depolarization signal.

It is noteworthy that the fibrous index reacts mainly to the particle compositional property changes of the sample, but minimally to the concentration of particles. Such a compositional measurement eliminates the need to know the total amount of water flow and is usable as a dynamic property indicating variable, as will be represented in section 4.3.

### 4.2 Balanced concentration coefficient

As discussed in sections 3.3 and 4.1, the extinction coefficient is relatively much more sensitive to the quantity of fines than fibers. This is due to the higher specific surface area of the fines compared to that of fibers: a certain amount of fines per gram scatters light many times more than the same amount of fibers per gram. The depolarization signal behaves in the opposite way: it is relatively more sensitive to fibers than fines.

The normal method in optical particle amount measurements is to refer and calibrate the results with the amount of dry matter analyzed in the laboratory. This is also the case with pulp and paper industry measurements. The sensitivity difference results in a large calibration factor variation between separate particle fractions. This variation in calibration can cause problems especially if the particle quality determination is disturbed for some reason and fines are interpreted as fibers or vice versa. Ideally, the particles would have the same calibration factor, so that the total consistency or concentration would remain error-free even if the different fractions could not be distinguished from each other.

Particle fraction sensitivities can be partially evened out by using a suitable model that takes into consideration both extinction and depolarization. The model used in the measurements of this work is based on the Euclidean distance of the extinction and depolarization coefficients from the origin in extinction–depolarization coordinate system. Here the origin still corresponds to water value measurements. This is designated as balanced concentration coefficient $\mu_B$ which was calculated as
\[
\mu_B = \sqrt{\mu_{\text{ext}}^2 + \mu_{\text{DP}}^2}.
\]

In the calculation the sensitivity differences between the different components are equalized, by which the fraction-wise calibration is harmonized better than in methods that use only the extinction or depolarization signal alone.

The extinction and depolarization coefficients of the sample and the balanced concentration coefficient formed based on them is shown in Fig. 16. The value of \(\mu_B\) follows the envelope curve of both source signals \(\mu_{\text{ext}}\) and \(\mu_{\text{DP}}\).

![Fig. 16. Balanced concentration coefficient based on Euclidean distance. The extinction coefficient \(\mu_{\text{ext}}\) is depicted by a gray solid line and the depolarization coefficient \(\mu_{\text{DP}}\) by a gray dotted line. Balanced concentration coefficient forms an envelope curve of both source signals thus harmonizing the response over all fractions.](image)

When pulp contents are compared fraction-specifically, also calibration must be done for each fraction due to the sensitivity differences. Even after the balanced concentration coefficient calculation, the fraction with fibrous material will require a different calibration than the fines fraction. In order to have comparable quantities for the different parts of the distribution, a weighting factor function can be used in the measurement to weight the quantities of the different materials by a factor corresponding to their response. The use of this weighting factor function for calibration will be described in section 6.1.
4.3 Fibrous index distribution

The DFA method is based on simultaneous qualitative and quantitative analysis of the fractionated sample flow. Quality is here described by the fibrous index and the balanced concentration $\mu_B$ is used as a variable describing the quantity.

The principle of the method is illustrated in Fig. 17. The fibrous index is presented in Fig. 17 a), and the concentration $\mu_B$ in Fig. 17 b), both as functions of flow. Fibrous index values are shown and considered in this example only for the moments when $\mu_B$ is greater than the limit value of 0.00035. Very small $\mu_B$ values are irrelevant because a small value means that there are no measurable amounts of particles at that flow point: the sample corresponds to water. Fig. 17 c) presents the formation of fibrous index distribution.

High fibrous index values indicate that fibers are present at the beginning of flow, and the fibrous index value decreases as the flow continues and the fibrous property of the particles reaching the measurement point decreases.

The classification of a sample begins with the definition of quality grades. In this example, the fibrous index is divided into 20 quality classes of 0.5 units each. This classification is described in Fig. 17 a) as horizontal dashed lines.

Those sample points where the numerical value of fibrous index is within a quality class are counted as belonging to that category. In the example, the lowest category between 0 and 0.5 is seen to include sample points with flow readings between 18 720 and 20 450 ml. Respectively, the next fibrous index category between 0.5 and 1.0 includes samples between flow moments of 18 630 and 18 720 ml. In this way, $\mu_B$ values in all moments in the flow are summed into some classified category.

The categorial particle concentration of the samples in the lowest class 0 to 0.5 is obtained from the corresponding area of the $\mu_B$ curve of the graph in Fig 17 b). This area is colored dark gray in the graph. Concentration of the depicted area is calculated as a Riemann sum of balanced concentration coefficient $\mu_B$ through flow points $i$ included in the category by using equation

$$\mu_B(FL_i) = \sum_{i=18 720 ml}^{20 450 ml} \mu_B(Q_i) \Delta Q = 8.75.$$  

This reading of 8.75 is placed on the fibrous index distribution graph as the first numerical value of the distribution. The corresponding fibrous index value is 0.25, the average value for the given category. In measurement, the sampling interval $\Delta Q$ has been 1.85 ml.
Fig. 17. Fibrous index distribution determination using DFA. The fibrous index in a) is divided into 20 quality classes of 0.5 units each. Sample points with a numerical fibrous index value within a quality class are counted as belonging to that category. In b) the categorial particle concentration of the samples in each quality class is obtained from the corresponding area of concentration $\mu_B$ curve. In c) Categorized concentration value is calculated as Riemann sum of $\mu_B$ and placed on the fibrous index distribution graph.
The particle concentration in the following category between 0.5 and 1.0 is calculated accordingly:

\[
\mu_B(FI_2) = \sum_{i=18.720 \text{ ml}}^{18.720 \text{ ml}} \mu_B(Q_i) \Delta Q = 0.80. \tag{21}
\]

This reading shifts to the second value of the fibrous index distribution at value 0.75 which is an average of 0.5 and 1.0.

When the whole sample is classified in this way, the distribution shown in Fig. 17 c) is obtained. In this example the low fibrous index values thus correspond to the quantity of non-fibrous particles, high values to the quantity of fibrous particles. The material with a high fibrous index is usually pure, non-fibrillated fiber, while the lowest fibrous index class contains fines and especially material that does not include polarization-inducing fibers. Material in the medium fibrous index range has partially retained its fiber-like nature by pulverization or fibrillation.

In this example, the number of fibrous index quality classes is 20, but it can basically be any other positive number. The larger the number of classes, the narrower the fibrous index bars in the distribution graph will be.

### 4.4 Size index

When analyzing samples that contain fibrous particles, the fibrous index can be applied as a primary measurement that allows the classification of the sample. For example in tube flow fractionation the fibrous index is able to clearly indicate if the sample material in the flow is fines or fibers.

Another new term, size index (SI), is defined as the ratio of long and short wavelength extinction coefficient. In this work size index is explained as extinction coefficient ratio of

\[
SI = \frac{\mu_{\text{ext}}(\text{NIR})}{\mu_{\text{ext}}(\text{Vis})}, \tag{22}
\]

where \(\mu_{\text{ext}}(\text{NIR})\) is the extinction coefficient at near infrared wavelength and \(\mu_{\text{ext}}(\text{Vis})\) depicts extinction coefficient at visible wavelength. The formation of size index as a function of flow is illustrated in Fig. 18. In Fig. 18 b) the two extinction coefficients are shown as a function of flow. The calculated size index is in Fig. 18 a).
Fig. 18. Size index variable is calculated as the ratio of extinction coefficients of NIR and Vis wavelengths. Size index as a function of flow is in the upper part of the figure and the corresponding extinction coefficients in the lower part of figure. At the beginning of flow, size index indicates the cross-sectional dimension of the fibers, and later in the fines fraction all particle dimensions influence the size index.

This size index term describes most strongly the particle dimension closest to the wavelength: in the case of non-fibrous fines and filler particles, the width, length, and depth parallel dimensions of the particle, and, in the case of fiber particles, the cross-sectional dimensions.

4.5 Size index distribution

Based on the size index, a distribution can be generated in the same way as the fibrous index distribution explained in section 4.3. The size index distribution can be calculated to include all particles in the entire measurement. In this case, the size
index is thought to be the primary measurement, suitable for situations where the aspect ratios of the particles are not very different from each other.

If the sample consists of both fibers and fine materials with different aspect ratios, their size index data will interfere with each other. In this case it is not possible to distinguish whether the numerical value of the size index is due to the cross-sectional dimension of the fiber or to the dimensions of the fines.

To avoid this problem, size index can be used as a secondary measurement of the fibrous index. The fibrous index can be used to identify whether the currently measured set of particles consists of fibers or fines. In this way, the fiber and fines fractions can have their own, separate size index distributions. The formation of the size index distribution of the fines fraction determined from the fibrous index is shown in Fig. 19. In Fig. 19 a), the flow moments at the beginning of the size index graph are interpreted as belonging to the fiber fraction, based on the fibrous index.

In the calculation of the fines size index distribution, these flow points containing fibers, marked in gray, are disregarded. Only the fines particles, arriving after flow moment of 18 600 ml, are taken into consideration when calculating the distribution. At the fiber fraction limit the size index signal is about 0.7 and it decreases as the flow progresses. This indicates that the particle size decreases as a function of flow.

The procedure is analogous to fibrous index calculation. The size index in Fig. 19 a) is divided into 20 quality classes of 0.05 units, and each quality class contains the sample points that include fines fractions whose numerical size index value is within the quality class. In Fig. 19 b) the categorial particle concentration of the samples in each quality class is obtained from the corresponding area of concentration $\mu_B$ curve, and in Fig. 19 c) the categorized concentration value is calculated as Riemann sum of $\mu_B$ and placed on the size index distribution graph.

In this example, the number of size index quality classes is 20, but like in the fibrous index distribution example, it can basically be any other positive number. The larger the number of classes, the narrower the size index bars in the distribution graph.
Fig. 19. Size index distribution of fines determination using DFA. The size index in a) is divided into 20 quality classes of 0.05 units. Sample points including fines fractions whose numerical size index value belongs to a quality class are counted as belonging to that category. In b) the categorial particle concentration of the samples in each quality class is obtained from the corresponding area of concentration $\mu B$ curve. In c) categorized concentration value is calculated as Riemann sum of $\mu B$ and placed on the size index distribution graph.
The fibrous index used as the primary measurement and the size index acting as the secondary measurement are described in Fig. 20. At the top of the figure is the fibrous index distribution, where the fines fraction is limited to the range 0 to 1 and fiber fraction to the range 1 to 10. Based on these fraction boundaries, a separate size index distribution has been formed for both fractions.

The fines fraction size indices have values below 0.75 as the amount decreases toward smaller size distribution values. The maximum readings of the distribution of the fiber fraction are also at 0.75 but are evenly distributed in both directions. This is partly due to the greater inhomogeneity of the fibers compared to fines, which produces noise in the measurement.

In any case, it can be concluded from the distribution that the sample in question has two different fractions: the fiber fraction in the range of 6 to 9 in fiber index and the fines fraction in the range of 0 to 1.

If the bar values in the fractions were summed together, a reading proportional to consistency would be obtained. Based on this, it could be concluded that there is more material in the fiber fraction than in the fines fraction because the total of the bar values is higher. However, these vertical axis balanced concentration $\mu_b$ readings have not yet been calibrated to correspond to real consistency readings, so there will be an error in the interpretation. Calibration for consistency values will be presented on chapter 6.
Fig. 20. Fibrous index distribution as the primary measurement, size index distribution as the secondary measurement. At the top of the figure is the fibrous index distribution, where the fines fraction is limited to the range 0 to 1 and fiber fraction to the range 1 to 10. Based on these fraction boundaries, a separate size index distribution has been formed for both fractions. Size index distributions for all fractions can be calculated based on the fibrous index and the size distribution data of different particle classes can be distinguished from each other. Only the width of the classification window used to determine the fibrous index limits the number of fractions and thus the number of fraction classes can be the same as the number of bars in the distribution.

The size indices seem to be within the same range in both fractions in Fig. 20. However, it should be noted here that the indices are not absolute size figures but rather indicative. Thus, the same numerical values of the size index for different particles do not mean that the dimensions of the particles are necessarily the same.

The cross-sectional geometry of fibers basically includes two fiber walls and a hollow lumen between them. Naturally there are also fiber walls above and below the lumen, but when those are transverse to the incoming direction of the light, they are partially transparent. Probably in the case of non-flattened fibers, the size index reacts through scattering to the dimensions of the fiber wall thickness. If, on the
other hand, the fibers are flattened, then the situation can be very different in terms of the size index.

### 4.6 Key characteristics

The distribution figures describe the status of the process and are informative, especially for process operators. From the distribution plot, one can see immediately the fibrous index distribution of the measured sample and, if necessary, the fractional size index distribution. In process control, however, distribution information is not useful as such but requires unambiguous numerical values.

As shown in the examples above, we can derive certain key characteristics from the distributions and depict quantities and properties of each fraction of the measured sample.

The total consistency of the sample is obtained by integrating the entire distribution (fibrous or size index distribution). When integrating the distribution by fractions we obtain fraction-specific consistencies: for example long-fiber, medium-fiber, and fines consistency. When particularly high accuracy is required, the quantity signal used for the consistency definitions should be calibrated by using a weighting factor function. However, even without calibration the ratio of the values describes the changes in the relative quantities of fines and fibers in relation to the total consistency.

We can also produce for example fraction-specific mean values, weighted mean values, or values based on distribution symmetry. The fraction-specific weighted mean describes the mean property of the fraction in question: as an example, the weighted mean of the fibrous index for the fines fraction in Fig. 20 is about 0.29, for the fiber fraction value it is about six. If the weighted mean values increase, it can be confirmed that the particles of that fraction have become more fibrous. Correspondingly, when the weighted mean values of the size index distribution decrease so does the mean particle size, and vice versa.
5 Performance of the DFA method

The DFA method solves several uncertainties related to fractionation conditions. The method appears to be substantially more independent of changes in sample consistency, water temperature and water flow rate compared to the flow-based method.

This chapter discusses the distribution of the sample into different fractions and, above all, the error related to the relative proportions of these fractions by two different methods of analysis. It is good to note that the variable describing the quantity in this chapter is the extinction coefficient, which has a different response to the consistency caused by the fibers and the consistency produced by the fines.

The fraction ratios calculated based on the extinction coefficient therefore do not directly produce the real fines content, instead giving an uncalibrated, extinction coefficient related fines fraction content. The real fines content requires consistency calibration, which will be more specifically discussed in chapter 6.

5.1 Linearity of optical measurements

Optical measurement methods are naturally suited for tube flow fractionation because of the relatively small sample volumes and concentrations. The properties of tube flow fractionation and optical measurement support each other, producing a very efficient combination for material analysis. Dilution of the sample by fractionation and the separation of the different particles into their own sets offer a significant advantage especially for optical measurement techniques.

Division calculation of signals supposes that the signals start from zero value in water reference and are linear. For extinction signals this is true at relatively low consistencies, and also the depolarization signal is somewhat linear at low consistency. However, linearity is not an absolute requirement but it improves the resolution of fractionating measurements when DFA is used.

In fractionation, the sample is divided over a long distance in the tube and thus it is diluted from the original consistency. This dilution keeps the extinction and depolarization signals in the linear range.

To ensure that the measurements are in the linear, single scattering region, two samples were measured with two different path lengths and at two wavelengths, visible (Vis) and near infrared (NIR).

The samples were pure eucalyptus pulp (Euca) and pure ground calcium carbonate (GCC). Different path lengths were implemented by using two separate
optical measurement modules installed on the same circulation loop, as seen in Fig. 21. The circulation loop is needed to avoid sample sedimentation and to keep the sample flow homogeneous. Continuously flowing sample also serves the averaging which is needed because of the inhomogeneous nature of fiber pulp.

![Diagram](image)

Fig. 21. Measurement arrangement for linearity check. Two modules with different path lengths ($L$) are in same sample circulation loop. The sample is pumped through the measurement modules back to the sample tank.

The lower module, number 2 in the circulation loop, was equipped with path length $L = 3.5$ mm and upper module 1 with path length $L = 1.5$ mm. Pure water measurement was done first, and these water measurements were used as reference points in the extinction measurements. This means that extinction value 0 corresponds to water absorption value at a given wavelength.

The extinction measurement results at Vis and NIR wavelengths are shown in Fig. 22 and Fig. 23, respectively, and the depolarization measurement results are shown in Fig. 24.
Fig. 22. Extinction coefficients obtained with two different path lengths at near infrared wavelength. Coefficients measured with eucalyptus fiber suspension on the left and calcium carbonate suspension on the right. Extinction remains linear under 0.4 mm⁻¹ values.

Fig. 23. Extinction coefficients obtained with two different path lengths at visible wavelength. Coefficients measured with eucalyptus fiber suspension on the left and calcium carbonate suspension on the right. Extinction remains linear under 0.4 mm⁻¹ values.
The measurement with a longer path length can be interpreted to be in the linear region if its extinction coefficient value is identical to the shorter path length measurement. At a consistency where the response of a longer path length measurement deviates from a shorter one, a nonlinear multiple scattering range is entered. Based on the results in Fig. 22 and 23 the region is linear enough, if the extinction coefficient is below 0.4 mm\(^{-1}\). This conclusion is valid at least for particles bigger than the GCC used in these studies.

![Fig. 24. Depolarization obtained with two different path lengths at the visible wavelength. Coefficients measured with eucalyptus fiber suspension on the left and calcium carbonate suspension on the right.](image)

In Fig. 24 the depolarization signals of the eucalyptus fiber sample are linear and unique up to value 0.4; for the GCC sample they seem to be nearly zero if the consistency is very low, under 0.1 Cs-%. The zero response means that the depolarization signal in low consistencies does not react to GCC and thus the measurement is sensitive only to the existence of fiber material.

Calcium carbonate is a birefringent material in the same way as the crystalline parts of cellulose fibers. The reason for the minimal response of calcium carbonate to the measurement of depolarization at low consistencies compared to fibers is likely to be in a different relationship between scattering properties and opacity. Small carbonate particles scatter light more strongly than fibers, being more opaque. In this way, the light rays passing through the fibers can react relatively more
strongly with the birefringent material, whereby the measured depolarization is also stronger. However, the assumption of linearity is only valid in a limited consistency range, and the linear range of the measurement will be reduced when the measurement distance increases. At low consistencies the depolarization measurement reacts to the amount of fibers whereas at higher consistencies, where multiple scattering occurs, it will react to all materials that cause scattering. Still, when compared to extinction measurement the depolarization measurement is less oversensitive to fillers or fines in relation to changes in consistency.

5.2 Effect of consistency variations on analysis methods

The consistency of the sample affects fractionation, causing error in flow-based analysis. This section describes the error caused by the consistency variation when using the FBA and the DFA method. The same test results are also examined for consistency calibration and consistency measurement in sections 6.1 and 6.2.

Materials and methods

The parameters and variables of the fractionation system used in this test are shown in Table 1. This test involved the measurement of only one light source operating at near infrared wavelength. As an exception to other measurements in this thesis, both extinction and depolarization measurements for fibrous index have been made at near infrared wavelength, while in all other tests the wavelength has been in visible. The optical path length of the cuvette is 2 mm.

Table 1. Parameters and variables used in consistency variation test.

<table>
<thead>
<tr>
<th>Parameter or variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate</td>
<td>5.7 l / min</td>
</tr>
<tr>
<td>Water temperature</td>
<td>25 °C</td>
</tr>
<tr>
<td>Length of fractionation tube (material: FEP)</td>
<td>100 m</td>
</tr>
<tr>
<td>Inner diameter of fractionation tube</td>
<td>16 mm</td>
</tr>
<tr>
<td>Diameter of fractionation tube coil</td>
<td>50 cm</td>
</tr>
<tr>
<td>Sample volume</td>
<td>200 ml</td>
</tr>
<tr>
<td>Wavelength 1 (Extinction and depolarization)</td>
<td>Near infrared</td>
</tr>
<tr>
<td>Wavelength 2 (Extinction)</td>
<td>-</td>
</tr>
<tr>
<td>Optical path length</td>
<td>2.0 mm</td>
</tr>
</tbody>
</table>
Five different pulp samples were measured at several consistencies between 1 and 16 g/l. Three of the samples were thermomechanical pulps (TMP) and two chemical pulp samples. Pulp type of samples were:

- Pine pulp (Pine),
- Eucalyptus pulp (Euca),
- Unscreened TMP (TMP),
- TMP reject refining feed (TMP BR) and
- TMP after reject refining (TMP AR).

The unscreened TMP is inherently rich in fines detached from the fibers and the fibers are broken and deformed. The fines of TMP are fibril-like and very small in size. The amount of fines in TMP is typically rather high, as seen also in this case.

In the TMP process the pulp is screened so that the non-separated fiber bundles or shives are directed to reject refining. The rejected pulp thus contains a lot of coarse fiber bundles and less fines than the accepted pulp. The target of reject refining is to refine the non-fibrous sticks into usable individual fibers. The TMP after reject refining has thus more fines material and the fibers are more finely divided than in the reject refining feed.

The chemical pulp samples, Euca and Pine, were non-refined and thus contain mainly unbroken fines and only small amounts of fines. The fines of chemical pulp samples are largely composed of parenchyma cells naturally present in hardwood. These differ greatly in size and composition from the fines of TMP.

**Results**

Of the results of this test, only the results of the TMP sample are presented by way of example. The equivalent results of the other samples are given in Appendix 1. Section 5.4 summarizes the results of all experiments.

The extinction coefficient of the TMP sample as a function of flow at four different consistencies is illustrated in Fig. 25. As the consistency increases from 2 to 15 g/l, the area covered by the extinction curve increases correspondingly.
Fig. 25. The extinction coefficient of the TMP sample as a function of flow at four different consistencies. A flow-based limit is set for 18 000 ml, before which the material is mainly fiber and after limit the fines. The area covered by the extinction curve increases in corresponding proportion to sample consistency.

In Fig. 25 a flow-based limit is set for 18 000 ml. Before the limit the material is mainly fiber, after the limit mainly fines. The increase in consistency slightly accelerates the arrival of particles in the measurement. In this case, as the arrival time accelerates, the first particles of the fines fraction will erroneously be mapped to the fiber fraction.

The corrective effect of the DFA method on the TMP sample consistency variations is seen in Fig. 26. The fibrous index indicates the conversion of sample material from fibers to fines. Fibrous index value 0.9 is used here as the limit value for fines. Based on the graphs, as consistency increases the limit value between fiber and fines decreases to the previous flow readings which was already visualized in Fig. 25. The black dotted line in Fig. 26 represents the fraction limit value of fibrous index: the region above it represents the fiber fraction (FR2), the region below the fines fraction (FR1).

The colored dashed lines starting from the intersection point of the fibrous index and the fraction limit describe the flow moments of the fraction change at different consistencies. The dots at the end of the dashed lines represent the displaced fraction limits in the extinction coefficient plots.
Fig. 26. The corrective effect of the DFA method on the TMP sample consistency variations. The black dotted line represents the fraction limit value in fibrous index. The intersection of fibrous indices and fraction limit value indicates the flow value where the fraction changes. The increasing consistency decreases the limit in flow value.

The fraction ratios of TMP samples generated based on the extinction coefficient areas are shown in Fig. 27 as a function of sample total consistency. Sample consistency has swept from 1 to 15 g/l.

The share of FR1 of the whole amount calculated according to the fixed fraction limit by FBA is shown with blue markers and the corresponding share calculated dynamically according to the DFA with orange markers. The measurements are the averages of five parallel measurements. Dotted lines indicate the linear regressions, continuous lines the standard deviation values of the measured points.
Fig. 27. Fines fraction (FR1) share as function of sample consistency in TMP sample. Blue and orange markers indicate the FR1 share calculated with FBA and DFA methods respectively. Dotted lines indicate the linear regressions, continuous lines the standard deviation values of the measured points. Sample consistency variations effects remarkably less when used DFA.

The fraction 1 share obtained by the DFA method remains almost unchanged in terms of consistency. On average, the increase is 0.0814 percentage points for Cs unit of 1 g/l. This consistency related error is about one hundredth compared to the flow-based method, where it is $-0.7081$ percentage points.

Uncertainty in sample preparation and dosing contributes to the FR1 share of the sample, which is reflected in the variation of the individual measurement points relative to the mean of the sample set.

This is caused by the strong tendency of fiber particles to sediment in aqueous suspension and it poses challenges to sample set dilutions and dosage. Taking a known sub-sample from a larger sample volume for dilution and dosing requires efficient mixing to ensure that the different particle types and sizes are homogeneously distributed in the volume. This kind of uncertainty in sample preparation and dosing contributes to the incorrect fraction shares of the pulp sample.
5.3 Effect of temperature variations on analysis methods

In order to study the effect of water temperature changes on fractionation results, a temperature test was executed with two different pulp samples. This section describes the results of this experiment for the operation of both the FBA method and the DFA method.

Materials and methods

In the test the water temperature was changed between 15 °C and 40 °C at intervals of 5 °C. The sample pulps were eucalyptus pulp and pine pulp in constant consistencies. The parameters used in fractionation are shown in Table 2.

Table 2. Parameters and variables in temperature effect study.

<table>
<thead>
<tr>
<th>Parameter or variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate</td>
<td>5.7 l/min</td>
</tr>
<tr>
<td>Water temperature</td>
<td>15–40 °C</td>
</tr>
<tr>
<td>Length of fractionation tube (material: FEP)</td>
<td>100 m</td>
</tr>
<tr>
<td>Inner diameter of fractionation tube</td>
<td>16 mm</td>
</tr>
<tr>
<td>Mean diameter of fractionation tube coil</td>
<td>50 cm</td>
</tr>
<tr>
<td>Sample volume</td>
<td>200 ml</td>
</tr>
<tr>
<td>Wavelength 1 (Extinction and depolarization)</td>
<td>Visible</td>
</tr>
<tr>
<td>Wavelength 2 (Extinction)</td>
<td>Near infrared</td>
</tr>
<tr>
<td>Optical path length</td>
<td>3.5 mm</td>
</tr>
</tbody>
</table>

All results analyzed in this section use the extinction coefficient of the visible wavelength range to measure the quantity of sample fractions.

Effect of temperature on the FBA method

The change in the extinction signals of pine and eucalyptus pulp caused by temperature changes is shown in Fig. 28. The peak position of fiber fraction at 15 °C in pine pulp is about 16 500 ml and changes by about 700 ml as temperature increases to 40 °C. The corresponding change of the fiber fraction peak position in eucalyptus pulp is about 400 ml with this temperature change of 25 °C.

The changes in the fines fraction are smaller than in the fiber fraction. The peak of the pine pulp changes from 18 500 ml to about 18 700 ml, the difference being about 200 ml. Peak transition of both pulp types are of the same order.
Fig. 28. Effect of fractionation water temperature on the attenuation signal in pine and eucalyptus pulps. Increasing temperature moves the extinction signals towards later flow values which is seen in both pulp samples. The vertical dashed line represents the flow-based fraction limit. The relative proportions separated by the fraction limit change significantly as the temperature changes.

In the figures a vertical dashed line represents the flow rate based fraction limit. The fraction limit of pine measurements in Fig. 28 is set to 18 000 ml in the distribution, which is the local minimum of 15 °C measured fractogram. This local minimum reveals that the fiber amount is decreasing and the fines amount increasing, and thus the sample material grade is changing in the flow. In the same way the limit is set for 18 300 ml for eucalyptus pulp.

When temperature increases the fractogram moves towards later flow values, which is seen with both pulp samples. Despite controlled flow conditions, the distribution along the flow has changed as function of temperature. This is just the problem with flow based fractional analysis: when sample components arrive to measurement at different times due to temperature changes, fraction determination is disturbed.
Effect of temperature on the DFA method

The change in the fibrous index distributions of pine pulp caused by temperature change is shown in Fig. 29. The distinguishable fiber and fines fractions corresponding to the fractograms in Fig. 28 are visible in the distributions. The fines fraction in the graphs is roughly in the fibrous index range of 0 to 2 and the fiber fraction in the range of 2 to 7. For comparison, all graphs show the distribution measured at 15 °C in red.

It can be seen from the distributions that they remain very similar even if the fractionation temperature changes significantly. Specifically, the fines fraction remains unchanged in relation to both the fibrous index and the shape of the distribution. Small changes in the fiber fraction are observed especially at temperatures of 35–40 °C compared to lower temperatures: the highest fiber index values are eliminated and the distribution shifts slightly toward lower readings.

Most probably, this is because tube flow fractionation with hot water does not separate the different particles as efficiently as it does at colder temperatures. Among the particles having a high fibrous index, there are overlapping ones with a lower fibrous index and thus the average reading of these becomes the fibrous index to be measured.
Fig. 29. Fibrous index distribution of pine pulp at six temperatures, DFA calculation.

The corresponding change in the fibrous index distributions of eucalyptus pulp caused by temperature change is illustrated in Fig. 30. The red graph also shows the 15 °C temperature distribution as a reference. In the same way the fibrous index distribution of the eucalyptus pulp sample has kept the fines and fibers fractions separate, as seen in figure.
When comparing the shapes of these distributions, the eucalyptus pulp has more deviation as a function of temperature but the fibrous index remains mainly in place here as well. A similar issue of fractionation resolution can also be seen here: as the temperature increases, the fiber fraction shifts toward lower fibrous index readings. The fines fraction here also appears to be moving toward lower fibrous index readings. The reason for this remains unclear.

**Summary of temperature effects**

In Fig. 31 fraction contents of both pulp samples calculated by using extinction coefficient in visible wavelength are presented. Fraction 1 that includes the fines fraction is marked as FR1 in the figures. The FR1 share for the whole amount calculated by FBA is shown with blue markers and the corresponding share calculated by DFA with orange markers. The measurements are averages of five parallel measurements. The dotted lines indicate the linear regressions, continuous
lines the standard deviation values of the measured points. The deviations are calculated as the variation of five parallel measurements in relation to average values.

**Fig. 31.** Fraction content as function of fractionation water temperature in eucalyptus and pine pulps. Blue and orange markers indicate the FR1 share calculated with FBA and DFA methods respectively. Dotted lines indicate the linear regressions and continuous lines the standard deviation values of measured points. The effect of temperature is remarkably smaller when using DFA.

The temperature of the fractionation water has a significantly smaller effect on the results obtained with the DFA method than with the FBA method. Based on the results for these pulp types, the changes caused by temperature are well controllable when using dynamic fractional analysis.
5.4 Effect of flow rate variations on analysis methods

The effect of water flow rate changes on fractionation results was studied at two different flow rates. This section describes the results of this experiment with regard to the operation of the analysis methods.

Materials and methods

The test was performed at two different fractionation water flow rates: 4.5 l/min and 5.6 l/min. Three parallel measurements were carried out for both flow rates. The sample was eucalyptus pulp with added GCC filler, 10% of the dry weight. The consistency of sample was 7 g/l. The parameters used in fractionation are shown in Table 3.

Table 3. Parameters and variables in flow rate effect study.

<table>
<thead>
<tr>
<th>Parameter or variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate</td>
<td>4.5–5.6 l/min</td>
</tr>
<tr>
<td>Water temperature</td>
<td>22 °C</td>
</tr>
<tr>
<td>Length of fractionation tube (material: FEP)</td>
<td>100 m</td>
</tr>
<tr>
<td>Inner diameter of fractionation tube</td>
<td>16 mm</td>
</tr>
<tr>
<td>Mean diameter of fractionation tube coil</td>
<td>50 cm</td>
</tr>
<tr>
<td>Sample volume</td>
<td>200 ml</td>
</tr>
<tr>
<td>Wavelength 1 (Extinction and depolarization)</td>
<td>Visible</td>
</tr>
<tr>
<td>Wavelength 2 (Extinction)</td>
<td>Near infrared</td>
</tr>
<tr>
<td>Optical path length</td>
<td>3.5 mm</td>
</tr>
</tbody>
</table>

As in the previous sections, all results analyzed in this section use the extinction coefficient of the visible wavelength range to measure the quantity of sample fractions.

Results

In Fig. 32 the fraction contents by using extinction coefficient at visible wavelength are presented. Fraction 1 that includes fines fraction is marked as FR1 in figures. The FR1 share for the whole amount calculated by FBA is shown with blue markers and the corresponding share calculated by DFA with orange markers. The measurements are averages of three parallel measurements. The dotted lines indicate the linear regressions and continuous lines the standard deviation values.
of the measured points. The deviations are calculated as the variation of parallel measurements in relation to average values.

![Graph showing Eucalyptus + 10% GCC fraction content as a function of fractionation water flow rate.](image)

**Fig. 32.** Fraction content as function of fractionation water flow rate in eucalyptus pulp added with 10% GCC. Blue and orange markers indicate the FR1 share calculated with FBA and DFA methods respectively. Dotted lines indicate the linear regressions and continuous lines the standard deviation values of measured points. The effect of flow rate is remarkably smaller when using DFA.

The flow rate of the fractionation water has a significantly less effect on the results obtained with the DFA method than with the FBA method. Based on these results, the changes caused by flow rate are well controllable when using dynamic fractional analysis.
5.5 Summary of flow condition variation effects

The effect of the fractionating variables described in the previous sections is summarized in Table 4. The first five rows describe the varied sample consistency effects with different pulp types, the next two rows concern the water temperature variation effects with two different pulp types and the last row shows the effect of varied water flow effect for one sample.

Table 4. Comparison between FBA and DFA methods when sample consistency, water temperature and flow rate varies. Mean error values and the corresponding standard deviations of 1 σ are shown.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cs g/l</th>
<th>T °C</th>
<th>Flow l/min</th>
<th>FBA Error %-point / g/l</th>
<th>DFA Error %-point / g/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>Varied consistency</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pine pulp</td>
<td>1–10</td>
<td>25</td>
<td>5.7</td>
<td>−0.534 ± 0.194</td>
<td>+0.003 ± 0.100</td>
</tr>
<tr>
<td>Eucalyptus pulp</td>
<td>2–16</td>
<td>25</td>
<td>5.7</td>
<td>−0.336 ± 0.108</td>
<td>−0.012 ± 0.054</td>
</tr>
<tr>
<td>Unscreened TMP</td>
<td>1–15</td>
<td>25</td>
<td>5.7</td>
<td>−0.708 ± 0.148</td>
<td>+0.078 ± 0.130</td>
</tr>
<tr>
<td>TMP reject refining feed</td>
<td>2–8</td>
<td>25</td>
<td>5.7</td>
<td>−0.433 ± 0.153</td>
<td>+0.035 ± 0.151</td>
</tr>
<tr>
<td>TMP after reject refining</td>
<td>2–8</td>
<td>25</td>
<td>5.7</td>
<td>−0.775 ± 0.152</td>
<td>+0.109 ± 0.266</td>
</tr>
<tr>
<td>Varied Temperature</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pine pulp</td>
<td>7</td>
<td>15–40</td>
<td>5.7</td>
<td>+0.237 ± 0.031</td>
<td>+0.020 ± 0.061</td>
</tr>
<tr>
<td>Eucalyptus pulp</td>
<td>7</td>
<td>15–40</td>
<td>5.7</td>
<td>+0.560 ± 0.038</td>
<td>+0.034 ± 0.041</td>
</tr>
<tr>
<td>Varied flow rate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eucalyptus pulp + 10% GCC</td>
<td>7</td>
<td>22</td>
<td>4.5–5.6</td>
<td>+5.649 ± 0.060</td>
<td>+0.730 ± 0.057</td>
</tr>
</tbody>
</table>

In the consistency test the high standard deviations are caused by uncertainties of sample preparation and dosages. In the other tests the same sample was used for all variations in temperature and flow without need for sample preparation or dilution. This reduces the standard deviation values.

The results are also illustrated in Fig. 33, which shows the errors and their standard deviations in different situations. The blue markers correspond to the results obtained by the DFA method and the orange markers correspond to the results obtained by the FBA method. On the left are the errors caused by the variation in sample consistency, in the middle the water temperature and on the right the water flow rate.
Fig. 33. The errors in FR1 share and their standard deviations in different situations. The blue markers correspond to the results obtained by the DFA method and the orange markers correspond to the results obtained by the FBA method. On the left are the errors caused by the variation in sample consistency, in the middle the water temperature and on the right the water flow rate.

Variations in sample consistency and variations in the temperature of the water used for fractionation are excellently corrected when using the DFA method. The proportion of FR1 remains the same within the $1\sigma$ uncertainty in all the situations considered in these experiments.

Changes in fractionation water flow rate are significantly less affected in the DFA method than in the FBA method. However, based on this experiment the DFA method leaves an error of just under 1%-point for each change at flow rate 1 l/min. The corresponding error with the FBA method is about fivefold, being just under 6 %-point.
6 Consistency measurements using DFA

Tube flow fractionation enables separate measurement of different particle types in the sample. This creates previously untapped opportunities for more efficient consistency measurement. These issues are of great importance due to the widespread need of consistency measurements and their high significance.

This chapter deals with the measurement of consistency based on the DFA method. The first two sections of this chapter deal with the measurements described in the previous section 5.1 for consistency calibration. Section 6.1 describes the operation of the weighting factor function used in calibration through these measurements, and section 6.2 examines the behavior of consistency responses obtained through calibration. Section 6.3 presents a study in which subsamples separated from a pulp sample are mixed in a known ratio and the performance of the calibration is monitored.

6.1 Calibration by weight function

The most important phase in consistency measurement is calibration and tuning the measurement to indicate actual consistency. If the calibration and tuning fail, the obtained results will be fundamentally incorrect.

Today, the most widely used optical consistency measurements do not fractionate but instead measure all-inclusive samples. In this case it is challenging to perform a calibration that considers changes in the relative amounts of different particles in the measurement object.

The DFA method solves this problem by enabling a flexible way to calibrate the measurement as a function of the fibrous index. In calibration, a dynamic weighting based on the FI variable is created. Fines particles with a low FI reading will thus have a different weighting than fibrous particles with a high FI reading.

Fig. 34 shows three different samples of the test described in section 5.1 at a consistency of 7 g/l. The samples are made of pine pulp, eucalyptus pulp, and TMP and their fibrous index distributions are seen in Fig. 34. a)–c), respectively. Based on these three samples, the weighting factor function in Fig. 34 d) is formed. This function weights the \( \mu_B \) readings corresponding to each fibrous index so that the total consistencies are as close as possible to the actual total consistency, in this case 7 g/l. Here, an exponential function is used as the weighting factor function of
where $C_1$ is the gain and $C_2$ the exponent used in the weighting function. In these samples the best fit is achieved by $C_1 = 0.0518$ and $C_2 = -0.14$; when these are used the $\mu_B$ readings correspond to the known consistency.

Fig. 34. Calibration by weight function. Three samples: a) pine pulp, b) eucalyptus pulp, and c) TMP at a consistency of 7 g/l are used for calibration. Weight function in d) is fitted to produce the total consistency of 7 g/l for each sample.
The shape of the function in Fig. 34 d) indicates that the subsamples with low fibrous index are more strongly weighted than those with higher ones. Here, the difference of gain between fibers and fines is rather small due to the use of the balanced concentration coefficient $\mu_B$ instead of the extinction coefficient $\mu_{ext}$ as seen in section 4.3. In this case, an exponential function was used for calibration, but other types of functions can be used as well. For example, power functions are used in the calibrations described later in this thesis.

6.2 Consistency measurement of different pulp types

In this section the results of the calibration obtained in section 6.1 are examined.

Fig. 35 shows the calibrated fibrous index distributions of samples at 7 g/l consistency. Fibrous index is on the horizontal axis, the calibrated consistency values on the vertical axis. The distributions were divided into two fractions with the limit value between them at the fibrous index value 0.6. The fines fraction includes values below 0.6, the fiber fraction values above it.

The chemical pulp samples, pine and eucalyptus, are shown in Fig. 35 a) and b), respectively. Chemical pulp fibers are more uniform and fibrous than mechanical pulp fibers, which is reflected in their higher fibrous index value when compared to TMP in Fig. 35 c). Probably the longer fiber length of pine pulp in comparison to eucalyptus pulp is visible: the distribution is clearly weighted towards higher fibrous values. The fines fraction of the chemical pulp used here includes less sample material in the range 0.3–0.6 and there are no particles in the range below 0.3. It can be concluded that the morphological differences between the chemical pulp and mechanical pulp fines are visible in the measurement.

The refined mechanical pulps (TMP) contain significant quantities of fines, with remarkably lower fibrous index than chemical pulp fines. The TMP sample is original, unscreened refined mechanical pulp and its fines content is the highest, while its fiber fraction contains fibers of different qualities evenly distributed in the fibrous index range of 0.6–1.4.

TMP reject pulp taken from a reject refining feed is shown in Fig. 35 d). The fines content of this screening reject is very low compared to the unscreened TMP sample, but the fiber fraction still includes significant amounts of fibrous particles, which is shown in the distribution values at fibrous index value 1.3. The graph in Fig. 35 e) shows results for a sample taken after reject refining. In refining, the quantity of fibrous material decreases, and especially the quantity of fines increases correspondingly.
Fig. 35. Fibrous distributions at 7 g/l consistency for a) chemical pine pulp, b) chemical eucalyptus pulp, c) unscreened TMP, d) TMP before reject refining, and e) TMP after reject refining. Eucalyptus has a smaller amount of fines than TMP samples.

The samples are very heterogeneous in nature, as seen in Fig 35. However, the same calibration is used for all samples. Consistency responses of diluted sample series can be obtained by integrating the distributions fraction-specifically. The obtained fraction integrals are then represented as a function of the actual consistency, as seen in Fig. 36. The actual consistencies are calculated for each dilution point using the standard laboratory analysis as baseline data.
Fig. 36. The measured consistency responses of five pulps as a function of actual total consistency: chemical pulps a) pine and b) eucalyptus; TMP pulps c) unscreened, d) before reject refining, and e) after reject refining. Total consistency is indicated with crosses, fiber consistency with circles and fines consistency with squares. All responses are linear up to 10 or even 15 g/l.

The cross ticks in Fig. 36 correspond to the total consistency, the circles the fiber consistency, and the squares the fines consistency. In all samples included in the calibration data, TMP, eucalyptus and pine pulps, the slope of total consistency is
close to value 1 over the whole consistency range as seen in Fig. 36. a)–c) respectively. This indicates that the same calibration can be used to describe the consistency of these three very different pulp types.

For comparison, Fig. 36. d) and e) also show the TMP reject pulps before and after reject refining. These differ substantially from those used in the calibration of unscreened pulps, producing a much weaker response. The reason could be that the reject pulp consists to a considerable extent of unrefined fiber bundles and shives. In laboratory analysis these coarse particles cause a strong effect on the mass, but the optical response is weak relative to the amount of dry matter.

Table 5 numerically summarizes the results shown in Fig. 36. The table shows the consistency ranges, fines contents, error rates and $R^2$ correlations for all sample pulps. There is no reference analysis for fines content, so these results are unverified.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cs g/l</th>
<th>Fines content</th>
<th>Error %</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pine pulp</td>
<td>1–10</td>
<td>5.7 ± 0.7</td>
<td>-2.2%</td>
<td>0.9957</td>
</tr>
<tr>
<td>Eucalyptus pulp</td>
<td>2–16</td>
<td>7.4 ± 0.6</td>
<td>+2.2%</td>
<td>0.9983</td>
</tr>
<tr>
<td>Unscreened TMP</td>
<td>1–15</td>
<td>71.3 ± 1.0</td>
<td>+1.0%</td>
<td>0.9998</td>
</tr>
<tr>
<td>TMP before reject refining</td>
<td>2–8</td>
<td>26.3 ± 0.7</td>
<td>-22.3%</td>
<td>0.9988</td>
</tr>
<tr>
<td>TMP after reject refining</td>
<td>2–8</td>
<td>34.3 ± 1.0</td>
<td>-27.0%</td>
<td>0.9994</td>
</tr>
</tbody>
</table>

As a result of this test, it can be concluded that the consistency measurements of TMP, pine and eucalyptus pulps were performed using the same calibration. The same calibration produces almost the same responses. The responses start from zero in water value and are linear, which allows the calibration to be performed with gain alone, without an offset term. Gain can be produced as a function of the fibrous index, giving the pulp's various particles just the right weight. The calibration sample was only one sample per pulp species, but it has achieved the same calibration for these three very different types of pulps.

### 6.3 Consistency measurement of TMP fractions

In optical consistency measurements, the biggest challenge is usually posed by changes in the relative amounts of different particle components, which calibration cannot always cover. This can cause even large errors in consistency measurement.
This experiment was performed to see how variations in the relative amounts of two completely different pulp components are controllable for consistency measurement.

**Materials and methods**

In this test, the functionality of the DFA method in measuring two different fractions of thermo-mechanical pulp TMP was studied. The original TMP was separated by screening the sample through 48 mesh wire. The R48 part was used as the long-fiber (LF) sample and P48 as the short-fiber (SF) sample. These parts were mixed using seven known proportions.

The total consistency of all resulting samples was standardized to 3 g/l. The measurement parameters used in the test are shown in Table 6.

**Table 6. Parameters and variables used in TMP test.**

<table>
<thead>
<tr>
<th>Parameter or variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate</td>
<td>5.60–5.64 l/min</td>
</tr>
<tr>
<td>Water temperature</td>
<td>24.6–25.0 °C</td>
</tr>
<tr>
<td>Length of fractionation tube (material: FEP)</td>
<td>100 m</td>
</tr>
<tr>
<td>Inner diameter of fractionation tube</td>
<td>16 mm</td>
</tr>
<tr>
<td>Mean diameter of fractionation tube coil</td>
<td>50 cm</td>
</tr>
<tr>
<td>Sample volume</td>
<td>200 ml</td>
</tr>
<tr>
<td>Wavelength 1 (Extinction and depolarization)</td>
<td>Visible</td>
</tr>
<tr>
<td>Wavelength 2 (Extinction)</td>
<td>Near infrared</td>
</tr>
<tr>
<td>Optical path length</td>
<td>3.5 mm</td>
</tr>
</tbody>
</table>

**Results**

Consistency calibration was performed using two samples, one sample of pure SF fraction and one sample consisting of 10% SF and 90% LF fraction, at 3 g/l consistencies. The resulting weight function was a power function of

\[
C_s = \sum_{F_I=0}^{10} 0.0321 \times F_I^{-0.0283} \times \mu_B. \tag{24}
\]

This function strongly emphasizes the smallest fibrous index values, which is seen in Fig. 37.
The fibrous index and the corresponding size index distribution of all measured samples are shown in Fig. 38. The figure shows the fibrous index distributions on the left and the corresponding size index distributions on the right. The topmost graph shows a sample containing only the LF fractions, and as it goes down, the SF fraction gradually increases. The bottom figure then shows a sample containing only SF fractions. The markings in the figure describe the LF/SF ratio. For example, 100/0 means a sample containing 100% LF fractions and 50/50 represents a sample with 50% of both SF and LF fractions.

When analyzing the results, fibrous index value 1.2 was selected as the limit between fines and fibers: fines below and fibers above that value. The sample with only the long-fiber fraction also contains fines because screening has not succeeded to absolutely removing them all. However, the amount of fines is remarkably smaller than in the short-fiber sample. In addition, the fibrous index maximum value is higher for the long-fiber sample which could mean that the finest fines material would be screened away with water removal.

The short-fiber sample, in the bottom graph of Fig. 38, contains mainly fines material but also a small amount of the fiber fraction material in the fibrous index region between 1.2 and 8. This indicates that also bigger, more fibrous particles can pass through the screen in a suitable orientation.
Fig. 38. Fibrous index and size index distributions of long-fiber (LF) and short-fiber (SF) samples mixed in different ratios. The markings in the figure describe the LF/SF ratio.

The size index distributions in Fig. 38 describe that the samples have two distinct size index groups, one with a size index class of about 0.7 and the other with a size index class of 0.9. These groups arise from the different shape and size factors of the particles in the fines and fiber fractions. The weights of the distributions clearly change when the SF fraction is added to the pure LF sample. Initially, in the LF
sample, the higher peak of the fiber fraction's size index distribution decreases in relation to the fines distribution portion as it moves toward the SF sample.

This can also be seen in Fig. 39, which shows the size index distributions of the fines fraction and fiber fraction obtained through the measurement. The graph on the left shows the size distributions of the SF sample, the distribution of the fines fraction in blue and the fiber fraction in orange. Correspondingly, the graph on the right shows the distributions of the LF sample.

The fines distributions depicted in blue thus describe particles that are between readings 0 and 1.2 on the fibrous index axis, and the fiber fraction distributions depicted in orange are particles above the 1.2 fibrous index reading. In this way, in addition to fraction-specific consistency measurements, the DFA method can be used to obtain fraction-specific size index distributions.

![Fig. 39. Size index distribution of short-fiber (left) and long-fiber (right) samples.](image)

The results of this test are summarized in Table 7. The 100/0 and 0/100 samples used in the consistency calibration are shown in bold. The weighted averages of the measured size index distributions are at the end of the table. The averages of the size indices of both the fiber and fines fractions remain quite unchanged, from which it can be concluded that the size index measurement is not remarkably disturbed by changes in the mixing ratios.
Table 7. Fractional consistencies and size index distributions of long-fiber (LF) and short-fiber (SF) samples mixed in different ratios. The samples used in consistency calibration are 90/10 and 0/100. Mean consistency and size index values and the corresponding standard deviations of 1σ are shown.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cs</th>
<th>Measured Cs [g/l]</th>
<th>Measured Size index</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LF/SF</td>
<td>g/l</td>
<td>Total</td>
</tr>
<tr>
<td>100/0</td>
<td>2.96</td>
<td>3.22 ± 0.14</td>
<td>2.63 ± 0.12</td>
</tr>
<tr>
<td>90/101</td>
<td>3.05</td>
<td>3.05 ± 0.08</td>
<td>2.29 ± 0.08</td>
</tr>
<tr>
<td>80/20</td>
<td>2.99</td>
<td>2.97 ± 0.10</td>
<td>2.02 ± 0.08</td>
</tr>
<tr>
<td>70/30</td>
<td>3.07</td>
<td>3.04 ± 0.12</td>
<td>1.90 ± 0.12</td>
</tr>
<tr>
<td>60/40</td>
<td>2.95</td>
<td>2.99 ± 0.12</td>
<td>1.69 ± 0.11</td>
</tr>
<tr>
<td>50/50</td>
<td>3.01</td>
<td>3.05 ± 0.08</td>
<td>1.55 ± 0.07</td>
</tr>
<tr>
<td>0/1001</td>
<td>2.99</td>
<td>2.99 ± 0.05</td>
<td>0.62 ± 0.04</td>
</tr>
</tbody>
</table>

1Samples used in calibration

The consistency measurements described in Table 7 and the corresponding total consistency analysis performed in the laboratory are shown in Fig. 40. The graphs are a function of the short-fiber (SF) content.

The figure shows the measured total consistency in blue and the corresponding laboratory consistency analyses in black. The measured total consistency readings correspond well even to small variations in sample consistency with more than 10% short-fiber content.

This error in pure LF sample is most likely due to problems with sampling. When taking a subsample of a larger sample volume for measurement, the sample must be mixed until homogeneous to make the sample as representative as possible. The sedimentation properties of the samples strongly influence the success of subsampling. Samples composed solely of fibers sediment very strongly, just like the LF sample here. It appears that a relatively larger amount of fibrous material has occurred in the subsample taken for measurement than in the original sample.

The error is caused by the higher fiber content, as can be inferred from the fact that there is no deviation in the fines Cs curve at that point unlike in the fiber Cs curve. In general, the fines Cs curve is smooth and the variations in overall consistency come from variations in fiber consistency. This variation is presumably due to the abovementioned sedimentation and sub-sampling problems.
Fig. 40. Consistency measurements and the corresponding total consistency analysis performed in the laboratory. The measured fines Cs increase and fiber Cs decrease when short-fiber content increases. The measured total Cs corresponds well with laboratory total consistency.

This experiment shows that widely varying mixtures of two very different components can be measured well by the DFA method. One sample at both ends of the range is sufficient for calibration. The values of 10% and 100% SF content have been used in this experiment. It appears that the fractional fines Cs and fiber Cs operate logically, which is very promising even though no actual laboratory reference for these is available here.
7 DFA in nanomaterial measurements

The number of industrial-scale processes producing nanofibrillated cellulose and cellulose nanocrystals is currently small. However, a lot of research into wood-based nanomaterials is going on, and as processes and applications develop in the future their production is expected to increase. Alongside the development of applications and processes also a new type of measurement technology is needed, and one potential solutions for this is the DFA method.

This chapter explains how the phenomena occurring in laboratory scale Masuko grinding are reflected in the measurements made by the DFA method. The raw materials for the samples were two different types of HW fibers which were made into a grinding series in two ways: with and without chemical pre-treatment.

The Materials and methods section describes the preparation of all sample sets. The results of the NFC sample set are described in section 7.1 and the results of the CNC sample series are described in section 7.2.

Materials and methods

For the test, four sets of samples were performed at different grinding levels. The samples were produced at the University of Oulu, Fiber and particle engineering laboratory. Two sample sets were made of bleached birch pulp, and two of bleached eucalyptus pulp. Of these two series, one was NFC and the other CNC. The samples were ground using a Masuko supermasscolloider.

Masuko supermasscolloider is a laboratory scale friction grinding machine that produces ultra-fine particles from bigger ones. The ultra-fine grinding occurs between two non-porous ceramic grinding stones. The Masuko grinder was MKCA6-2J (Japan). The clearance between the upper and lower stones is adjustable in 10 µm increments and it has a strong effect on the particle size and quality of the refining product.

No chemical treatment was used in the manufacture of the NFC material, the fibers were ground as such. The NFC suspensions were ground at a consistency of 1.5 Cs-%. The pulps were passed through the grinder up to 20 times, using negative clearance values of −20 µm, −40 µm, −60 µm, −80 µm, −90 µm and −100 µm to obtain viscous NFC hydrogels.

The CNC suspensions were ground at 2.0 Cs-%. Before grinding the samples were subjected to chemical pre-treatment by deep eutectic solvent for 1 hour at a temperature of 100 °C. The pre-treatment dissolves the amorphous regions of the
fibers, allowing the crystalline regions to be separated by reasonably light mechanical grinding. The used deep eutectic solvent was a combination of choline chloride and oxalic acid (Sirviö, Visanko & Liimatainen, 2016).

As reference measurements, the samples were subjected to fiber analyses with a Valmet FS5 and some of the samples were imaged with a field-emission scanning electron microscope (Zeiss ULTRA plus, Germany). The results of the reference analysis of the NFC series are in Table 9 in section 7.1 and the results of the reference analysis of the CNC series are in Table 10 in section 7.2. The parameters used in fractionation are in Table 8.

Table 8. Fractionation parameters and variables in nanomaterial measurements.

<table>
<thead>
<tr>
<th>Parameter or variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate</td>
<td>0.39–0.45 l/min</td>
</tr>
<tr>
<td>Water temperature</td>
<td>20.7–23.3 °C</td>
</tr>
<tr>
<td>Length of fractionation tube (material: FEP)</td>
<td>50 m</td>
</tr>
<tr>
<td>Inner diameter of fractionation tube</td>
<td>4 mm</td>
</tr>
<tr>
<td>Mean diameter of fractionation tube coil</td>
<td>22 cm</td>
</tr>
<tr>
<td>Wavelength 1 (Extinction and depolarization)</td>
<td>Visible</td>
</tr>
<tr>
<td>Wavelength 2 (Extinction)</td>
<td>Near infrared</td>
</tr>
<tr>
<td>Optical path length</td>
<td>1.5 mm</td>
</tr>
<tr>
<td>Sample volume</td>
<td>3 ml(^1)</td>
</tr>
<tr>
<td>Sample consistency</td>
<td>1 g/l(^2)</td>
</tr>
</tbody>
</table>

\(^1\)6 ml in sample NFC Birch 23 500 kWh/t  
\(^2\)0.5 g/l in sample NFC Birch 23 500 kWh/t

Flow velocities were between 0.39 and 0.45 l/min and the measured water temperature between 20.7 and 23.3 °C. Sample consistency was 1 g/l, the only exception being the last NFC birch which was so gelatinous that feeding it to fractionation without dilution was not possible. The consistency of this sample was therefore halved and the volume doubled.

7.1 Nanofibrillated cellulose measurements

The reference measurement result matrix for the NFC samples is in Table 9. Fiber dimensions and fines A content were measured with a Valmet FS5 fiber analyzer. Fiber width was calculated as length-weighted average fiber width. The fines A % represents flake-like fines (type A) as percentage of the projection area of all measured particles. Particles shorter than 0.2 mm are included in fines A. Fiber
length $L_c(l)$ is the length-weighted average fiber length. The fiber class limit was here set to zero, so that all detected particles are considered when calculating the dimensions of the fibers, including those belonging to the fines. Fibrillation % indicates the projection area of the attached fibrils in relation to the projection area of the entire fiber, scaled into a percentage.

Table 9. NFC sample reference analysis results.

<table>
<thead>
<tr>
<th>SEC kWh/t</th>
<th>Time min</th>
<th>$L_c(l)$ mm</th>
<th>Fiber width µm</th>
<th>Fines A %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Birch</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0.555</td>
<td>16.92</td>
<td>14.51</td>
</tr>
<tr>
<td>100</td>
<td>7</td>
<td>0.559</td>
<td>17.17</td>
<td>14.73</td>
</tr>
<tr>
<td>300</td>
<td>11</td>
<td>0.559</td>
<td>17.27</td>
<td>14.89</td>
</tr>
<tr>
<td>700</td>
<td>18</td>
<td>0.551</td>
<td>17.18</td>
<td>15.52</td>
</tr>
<tr>
<td>1300</td>
<td>30</td>
<td>0.51</td>
<td>16.23</td>
<td>16.4</td>
</tr>
<tr>
<td>2400</td>
<td>43</td>
<td>0.413</td>
<td>13.53</td>
<td>19.22</td>
</tr>
<tr>
<td>3800</td>
<td>54</td>
<td>0.143</td>
<td>7.1</td>
<td>48.36</td>
</tr>
<tr>
<td>6100</td>
<td>75</td>
<td>0.124</td>
<td>7.4</td>
<td>52.47</td>
</tr>
<tr>
<td>9500</td>
<td>94</td>
<td>0.071</td>
<td>5.94</td>
<td>69.22</td>
</tr>
<tr>
<td>14300</td>
<td>120</td>
<td>0.048</td>
<td>3.48</td>
<td>88.15</td>
</tr>
<tr>
<td>20000</td>
<td>135</td>
<td>0.04</td>
<td>2.32</td>
<td>96.11</td>
</tr>
<tr>
<td>26200</td>
<td>147</td>
<td>0.037</td>
<td>1.91</td>
<td>97.26</td>
</tr>
<tr>
<td>Eucalyptus</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0.567</td>
<td>17.46</td>
<td>16.22</td>
</tr>
<tr>
<td>100</td>
<td>8</td>
<td>0.568</td>
<td>17.67</td>
<td>17.42</td>
</tr>
<tr>
<td>400</td>
<td>14</td>
<td>0.573</td>
<td>17.82</td>
<td>17.05</td>
</tr>
<tr>
<td>900</td>
<td>24</td>
<td>0.547</td>
<td>17.35</td>
<td>18.22</td>
</tr>
<tr>
<td>1700</td>
<td>38</td>
<td>0.336</td>
<td>12.75</td>
<td>28.5</td>
</tr>
<tr>
<td>3400</td>
<td>62</td>
<td>0.152</td>
<td>8.41</td>
<td>47.21</td>
</tr>
<tr>
<td>6100</td>
<td>85</td>
<td>0.059</td>
<td>4.41</td>
<td>80.13</td>
</tr>
<tr>
<td>10300</td>
<td>123</td>
<td>0.04</td>
<td>2.64</td>
<td>97.5</td>
</tr>
<tr>
<td>17500</td>
<td>187</td>
<td>0.039</td>
<td>1.72</td>
<td>99.6</td>
</tr>
</tbody>
</table>

The specific energy consumption rises very high in these grinding series and results in very fine particle material.

The FESEM images of NFC samples at four SEC levels are seen in Fig. 41. Fig. 41 a) shows the original, unground birch pulp, Fig. 41 b) the original Eucalyptus pulp. Fig 41 c) shows the birch at 3800 kWh/t and d) eucalyptus at 1700 kWh/t grinding level. Figs. 41 e) and f) the fibers are already severely broken and abundant fibril-like material is present. The lower Figs. 41 g) and h) show the
samples resulting from the grinding series, consisting almost exclusively of sub-micron material.

As can be seen from the microscope images, the grinding has not actually produced macro fibril material. The surface layers of fibers have begun to break up from to a much finer size than the fibrils produced by the normal refining process. Birch fibers require more energy than eucalyptus fibers to achieve a fine-grained finish.
Fig. 41. FESEM images of NFC samples, birch (left) and eucalyptus (right) with different specific energy consumption grinding levels. The original, unground pulps are in a) and b), and with increasing grinding levels the fibers are first severely broken with abundant fibril-like material present in c)–f) and finally consist almost exclusively of sub-micron material as seen in g) and h).
Detailed and enlarged FESEM images from the last grinding points are shown for birch and eucalyptus in Figs. 42 a) and b), respectively. Both of these consist mainly of very thin fibrils in the nanometer scale.

![Detailed FESEM images from the last grinding points of a) birch and b) eucalyptus pulp series. Both consists mainly of very thin fibrils in the nanometer scale.](image)

The fibrous index and size index distributions generated by the DFA method for the NFC eucalyptus sample are shown in Fig. 43. Both distributions develop as expected: the distribution shifts toward the lower readings as grinding progresses. The fibrous index and size index distributions resemble each other in shape, and in this review of grinding we can focus on tracking the phenomena of the size index distribution.

At the beginning the measurement indicates that the particle size distributions are still quite narrow. When grinding increases, material begins to detach from the surface of the fibers, which is reflected in a slightly increasing consistency reading on the left side of the fiber distribution. At the same time the fiber distribution shifts towards slightly smaller size index readings.

Gradually, the amount of material detached from the fibers increases and the surface area of the original fiber distribution decreases, shifting towards smaller readings. At the grinding level of 6100 kWh/t, the peak of the initial, continuously decreasing fiber distribution is at the size index reading 0.5 and after this the material of this state disappears completely.

Towards the end of grinding the size index distribution of the fines material narrows again as the particles are split into the same size.
Fig. 43. Fibrous index and size index distributions of Masuko ground NFC eucalyptus pulp. As grinding progresses, both distribution shift toward lower readings. The size index distribution shifts from the initial narrow distribution of fibrous material through the intermediate steps to the narrow fines distribution of the rest.
For the imaging reference measurement, the sample consistencies were adjusted to between 0.08 and 0.1 g/l in the laboratory. Consistency adjustment of the FS5 measurement was disabled. Sample consistency was measured by drying and weighing the amount of dry matter. Thus, the gravimetric consistency was determined and kept constant for all samples to be measured. Gravimetric consistency determination could be performed with a resolution of 0.02 g/l.

The imaging fiber measurement of the Valmet FS5 results in a consistency determination based on the shape and amount of particles.

Results of the gravimetric consistency determination of all NFC eucalyptus samples and the corresponding consistency readings seen by the imaging measurement are shown in Fig. 44. The gravimetric consistencies are drawn with blue and the results of the imaging consistency measurement with orange color. The ratio of these two consistency values is shown in the figure with gray bars.

**Fig. 44.** The gravimetric consistency determination results of all NFC eucalyptus samples (blue) and the corresponding consistency seen by the imaging measurement (orange). The ratio of the consistencies is shown with gray bars. The particle size of the samples at the last two grinding levels goes partially below the optical resolution of the imaging measurement, which is reflected in a decrease in the percentage of imaging consistency.
In the figure, the consistency information obtained with the two different methods show some differences. At the beginning of the series, up to 1700 kWh/t grinding, the consistency obtained by imaging is on average about 18% higher than the gravimetric consistency. The ratio of the consistency obtained by imaging vs. gravimetric consistency decreases significantly in the measurements of the last two grinding levels. This is most likely because the imaging measurement is no longer able to distinguish the smallest particles so that the calculation cannot produce actual consistency information based on the image information.

The ratio between these consistencies is interesting with regard to the DFA results: from the perspective of consistency, this ratio roughly describes the proportion of particles below the imaging resolution in the total particles.

Of course it is not possible to make an exact analysis based on this value, but the ratio makes it possible to look at which size index region the resolution limit of the imaging measurement is.

Based on Fig. 44, the imaging consistency ratios of the last two samples in the series are 65% and 34%, respectively. Similarly, in Fig. 43 the size index distribution of the 10 300 kWh/t sample can be seen to have a limit at about size index 0.3; this size index divides the distribution so that 65% of the consistency is above that limit, the remaining 35% below it. Correspondingly, for the 17 500 kWh/t sample the size index limit that divides the distribution in the percentage ratio of 66 / 34 is slightly below 0.3. Thus the resolution limit of the imaging measurement can be cautiously estimated to be at about size index reading 0.3 for an NCF eucalyptus sample.

The fiber index and size index distributions of the NFC birch sample are seen in Appendix 2. These distributions develop in much the same way as the eucalyptus, except that the birch fibers require more energy to achieve a similar grinding result. The resolution limit of the imaging measurement for the NFC birch measurement series also settles very similarly around the size index value 0.3.

### 7.2 Cellulose nanocrystal measurements

The CNC sample sets were first prepared by chemical pre-treatment, followed by Masuko grinding. The reference measurement result matrix for the CNC samples is in Table 10. The same methods and settings as for the NFC measurements presented in section 7.1 have been used also for the CNC sample reference measurements.
The table shows the effect of chemical treatment on particle size. Even before grinding, the particle lengths are very small compared to chemically untreated fibers, with lengths of 0.555 mm for birch and 0.567 mm for eucalyptus according to Table 9. The amount of fines is also over 95% at the beginning of both sets. The average particle widths are initially more than 10 µm but drop significantly already during the first grinding step.

The FESEM images of CNC samples are seen in Fig. 45 at three SEC levels. Fig. 45 a) shows the original, unground but chemically treated birch pulp while in Fig. 45 b) is the corresponding eucalyptus pulp. The fibers are gradually cleaved at this stage, but still coarse. The Figs. 45 c) and d) show birch and eucalyptus at 1300 kWh/t grinding levels. At the final points the coarse particle material has already completely disappeared (Figs. 45 e) and f)).
Fig. 45. FESEM images of CNC samples, birch samples on the left and eucalyptus samples on the right. In a) is the original, unground birch pulp with chemical pre-treatment and b) is the corresponding original Eucalyptus pulp. Figures c) and d) show 1300 kWh/t grinding for birch and eucalyptus, respectively. At points e) and f) the fibers are already severely broken and also fibril-like material is absent, unlike in the corresponding NFC samples.

Detailed FESEM images from the last grinding points are shown in Fig. 46, birch in a) and eucalyptus pulp in b). Both consist mainly of very fine material, but the shape is not as fibrillated than in the NFC seen in Fig. 42: the particles are shorter but wider compared to the final samples of the NFC series.
Fig. 46. Detailed FESEM images from the last grinding points of the CNC series: a) birch and b) eucalyptus pulp series. The particles are shorter but wider compared to the final samples of the NFC series.

The fibrous index and size index distributions generated by the DFA method for the CNC eucalyptus sample are shown in Fig. 47. Similar to the NFC, both distributions shift toward lower readings.

However, here the initial distributions are broader and more weighted toward lower values. This clearly indicates the fiber breakdown caused by the chemical pre-treatment. The fibrous index distribution starts at approximately the same reading of less than 7 as the original pulp in Fig. 43, but the distribution is very flat compared to the original.

Correspondingly, the size index distribution is flatter but also starts from a lower size index value than the original. The lower reading is probably caused by changes in the fiber wall: material has likely been dissolved from the wall and the fiber wall thickness has thus decreased from the original.

There is not much change in the first three distributions; the fibrous index distribution narrows slightly, and both distributions shift slightly lower. With grinding energy of 8400 kWh/t the distributions have already narrowed significantly. In the final situation, however, readings as small as in the final NFC situation are not achieved: the size index distribution of the final sample is between 0.35 and 0.45, while for NFC it was almost completely below 0.3.
Fig. 47. Fibrous index and size index distributions of Masuko ground eucalyptus CNC sample. The chemical pre-treatment is seen as broad distributions of upstream samples. Both distributions develop as grinding progresses, and the distribution shifts toward lower readings.

The gravimetric consistency determination results of all CNC eucalyptus samples and the corresponding consistency readings seen by the imaging measurement are shown in Fig. 48, gravimetric consistencies with blue and the results of the imaging consistency measurement with orange color. The ratio of these consistency values is shown in the figure with gray bars.
Fig. 48. The gravimetric consistency determination results of all CNC eucalyptus samples (blue) and the corresponding consistency readings seen by the imaging measurement (orange). The ratio between the consistency obtained by the imaging and gravimetric consistency is shown with gray bars. The particle size of the samples of the last two grinding levels goes partially below the resolution of the imaging measurement, which is reflected in a decrease in the percentage of imaging consistency.

As shown in Fig. 48, at the last two grinding levels, the imaging measurement readings are only about 50% and 30% of the gravimetric consistency results. The size index reading of the distributions that divides the sample in these ratios can be estimated to be in the range of 0.43 to 0.45. This is significantly higher than the estimated 0.3 for NFC samples. This confirms that for such different types of particles, the readings are not directly comparable. The correspondence of the size index to different particles needs to be clarified in future studies.
8 DFA in microfibrillated cellulose measurements

This chapter explains how the phenomena occurring in LC refining are reflected in the measurements made using the DFA method. Samples refined at two different consistencies were used in the experiment. The obtained results are presented in relation to the SEC.

Materials and methods

Sample material was produced in another project by a laboratory-scale industrial refiner, with the target of producing microfibrillated cellulose. The sample production process and extensive reference measurements are excellently documented by Sajaniemi (2018) and Sjöström (2018).

The refined sample was bleached birch pulp. Two sample series refined at different consistencies, were used in the experiment. Both series were refined with high load, meaning a small gap between the refiner stator and rotor.

The first series was started at consistency 6.1 Cs-%, and over SEC 500 kWh/t it was diluted to 4.1 Cs-% to prevent refiner heating and pressure problems caused by the increasing pulp viscosity. This first sample series was named HCHL (High Consistency, High Load). The second sample series was refined at a lower consistency of 3.5 Cs-% and named as LCHL (Low Consistency High Load). Both sample series represent different specific energy consumptions at 500 kWh/t intervals: LCHL up to 2000 kWh/t and HCHL up to 2500 kWh/t.

The parameters and variables of the fractionation and measurements used in the test are shown in Table 12.

As a reference, all samples were measured by Valmet FS5 fiber analyzer which enables versatile fiber property analysis by an ultra-high density imaging technology. The °SR value was also determined for all samples.

In this analysis the width limit of particles classified as fibers was 5 µm. Key fiber analysis results from the FS5 and the determined °SR values are shown in Table 11. The results include the mean values and standard deviations of five parallel measurements.
Table 11. Fiber properties by FS5 and °SR values. Mean values and the corresponding standard deviations of 1 σ are shown.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fiber width (µm)</th>
<th>Fines A (%)</th>
<th>Lc(l) (mm)</th>
<th>Fibrillation (%)</th>
<th>°SR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>20.39 ± 0.03</td>
<td>18.82 ± 0.23</td>
<td>0.876 ± 0.005</td>
<td>0.81 ± 0.03</td>
<td>35</td>
</tr>
<tr>
<td>LCHL 500</td>
<td>22.03 ± 0.08</td>
<td>50.00 ± 0.21</td>
<td>0.429 ± 0.002</td>
<td>4.03 ± 0.05</td>
<td>88</td>
</tr>
<tr>
<td>LCHL 1000</td>
<td>21.32 ± 0.07</td>
<td>70.08 ± 0.29</td>
<td>0.236 ± 0.002</td>
<td>6.03 ± 0.06</td>
<td>95</td>
</tr>
<tr>
<td>LCHL 1500</td>
<td>20.41 ± 0.04</td>
<td>82.92 ± 0.11</td>
<td>0.168 ± 0.001</td>
<td>7.43 ± 0.20</td>
<td>95</td>
</tr>
<tr>
<td>LCHL 2000</td>
<td>19.89 ± 0.07</td>
<td>89.87 ± 0.11</td>
<td>0.140 ± 0.001</td>
<td>7.65 ± 0.41</td>
<td>95</td>
</tr>
<tr>
<td>HCHL 500</td>
<td>21.14 ± 0.07</td>
<td>41.46 ± 0.16</td>
<td>0.548 ± 0.005</td>
<td>3.01 ± 0.06</td>
<td>84</td>
</tr>
<tr>
<td>HCHL 1000</td>
<td>21.63 ± 0.06</td>
<td>56.62 ± 0.22</td>
<td>0.345 ± 0.001</td>
<td>4.34 ± 0.11</td>
<td>95</td>
</tr>
<tr>
<td>HCHL 1500</td>
<td>21.81 ± 0.09</td>
<td>63.26 ± 0.18</td>
<td>0.277 ± 0.001</td>
<td>4.91 ± 0.08</td>
<td>&gt;95</td>
</tr>
<tr>
<td>HCHL 2000</td>
<td>21.64 ± 0.02</td>
<td>77.08 ± 0.19</td>
<td>0.190 ± 0.001</td>
<td>6.01 ± 0.15</td>
<td>93</td>
</tr>
<tr>
<td>HCHL 2500</td>
<td>20.72 ± 0.08</td>
<td>88.46 ± 0.12</td>
<td>0.145 ± 0.001</td>
<td>6.76 ± 0.26</td>
<td>84</td>
</tr>
</tbody>
</table>

As seen in Table 11, in both sample series the fines content and fibrillation increase with increasing refining energy while the fiber length decreases. In both sample series the width of fibers first begins to increase with refining, then flattens and turns downward.

Schopper-Riegler value, which normally describes refining, ceases to function in these samples. This is because the particle size is reduced to such an extent that the required fiber network is not formed on the wire of the SR cell and thus all particles pass through the wire. The size of free holes in wire is 152.5µm x 246.7 µm (Internal Organization for Standardization, 1999).
Table 12. Fractionation parameters and variables in MFC test.

<table>
<thead>
<tr>
<th>Parameter or variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate</td>
<td>0.39–0.45 l/min</td>
</tr>
<tr>
<td>Water temperature</td>
<td>23 °C</td>
</tr>
<tr>
<td>Length of fractionation tube (material: FEP)</td>
<td>50 m</td>
</tr>
<tr>
<td>Inner diameter of fractionation tube</td>
<td>4 mm</td>
</tr>
<tr>
<td>Mean diameter of fractionation tube coil</td>
<td>22 cm</td>
</tr>
<tr>
<td>Wavelength 1 (Extinction and depolarization)</td>
<td>Visible</td>
</tr>
<tr>
<td>Wavelength 2 (Extinction)</td>
<td>Near infrared</td>
</tr>
<tr>
<td>Optical path length</td>
<td>1.5 mm</td>
</tr>
<tr>
<td>Sample volume</td>
<td>5 ml</td>
</tr>
<tr>
<td>Sample consistency</td>
<td>1 g/l</td>
</tr>
</tbody>
</table>

Five parallel fractionation measurements were made on each sample at 1 g/l consistency. The resulting balanced concentration coefficients were calibrated by the weight function of

\[ C_s(FI) = 0.1913 \times FI^{-0.406} \times \mu_B(FI). \]  

\[ (25) \]

The parameters of the calibration function were obtained using all samples in both series and their five parallel measurements.

**Results**

The averaged distributions were calculated using each of the five parallel distributions generated by the DFA algorithm. The resulting fibrous index and size index distributions of LCHL and HCHL samples are shown in Fig. 49 and 50 respectively.

The fibrous index distributions are shown on the left and the corresponding size index distributions are on the right. Distributions of pre-refined reference pulp sample are shown at the top of the figure, and from there the degree of grinding increases, being highest in the bottom figure.

It is difficult to distinguish at which FI readings the particles are truly fines according to the classification of the imaging system. It can be seen from Table 11 that the LCHL 500 sample has a 50% fines A content. From the fibrous index distribution in Fig. 49 the 50/50 center of gravity of the LCHL 500 sample distribution is at about FI reading 5. Thus for this distribution the limit between fines and fiber fractions should be in that range.
However, the next sample LCHL 1000 contains about 70% of fines A and thus about 30% fibers. If the fines limit were set at FI reading 5, then all the material in this sample would be fines.

In the mechanical manufacturing process of MFC, the aim of strong refining is to convert fibrous material into microfibril material. There are phases in the breakdown of fibers where the fibers are clearly not classifiable as fines but are also not fibrous. The limit value for fines is at FI reading 1.2.

Fig. 49. Fibrous index (left) and size index (right) distributions of low consistency and high load (LCHL) refined sample with different refining degrees. The specific energy consumption in the top graphs is 100 kWh/t and increases downwards in the figure. The fibrous index limit value between weakly and strongly fibrous materials is 1.2.

The fibrous index distribution reacts significantly to increasing SEC. Initially the center of gravity of the fiber fraction on the FI axis is approximately at value 8,
then decreases with refining until the final reading is about 0.8. At the same time
the fines amount between values 0 and 1.2 increases.

In the size index distributions three separate peaks begin to stand out. The peak
of the highest reading gets narrower as refining progresses.

Similar effects are seen in the HCHL sample in Fig. 50, but here the decrease
of the center of gravity on both the FI and SI axis is not as strong as with LCHL.
At the last refining level of 2500 kWh/t all particles are just below the fines limit,
whereas in the LCHL sample all the material was clearly below the limit already at
2000 kWh/t refining degree.
Fig. 50. Fibrous index (left) and size index (right) distributions of high consistency and high load (HCHL) refined sample at different refining degrees. The specific energy consumption in the top graphs is 100 kWh/t and increases downwards in the figure. The fibrous index limit value between weakly and strongly fibrous materials is 1.2.

The key figures of all samples are in Table 13. The same phenomena as those shown in Fig. 49 and Fig. 50 are grouped into numerical values. The standard deviation values are included for the mean values of 5 parallel measurements.
Table 13. The key figures of LCHL and HCHL refining sample series measured by DFA method. Mean values and the corresponding standard deviations of 1 σ are shown.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fibrous index</th>
<th>Size index</th>
<th>Fines content</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fibers</td>
<td>Fines</td>
<td>Fibers</td>
</tr>
<tr>
<td>Reference</td>
<td>7.79 ± 0.05</td>
<td>0.56 ± 0.16</td>
<td>0.668 ± 0.003</td>
</tr>
<tr>
<td>LCHL 500</td>
<td>4.80 ± 0.06</td>
<td>0.51 ± 0.07</td>
<td>0.486 ± 0.006</td>
</tr>
<tr>
<td>LCHL 1000</td>
<td>2.17 ± 0.02</td>
<td>0.41 ± 0.08</td>
<td>0.416 ± 0.001</td>
</tr>
<tr>
<td>LCHL 1500</td>
<td>1.36 ± 0.01</td>
<td>0.49 ± 0.10</td>
<td>0.387 ± 0.002</td>
</tr>
<tr>
<td>LCHL 2000</td>
<td>1.97 ± 0.56</td>
<td>0.59 ± 0.06</td>
<td>0.744 ± 0.180</td>
</tr>
<tr>
<td>HCHL 500</td>
<td>6.31 ± 0.10</td>
<td>0.56 ± 0.14</td>
<td>0.533 ± 0.004</td>
</tr>
<tr>
<td>HCHL 1000</td>
<td>3.27 ± 0.02</td>
<td>0.42 ± 0.03</td>
<td>0.445 ± 0.001</td>
</tr>
<tr>
<td>HCHL 1500</td>
<td>2.63 ± 0.01</td>
<td>0.35 ± 0.03</td>
<td>0.429 ± 0.002</td>
</tr>
<tr>
<td>HCHL 2000</td>
<td>1.57 ± 0.01</td>
<td>0.37 ± 0.07</td>
<td>0.405 ± 0.002</td>
</tr>
<tr>
<td>HCHL 2500</td>
<td>2.46 ± 0.95</td>
<td>0.72 ± 0.06</td>
<td>0.475 ± 0.075</td>
</tr>
</tbody>
</table>

For comparison, the fines A content result of FS5 and the fines content obtained with DFA are shown in Fig. 51. The fines A content develops in a different way compared to the fines content of DFA, but both demonstrate that LCHL refining is more efficient for generating fines material than HCHL. When monitoring the progress of the MFC refining process by means of DFA, it could be good if the fines limit is dynamic instead of a fixed FI value.

The difference in the shape of the curves is due to the difference between the two measurement methods. Imaging measurement produces an absolute reading when classifying particles as either fibers or fines based on morphology. The DFA method is more relative: strongly refined fibers are fibrillated and broken but from an imaging point of view they still match the morphological dimensions of fibers.
Fig. 51. Effect of refining energy on Fines A % as seen by the imaging system and the fines content of DFA.

The results show clear differences between the two different refining sets. High consistency refining requires more energy to achieve the same level of refining as low consistency refining. These changes appear very parallel in both the DFA method and the imaging FS5. Compared to the imaging method, the DFA method produces less detailed information, it shows more an overview of the state of the process.
9 Discussion

This study investigated an improved analysis method for fractionated samples to exploit the full potential of tube flow fractionation. This potential means more versatile and undisturbed measurement results as well as the possibility to simplify the tube flow fractionation system.

Section 9.1 discusses the advantages of the method developed in the work. Section 9.2 deals with the evaluation of the consistency measurement results obtained in the study. The applicability of the method for monitoring the production of cellulose micro- and nanomaterials by refining or grinding is discussed in section 9.3. Proposed future research topics are presented in section 9.4.

9.1 Advantages of Dynamic Fractional Analysis

In general, non-imaging optical measurements of suspensions in the pulp and paper industry operate as indirect methods, utilizing changes in the optical properties to monitor changes in the sample properties. The optical properties measured are most commonly related to scattering by particles, absorption in the sample material, or depolarization. The propagation of light in a sample depends on the combined effect of all these optical phenomena.

For example, consistency is proportional to the scattering coefficient of the suspension [1/mm] which indicates the spatial frequency of scattering events encountered in the light path. This spatial scattering frequency is thus proportional to the number of solid particles in the surrounding matrix.

Different particles have their own scattering efficiency properties. As the particle size decreases, approaching the wavelength used, the scattering coefficient typically increases. Thus, when measuring consistency [g/l] based on the amount of scattered light, a sample consisting of small particles scatters more strongly than a corresponding sample of larger particles. As a result, larger particles require a higher weighting factor (calibration gain) than smaller particles to obtain the correct quantity or consistency results.

Especially pulp suspensions contain a wide variety of particles with different optical properties, wherein the weight factor of the response is dependent on the distribution of the particles. When using scattering measurements, the more the size distribution of the suspension is weighted into small particles, the lower the weighting factor should be to produce the correct consistency reading.
This works well when the distribution remains constant and the relative amounts of different particles in the suspension do not change. However, almost always in industrial samples the relative amounts of these different particles vary greatly, which poses the greatest challenges for both consistency measurement and other optical measurements.

Tube flow fractionation alleviates this problem by arranging the particles of a sample suspension in order of their flow resistance. Flow resistance correlates with particle size and aspect ratios, which is reflected in the fractionation of the particles. Particles will be arranged principally in order of size, but the low aspect ratio also enhances the propagation of fibers. This separation of particle sets with different measurement responses is the most significant advantage of fractionation.

Tube flow fractionation carries out the sample pretreatment, and the actual measurement following this pretreatment plays a significant role in the generation of information. The fractionation pretreatment step supports the measurement by providing the abovementioned separation, and the measurement step must be able to take full advantage of this pretreatment so that weaknesses in the reproducibility of fractionation can be dynamically compensated. This advantage of fractionation can be fully exploited by the new DFA algorithm.

The sample dilution phenomenon occurring in tube flow fractionation is the first key factor allowing the implementation of DFA. Figs. 12–14 show that the sample moves to a more linear range of optical properties when diluted to low consistency. When the sample consistency is in a linear range with respect to the optical properties, the pure water around the sample can be used as a reference. In this case, the zero point of the measurement response represents this water value.

When linear and zero originating consistency dependent signals are obtained with dilution, the relative values calculated by these can be utilized. The nature of these signals in relation to each other changes dramatically when compared to looking at them individually.

The signals examined in this work are spectral extinction coefficients and depolarization, presented in section 2.6. These signals individually respond to the amount of material in the sample, i.e. consistency, each with its own specific response. The depolarization signal characteristically reacts to the amount of birefringent material contained in the wood fibers, whereas extinction reacts to the changes in scattering caused by the variation in the ratio between particle morphology and size and wavelength.

The ratios of these differently responding consistency signals produce consistency-independent quality signals or indices. These quality monitoring
fibrous index and size index are another key finding in the DFA method, allowing continuous quality monitoring of a flowing sample. Compared to the earlier flow-based analysis method, this continuous quality monitoring remarkably reduces the requirements for accurate sample consistency, temperature and flow rate control.

The effect of sample consistency on fractionation is described in section 5.1. Perhaps this is best illustrated in Fig. 26, where the TMP sample is fractionated at three different consistencies of 2, 9, and 15 g/l with constant temperature and flow rate. The figure shows how the sample is distributed over a longer distance in flow tube as the consistency increases, with the first fibrous particles reaching the measurement point significantly earlier than in the samples at lower consistency.

As the sample is distributed over a longer distance due to the consistency, the boundary between the fiber and fines fraction also comes earlier. However, the fibrous index makes it possible to dynamically detect at which flow point the fraction boundary changes and thus the changing consistency cannot cause a significant error in the shares of the fractions. Similar phenomena to fractional boundaries are caused by temperature changes, described in section 5.2, and flow rate, described in section 5.3.

When examining the effects of varying fractionation conditions on the fraction shares, variation is observed between parallel sample sets. This is particularly evident in the consistency change studies in Fig. 27 as well as in Fig. 31, which consider the effect of fractionation water temperature. In measurements at different consistency or temperature points, the values are sometimes below, sometimes above the linear regression.

These deviations are repeated in the same way when analyzed by the DFA method and the FBA method: if a point of the DFA is above the linear regression, so is the corresponding point of the FBA. This is probably caused by the uncertainty associated with taking several parallel sub-samples. It is very difficult to keep the fiber suspension homogeneous and thus a small subsample separated from it does not fully represent the original sample. Despite these uncertainties, it can be seen from Fig. 33 that the DFA method reduces or even eliminates the errors caused by changes in the conditions.

For consistency changes from 2 to 8 g/l and temperature changes from 15 °C to 40 °C, the standard deviation of the parallel measurements covers the error-free situation. Using DFA, the change in flow rate of 1 l/min causes a 0.73 %-point error to the fraction share; when using FBA the corresponding error is 5.7 %-point.
9.2 New aspects in consistency measurement

Consistency measurements by the DFA method are described in chapter 6. Certain specific features make the method very promising for use in consistency measurements even in an industrial environment. The first of these features is that the fractionation itself makes the particle sets with different characteristic optical responses measurable separately from each other. Secondly, the dilution in fractionation enables optical measurements for the linear and zero originating operating range. The third special feature is the fibrous index which monitors the quality of the particles produced by the DFA algorithm, thereby significantly reducing the requirements for fractionation flow control.

With these factors, a fibrous index distribution is obtained in which each element of the distribution represents a zero originating and linear consistency related response of each quality class. For such a distribution, it is then possible to produce a calibrated consistency distribution with the weighting factor function alone or with a fractional gain value.

In section 6.2, a common consistency calibration was performed for three very different pulp sets using only one, 7 g/l consistency point for each pulp type (Eucalyptus, Pine and TMP). The fibrous index distribution in Fig. 34 shows well that the TMP contains more fines and its fiber fraction is less fibrous compared to chemical pulps. The resulting calibration can produce identical total consistency responses for all three sample series to be calibrated according to Table 5. With the fractionation parameters described in the table, the responses continued to be linear up to a consistency of 15 g/l and the consistency points remained well along the same line.

The TMP pulps before and after reject refining, included by way of example in the tests, do not follow the same response curve, causing consistency readings that are approximately 30% lower than actual. This is probably due to the coarse material that is typically richly present in these separated reject pulps and raises the dry weight but is less optically effective.

Fig. 25 shows how the TMP sample dilutes as it progresses through the fractionation tube. According to the figure, the first particles of a sample with a consistency of 15 g/l arrive at a flow point of about 16 000 ml according to the flow measurement. The last particles come just after the flow point of 19 500 ml. A rough estimate is that a sample with an initial sample volume of 200 ml was divided into a volume of 3000 ml, i.e. 15 times the original volume. If the particles of the sample...
were evenly distributed in terms of consistency in a volume of 3000 ml, then the consistency of the 15 g/l sample in the measurement would be 1 g/l.

In this work the factors influencing dilution were not focused on, and ready-made solutions were used instead. Optimizing the sample volume for sample consistency, for the length and diameter of the fractionation tube, and for flow variables would be a subject for separate, future studies. The dilution phenomenon appears to work reproducibly, which is supported by all the results presented in this work.

When compared with methods measuring all-inclusive samples, the combination of fractionation and DFA provides a significant improvement that takes into account the optical interaction differences between the particle sets.

It is revolutionary that separate fiber and fines consistency calibrations can be done by only a priori total consistency information as shown in chapter 6.3. Another remarkable finding is that the same calibration can be used for totally different pulp samples, as seen in the test with a long-fiber and short-fiber mix.

### 9.3 Potentiality of DFA in micro- and nanomaterial monitoring

In addition to consistency measurement, fractionation also enables the monitoring of fiber refining or grinding based on the fibrous index distribution. Fibrous index is an effective variable, especially when the suspension consists of fibers and fines detached from the fibers. The size index distribution becomes increasingly important when nanomaterials appear in the suspension during refining or grinding.

The use of the size index works at least when the material of the suspension remains the same, as in a refining or grinding process, in which case the spectral absorption coefficient of the material remains essentially constant.

The distribution diagrams are informative and describe well the state of the particle suspension being measured. For example, in an industrial control room environment where humans are monitoring the state of a process, such a distribution diagram will be useful. Numerical indicators calculated from the distribution are useful when individual values are required, for example for the use of control automation systems.

The imaging fiber analyzer was used as a reference device in the studies. Measurements with the DFA method cannot produce as detailed information as obtained by this kind of microscopic imaging and image analysis. However, fractionation complements the measurement by making the material below the microscopic resolution more visible. In the future, a combination of imaging
measurement and the fractional DFA method may provide an efficient package where the DFA yields information especially on the nanoscale materials.

Using the DFA method, the transformation of fiber particles to nanoscale materials due to grinding are systematically displayed. The aberrant formation of cellulose nanocrystals relative to nanofibrillated cellulose was clearly and logically distinguished in the measurements.

Interesting observations are the results presented in sections 7.1 and 7.2, where we can conclude based on the gravimetric and imaging consistencies that in these test samples the material below the numerical size index value 0.3 is below the resolution limit of the imaging measurement. This will require further research in the future, but at this stage this is already a very promising result. Nanoscale materials require measurement technologies applicable to the process conditions, and this is exactly it.

### 9.4 Future research topics

The resolution limit of the size index mentioned above is one important research topic for the future. It is good to find out the absorption and scattering factors that affect the formation of the size index.

In the future more studies into calibration are needed to optimize the calculation of the calibration weight function and possibly to assist the calibration by simultaneous size index information.

It is important to understand that measurement resolution depends on how effectively the different particles can be separated in fractionating sample handling. If different particles arrive simultaneously to measurement, the result is a combination of particle properties and relative particle amount. In some cases it is sufficient to distinguish the fibrous particles from other particles, usually smaller and different in the aspect ratio than the fibrous ones.

For example, in pulp processes where the suspension consists mainly of tracheid fibers and parenchyma cells, the greatest importance in the measurement could be to separate these two different fractions from each other. In applications where the fibrous material consists of different tracheid fibers and also the fines material contains fractions of different composition and efficiency for the process, the requirements for the measurement resolution are significantly higher. Any improvement in resolution usually occurs at the expense of response time.

In future studies it will be necessary to optimize these fractionation related variables to obtain the best solution for each purpose. For example, the dimensions
and materials of the fractionation tube, the optimal ranges of flow rate range and temperatures affect how well the different particles are separated from each other during fractionation. In continuous measurement, it is good to also consider the water consumption, which favors a small diameter tube.

The applications considered in the work are related to the paper and pulp industry, but the method is also applicable to many other areas as well: environmental measurements, mineral industry, food industry or medical monitoring, to name just a few. This wide applicability is made possible by the fact that tube flow fractionation and its phenomena as well as optical measurement technology are highly scalable. In this area here is a huge amount of things to explore in the future.
10 Conclusion

The main goal of the work was to verify the functionality of a new analysis method of tube flow fractionated samples. Compared to the currently known Flow Based Analysis (FBA) method, the new Dynamic Fractional Analysis (DFA) method significantly reduces the measurement error introduced by variables related to fractionation.

The main variables, water temperature, flow rate and sample consistency, change the particle distribution with respect to flow moments. The FBA method analyses the distributions against constant flow moments, as the variations of these flow variables result in error in the fractional analysis. In this work the changes in the proportion of the fines fraction were parallelly analyzed by FBA and DFA when the fractionation variables were changed at given steps.

For consistency changes of 2 to 8 g/l and temperature changes of 15 °C to 40 °C, the standard deviation of parallel measurements covers the error-free situation. Using DFA, the change in flow rate of 1 l/min causes a 0.73 %-point error to the fraction share, whereas using FBA the corresponding error is 5.7 %-point.

Certain specific features make the method very promising for use even in industrial environments. These key features concerning DFA method are listed here:

1. The separation of particles by tube flow fractionation makes the sets of particles with different characteristic optical responses measurable separately, without interference from each other.
2. The dilution by fractionation obtains optical measurements for the linear and zero originating operating range.
3. The linear and zero originating signal responses allow the use of simple division operation to obtain a fibrous index monitoring the quality of the particles in the flow.
4. With parallel fibrous index and consistency signals, a fibrous index distribution is obtained in which each element of the distribution represents a zero originating and linear consistency related response of each quality class.
5. For such a distribution, it is then possible to produce a consistency calibrated fibrous index distribution with the suitable weighting factor function.
6. From consistency calibrated fibrous index distributions, the fractional consistencies can be calculated as partial integrals.
7. From fractional consistencies for example the fines fraction or other fraction shares can be calculated.
8. In parallel with the fibrous index, a size index distribution can be created to monitor the particle size related index.

9. From fibrous and size index distributions the fractional gravity centers or other characteristics can be determined, which can be used for example, to describe the progress of the refining or grinding process.

The linear response starting from zero provides the possibility of linear single-point calibration. Because of this, only a gain factor as a function of the fibrous index is needed for real calibration over a wide consistency range. The number of calibration samples required is reduced, and this in turn will lower the start-up cost of the device in process consistency measurement applications. For unscreened TMP and eucalyptus pulp even 15 g/l consistency samples remained in the linear range when comparing the measured consistency response to real consistency.

When fractionation is used, the refining and grinding of fibers can be monitored by means of the fibrous index. The treatment of the fibers is reflected in a decrease in the fibrous and size indices.

Specific measurement of micro- and nanofibrillated material will be possible without disturbance from the bigger components in samples. The measurement of MFC and NFC processes is a novelty, because no fast responding methods for suspensions containing both big particles and nanoscaled particles have so far been available. There is an increasing need for micro- and nanoscale material measurements, and in this field the DFA method will give cost and material reductions by enabling faster, more accurate process control.

Due to the scalability of the tube flow fractionation phenomenon, the DFA method is probably applicable also to many other areas as well, for example to environmental measurements, mineral industry, food industry or medical monitoring. The method has great potential and the future will show how widely the measurement method presented in this work will be yet used.
List of references


Appendices

Appendix 1  Effect of consistency variations
Appendix 2  The distributions of the NFC and CNC birch samples
Appendix 1 Effect of consistency variations

Fig. 1. Effect of consistency variation on fraction 1 share obtained by FBA and DFA methods on Eucalyptus pulp.

Fig. 2. Effect of consistency variation on fraction 1 share obtained by FBA and DFA methods on Pine pulp.
Fig. 3. Effect of consistency variation on fraction 1 share obtained by FBA and DFA methods on TMP before reject refining.

Fig. 4. Effect of consistency variation on fraction 1 share obtained by FBA and DFA methods on TMP after reject refining.
Fig. 5. Effect of consistency variation on fraction 1 share obtained by FBA and DFA methods on unscreened TMP.
Appendix 2 The distributions of the NFC and CNC birch samples

Fig. 1. Fibrous index and size index distributions of Masuko ground NFC birch pulp. As grinding progresses, both distribution shift toward lower readings. The size index distribution shifts from the initial narrow distribution of fibrous material through the intermediate steps to the narrow fines distribution of the rest.
Fig. 2. Fibrous index and size index distributions of Masuko ground birch CNC sample. The chemical pre-treatment is seen as broad distributions of upstream samples. Both distributions develop as grinding progresses, and the distribution shifts toward lower readings.


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