Image-based quantitative infrared analysis and microparticle characterisation for pulp and paper applications

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Akademisk avhandling som med tillstånd av KTH i Stockholm framlägges till offentlig granskning för avläggande av teknisk doktorsexamen fredagen den 12 februari kl. 10:00 hos Innventia, Drottning Kristinas väg 61, Stockholm.
When you walk to the edge of all the light you have and take that first step into the darkness of the unknown, you must believe that one of two things will happen:

There will be something solid for you to stand upon, or, you will be taught how to fly.

– Patrick Overton
Abstract

Measurements of process variations and particle morphology are widely employed in the pulp and paper industry. Two techniques with high potential, infrared thermography and microparticle characterisation, are mainly used qualitatively. Quantitative thermography requires knowledge of the emittance, a material property which has not been measured under many process-relevant conditions. Quantitative characterisation of microparticles, e.g. pulp fines and mineral fillers, requires the analysis of a large number of particles, which can be accomplished using flow microscopes. Flow microscopes for pulp analysis have had insufficient spatial resolution to resolve fines and fillers. Additionally, there has been a lack of methods which can differentiate between fines and fillers in a mixed suspension.

State-of-the-art instruments for particle image analysis were evaluated and compared to laser diffractometry, a measurement method based on scattering by diffraction. Laser diffractometry was found to be highly sensitive to the complex refractive index of the particles, and especially to its change due to moisture absorption. A high-resolution imaging flow cytometer and a high-resolution fibre analyser were found to be complementary for characterisation of pure fines and fines/filler mixtures, and superior to laser diffractometry. A method for differentiating between fines and fillers in a suspension based on their autofluorescence and side-scattering was proposed and qualitatively evaluated.

Furthermore, a method for measuring the directional and integrated emittance of paper was developed and its accuracy was determined. Measurements on a wide range of samples showed that the emittance of fibre-based materials vary significantly with wavelength, pulp type, observation angle, and moisture content. By applying measured quantitative values of the emittance, the thermal energy emitted by sack paper samples during mechanical deformation could be quantitatively calculated. The increase in thermal energy at the time of rupture was found to correlate well with the elastic share of the mechanical energy that was stored in the sample during its elongation.

In summary, the results of this work have facilitated the use of quantitative microparticle analysis and infrared thermography for pulp and paper applications.
Keywords

Metrology, imaging, pulp, paper, board, stock, papermaking, refining, fibre treatment, fibrillation, fines, filler, morphology, classification, flow microscopy, fibre analyser, flow cytometry, laser diffraction, laser diffractometry, imaging particle analysis, dynamic image analysis, process variation, thermography, emittance, emissivity, NDT, infrared, MWIR, LWIR, goniometer
Sammanfattning


Högupplösta mätinstrument för bildbaserad mikropartikel-karakterisering utvärderades och jämfördes med en laserdiffraktometer, en mätmetod baserad på ljusspridning genom diffraction. Laserdiffraktometerns mätresultat påverkades starkt av det brytningsindex som antogs för provet, och hur brytningsindexet ändrades med fukthalt. En högupplöst bildbaserad flödescytometer och en högupplöst fibermätare konstaterades komplementera varandra vid mätningar av måldens finmaterial. De var även pålitligare än laserdiffraktometern vid mätningar av organiskt finmaterial. En metod för att skilja mellan organiskt och oorganiskt finmaterial i en måld baserat på deras autofluorescens och ljusspridning presenterades och utvärderades kvalitativt.


Sammanfattningsvis har resultaten av detta arbete möjliggjort kvantitativ användning av mikropartikel-karakterisering och infraröd termografi i massa- och papperstillämpningar.
After my M.Sc. in astronomy, I was pretty sure that I wanted to pursue PhD studies. At the time, I could not have imagined where I would end up, but I’m very pleased with where I did. Being an industrial PhD student has been highly rewarding. I want to thank Innventia, KTH Royal Institute of Technology, the Swedish Energy Agency, and Önnesjöstiftelsen for giving me this opportunity.

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This time has brought a lot of changes, among them the passing of my mother. I regret that she did not live to share this time with me. I am grateful for the friends and family which have done so, and filled my life with love, food and geekdom. Another change is that of my name and personal pronoun, to ones that I feel resonate more with myself. It seems that, during the development of knowledge and methods, we may also develop ourselves.

Stockholm, January 2016
Kari Hyll
Contributions to appended papers

Paper A


Hyll was the only contributor, aside from standard language feedback.

Paper B


Hyll was responsible for the evaluation, selection and procurement of the ImageStream instrument, and developed its application on stock samples. Hyll procured suitable calibration material, carried out part of the ImageStream measurements, and made the mixing-rule calculations of the refractive indices, the uncertainty analysis, the data analysis routines, and data interpretation.

Paper C


Hyll carried out the ImageStream measurements. Hyll made the largest share of the data analysis and presentation, and calculated the key factors made on measurements on the refiner segments.

Paper D


Hyll researched the theoretical foundations of the method and participated in the construction of the goniometric setup. Hyll performed the evaluation measurements and error analysis, and the FTIR verification measurements.
Paper E


Hyll performed the experiments and the data analysis and presentation. Hyll evaluated a proposed mixing rule formula for the emittance of wet paper.

*Paper F*


Hyll carried out the thermographic measurements and the entire data analysis, and also presented the research at the Paper Physics Conference 2012, Stockholm.

**List of related publications**


*Comparison of optical methods for fines and filler characterization*, Master thesis work by Farnaz Faranani, supervised by Kari Hyll, KTH Royal Institute of Technology, Dept. of Fibre Technology, 2016


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1. Introduction

The paper and board industry is the largest forest-based industry in Sweden [1]. The basis of paper is pulp that is made from wood, see Figure 1. The most important part of the pulp is the fibre, but the pulp also contains smaller, micrometre-sized particles that are called fines. Before being used in the paper machine, additives and mineral filler particles such as clay and chalk are mixed into the pulp. The resulting suspension, whose composition is around 96% water and 4% solids material, is then called a stock. The micrometre-sized fillers decrease the strength of the paper, but improve light scattering and thus make the paper less transparent. Too much added filler would make the paper weak. Too many fines would make the paper compact and difficult to dewater on the paper machine. Thus, knowledge on the stock composition and on the morphology (size, shape) of the fibres, fines and fillers helps to control the papermaking process and the properties of the final product.

Image-based instruments called fibre analysers have been used since the 1980’s to measure the morphology of fibres. The instruments are in principle microscopes that measure on a flowing particle stream, which allows many
particles to be analysed in a short amount of time. Papermaking uses tonnes of stock during a single day, but most measurement instruments can only measure a few decilitres. If that small volume differs from the rest of the stock, the measurement may give a flawed impression of its composition as the composition can vary with time. To compensate for this, more measurements can be made, which however require the analysis to be fast. The variations over time can then also be detected. When many particles are measured, statistical calculations can be made, and representative measurement results are obtained. Fibre analysers solve most of these issues. However, their ability to analyse small particles has been limited. Thus, it has not been possible to analyse fines and fillers in a statistical way, with the exception of the largest fines. Other measurement methods which can detect small particles are unable to measure their shape and to distinguish between fines and fillers.

Industrial paper and boardmaking is an advanced and largely automated process. In the paper machine, the stock is pumped onto a wire mesh where it forms a wet fibre network called the web. The web can be up to 10 m wide and move with speeds up to 2000 m/min. It is difficult to distribute the stock and its particles uniformly on the wire mesh. Because of this, spatial variations in particle concentration occur. As a result, the properties of the produced web are non-uniform, for example in terms of its local fibre and fines concentration, but also in its moisture. To detect and compensate for variations in the web, the web is continuously scanned with measurement sensors. Current sensors only cover a small area of the web. Thus, variations which change rapidly may be missed. A potent method for detecting such variations is thermography, see Figure 2.

![Figure 2. An infrared thermographic image showing moisture variations on the reel of a paper machine, where the finished product is rolled up (courtesy of Catherine Östlund).](image)

Thermography detects infrared radiation and converts this information into a temperature image. The technique can detect temperature variations,
which tend to correlate with moisture. Moister areas in the web are usually characterised by lower temperature due to a more pronounced evaporative cooling, while drier areas have higher temperature. However, to measure absolute, quantitative temperature values with thermography, the emittance, a material property, of the motive has to be known. The emittance is a measure of how efficiently a material emits heat. Partly due to the lack of process-relevant emittance values, thermography is not yet established as a continuous web inspection method.

The first contribution of this thesis work is that methodology and instruments developed for life science applications can be applied in the pulp processing to characterise a larger share of fines and filler particles. As the methods are image-based, they also provide shape and textural information about the particles. A method which can tell mineral fillers and pulp fines apart, and analyse them as separate groups, has also been demonstrated. This will make it possible to better control the papermaking process, and has future potential, for example in the characterisation of recycled pulp.

The second contribution of this work is the newly developed method which can measure emittance values relevant to applications in a paper mill. Measured emittance values of a wide range of fibre-based samples have been published, and are thus easily accessible for future thermographic studies. The influence of parameters that had not previously been studied, such as temperature and direction of observation, was determined. A model for predicting the emittance of a sheet with varying moisture content was presented. This will make it possible to do thermographic measurements with higher accuracy. It was also demonstrated how such a study could provide new knowledge related to the physical mechanisms behind the rupture of paper.

1.1. Problem statement

Measurements of the composition and morphology of the stock and of the variations in the web allow for the analysis and control of the process and of the finished product. Two methods with high potential for quantitative analysis, image-based characterisation of the micron-sized fine fraction of a stock, and two-dimensional thermographic analysis of paper, are today mainly used qualitatively.

Current instruments for stock characterisation have insufficient spatial resolution to characterise the fine fraction. Additionally, it is not possible to differentiate between the most common particle types in the fine fraction, i.e. pulp fines and mineral fillers. This makes the production process more
difficult to control. The first question is then: can we find and apply a better and more suitable measurement technique?

Quantitative thermographic imaging requires knowledge of the emittance of the observed material. The emittance of paper cannot be theoretically predicted; it has to be measured. In the case of paper, only very few measurements have been performed for conditions that are encountered in the papermaking process. No emittance measurement method that allows for variation of temperature, observation angle and moisture ratio exist. The second question is then: can we develop and apply a measurement technique that will provide the lacking emittance data?

1.2. Objective

The aim of this work is to facilitate the quantitative use of 1) image-based microparticle characterisation of the fine fraction of a stock, and 2) 2D thermal analysis, by applying technological developments and increasing the measurement accuracy. The best current method for morphological characterisation of the fine fraction of a stock, including the differentiation between pulp fines and mineral fillers, is to be identified and evaluated. A measurement method needs to be developed and emittance values for fibre-based materials under various process-relevant conditions are to be measured.

1.3. Methodology

A thorough literature study on fines and filler characterisation identified the advantages and limitations of different measurement methods. Several commercially available instruments developed for applications outside the pulp and paper industry were evaluated on stock samples. The most promising instruments, an imaging flow cytometer and a laser diffractometer, were then compared to state of the art analysers developed for stock characterisation. The instruments were verified using calibration particles with optical properties similar to those of wet pulp. The two instruments showing the best performance were applied in a study of the influence of refining on the morphology of fibres and fines. In addition, with one of the methods, a method for separating fines and fillers based on differences in light absorption and light scattering was proposed and qualitatively evaluated.

The literature on emittance measurement methods and reported emittance values of paper and similar materials was summarised and reviewed. A new angle-resolved goniometric emittance measurement method suitable for various fibre-based samples exposed to different temperatures and moisture
ratios was developed. Followed by verification testing and error analysis of the system, a large number of angle-resolved emittance measurements were made on paper and board under conditions similar to those at different stages in the papermaking process. The applicability of measured emittance values to quantitative thermographic measurements was demonstrated in some experiments where the dissipated energy during the rupture of a paper sample was compared with the applied mechanical energy during the tensile test.

1.4. Overview

This thesis is organised in nine chapters. Chapter 1 comprises this introduction. In Chapter 2, the papermaking process from the stock to the finished sheet is presented. Relevant measurements at different stages of the process are introduced. Chapter 3 comprises the fundamental theory behind optical, image-based measurements. Chapter 4 explains how the theory is applied in particle size analysis and infrared thermography. Chapter 5 presents the experimental procedures of the fine material characterisation. First, the measurement instruments used in the studies are explained in detail. Then, the experiments are described. Chapter 6 presents the experimental methods of the emittance measurements and the thermographic application. Chapter 7 and Chapter 8 present and discuss the results from the experimental work of the fine material characterisation and the emittance measurements, respectively. In Chapter 9, the main results of this work are summarised and suggestions for future work are given. After the bibliography, an appendix provides a gallery with highlights of measured particle images, and a list of symbols and abbreviations.
2. Pulp and papermaking

2.1. The forest-based industry

Forests are a renewable resource that covers 55% of the area of Sweden [4]. The forest-based industry accounts for around 10% of the employment and export in the Swedish industry and had an annual turnover of 197 billion SEK in 2013.

Recently, two major trends have been changing the situation for wood-based products in general and fibre-based products in particular. The first trend is the digitalisation of information, which has resulted in a decreasing demand of printing paper. This change has initiated the research on new, high-value products that can be derived from wood pulp. Packaging paper, board and tissue products, however, still see high demand, and are believed to grow in the future. The second trend is the conversion from an oil-based economy to a sustainable, resource-efficient economy. As wood is renewable, widely available and not used as a food source, it is a sustainable raw material for new materials. Pulp-based biocomposites, transparent barriers from cellulose nanofibrils (CNF), and carbon fibres and fuel based on lignin are examples. The research has also created a demand for methods to characterise the new products.

Though much attention is given to new products, the paper and board industry remains the largest sector within the Swedish forest-based industry [5], and is likely to remain so for years to come. The forest-based industry has set a goal to become 15% more energy-efficient by the year 2020 [5], and an important part will be achieved by implementing new technology and the continued optimisation of the papermaking process. Due to the large volumes handled in pulp and paper processes, even a comparatively small increase in efficiency due to improved measurements may save significant energy and money.

The following sections give a short overview on the papermaking process.

2.2. Pulp and stock

The basis of paper and board is pulp made from wood. Wood consists mainly of fibres, ray- and vessel cells, bound together by a lignin matrix. A typical
softwood (SW) fibre is 30-70 µm wide and 2-5 mm long, and can be imagined as a hollow cylinder. The fundamental building block of the fibre is the elementary fibril, an aggregate of cellulose molecules 3-5 nm wide and around 0.1-1 µm long, see Figure 3 [6-8]. Elementary fibrils aggregate with themselves and with hemicellulose to form nanofibrils and microfibrils, here defined as fibrils with a diameter of 0.005-0.1 µm and 0.1-1 µm, respectively. Nano- and microfibrils aggregate with lignin into macrofibrils, here defined as fibrils thicker than 1 µm, and also to build up the three primary layers of the fibre wall, which lie between the middle lamella and a hollow space called the lumen. In the outer layer of the fibre, the primary wall, the fibrils are bound together with pectin and oriented cross-wise. If exposed to force, the primary wall tends to break into flaky fragments. The secondary wall is mainly built by fibrils oriented in the same direction, bound together by lignin. When exposed to gentle force, the fibrils are raised to the surface and may be detached from the fibre relatively intact.

Figure 3. The structural components of wood [based on 9].

In the pulping process, the goal is to release the fibres from the matrix by mechanical forces or by chemically dissolving the lignin, which represents the glue that holds the fibres together. Mechanical pulping tears apart the fibres, resulting in a pulp with a wide size and shape distribution. Thermo-mechanical pulp (TMP) is the most common mechanical pulp. Chemical pulping gives a pulp with stiff, relatively intact fibres and a narrower size and shape distribution. Sulphate kraft pulping is the most common chemical pulping process. After pulping, the pulp may be chemically bleached to remove additional lignin and turn the brownish colour into white. The biggest difference between these two processes is that the mechanical pulping process has a yield, i.e. the ratio between the amount of produced pulp and the initial amount of wood, of close to 100%, while the yield of the chemical pulping process is only around 50%.

Bleached chemical kraft pulp is the most common pulp type. Its intact fibres give a bulky network that has low strength. The bonding strength is related to both the contact area and number of contact points between the particles,
which in turn are related to their specific surface area. To improve the bonding strength of the final product, chemical pulp is generally subjected to a mechanical treatment, refining. The refining process affects the morphology of the pulp fibres in several ways, see Figure 4. During refining, internal fibrillation weakens the bonds between elements in the fibre wall. This treatment makes the fibre more flexible and able to make contact at more points in a fibre network. Internal fibrillation also allows the fibre to swell, and the lumen of the fibre to collapse more easily. External fibrillation raises fibrils to the surface, see Figure 4, further increasing the specific surface area. Refining also affects the size distribution of the pulp, for example the length distribution, by the creation of fibre fragments and fines.

Figure 4. Effects of refining on a fibre. Top row: fibre shortening. Bottom row (left to right): Original fibre wall and lumen, internal fibrillation, external fibrillation, a collapsed fibre, and free fines.

Fines are commonly defined as the fraction of a pulp that passes a screen with Ø76 µm holes (200 mesh) in the Britt Dynamic drainage Jar (BDDJ). The hole size was originally chosen to mimic the openings of the forming wire in a paper machine [10]. As the screening is based primarily on length, most fibres do not pass the Ø76 µm holes. Instead, fines comprise smaller particles like ray cells, flaky fragments from the fibre wall, and fibrils of different sizes, see also the Appendix. In mechanical pulp, a large amount of fines are created in the pulping process. In chemical pulp, the relatively small share of fines that is present in the pulp before refining are called primary fines, while the fines that are produced during refining are called secondary fines.

Papermakers have always been interested in fines, as they influence many product properties. The impact on product properties differs dependent on the pulp type (mechanical or chemical) from which the fines originate, and on their size and shape (fibrillar, flaky, chunky). The primary fines of chemical pulp contain a high share of chunky ray cells, while the secondary fines are mainly fibrillar [11]. Both primary and secondary chemical fines increases strength properties, but secondary fines have a stronger effect [12]. The stronger effect is partly attributed to the flexibility and high specific
surface area of the fibrils, which create many contact points between particles [12-14]. Increased amount of mechanical pulp fines improves light scattering in the sheet, while chemical pulp fines have little or adverse effect [13]. All fines increase sheet density, impair drainability and make the paper more difficult to dry, but fibrillar fines have a larger impact than flaky fines or ray cells [12, 13, 15].

For many paper grades, the pulp is mixed with mineral fillers and a smaller amounts of additives (starch, retention aids, dyes), before being pumped to the paper machine. This mixture is then called a stock. In this thesis, the fraction of a stock which passes a Ø76µm mesh will be called the fine fraction, and may thus contain both fines, fillers, and other micro- and nano-particles, see Figure 5. Mineral fillers are used to make the paper less transparent, but also to decrease raw material costs. Fillers are cheaper than fibres, and as fillers absorb less water than fibres, they require less energy to dry. The transparency is reduced as the fillers are efficient light scatterers. Individual filler particles have a size range of 0.1-5 µm with a mean size around 0.5 µm [16, 17]. As will be seen in the following chapter, the size is chosen so that the scattering of visual light can be maximised due to resonance effects. If the shape is also platy, as for kaolin and talc, the light scattering is further increased [18]. A disadvantage of fillers is that they reduce the strength and increase the density of the product. However, if the particle size is large and the shape is scalenohedral or aggregated, the density increase can be reduced when compared with the use of smaller, spheroid or platy fillers [18, 19].

![Figure 5. Typical widths of some particle types in a fine fraction.](image)

In the stock, fibres, fines, and fillers are often encountered as larger structures, e.g. loose flocs/agglomerates, or dense aggregates. Aggregates may be remnants from the filler production process, due to insufficient dispersion. Flocculation may be induced deliberately through chemical additives, in order to retain particles in the papermaking process, but also occur naturally, especially when the concentration is high. Small particles,
e.g. fines and fillers, are especially prone to flocculation due to their high specific surface area [20].

2.3. Papermaking

When pumped to the headbox, the stock is diluted and the resulting suspension has a concentration of approximately 99% water and 1% dry substance (fibres, fines, and additives), corresponding to a moisture ratio, $MR$, of 99. The moisture ratio is defined as the mass of the water divided by the mass of the dry substance. The temperature of the suspension is 40-50°C.

The headbox distributes the suspension onto a supportive wire. This continuous wire can be 10 m wide and move at speeds up to 2000 m/min. The dewatering process starts as the wire retains the solid particles of the suspension and a fibre network, called the web, is eventually formed. It is difficult to achieve a uniform distribution of the solid substance in both the machine-direction (MD) and the cross-direction (CD) of the paper machine. The suspension itself may also be non-uniform due to particle flocculation/agglomeration. The result is a non-uniform distribution of particles in the web, which may also be referred to as grammage variations or formation.

After the initial wire dewatering, the web contains 80% water and 20% dry substance, corresponding to a moisture ratio of 4, see Figure 6. The edges of the web may be trimmed away and recycled into the stock as broke.

![Figure 6. Illustration of the different sections of a paper machine and the decrease in the moisture ratio during the process [21].](image-url)
The web then enters the press section, where it is compressed in several press nips between press felts. Water is mechanically squeezed out and taken up by the felts. After pressing, the web has 40-50% dry substance and a moisture ratio of approximately 1. At this stage, the web network contains air-filled pores, and the remaining water is mainly located inside the fibre wall, or bound to the surface of the fibres and the fines. This water is difficult to remove mechanically.

The remaining water is therefore evaporated in the drying section, where the web is heated through steam-heated drying cylinders to temperatures of 50-100°C. The process consumes much more energy than the mechanical dewatering process. Due to the large production volumes, a small saving in drying energy makes a significant difference in production cost and speed of the papermaking process. If the web is non-uniform in its solids material content, the areas of the web that have more particles will also contain more water, and take a longer time to dry. Correspondingly, areas with fewer particles contain less water and will dry faster.

At the end of the drying section, the web has approximately 4% water and 96% dry substance, corresponding to a moisture ratio around 0.04. The web may be calandered, i.e. pressed between hot cylinders to make the surface smoother. This also compresses the sheet, reducing the volume of air inside the web, which, as will be explained in the next chapter, decreases the light scattering in the sheet and increases its transparency. Finally, the web is rolled onto a pope cylinder.

Samples of the finished paper are evaluated in order to assess the product quality. However, it is desired to detect variations and problems in real-time, as the process can then be adjusted to compensate deviations. Thus, measurements are made over the entire production chain.

### 2.4. Stock characterisation

Traditionally, many stock characterisation methods have been gravimetric or based on dewatering resistance. The dewatering resistance methods, for example the Schopper-Riegler test, mimic the dewatering through the wire of a paper machine, which goes slower if fines fill the pores in the network or the fibres are fibrillated. Gravimetric methods, for example the Britt Dynamic Drainage Jar (BDDJ), determine the weight share of the sample that passes a screen with a certain hole size. As these methods only give indirect information about the morphology of the particles, and can be sensitive to changes in pulp morphology, optical static microscopy has been used as a qualitative complement.
In static microscopy, a small drop of pulp is fixated on a glass slide, and the slide is imaged at high magnification. Contrast-enhancing techniques can be used to make the particles more visible, see an example in Figure 7. Static microscopy provides high spatial resolution but has the disadvantage that it is labour-intensive and that only a few particles are imaged at the same time. Thus, it is difficult to obtain statistically representative quantitative results.

![Microscopy image of the same area in a mixture of fines and fillers, with and without contrast-enhancing techniques. Left: Brightfield; no contrast enhancement. Right: Phase contrast enhancement (courtesy of Joanna Hornatowska).](image)

In the 1980's, flow microscopes for pulp analysis were developed [22]. These so-called fibre analysers combine measurements on flowing pulp with image analysis to obtain quantitative information on a large number of particles. The spatial resolution of most fibre analysers has been sufficient to measure the morphology of the fibres, for example their length, width, curl, and number of kinks, but not to measure micrometre-sized features such as external fibrillation, fillers or a large share of the fines [23, 24]. Fines and fillers have instead been characterised, separately, through static microscopy, laser diffractometry, or gravimetric methods (see Paper A). However, recent development in the resolution of flow microscopes has opened up the possibility for detecting smaller particles, coarse fibrillation, and also the fibre wall thickness [25-28].

Fines and fillers have similar size, behave similar in the process, and often end up in the same fine fraction. Examples include fine fractions from the white water of a paper machine, which contains particles that are not retained by the wire, broke which is recirculated in the process, and pulp made from recycled paper. As fines and fillers have different impact on product properties, it would be beneficial to be able to distinguish between them. If the absolute amount of fines and fillers in a certain sample could be
measured in a simple way, the production process could be better controlled, with potential raw material and energy savings. Currently, no single measurement system is capable of differentiating between fines and fillers, or to simultaneously characterise their morphology.

2.5. Web and sheet characterisation

The produced web on a paper machine is commonly monitored by a Quality Control System (QCS), see Figure 8. In a QCS, single spot sensors traverse the web and collect various electromagnetic signals, which are then related to product properties such as thickness, grammage, moisture, or filler content. The measurement results are used to control the product properties so that they comply with the product specifications. Only a small share of the total produced area, less than 1 ‰, is analysed. In addition, as the web may move with speeds of up to 2000 m/min, the existing QCS on paper and board machines give only limited possibilities to detect short-term variations in the product properties.

When the QCS were introduced, spot sensors were used as they have a high sampling rate and the integrated signal data required less data handling capacity. However, improvements in the frame rate of video recorders and computer memory have opened up the use of image-based sensors. As images give information in two dimensions, it is possible to cover the entire produced area. Image-based web inspection have been used e.g. to detect holes in the web [30], and to monitor variations in grammage and topography [31, 32]. By stitching an image sequence together, 2D Fourier analysis may be performed, and the detected temporal variations can be linked to specific variations in the process [32].
All the mentioned measurements require the web to be illuminated, after which the reflected (back-scattered) or transmitted light is collected. However, an inspection system would be more flexible and robust without the dependence on illumination. An example of such a passive technique is thermography, which utilises the infrared radiation emitted by all materials which have a temperature above the absolute zero. The measured infrared radiation is then converted to a temperature image. Thermography has been used for qualitative inspection and research in the pulp and paper industry for more than 30 years [33, 34], but its on-line use is still under development [35].

As previously mentioned, the finished paper sheet is tested to verify its quality. Optical analysis is made to determine that the paper is sufficiently white and non-transparent, and mechanical analysis is made to verify the strength of the paper. The grammage (mass of solid material per unit area) and thickness is also measured so that the density and its inverse, the bulk, can be calculated. In paper and board making, it is often desired to have high sheet strength while maintaining a high bulk. If the bulk is high, less raw material is required and less energy is needed to dry the sheet. However, as the surface of a paper is difficult to define, thickness and bulk measurements can have high measurement uncertainty.

Mechanical properties are measured by subjecting a paper sample to deformation and recording the energy required to rupture the sheet. Commonly measured are the tensile strength, tensile stiffness, tensile energy absorption, and stretch at break, which are measured in the in-plane direction, and the z-strength, which is measured in the out-of-plane direction. The mechanical properties are often normalised by the grammage to obtain an index, e.g. the tensile index.

Many of the morphological properties of the stock influence the sheet properties. Ideally, it would be possible to model and predict the final product properties based on an analysis of the stock composition. However, the relationships are complex, and disparate results are often reported. In chemical softwood pulp, increased fibre length adversely affects the formation, but improves tensile index up to a certain length [36]. Some studies suggest that external fibrillation increase tensile index, while other instead attribute the increase to only internal fibrillation [37]. Some studies report that z-strength increases with amount of fines, while other see no correlation [38]. The overall most influencing parameter is the fibre wall thickness. As previously mentioned, external fibrillation and fibre wall thickness have only recently become possible to measure with fibre analysers. Thus, the improved metrology may facilitate increased efforts in linking stock properties to product properties.
3. Theory

3.1. Interaction between electromagnetic radiation and matter

All what we observe with our eyes and process by the visual perception system in our brain is a “finger print” of light interacting with matter and surface roughness. If a surface, i.e. the outermost atomic layer, is illuminated with white light, the surface may reflect the light, specularly, like a polished mirror, or diffusely, like chalk. The material below the surface may transmit, absorb, or re-radiate the incident light. If a portion of the incident white spectrum is absorbed and the rest is reflected or re-radiated, the surface will then be interpreted as a coloured object by our brain. Our visual system is thus an excellent, but very subjective, detector of different materials and surface properties, but it uses only a narrow wavelength band of the large electromagnetic spectrum, as shown by the VIS range (wavelengths 0.4-0.7 µm) in Figure 9.

![Electromagnetic Spectrum](image)

Figure 9. The electromagnetic spectrum, with the ultraviolet (UV), visual (VIS), near-, short-, mid-, and long-wavelength infrared (NIR, SWIR, MWIR, LWIR), and microwave wavelength ranges shown [based on 39].

Outside the visual range, “light” is referred to as electromagnetic radiation, and instead of illumination, one talks about irradiance. Due to its dual nature, electromagnetic radiation may be regarded as either particles or waves, usually dependent on the application. Its wave nature implies that electromagnetic radiation has an amplitude, a wavelength, a phase, and may be polarised in different directions. Its particle nature implies that electromagnetic radiation may only be detected as discrete bundles of
energy: photon quanta. The energy of a photon is inversely proportional to its wavelength. The more energetic UV radiation is useful for observing small particles and may also cause fluorescence, i.e. re-radiation of less energetic radiation, while thermal infrared is sensitive to absorption by molecular vibrations in the material and can thereby quantify chemical properties, e.g. the water content of a material. This thesis work investigates the potential of quantitative measurements on paper, pulp and particles by applying imaging sensors, mimicking the eye, but operating over a much larger wavelength region, from the ultraviolet (UV) to the long wavelength thermal infrared (LWIR).

The interaction between paper and electromagnetic radiation is studied in the field of paper optics. Most studies in paper optics focus on the final, dry sheet, in which recent modelling has included fines and filler particles [40, 41]. When papermaking suspensions and have been the focus of studies, relatively little attention has been given to fines or fillers [22, 42, 43]. As fibres are large, their interaction with electromagnetic radiation can be predicted by geometrical optics. It will be seen that, when the particles are small, greater attention must be paid to how their optical properties vary with moisture content.

Imagine that a collection of particles is irradiated by a beam of electromagnetic radiation, see Figure 10.

![Figure 10. Illustration of transmission, absorption and scattering (reflection, refraction, diffraction) of the incident radiation. The transmission and reflection hemispheres are also defined.](image-url)

The radiation that exits the collection in the forward direction is said to have been transmitted. If a detector is placed on the other side of the suspension,
the measured power, or flux, of the transmitted radiation will be lower than that of the original beam. The loss in power is called extinction. Extinction occurs through scattering or absorption. In this thesis, the treatment of scattering will be limited to the most common scattering process, elastic scattering, which redirects the radiation but does not remove energy from it. Absorption removes energy from the original beam by changing its frequency (wavelength).

The ability of a medium to attenuate a beam can be quantified by measuring the transmitted, reflected, or absorbed power, and relating it to the power $P_0$ [W] of the incident beam. The reflectance $\rho$, transmittance $\tau$, and absorptance $\alpha$ are thus defined:

$$\rho = \frac{P_r}{P_0}, \quad \tau = \frac{P_t}{P_0}, \quad \alpha = \frac{P_{abs}}{P_0}$$  \[Eq. 1\]

where $P_r$, $P_t$ and $P_{abs}$ is the power of the reflected (back-scattered), transmitted, or absorbed radiation, respectively. As it is difficult to measure the power loss by absorption, the absorptance is often derived from reflectance and transmittance measurements. According to energy conservation laws, the sum of transmission, reflection, and absorption must equal unity.

$$\alpha(\lambda,\theta) + \rho(\lambda,\theta) + \tau(\lambda,\theta) = 1$$  \[Eq. 2\]

Transmission, reflection and absorption are macroscopic manifestations of microscopic interactions between irradiance and matter and depend on the incidence angle $\theta$, i.e. the angle between the incident direction and the normal to the surface, and the wavelength $\lambda$. The complex refractive index $\tilde{n}$ is used to describe how the electromagnetic radiation is changed when it propagates through a medium:

$$\tilde{n}(\lambda) = n(\lambda) + i\kappa(\lambda)$$  \[Eq. 3\]

where the real part $n$ is simply called the refractive index, and $\kappa$ is called the extinction coefficient. In the remainder of the text, the wavelength dependence of the complex refractive index will be implicit. The refractive index mainly relates to scattering processes, while the extinction coefficient mainly relates to absorption processes. Colour changes, fluorescence and thermal emission are effects of absorption processes.

A refractive index is only well-defined for a homogeneous medium. Thus, many particles and materials will have an effective refractive index, representing the combined effect of the constituent materials and their
refractive indices. This can be exemplified by considering a stock, where the particles are immersed in water. Two of the main components of wood, cellulose and hemicellulose, are hydrophilic. Lignin is hydrophobic, but constitutes a smaller share of the substance. Thus, fibres and fines are overall hydrophilic and absorb water into their structure and also increase in size, i.e., they swell.

As the refractive index of water is lower than that of dry fibres and fines, see Table 1, their refractive index decreases as they absorb water. As fines can hold more water than fibres [44], their refractive index is lowered more. The exact refractive index of wet fibres or fines does not appear to have been measured. However, volume-based mixing rules can be used to estimate the effective refractive index of an inhomogeneous particle or a particle mixture [42, 45].

Table 1. Refractive indices of some substances relevant to papermaking. Extinction coefficient values $< 10^{-4}$ were regarded as negligible.

<table>
<thead>
<tr>
<th>$\lambda_{500\text{nm}}$</th>
<th>Air $n$</th>
<th>Water $n$</th>
<th>Cellulose $n$</th>
<th>Hemicellulose $n$</th>
<th>Lignin $n$</th>
<th>PCC $n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\kappa$</td>
<td>0</td>
<td>0</td>
<td>0.001</td>
<td>0.025</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ref.</td>
<td>[46]</td>
<td>[47]</td>
<td>[48]</td>
<td>[49, 50]</td>
<td>[49]</td>
<td>[16, 51]</td>
</tr>
</tbody>
</table>

When radiation strikes a boundary between two media, no absorption or scattering occur if their refractive indices are identical. In most cases, they are not, and the changes to the electromagnetic radiation depend on the refractive index contrast. The refractive index contrast is given by the relative complex refractive index $m$. For a particle immersed in water, the relative refractive index is expressed as:

$$m = \frac{\tilde{n}_{\text{particle}}}{\tilde{n}_{\text{water}}} \quad \text{[Eq. 4]}$$

A particle with a relative refractive index that is close to unity is said to be optically soft. Otherwise, it is said to be optically hard. Fines are examples of optically soft particles. As fines absorb much water, they will have a low refractive index contrast relative to the surrounding water. They will interact little with incident radiation, and will thus be difficult to detect in an optical measurement. Most papermaking fillers are hydrophobic [52]. Thus, they change little in refractive index when immersed in water, their refractive index contrast is high, and they are optically hard. As will be seen in the following section, the size and shape of the particles and the wavelength of the electromagnetic radiation also influence the scattering.
3.2. Scattering

Scattering is a boundary phenomenon that occurs when an electromagnetic wave encounters a medium with a different refractive index. In addition to the relative refractive index, the most important parameter for the scattering of electromagnetic radiation by a particle is the relative size $x$. The relative size indicates how large the particle is compared to the wavelength of the incident radiation:

$$x = \frac{2\pi d}{\lambda}$$  \hspace{1cm} \text{[Eq. 5]}

where $\lambda$ [m] is the wavelength and $d$ [m] is a characteristic dimension of the particle, see also Figure 11. For a spherical particle, $d$ would be its diameter. For a cylindrical particle, the best choice of characteristic dimension is not obvious. Area-equivalent diameter or semi-major axis has been suggested [53].

![Figure 11. Relative size ($x$) vs. wavelength ($\lambda$) and characteristic dimension ($d$), shown with logarithmic scale. The scattering regimes for various particles and wavelength ranges are also shown [inspired by 41].](image)

If a single particle is irradiated by a monochromatic beam of electromagnetic radiation, the total power $P_{sc}$ [W] scattered in all directions can be described as:

$$P_{sc} = I_0 C_{sc}$$  \hspace{1cm} \text{[Eq. 6]}
where $I_0 \, [W/m^2]$ is the irradiance of the emitted beam, and $C_{sc} \, [m^2]$ is the scattering cross-section. In radiometry the term intensity, or more correctly radiant intensity, refers to radiant power per steradian [W/sr] [54]. However, in the context of measurement of radiation with a detector, the power measured over a certain detector area, i.e. the detector output, is commonly called intensity, despite being an irradiance. Due to the common use of “intensity” when relating to the output of a measurement instrument, intensity will be used in the rest of this thesis as replacement of irradiance.

The cross-section in Eq. 6 can be thought of as the area overlap between the collimated irradiating beam and the particle. It is a function of particle shape, size, material, wavelength and direction. The cross-section can be given by:

$$C_{sc} = \frac{1}{k^2} \int D_{sc}(\Omega, m, x) d\Omega$$  \hspace{1cm} [Eq. 7] \\

$$d\Omega = \sin \theta d\theta d\phi$$  \hspace{1cm} [Eq. 8]

where $\Omega \, [sr]$, $\theta \, [rad]$ and $\phi \, [rad]$ are the scattering solid angle, polar angle and azimuthal angle, respectively, see Figure 12, $k \, [m^{-1}]$ is the wave number, and $D_{sc}$ will be called the directional scattering function [55].

![Figure 12. Illustration of the scattering of an incident beam into a solid angle element $d\Omega$, either in-plane (specularly) or out-of-plane (diffusely). The polar angle $\theta$ and the azimuthal angle $\phi$ are also shown [based on 56].](image)

The intensity scattered in a specific direction, for example that of a detector, can then be obtained by combining Eq. 6 and Eq. 7:
\[ I_{sc} = \frac{I_0}{k^2R^2}D_{sc}(\Omega,m,x) \]  

[Eq. 9]

where \( I_{sc} \) [W/m²] is the intensity of the scattered beam and \( R \) [m] is the distance between the particle and the detector. Eq. 9 tells us that the directional scattering function \( D_{sc} \) can be obtained by angle-resolved measurements of the scattered intensity. \( D_{sc} \) can also be theoretically predicted by solving Maxwell’s equations under the boundary conditions imposed by the size and shape of the particle. The most widely used solution for scattering of single-particle type is the Mie theory [57]. It was developed for spherical particles of any size. For a spherical particle, the dependence on the solid angle \( \Omega \) is reduced to a dependence on only the polar angle \( \theta \). If the radiation is unpolarised, the Mie theory gives the directional scattering function as:

\[ D_{sc}(\theta,m,x) = \frac{1}{2}\left(|S_1(\theta,m,x)|^2 + |S_2(\theta,m,x)|^2\right) \]  

[Eq. 10]

where \( S_1 \) and \( S_2 \) are scattering amplitude functions for the two states of polarisation, given by:

\[
\begin{align*}
S_1(\theta,m,x) &= \sum_{j=1}^{\infty} \frac{2j+1}{j(j+1)} \left[ a_j(m,x)\zeta_j(\theta) + b_j(m,x)\psi_j(\theta) \right] \\
S_2(\theta,m,x) &= \sum_{j=1}^{\infty} \frac{2j+1}{j(j+1)} \left[ a_j(m,x)\psi_j(\theta) + b_j(m,x)\zeta_j(\theta) \right]
\end{align*}
\]  

[Eq. 11]

The functions \( a(m,x) \), \( \zeta(\theta) \), \( b(m,x) \), and \( \psi(\theta) \) are based on Legendre and Riccati-Bessel functions, and can be found in textbooks on light scattering [58]. A feature of Mie scattering is resonance effects, which occur when the size of the particle is of the same order of magnitude as the wavelength. Resonance can increase the intensity of the scattered radiation significantly.

As the Mie theory is complex, simpler approximations are used whenever possible. Which approximations that can be used depend on the relative size and the relative refractive index of the particles, see Figure 13. For particles which are small relative to the wavelength of the illuminating radiation, i.e. \( x << 1 \), the Rayleigh approximation can be used. For particles much larger than the wavelength, \( x >> 1 \), geometrical optics or the Fraunhofer approximation can be used. If the relative size is around unity, there are few other options than to use the Mie theory. However, additional options are available if the particles are optically soft. Then, the Rayleigh-Gans approximation can be used.
approximation may be used for particles with relative size around unity, and the anomalous diffraction theory (ADT) if the relative size is large \[45, 53, 59\].

Figure 13. Illustration of approximate scattering regimes versus logarithmic relative size and refractive index, at visual wavelengths. Approximate regimes for various papermaking particles are also illustrated.

In the Rayleigh regime, as \(x \to 0\), the Mie equation (Eq. 10) approximates to [60]:

\[
D_{sc}(\theta,m,x) = \frac{x^4 d^2}{2} \left( \frac{m^2-1}{m^2+2} \right)^2 \frac{8\pi^4 d^6}{\lambda^4} \left( \frac{m^2-1}{m^2+2} \right)^2 (1+\cos^2 \theta) \tag{12}
\]

As the scattering intensity is proportional to \(d^6\), a small decrease in size will give a large decrease in scattering. Additionally, if \(m\) is only weakly dependent on the wavelength, the intensity is proportional to \(\lambda^{-4}\).

For large and opaque particles \((x >> 1, \ m >> 1)\), the Fraunhofer approximation is applicable, and the directional scattering function is given by [61]:

\[
D_{sc}(\theta,x) = x^4 \left( \frac{J_1(x \sin \theta)}{x \sin \theta} \right) = \frac{16\pi^4 d^4}{\lambda^4} \left( \frac{J_1(x \sin \theta)}{x \sin \theta} \right) \tag{13}
\]

where \(J_1\) is the first-order Bessel function of the first kind. The periodical \((\cos, \sin)\) parts of \(D_{sc}\) create intensity maxima and minima at certain angles.
\( \theta \). The directions of scattering can be coarsely grouped into forward-scattering (FSC) and back-scattering (BSC). FSC is scattered at angles \(-90 < \theta < 90^\circ\) relative to the irradiating beam, i.e. corresponding to the transmission hemisphere, see Figure 10 and Figure 14. BSC is scattered in the \(\pm(90^\circ-180^\circ)\) range relative to the irradiating beam, i.e. corresponding to the reflection hemisphere. Based on the macroscopic changes to the scattered electromagnetic wave, the scattering is classified as reflection, refraction or diffraction.

\[ \text{Rayleigh regime} \quad (d \sim \lambda/10, \ x \sim 0.6) \]

\[ \text{Mie regime} \quad (d \sim \lambda/4, \ x \sim 1.6) \]

Figure 14. Definitions of scattering directions: the back-scattering (BSC) hemisphere, the forward-scattering (FSC) hemisphere, specific side-scattering (SSC), and specific forward-scattering (SFSC). The reflection, refraction and diffraction types of scattering are also illustrated.

As the angles 0° and ±90° give special cases in many scattering equations, the term specific forward scattering (SFSC) is introduced for the scattering at 0° angle, and the term side-scattering (SSC) for the scattering ±90° (perpendicular) to the irradiating beam. For small particles falling into the Rayleigh regime, the scattering intensity has its maxima at 0° and 180° and its minima at ±90° (Eq. 12). Thus, the BSC intensity is relatively strong. With increasing size, the SSC and SFSC increase, see Figure 15. For large particles falling into the Fraunhofer regime, the intensity peaks at 0°, and SFSC dominates (Eq. 13). The increase in FSC is mainly attributed to diffraction.
As previously mentioned, the Mie theory was developed assuming a spherical and homogeneous particle. Otherwise, its shape and texture significantly impacts its scattering. Many papermaking particles are approximately cylindrical in shape. At sharp edges, for example the ends of a cylinder, scattering due to diffraction increases. The phenomenon is called end effects. It has been proposed that the end effects of a cylinder can be ignored if the aspect ratio (length divided by width) is sufficiently large, e.g. > 3 [63]. Then, the scattering cross-section of a finite cylinder could be obtained by multiplying the cross-section per unit length of an infinite cylinder with the length of the finite cylinder [58]. However, if the conditions of the Rayleigh-Gans approximations are applicable, it would be a better choice for predictions of the scattering by a finite cylinder, as it is valid for particles of any shape [59].

Scattering by a single particle is rarely encountered in reality. The scattering by a medium can be treated similarly to single particle scattering provided that certain conditions are met. First, the particles must be packed sparsely enough that their scattering effect on each other is negligible compared to the scattering effect of the external, incident radiation [59]. Secondly, the distances between the particles should be random, so that their scattering is incoherent, and the total number of particles should be large. If these conditions are fulfilled, the scattering is said to be independent, or of single-particle type, and the Mie theory can be applied by adding the cross sections of all particles in the irradiated volume of the medium [55]. A dilute suspension is an example of a medium with independent scattering. If the conditions are not fulfilled, the scattering is dependent, and the propagation of radiation is more complex to predict due to multiple scattering effects. An example of a material exhibiting dependent scattering is paper, where the distances between the particles are random, but their packing can be tight [40, 41].
3.3. Absorption

Atoms and molecules can only exist in certain discrete energy states. For liquids and solids, the energy states are so closely spaced that they form continuums, or bands. However, there are absorption gaps of energies not covered by any band. Changes to the atoms or molecules, such as excitation, translation or vibration, can only happen by absorption of a photon or another energetic interaction with the right energy.

Even if a structure is irradiated by a photon suitable to lift it to a certain absorption band, it is not given that absorption occurs. At every interaction, a photon has a finite chance of being absorbed. A glossy high reflecting surface or a fully transparent medium are examples of little or no absorption. On the other hand, a porous medium would give ample multiple scattering and higher chance of absorption. An example of a porous medium is the fibre network of a paper sheet.

If the photon is absorbed, it is often re-radiated at wavelengths longer than that of the absorbed radiation. Two such processes are the emission of thermal radiation and fluorescence. If the absorbed radiation matches translation or vibration bands in the molecule or structure, the temperature of the material increases. The energy may then be re-radiated as thermal radiation. All objects with temperatures above the absolute zero emit thermal radiation. The emission of a perfect emitter, a so-called blackbody, is only a function of temperature and wavelength, and is given by Planck’s law. Planck’s law expresses the spectral radiance $B_{BB}$ [Wm$^{-2}$sr$^{-1}$] emitted by a blackbody as:

$$B_{BB}(\lambda,T) = \frac{2hc^2}{\lambda^5} \frac{hc}{e^{\frac{hc}{\lambda k_B T}} - 1}$$  \[Eq. 14\]

where $h$ is Planck’s constant (6.63 x 10$^{-34}$ J/s), $c$ is the speed of light in vacuum (3.00 x 10$^8$ m/s), $k_B$ is Boltzmann’s constant (1.38 x 10$^{-23}$ J/K), and $T$ [K] is the temperature. For normal environmental temperatures the emitted radiation is strongest in the infrared wavelength range. For example, at temperature 23°C, the peak lies at a wavelength of 10 µm. Most real materials are not blackbody radiators. Instead, they emit only a fraction of that of a blackbody, and are called greybodies:

$$B_{obj}(\lambda,T) = \varepsilon \cdot B_{BB}(\lambda,T)$$  \[Eq. 15\]

where $\varepsilon$ is the emittance, or emissivity, of the material. The emittance is a material parameter which can vary with wavelength, temperature,
observation angle, and composition. It can only rarely be theoretically predicted. Instead, it has to be measured. Under steady-state conditions, and if other absorption processes are negligible, the emittance is equal to the absorptance:

\[ \varepsilon(\lambda, \theta) = \alpha(\lambda, \theta) \]  

[Eq. 16]

Recalling Eq. 2, we get:

\[ \varepsilon(\lambda, \theta) = 1 - \rho(\lambda, \theta) - \tau(\lambda, \theta) \]  

[Eq. 17]

Thus, a common way of measuring the emittance is to measure the reflectance and transmittance with a spectrophotometer. However, it can also be measured by reference techniques, where the emitted thermal radiation from an object with unknown emittance is compared to that emitted from an object with known emittance.

Fluorescence occurs when an atom or molecule is excited to an excited singlet state by absorbing a photon matching an absorption gap. If the irradiating photon has too little energy, no absorption occurs. If it has too much energy, fluorescence may still occur, with the excess radiation dissipated as heat. The atom or molecule keeps the excited states for a few nanoseconds. During this time, some of the excitation energy is dissipated, and some is lost in interactions with the molecular environment. When the atom or molecule drops to its lower energy level, it emits a photon, the fluorescence, see the illustration in Figure 16.

![Fluorescence illustration](image)

*Figure 16. Fundamentals of fluorescence [based on 64]*

Most fluorescence is of the Stoke’s type, where the wavelength of the emitted photon is longer than the wavelength of the absorbed photon. The difference
in wavelength is useful as it allows emitted photons to be distinguished from the irradiating photons.

Compounds which exhibit fluorescence are called fluorophores. Measured fluorescence is the integrated emission from the fluorophores over entire volume of the particle. Thus, smaller particles will have weaker fluorescence. Under well-controlled conditions of particles with similar size, this can be used to estimate particle thickness. When fluorescence is utilized in measurements, the sample is often stained with fluorescent dyes containing strong, specific fluorophores which bind well to the compounds of the sample. Many materials also contain inherent fluorophores, and the fluorescence from unstained samples is called autofluorescence.

The autofluorescence of pulp is commonly associated with lignin, whose emission is strongest for ultraviolet (UV) excitation wavelengths [65]. However, if the concentration of lignin is high, fluorescence at UV and blue wavelengths has a large probability of being re-absorbed by the sample. Due to this self-absorption, the fluorescence intensity may decrease when the lignin concentration is increased [66]. To circumvent the self-absorption, it has been proposed that a red excitation wavelength (630 nm) could be used instead [67]. Bleached chemical pulps have low lignin content. However, autofluorescence from pure cellulose has also been detected, and at least one study detected autofluorescence from bleached kraft softwood (BKSW) at UV excitation wavelengths [67].

The autofluorescence from thinner fines, such as microfibrils, may be weak and thus require staining. The compounds of a fibre are not equally easy to stain. Lignin is relatively easy to stain. Acidin orange, which binds to lignin, may be dripped directly into a sample. The sample can then be measured after a quick stirring. Cellulose and hemicellulose, which are dominant compounds in fibrils, are relatively difficult to stain. Dyes such as Calcofluor White and Congo red may require 1 hour heating it uniform temperature to bind to the cellulose [68, 69]. Thus, staining of cellulose is mainly made by laboratory microscopists, and not as a part of an automated process analysis.

3.4. Imaging

In imaging, the photons emitted or scattered from a motive are detected by a 2D array of detector elements. The area of the motive which is imaged into the camera is called the field of view (FOV), see Figure 17. A single detector element is called a pixel, and has a finite size given by the pitch (pixel to pixel distance). The area of the motive which is imaged onto a single pixel is called the instantaneous field of view (IFOV). The most common 2D arrays of pixels are charge-coupled devices (CCD) and complementary metal oxide
semiconductors (CMOS). The absorbed photons create a photoelectric current in the pixel sensor which is proportional to the intensity of the radiation. The voltage, or charge built by the current, is then digitised to an intensity value.

An optical system is needed to guide and focus the radiation from the object to the detector. Lenses, mirrors, filters, gratings and beam-splitters may all be part of an optical system. Glass is the most common material for lenses, and can be used for wavelengths between 360 nm (near-UV) to 1300 nm (near-IR, NIR).

![Diagram](image)

**Figure 17. Illustration of field of view (FOV) and instantaneous field of view (IFOV) in the vertical direction.**

A large number of factors influence the quality of an image, and thus the possibility to extract information from it. The most important quality aspect is the resolution. In an imaging system, it traditionally refers to the possibility of distinguishing two high contrast features from each other when they are very close. Geometrical constraints on the resolution include the diffraction limit, the pixel size, the distance to the motive, and aberrations from the optical system. Other factors include noise from the detector and the surroundings, the contrast, the focus, particle motion, and sampling constraints.

Due to diffraction in the optical system, no detail is ever imaged perfectly sharp. Instead, the radiation from the feature is spread out in a way that is dependent on the wavelength of the radiation and the size of the objective in the optical system. As mentioned above, if two details are sufficiently close, they become indistinguishable. Using visual light, the smallest separation to be resolved is approximately 200 nm. Using long-wavelength infrared (LWIR) radiation, the limit is approximately 7 µm. Even if two details are theoretically distinguishable, the CCD detector must be able to capture the difference. Thus, the pixel size also limits the resolution, see **Figure 18.**
In practice, the resolution is not limited by the geometrical constraints, but by noise and the contrast of the motive [71]. All measurements have some level of noise, which can come from the detector and from the surroundings. If the noise is high, the signal from a feature must be higher than the noise in order to be distinguishable, i.e. the contrast $C$ must be high:

$$C = \frac{I_{\text{obj}} - I_{\text{bg}}}{I_{\text{bg}}}$$  \[\text{Eq. 18}\]

where $I_{\text{obj}}$ and $I_{\text{bg}}$ are the intensity of the object and background, respectively. Scattering and absorption create contrast by removing irradiance, making the object look darker than the background. If the refractive index contrast between a small particle and the surrounding is large, the scattering is high, resulting in a good image contrast. Contrast may also be increased through fluorescent staining, which would make the motive emit more radiation. It would then look brighter than the background. The limitations imposed by the contrast and noise on the size $d$ of a resolvable detail can be expressed as:

$$d = \left(\frac{k^2}{N_p C^2}\right)^{-1}$$  \[\text{Eq. 19}\]
where $N_p$ is the number of detected photons per unit area in the image, i.e. the signal, and $k$ is a noise-related quantity with a typical value of $k = 5$ [71]. The influence of the noise and contrast is illustrated in Figure 19.

![Figure 19. Illustrations of the influence of contrast and resolution and contrast and noise on the image quality [based on 72, 73].](image)

So far, the resolution in the image plane has been considered, i.e., it has been assumed that the particle is in focus. An object will look sharp if it is positioned so that it is imaged in the focal plane of the optical system. There is a range of distances from the focal plane where the sharpness is acceptable. That range is called the depth of focus or depth of field, see Figure 20.

![Figure 20. Illustration of depth of field and its impact on the image quality [based on 74].](image)
The depth of field is inversely proportional to the magnification of the optical system, so that a higher magnification gives a narrower depth of field. The depth of field is one of the most limiting factors in flow microscopes such as fibre analysers. As the particle movement in flow microscopes is not fully restricted, the depth of field thus needs to be wide. Simultaneously, a high magnification is desired. Some contrast enhancing techniques which are used for fibre characterisation, like phase contrast microscopy, cannot be used in flow microscopes as they would too severely narrow the depth of field [75].

Finally, it should be noted that sufficient resolution does not imply detection, or vice versa. An object can be much larger than the resolution and still not be detected in an image if its intensity relative to the noise, i.e. its contrast, is too low. Objects can be detected even though they are smaller than the resolution, provided that their contrast is large enough. This fact is utilised in fluorescence microscopy, where fluorescent stains are used to increase the intensity of features, and thus their contrast. However, while an object may be detected (counted) even though it is smaller than the spatial resolution, the object size cannot accurately be determined from the image in this case.
4. Optical measurements

4.1. Particle size analysis

Knowledge of the size and shape of particles enable prediction of product properties, process control and process evaluation. Optical measurement methods are powerful as they are non-destructive and fairly easy to automate. However, as was seen in the previous chapter, their use is limited by the optical properties of the sample.

An ideal particle size analyser is able to measure both the smallest and largest particle in a sample. If the sample is polydisperse, i.e. has a wide range of sizes, the task can be challenging. If a scattering theory is used to interpret the data, it must be valid for the entire range of particle sizes. The spatial resolution of the system must be good enough to detect the smallest particle. Simultaneously, the field of view must be big enough to cover the largest particle. Thus, the size range of the instrument should be as wide as possible. If there is a pump or fluidics system, its channels must be wide enough not to be plugged by large particles. But the channels must also be narrow enough so that particles don’t move out of the depth of field. In reality, any measurement system must make compromises.

A comprehensive review of particle size characterisation was made in Paper A. Three methods based on scattering and/or absorption: imaging particle analysis, laser diffractometry, and flow cytometry, are detailed below. Their strengths and limitations are summarised in Table 2.

<table>
<thead>
<tr>
<th></th>
<th>Imaging particle analysis</th>
<th>Laser diffractometry</th>
<th>Flow cytometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical size range</td>
<td>0.2-9000 µm</td>
<td>0.002-3000 µm</td>
<td>0.2-120 µm</td>
</tr>
<tr>
<td>Strengths</td>
<td>High resolution</td>
<td>Good statistics</td>
<td>Good statistics</td>
</tr>
<tr>
<td>Limitations</td>
<td>Bad statistics, laborious</td>
<td>No shape, no count</td>
<td>No shape, narrow size range</td>
</tr>
<tr>
<td>Inherent weighting</td>
<td>Number</td>
<td>Volume</td>
<td>Number</td>
</tr>
</tbody>
</table>

Table 2. Strengths and limitations of some optical size characterisation techniques.
The first method, imaging particle analysis, uses quantitative microscopy on fixed or flowing samples to infer the particle size. An imaged particle will subtend a certain pixel area on the detector. By knowledge of size of the IFOV, the true size of the particle can be calculated. The (projected) shape can also be obtained, which is a unique feature of imaging particle analysis. The difficulty is to determine which pixels in the image that belong to the particle, and which pixels that are background or noise: the segmentation or binarisation step [76, 77], see Figure 21.

![Figure 21. Demonstration of segmentation (binarisation). Left: Original greyscale image. Middle: Segmented using a low threshold value. Right: Segmented using a high threshold value.](image)

Segmentation is usually based on an intensity threshold value. Only pixels classified as belonging to a particle are used in the calculation of particle size. Thus, at least one pixel in the imaged particle must have sufficient intensity to reach above the threshold if the particle is to be accounted for. In practice, more than one pixel is required, as single pixels are often attributed to noise and removed. If parts of the particle have insufficient intensity, the particle size may be underestimated if the threshold value is high, see Figure 22. However, a too low threshold value can lead to an overestimation of the size. That the size of the particle is dependent on the threshold value is called the quantization error [78]. Dependent on the noise level and the contrast, it can be difficult to find an optimal threshold value. As mentioned in the previous section, a low refractive index contrast will give a low image contrast. Thus, fines and external fibrillation can be difficult to segment from a water background.

The alignment of the particle relative to the centre of the pixel can introduce a positioning error [78]. Due to bad positioning, the radiation from the particle can be spread out over several pixels, making it look larger but fainter, see again Figure 22. This error is particularly important if the size of the particle is similar to the pixel size. Finally, sampling constraints must be considered for accurate representation of the particle. According to the sampling theorem, to accurately reproduce one “line pair”, you need at least two pixels. At least three pixels are required to determine a shape. Thus, an instrument with a pixel resolution of 1 µm could characterise particles larger than 3 µm with some degree of accuracy.
The second method, laser diffractometry, is based on the inverse scattering problem, i.e. to recover the size of a particle based on measurements of its directional scattering distribution. In the previous chapter, it was seen that the intensity and direction of electromagnetic radiation scattered by particles is dependent on their size, shape and complex refractive index. Thus, in order to solve the inverse scattering problem, the shape and the refractive index must be reduced from the equation. The shape is reduced by assuming that the particles are spherical. Due to the assumption of sphericity, the output of a laser diffractometer is given as sphere-equivalent diameter (SED). The SED is the diameter that a sphere with the same volume as the particle would have, see Figure 23. As SED is the only output provided by laser diffractometry, the technique cannot be used to directly infer particle shape.

The refractive index is reduced either by employing the Fraunhofer approximation, or by requiring that it is known by the user. As was seen in Eq. 13, the Fraunhofer approximation does not require the refractive index.
However, it is only an accurate model for particles larger than about 25 µm [80]. For other sizes, the Mie theory should be used, and the refractive index must be known by the user. Scattering by diffraction cannot be used to resolve sizes below the diffraction limit: approximately 0.2 µm. To infer smaller sizes, the polarisation state of the light may be used [81]. The resolution of a laser diffractometer is usually tested on gold spheres with high refractive index. Thus, it is not certain that the resolution is the same for particles with other geometries and lower refractive index.

The third method, flow cytometry, utilises both scattering and absorption to characterise particles. Before measurement, the sample is often stained with a fluorescent dye. Hydrodynamic focusing is used to focus the sample suspension into a thin, flowing stream. The stream is illuminated by a laser for scattering measurements, and one or more lasers for fluorescent excitation. The specific forward-scattering (SFSC, $\theta = 0^\circ$), side-scattering (SSC, $\theta = 90^\circ$), and fluorescent intensities are then measured. In flow cytometry literature, SFSC is said to be related to particle size, while SSC is said to be related to particle texture, and, to a lesser degree, size [82, 83]. The reasoning for the latter is that irregular surfaces or structures increase scattering to the sides. The information is used to qualitatively classify particles. Particle size may also be obtained through a reference approach, where calibration particles with well-known size and optical properties are measured. The SFSC and SSC of the calibration particles are then compared to that of the sample, and give a circle-equivalent diameter (CED). Silica microspheres are increasingly used as calibration particles, as their optical properties are similar to biological samples [84, 85].

Finally, the presentation of the data should be addressed. Particle size data is usually given as a distribution, e.g. a histogram, from which mean values and other statistics can be calculated, see Figure 24. If every particle is given equal importance, or weight, in the histogram, the data is said to be number-weighted. In some applications, longer or bigger particles may be more important than smaller. If the occurrence of particles is length-, area- or volume-weighted, the impact of the size on the product properties can be more easily inferred from the distribution. For example, length-weighting is common in stock characterisation in order to account for the higher mass of the longer particles. A weighted mean value $x_{w,j}$, for example the mean value of a histogram bin, is calculated as:

$$x_{w,j} = \frac{\sum_{j=1}^{N} x_j \cdot w_j}{\sum_{j=1}^{N} w_j}$$

[Eq. 20]
where \( x_j \) is the un-weighted mean value of the \( j \):th particle and \( w_j \) is the value of its weight. In number-weighting, all \( w_j \) are set to unity. If a volume-weighted length was to be calculated, \( x_j \) would be the length of an individual particle, and \( w_j \) would be its volume. Techniques which measure individual particles, e.g. imaging particle analysis, are inherently number-weighted. Other techniques have different weightings, for example volume-weighting in the case of laser diffractometry. If data from two different measurement instruments are to be compared, both the compared property and the weighting must be the same [86, 87].

![Figure 24. Example of a fibre length distribution where different weightings (number, length, volume) have been applied to the same data. Particles with a length shorter than 100 µm (grey shaded area) were not included in the analysis.](image)

4.2. Thermography

In thermography, the thermal emission from an object is measured by a 2D pixel array sensitive to infrared radiation, usually as a function of time in a video sequence. Most thermographic cameras operate in either the MWIR wavelength range (3.0-5.0 µm) or the LWIR wavelength range (7.5-13.0 µm) due to limitations of the sensor materials and absorption bands in the atmosphere. The detected infrared radiation can then be converted to a temperature image via Planck’s law, by providing the emittance of the measured object (Eq. 14, Eq. 15).

Some additional considerations must be made during thermographic measurements, compared to visual imaging. The sample, the detector and the surrounding all emit thermal radiation. Thus, the noise can be very high. MWIR cameras generally use an array of photon-counting detector elements, which are cooled to minimise emission from the detector itself. LWIR cameras use an array of uncooled microbolometers. Microbolometer
cameras have traditionally been cheaper but less sensitive and with a lower frame rate than cooled cameras. However, due to intensive development, they are quickly approaching the performance of cooled detectors [88]. If the emittance of the sample and the surrounding is equal, the contrast in a thermographic image is given by:

$$C = 100 \cdot \frac{hc}{\lambda k_B T_{\text{sample}}} \frac{T_{\text{sample}} - T_{\text{amb}}}{T_{\text{sample}}}$$  \hspace{1cm} \text{[Eq. 21]}

where $T_{\text{sample}}$ and $T_{\text{amb}}$ are the temperatures of the sample and the surroundings, respectively, and the other parameters are the same as for Eq. 14 [71]. This implies that, if the sample and the surroundings have the same temperature and the same emittance, there will be no image contrast. To achieve a temperature difference, the sample may either be heated or cooled. Heating is preferred as this will increase the number of emitted photons, providing a stronger signal. An apparent temperature contrast is also created if two objects with the same temperature have different emittance.

It was stated in the papermaking section that the web may have a wide range of temperatures and moisture ratios during the papermaking process, i.e. those parameters vary in time. It was also mentioned that a non-uniform distribution of particles in the web results in moisture variations. Due to evaporative cooling, wetter areas of the web get a lower temperature than drier areas, creating a temperature contrast. The temperature differences make it therefore possible for thermography to be used for monitoring variations in the web, see Figure 25.

![Figure 25. Example of a visual (left) and infrared thermographic (right) image of the produced web (pope) on a paper machine. It can be noted that the web is viewed at a range of observation angles due to the cylindrical shape of the pope.](image-url)
Thermography cannot only be used for studying the non-uniformity of the papermaking process. When a paper sheet ruptures, heat is released. The same applies to absorption processes, where heat is released due to the adsorption of the water to the cellulosic surface. Thus, thermography may also be used to study the deformation of or absorption by paper and board, provided that quantitative temperature values can be measured with high accuracy.

The accuracy of the emittance influences both qualitative (relative) and quantitative (absolute) thermographic measurements. The influence on quantitative measurements is however much larger. An emittance error of 15% could introduce an error of 3% to the measured object temperature in Kelvin or Celsius [89]. For example, using an emittance of 0.82 when the true emittance is 0.71 would impart an error of 10°C, if the measured object temperature is 70°C. Despite this, generic, tabulated emittance values are often used in thermographic analysis. In the pulp and paper industry, this can partly be explained by a lack of studies where the emittance of fibre-based materials has been measured. As the emittance may vary with wavelength, observation angle (direction), surface roughness, and web composition (including moisture), the influence of all these factors on the emittance must be accounted for. There is partly a lack of appropriate methods for performing such measurements. In previous studies, some of the reported results are contradictory [90-92]. Thus, new methods and additional measurements would aid in determining suitable emittance values for pulp and paper applications.
5. Methods for fine material characterisation

5.1. The ImageStream imaging flow cytometer

The ImageStream\textsuperscript{X} MarkII imaging flow cytometer from Merck Millipore is developed for life science applications in e.g. microbiology, biochemistry, and medicine related topics. An idea devised in this thesis work was to evaluate the cytometer for use with particles present in a papermaking stock. The first results of these measurements are presented in Paper B and Paper C. As these studies comprise the first reported use of an ImageStream for pulp and paper applications, some attention will be given to the properties of the instrument and the changes made to adapt the analysis to stock samples.

In the ImageStream, the specific forward-scattering (SFSC) detector of a traditional flow cytometer has been replaced by a CCD, thus providing an image instead of the integrated intensity of the particle. The ImageStream system used in the studies presented in this thesis had four illumination sources, together allowing a wide range of optical signals to be collected. The illumination sources comprise a multispectral source for transmitted light (brightfield), a 488 nm laser for fluorescent excitation, a 785 nm laser for side-scattering (SSC) measurements, and an 830 nm laser for flow calibration. The power of the 830 nm laser cannot be controlled in the user interface, while the intensity of the other lasers can be varied. The brightfield source illuminates at an angle of 0° relative to the detector, while the lasers illuminate at angle 90°. The light is directed to a filter stack which spectrally divides it into six different wavelength ranges referred to as “channels”, see Figure 26.

The ImageStream camera uses time-delay-integration. This means that the charges created by the irradiance from the motive are continuously shifted from pixel to pixel down the detector, parallel to the axis of flow. Thus, the signal can be gathered from each particle for a longer amount of time, increasing the possibility of detecting faint objects. To synchronise the camera with the particle flow, 0.1 µm polystyrene spheres called “SpeedBeads” are mixed into the flow. These are illuminated by the 830 nm laser, and the scattered light is used to calculate the flow speed. As the SpeedBeads are mixed with sample particles, they must be removed from the data set in order not to disturb the measurement result. An automatic
routine for removal of images containing SpeedBeads was available. However, it was found that the routine also removed images containing fines and fillers of similar size. Thus, the routine was disabled and two different approaches were taken to remove the SpeedBeads: one approach for samples containing fines only, and one approach for samples containing fillers.

![ImageStream channels](image)

**Figure 26.** Example of the six image channels of the ImageStream, each corresponding to a specific wavelength range, and the composite of three of the six channels (rightmost image).

For samples containing fines only, the high SSC of the Speedbeads was utilised. Due to the high refractive index of polystyrene, 1.59, and the fact that the SpeedBeads do not absorb water, they had higher SSC intensity than fines at a given size. It was found that this could be used to differentiate the SpeedBeads from fines particles. In practice, the sizes and SSC intensities which were characteristic of the Speedbeads were identified, and the settings were adapted so that particles within that range were not included in the data. The probability of correct classification was estimated to be approximately 99%. However, as both the refractive index and size of the SpeedBeads were similar to that of mineral fillers, the same principle could not be used to differentiate between the two. Fluorescent beads were evaluated as a replacement for the SpeedBeads, however, their intensity was overly strong at the excitation levels needed in some practical applications. Instead, it was found that the fillers themselves could replace the SpeedBeads as particles for flow speed synchronisation. Thus, when samples containing fillers were run, the SpeedBead pump was disabled, and the data acquisition was delayed to allow the present beads to leave the system.

Three different microscope objectives were available for the ImageStream system used in the studies made for this thesis, providing 20X, 40X, and 60X magnification, respectively. The objectives were mounted on a moving,
automated slide and could be switched via the user interface. After a change in magnification, the flow speed was automatically adapted to minimise motion blur. Each objective provided a different resolution, field of view, and depth of field, see Table 3.

**Table 3. Properties of the ImageStream system using different objectives.**

<table>
<thead>
<tr>
<th>Magnification</th>
<th>IS60X</th>
<th>IS40X</th>
<th>IS20X</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resolution per pixel</td>
<td>0.33 µm</td>
<td>0.5 µm</td>
<td>1.0 µm</td>
</tr>
<tr>
<td>Field of view</td>
<td>40 µm x 170 µm</td>
<td>60 µm x 256 µm</td>
<td>120 µm x 512 µm</td>
</tr>
<tr>
<td>Numerical aperture</td>
<td>0.9</td>
<td>0.7</td>
<td>0.5</td>
</tr>
<tr>
<td>Depth of field</td>
<td>2.5 µm</td>
<td>4.0 µm</td>
<td>8.0 µm</td>
</tr>
<tr>
<td>Flow speed</td>
<td>40 mm/s</td>
<td>40 mm/s</td>
<td>60 mm/s</td>
</tr>
</tbody>
</table>

With a narrow depth of field, it is important to restrict the in-plane motion of the particles. As with other flow cytometers, the ImageStream uses a sheath fluid to hydrodynamically focus the sample suspension into a narrow stream. The sheath fluid creates a laminar flow, and the speed and pressure of the respective fluids ensure that they are not mixed. The sheath fluid is ideally the same as the suspension medium of the sample. In the studies made for this thesis, MilliQ ultrafiltered water was used as sheath.

Another purpose of the hydrodynamic focusing is to ensure that each image contains a single particle. If the concentration is high, this is difficult to achieve. Furthermore, the transmission-based sensor which measures the volume drawn into the flow cell starts to malfunction. In practice, a share of images is either empty, contains multiple particles, or contains a single particle that is too out of focus for reliable size analysis. As already indicated, it is possible to impose restrictions on the data collection, so that only images fulfilling certain criteria are saved. To reduce the amount of empty or overly blurry images, a restriction was set on the value of image root-mean-square (RMS) gradient. The RMS gradient is somewhat similar to the image contrast.

The system is designed for a small sample volume, between 15-200 µL, which is put into an Eppendorf tube (see Figure 27). As the fluidics channels are narrow, filtering the sample through mesh with Ø75 µm holes is recommended by the manufacturer. For fine fraction samples, this filtering step is automatically performed when the fine fraction is obtained. A single measurement of 10 000 particles took around 2 minutes for a well-concentrated sample, and up to 15 minutes for a very dilute sample. The ImageStream system that was used in the studies of this thesis was equipped with an AutoSampler, allowing up to 96 samples to be measured in an automated procedure. Then, a 96 well plate is used instead an Eppendorf tube (see Figure 27). When a well is to be analysed, the sample is drawn and dispensed five times before it is pumped to the flow cell, so that sedimented
particles are agitated. In this work, the 96 well plates were covered with a Sigma-X coverfilm to prevent evaporation of the sample during the several hours of unattended operation. Additionally, a sample of pure water was measured between every sample type in order to minimise carryover between the samples.

It should be mentioned that, at the magnifications provided by the ImageStream system, greater attention to contamination must be paid than what is standard in pulp analysis. Yeast, mold and bacteria may be challenging to differentiate from sample particles. Jars and equipment (e.g. the BDDJ) must be very well cleaned, as fine particles from previous samples may otherwise remain. A biocide should be added when the sampling is made to prevent microbiological growth, and the samples should be stored in a refrigerator. The measurements should then be made as soon as possible after the sample has been removed from the refrigerator.

Once the data is collected, an image-analysis software package associated with the ImageStream equipment, IDEAS, is used for analysis. The images for every particle and each channel are saved for optional inspection. Image processing is automatically performed to adjust the background of the images. The segmentation step is then performed, based on a default or user-adapted algorithm called a mask. Several algorithms can be combined based on Boolean logic. Due to the low contrast of the fines, they were challenging to segment. A combination of erosion, skeleton, and active contour (morphology) algorithms [93-95] was found to give the best segmentation for fines, see Figure 28. However, the same algorithm tended to oversize larger fillers due to bright halos caused by edge diffraction.
After segmentation, a wide range of parameters can be extracted in the form of number-weighted values for every particle. If another weighting is desired, it needs to be applied by importing the data to another software, e.g. Matlab. In this work, the total intensity (sum of the intensity of all pixels), median intensity, area (sum of the size of all pixels), perimeter (boundary length), length, minimum thickness, and maximum thickness were extracted. An average width was calculated from the minimum and maximum thicknesses. The length and the thickness were based on algorithms similar to the skeleton, and thus traced the particle shape.

In the analysis software, different subsets of particles can also be identified and separately analysed, provided that their parameter values are distinctly different. The differentiation is done by enclosing particle subsets by regions in a scatterplot, which is standard in flow cytometry, see Figure 29.

Figure 28. Five ImageStream segmentation algorithms (masks) applied to the same particle. The yellow area is the segmented (binarised) part of the particle.

Figure 29. Example of a density scatterplot where the colour scale - from blue to red - represents increasing relative occurrence (left), and a scatterplot with a defined region (right), from the ImageStream analysis software (IDEAS). Each dot represents a particle.
5.2. The L&W Fiber Tester and Fiber Tester Plus fibre analysers

In contrast to the ImageStream that was just introduced to pulp and paper applications, fibre analysers are well-established in paper mill laboratories. While the ImageStream cannot analyse fibres due to their large size, fibre analysers are adapted to fibre measurements. Many brands are available, for example the FiberLab (Metso Automation), the PulpEye (PulpEye), the FQA (OpTest), the MorFi (Techpap), and the L&W Fiber Tester (ABB Lorentzen & Wettre).

In this work, the L&W Fiber Tester (FT) and L&W Fiber Tester Plus (FT+) were used to evaluate the morphology of pulp (Paper B and Paper C). The properties of the instruments are summarised in Table 4. As the spatial resolution of the FT+ was not available, an approximate value was calculated based on the image size in pixels and the measured size of reference particles with known size.

Table 4. Properties of the L&W Fiber Tester (FT) and L&W Fiber Tester Plus (FT+) [27, 96, 97].

<table>
<thead>
<tr>
<th></th>
<th>FT</th>
<th>FT+</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resolution per pixel</td>
<td>~10 µm</td>
<td>~4 µm</td>
</tr>
<tr>
<td>Field of view [pixels]</td>
<td>1280 x 1024</td>
<td>2452 x 2054</td>
</tr>
<tr>
<td>Output available for each particle</td>
<td>Length, width, “shape”</td>
<td>Length, width, “shape”, “macrofibril” area, “macrofibril” perimeter</td>
</tr>
<tr>
<td>Examples of other outputs</td>
<td>Kink, curl, coarseness, fines content</td>
<td>Kink, curl, coarseness, fines content, share of P-fines and S-fines, total volume of fibres</td>
</tr>
<tr>
<td>Default fibre criteria</td>
<td>Aspect ratio (AR) ≥ 4, width &lt; 75 µm, “Shape” &gt; 50%, size ≥ 5 pixels</td>
<td>Aspect ratio (AR) ≥ 4, width &lt; 75 µm, “Shape” &gt; 50%,</td>
</tr>
<tr>
<td>Fines criteria</td>
<td>Length &lt; 100 µm (TAPPI-standard) or &lt; 200 µm (ISO-standard)</td>
<td></td>
</tr>
<tr>
<td>Weighting</td>
<td>Number, width, length (standard), area, volume</td>
<td></td>
</tr>
</tbody>
</table>

In a measurement, around 200 ml of pulp with dry fibre weight of approximately 0.1 g is put into a beaker and drawn into the instrument. The sample is automatically diluted to suitable concentration. First, half the sample is measured. Then, the second half is measured, and the two measurements are compared to verify the reproducibility of the analysis.

The segmentation algorithms used to binarise the obtained greyscale images are proprietary of the instrument supplier. The original images are not stored, unless an image-saving setting is enabled. From the binarised images, the area $A$ and perimeter $P$ are calculated. For a particle with cylindrical shape,
its 2D projection is a rectangle, and the area and perimeter is related to the length $L$ and width $W$ as follows [98]:

$$\begin{align*}
P &= 2L + 2W \\
A &= L \cdot W
\end{align*}$$  \[\text{Eq. 22}\]

The equation system given in Eq. 22 is solved to give the length and width [99]. Note that, as the length and width are calculated, they can exhibit a wider range of values than just a multiple of the pixel size. Because of this, the length and width may be expressed as a fraction of the pixel size, i.e. apparently more accurate than the resolution [27]. The solution to the equation system is:

$$\begin{align*}
L_{RE} &= \frac{P}{4} + \sqrt{\frac{P^2}{16} - A} \\
W_{RE} &= \frac{P}{4} - \sqrt{\frac{P^2}{16} - A + \text{offset}}
\end{align*}$$  \[\text{Eq. 23}\]

where the subscript $RE$ stands for rectangle-equivalent, and the width offset is added based on previous calibration measurements [100]. Due to the offset, the width may be larger than the length for particles with low aspect ratio.

To calculate the shape $S$ [%], also called the shape factor, form factor, or shape ratio, the projected length $L_P$, which is close to the distance between the end points of the particle, is divided by the rectangle-equivalent length [101]:

$$S = 100 \cdot \frac{L_P}{L_{RE}}$$  \[\text{Eq. 24}\]

Kink, which is another shape-related parameter, is defined as a sharp bend, whose direction is given by the kink angle [°].

Based on their number-weighted length and width, particles are classified into e.g. fibres, fines, and wide objects. The fibre and fines classifications are given in Table 4. The fines content $FC$ [%] of the respective instrument is then defined as:
where $N$ stands for the number of particles that are classified as fines or fibres.

In the analysis software of the FT+, the fibril area and fibril perimeter are calculated as the area and perimeter of macrofibrils attached to the fibre, relative to the total area and perimeter, respectively [99].

$$\begin{align*}
A_{\text{fibrils}} &= 100 \cdot \frac{A_{\text{fibrils}}}{A_{\text{fibre + fibrils}}} \\
P_{\text{fibrils}} &= 100 \cdot \frac{P_{\text{fibrils}}}{P_{\text{fibre + fibrils}}} 
\end{align*}$$  \hspace{1cm} [Eq. 26]

The fibrils are differentiated from the fibre through an erosion algorithm [99]. The fibrils of external fibrillation may have wide range of widths and their detection will be dependent on their intensity and contrast. Thus, fibrils thinner than the spatial resolution may be detected, but the calculation of their area and perimeter is dependent on the resolution.

The FT+ classification of the fines into P-fines or S-fines is based on a combination of the width and the length of the fines particle, on the number-weighted data. The specific threshold values for the length and width are proprietary of the instrument supplier. However, P-fines and S-fines are assumed to be coarser and slimmer, respectively. The P-fines and S-fines are then quantified as a share of the total number of fines, i.e. a fines content:

$$\begin{align*}
FC_{\text{P-fines}} &= 100 \cdot \frac{N_{\text{P-fines}}}{N_{\text{fines}}} \\
FC_{\text{S-fines}} &= 100 \cdot \frac{N_{\text{S-fines}}}{N_{\text{fines}}} 
\end{align*}$$  \hspace{1cm} [Eq. 27]

where $N$ is the number of P- or S-fines.
When the data is exported, different weightings may be applied. By default, all parameters mentioned in this section are reported as length-weighted values.

5.3. The Mastersizer2000 laser diffractometer

In the study presented in Paper B, the Mastersizer2000 laser diffractometer from Malvern Instruments was used in addition to the already presented instruments. The Mastersizer utilises the direction and intensity of the diffracted light to infer the particle size. The instrument is equipped with two illumination lasers: a blue with wavelength 466 nm, and a red with wavelength 633 nm. A range of 52 detectors is positioned around the flat flow cell, see Figure 30. The purpose of the blue laser and the backscatter detectors is to allow the detection of particles with sizes in the Rayleigh-regime. Based on the information supplied by the manufacturer, the polarisation state of the light is not utilised [102].

![Figure 30. Principle of the MasterSizer2000 laser diffractometer [based on 103].](image)

The instrument is adapted for a sample volume of 60 ml. The sample is dropped into a disperser unit, and additional sample or water is added until the light obscuration is within a certain range. Three measurements are then automatically made on the same sample. The disperser unit is manually cleaned with water, and the next measurement can be performed.

The data is then analysed using associated software. The light scattering model is chosen, and if the Mie theory is used, the complex refractive index must be provided. It is possible to set different refractive indices for the blue wavelength (the 488 nm laser) and the red wavelength (633 nm), thus accounting for spectral variations in the refractive index. However, only a single refractive index may be set for each sample. Thus, choosing a refractive index for an inhomogeneous sample containing materials with different refractive indices can be challenging.
Some additional model parameters can be adjusted, for example if the sample is known to be unimodal (have a single peak) or bimodal (have two peaks). Otherwise, a general model is used. The particle shape can also be specified as irregular or smooth. However, the difference in the calculation for the two cases is not detailed [103]. In the studies made for this thesis, the general model for irregular particles was used.

The data is exported as volume-weighted histogram values, calculated with user-defined limits and bin widths. The volume-weighted data may be converted to number-, length-, or surface area-weighted, but it is not advised for samples containing a significant share of sub-micron material [103].

5.4. Evaluation and comparison of instruments

There is an increased interest in the use of the micro- and nanosized material in a papermaking stock, e.g. pulp fines and mineral fillers. An example of such use is to fractionate the stock with screens or hydrocyclones, and return controlled amounts of fines and/or fillers with desired quality. However, convenient methods for evaluating the fractionation result are lacking. Previously, fines and fillers have often been analysed separately. The literature review presented in Paper A showed that many studies have used laser diffractometry to characterise fines and fillers, due the wide size range and high resolution claimed for the method. In these studies, little attention was given to the scattering theory used to calculate the result, or to the refractive index of the particles. Due to the lack of shape information, the results were also difficult to interpret. Recent development in the resolution of flow microscopes gives reason to investigate if they can now provide a more reliable characterisation of fines and fillers.

Thus, the aims of the study presented in Paper B were to 1) evaluate the performance of an instrument when measuring on pure fines, pure fillers, and a mixture of fines and fillers, 2) investigate instrument performance at its resolution limit using calibrated “fines mimicking” particles, and 3) investigate if morphological information from imaging instruments could be used to improve the interpretation of the laser diffractometry results. This was done by comparing laser diffractometry measurements to measurements obtained with flow microscopes with spatial resolution ranging from 0.33-10 µm/pixel. As previously mentioned, 0.5 µm is a common size for filler particles. Thus, a resolution of 0.33 µm should give the possibility of detecting a large share of the fillers, which has not been previously possible using flow microscopy.

The investigated instruments were the Mastersizer2000 (MS), the ImageStreamX MarkII (IS), and the L&W Fiber Tester (FT) and L&W Fiber
Tester Plus (FT+). The first instrument was based on laser diffractometry, while the others were flow microscopes. All three magnifications of the IS were used (20X, 40X, 60X), but only the brightfield channel, see Figure 26. The properties of the instruments are summarised in Table 5.

**Table 5. Properties of the evaluated measurement instruments. MS: Mastersizer. IS: ImageStream. FT: L&W Fiber Tester. FT+: L&W Fiber Tester Plus.**

<table>
<thead>
<tr>
<th></th>
<th>MS</th>
<th>IS60X</th>
<th>IS40X</th>
<th>IS20X</th>
<th>FT+</th>
<th>FT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detection limit</td>
<td>~ 20 nm</td>
<td>0.33 µm</td>
<td>0.5 µm</td>
<td>1.0 µm</td>
<td>~ 4 µm</td>
<td>~ 10 µm</td>
</tr>
<tr>
<td>Field of view or max. size</td>
<td>2 mm</td>
<td>2 mm</td>
<td>2 mm</td>
<td>2 mm</td>
<td>2 mm</td>
<td>2 mm</td>
</tr>
<tr>
<td>Raw data weighting</td>
<td>Volume</td>
<td>Number</td>
<td>Number</td>
<td>Number</td>
<td>Number</td>
<td>Number</td>
</tr>
<tr>
<td>Used output</td>
<td>SED</td>
<td>Length, width, area, perimeter</td>
<td>Length, Width</td>
<td>Length, Width</td>
<td>Length, Width</td>
<td>Length, Width</td>
</tr>
</tbody>
</table>

The samples comprised three different pulps, one type of filler, a mix of pulp and filler, and silica spheres of various sizes. The pulps were unbleached chemical softwood (UKSW), bleached chemical hardwood (BKHW), and TMP. The filler comprised precipitated calcium carbonate (PCC), and the mixed sample was made by blending 10% of the PCC with 90% UKSW, by weight. The samples were screened in a Britt Dynamic Drainage Jar (BDDJ) with Ø76 µm holes. Thus, fine fractions from each sample were obtained. For the mixed sample, it was estimated that the screening changed the relative composition to 85% PCC and 15% UKSW fines, by weight. The reason was that the majority of PCC particles were small enough to pass the mesh, while only a minority of the pulp particles passed.

Silica nano- and microspheres were used as calibration material to enable evaluation of the resolution and the measurement uncertainty of the instruments on particles with optical properties similar to those of wet pulp. The sizes of the silica microspheres, 7 µm, 2 µm, 350 nm, and a mixture of 20 and 80 nm spheres, were selected based on the limit of the instruments’ resolution. Rod-shaped calibration particles in the same size range would have been preferable, but were not commercially available.

For the analysis of the laser diffractometry data, the complex refractive index was required. No measured values for wet pulp or wet fines could be found, though two studies reported calculated values for wet pulp [42, 104]. One of the studies used the refractive index value calculated for wet pulp also for wet fines [104]. Thus, it was not taken into account that fines can hold more water than fibres [44]. Surprisingly, only a single study where laser diffractometry was used to characterise fines reported the refractive index [105]. In that case, no motivation for the value used (1.53) was given. No
value for an inhomogeneous mixture or fines and fillers was available. Thus, the refractive index values were calculated based on the following linear, volume-based mixing rules:

\[
\tilde{n}_{\text{fibre,dry}} = (F_{\text{cellulose}} \cdot \tilde{n}_{\text{cellulose}}) + (F_{\text{hemi}} \cdot \tilde{n}_{\text{hemi}}) + (F_{\text{lignin}} \cdot \tilde{n}_{\text{lignin}}) \quad \text{[Eq. 28]}
\]

\[
\tilde{n}_{\text{fines,wet}} = (F_{\text{H}_2\text{O,fines}} \cdot \tilde{n}_{\text{H}_2\text{O}}) + (F_{\text{dry,fines}} \cdot \tilde{n}_{\text{fibre,dry}}) \quad \text{[Eq. 29]}
\]

\[
\tilde{n}_{\text{mix,wet}} = (F_{\text{PCC}} \cdot \tilde{n}_{\text{PCC}}) + (F_{\text{fines,wet}} \cdot \tilde{n}_{\text{fines,wet}}) \quad \text{[Eq. 30]}
\]

where \( F \) is the estimated volume percentage of the compound in the pulp, see Table 6, “hemi” is an abbreviation for hemicellulose, and the refractive indices of the individual components are given in Table 1. A similar approach was used in a study of soils, which found the results to be satisfactory [106].

Table 6. Estimated volume fractions of the different compounds in the various samples.

<table>
<thead>
<tr>
<th></th>
<th>UKSW</th>
<th>BKHW</th>
<th>TMP</th>
<th>Mix</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>( F_{\text{cellulose}} )</td>
<td>67%</td>
<td>70%</td>
<td>35%</td>
<td>67%</td>
<td>[44, 107]</td>
</tr>
<tr>
<td>( F_{\text{hemi}} )</td>
<td>25%</td>
<td>27%</td>
<td>30%</td>
<td>25%</td>
<td>[44, 107]</td>
</tr>
<tr>
<td>( F_{\text{lignin}} )</td>
<td>8%</td>
<td>3%</td>
<td>35%</td>
<td>8%</td>
<td>[44, 107]</td>
</tr>
<tr>
<td>( F_{\text{H}_2\text{O}} )</td>
<td>78%</td>
<td>78%</td>
<td>63%</td>
<td>22%</td>
<td>[44]</td>
</tr>
<tr>
<td>( F_{\text{fines,dry}} )</td>
<td>22%</td>
<td>22%</td>
<td>37%</td>
<td>6%</td>
<td>[44]</td>
</tr>
<tr>
<td>( F_{\text{PCC}} )</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>72%</td>
<td>Estimation</td>
</tr>
</tbody>
</table>

The complex refractive indices that were used when evaluating the laser diffractometry data are given in Table 7.

Table 7. Derived or published refractive indices and extinction coefficients used in the Mastersizer setting for the measured samples. All values are for particles immersed in water. Extinction coefficients smaller than \( 10^{-4} \) were regarded as negligible.

<table>
<thead>
<tr>
<th></th>
<th>( n )</th>
<th>( \kappa )</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>UKSW fines</td>
<td>1.38</td>
<td>1.37</td>
<td>Mixing rule</td>
</tr>
<tr>
<td>BKHW fines</td>
<td>1.37</td>
<td>1.37</td>
<td>Mixing rule</td>
</tr>
<tr>
<td>TMP fines</td>
<td>1.43</td>
<td>1.41</td>
<td>0.004</td>
</tr>
<tr>
<td>PCC</td>
<td>1.59</td>
<td>1.59</td>
<td>0</td>
</tr>
<tr>
<td>Mix</td>
<td>1.53</td>
<td>1.53</td>
<td>0</td>
</tr>
<tr>
<td>Silica</td>
<td>1.43</td>
<td>1.43</td>
<td>0</td>
</tr>
</tbody>
</table>

The Mastersizer results were exported as volume-weighted SED distributions. The data from the image-based instruments was exported as
number-weighted length and width for every particle. From the ImageStream, the area and perimeter was also exported. In Matlab, the aspect ratio was calculated as the length divided by the width. In order to make the data from the image-based instruments comparable to the Mastersizer results, it was converted to volume-weighted SED. To calculate a volume, it is necessary to assume the particle shape. If the aspect ratio of the particle was \( \leq 1.33 \), the particle was assumed to be spherical. Otherwise, it was assumed to be cylindrical, see Table 8.

**Table 8.** Equations used to calculate the volume, circle-equivalent diameter (CED) and sphere-equivalent diameter (SED) in the spherical and cylindrical particle case.

<table>
<thead>
<tr>
<th>AR ( \leq 1.33 )</th>
<th>AR ( &gt; 1.33 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{L}{W} )</td>
<td>( \sqrt[3]{4WL} )</td>
</tr>
<tr>
<td>( CED = \frac{L}{W} )</td>
<td>( CED = \left( \frac{4WL}{\pi} \right)^{1/2} )</td>
</tr>
<tr>
<td>( V = \frac{\pi(SED)^3}{6} )</td>
<td>( V = \frac{\pi W^2 L}{4} )</td>
</tr>
<tr>
<td>( SED = CED )</td>
<td>( SED = \left( \frac{3W^2 L}{2} \right)^{1/3} )</td>
</tr>
</tbody>
</table>

The accuracy and uncertainty of the measurements were evaluated from silica spheres’ data. The accuracy was estimated as the difference between the measured average SED and the diameter specified by the manufacturer divided by the specified diameter. For the image-based instruments, the repeatability was evaluated as the \( 1\sigma \) standard deviation of the calculated SED within each sample. For the laser diffraction meter, a corresponding standard deviation was calculated from the span of the distribution. The reproducibility was evaluated as the \( 1\sigma \) standard deviation of the mean SED of two independent samples for the laser diffraction meter, FT, and FT+, and five independent samples for the ImageStream. The total measurement uncertainty was then calculated as the quadratic sum of the repeatability, reproducibility and the stated uncertainty of the diameter of the silica spheres.
Histograms were calculated from the image-based instruments’ data. First, the data was normalised by the total number of particles to obtain the relative frequency. Then, two sets of histograms were made: one for comparison between the Mastersizer data and the data from the image-based instruments, and one for comparison between the image-based instruments only. For the comparison with the Mastersizer data, a volume-weighted distribution was calculated with the same bin widths (class width) and limits as the data exported from the Mastersizer. The same bin widths were used for all instruments. For the comparison between the image-based instruments, the data was area-weighted and presented as relative frequency in a histogram, see the left side of Figure 31. The bin width was adapted to the resolution of the instrument, so that high-resolution data was binned more narrowly. To make the histograms comparable even though the bin widths were different, the data was normalised by the bin width in order to obtain a relative density, see the right side Figure 31.

![Figure 31. Illustration of relative frequency distribution (left), and relative density distribution (right) calculated from the same UKSW data. In a relative density distribution, the effect of differences in bin width is compensated for.](image)

### 5.5. Application in a study of refining

In chemical pulp, the initial fines content after pulping is comparatively low. Instead, fines are created during a consecutive mechanical fibre treatment process, refining. Many of these so-called secondary fines are small, slim and fibrillar. Largely due to the limited resolution of flow microscopes used in the pulp and paper industry, the morphology of chemical fines has rarely been quantitatively characterised.

During refining, fibres may also undergo external fibrillation, i.e. the partial release of fibrillar material from the surface, however still attached to the
fibre surface. While optical quantitative analysis of fibrillation is available, it has not been possible to link the fibrillation to the other morphological properties of the fibre. Thus, a study was made with the aim of applying the development in flow microscopy to increase the knowledge on the morphology of chemical fines, and how it is influenced by refining (*Paper C*). Additionally, new image analysis routines for the quantification of external fibrillation were utilised.

Bleached chemical softwood pulp (SW) was refined with a Voith LR industrial-like laboratory refiner, see *Figure 32*.

*Figure 32. The Voith LR laboratory refiner. The five segments used in the study are also shown (conical segments to the left, disc segments to the right).*

In the refiner, the intensity and energy may be controlled. The intensity is related to the force exerted by each impact onto the fibres in the refining gap, and may be expressed by the Specific Edge Load (SEL, Ws/m). The energy expended in the refining process is related to the total number of impacts on the fibres, and is usually expressed by the Specific Refining Energy (SRE, kWh/t). In industrial refining, where the pulp passes only once through a refiner, typical SREs for bleached chemical softwood fibres are in the range of 50 to 200 kWh/t. In laboratory refining, the pulp passes the refiner several times until the target SRE is reached. In this study, the pulp was sampled when the accumulated refining effect accounted to 0, 50, 100, 200, 300, and 400 kWh/t SRE, respectively.

Dependent on the design of the segment used in the refiner, certain fibre treatment may be emphasised. Five different segments, spanning a wide range of geometries, were used in this study, see *Table 9*.
Table 9. Characteristics of the segments used in the industrial-like laboratory refiner. $W_{\text{bar}}$: Bar width. $W_{\text{groove}}$: Groove width. BEL: Bar Edge Length.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Type</th>
<th>$W_{\text{bar}}$ [mm]</th>
<th>$W_{\text{groove}}$ [mm]</th>
<th>Cutting angle [°]</th>
<th>BEL [km/rev]</th>
<th>SEL [Ws/m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>Conical</td>
<td>3</td>
<td>12</td>
<td>20</td>
<td>0.018</td>
<td>2.5</td>
</tr>
<tr>
<td>C2</td>
<td>Conical</td>
<td>3</td>
<td>12</td>
<td>60</td>
<td>0.020</td>
<td>2.5</td>
</tr>
<tr>
<td>D1</td>
<td>Disc</td>
<td>3</td>
<td>12</td>
<td>60</td>
<td>0.317</td>
<td>2.0</td>
</tr>
<tr>
<td>D2</td>
<td>Disc</td>
<td>2</td>
<td>3</td>
<td>40</td>
<td>0.088</td>
<td>0.8</td>
</tr>
<tr>
<td>D3</td>
<td>Disc</td>
<td>1</td>
<td>1.3</td>
<td>30</td>
<td>0.032</td>
<td>0.1</td>
</tr>
</tbody>
</table>

The SEL was chosen based on experience of the optimal performance of the respective segment. The selection of segment D3 deserves a comment. D3 has a very fine design and was originally designed for refining hardwood (HW). Here, it was used for softwood for exploratory purposes. During the refining trials, it required a substantially higher pressure difference in order to maintain the flow through the refining gap. After the refining trial, the refiner was opened, and a high share of the grooves of the segment was found to be plugged.

The refined pulp samples were characterised by Schopper-Riegler (SR) drainage measurements and with the L&W Fiber Tester Plus (FT+) fibre analyser. Length, width, fibril area, and fibril perimeter were obtained for each particle longer than 200 µm. Additionally, kink per mm, share of P-fines, share of S-fines, and total fines content for each sample were obtained. The fines were defined according to ISO 16065-2, i.e. particles shorter than 200 µm, and the fines content was defined according to Eq. 25.

The pulp samples refined with segments C2, D1, D2 and D3 were screened with a BDDJ to obtain fines fractions, using the modified procedure described in Section 5.1. The fines fractions were measured with the FT+ and the ImageStream. For each sample, 100 000 particles were measured with the FT+, and 50 000 particles with the ImageStream. From the FT+, length and width data were exported for each particle, and the share of P-fines and share of S-fines for each sample. From the ImageStream, the length and width data were exported for each particle. As the ImageStream cannot measure fibres, a fines content could not be determined.

Matlab was used for the final analysis and visualisation. The aspect ratio was calculated from the FT+ and ImageStream data. Based on the data for each particle, relative frequency distributions were made. The distributions were length-weighted to adhere as closely as possible to standardised procedures [109]. The measurement uncertainty was estimated through the reproducibility, i.e. the standard deviation at 1σ level of the five mean values (one for every segment) measured for the unrefined pulp (0 kWh/t).
Refining theories attempt to predict the refining result by the calculation of different refining descriptors [110]. The refining descriptors are based on conditions of the refining process, the geometry of the segments, and sometimes also the morphology of the fibres. In addition to the SEL, the Cutting Edge Length (CEL), Modified Edge Length (MEL), Specific Surface Load (SSL), and C-factor refining descriptors were calculated [111-114].

Finally, laboratory sheets were made from each pulp sample that had been refined at a SRE of 400 kWh/t. Grammage, thickness, tensile strength, tensile stiffness, stretch at break, and tensile energy absorption were measured on the sheets according to standard procedures. Density and its inverse, bulk, were also determined.

5.6. Principle for fines and filler differentiation

In the literature review presented in Paper A it was seen that traditional flow cytometry had been used to indirectly estimate the size and shape of fines [115, 116]. It was also found that the technique could be used to differentiate between different types of particles. For example, it had been used to differentiate between mechanical pulp fines and wood pitch [117], and between wood pitch and fillers [118]. As already mentioned, no quantitative method exists which can differentiate between fines and fillers. Throughout this thesis work, experience was gained on the difference in optical properties between wet fines and fillers. Fillers were noted to have high SSC but negligible autofluorescence when excited with 488 nm light. Fines were noted to have low SSC but to exhibit some autofluorescence. Thus, an idea was devised to use imaging flow cytometry to 1) differentiate between fines and fillers based on these differences, and 2) measure the size and shape of the respective particle type. The principle was evaluated in a Master thesis project that was supervised by the author of the present thesis [119]. Due to lack of time for complementary analysis, these results have not been published yet, but some key results are presented in the following pages and in Section 7.4.

Three of the samples from the study presented in Paper C were used for evaluating the differentiation principle: UKSW pulp, PCC filler, and a mixture of 90% UKSW and 10% PCC, by weight. As previously mentioned, the sample was estimated to contain around 85% PCC and 15% fines after the screening using a BDDJ. The samples were measured with the ImageStream at 60X magnification, providing a spatial resolution of 0.33 µm/pixel. For all samples, the power of either the 488 nm excitation (EXC) laser or the 785 nm SSC laser was varied, while the power of the other laser was held constant, see Table 10. The aim was to identify the optimal laser power for differentiating between the particles.
Table 10. Evaluated power levels for the excitation (EXC) or side-scattering (SSC) laser, while the other laser was held at constant power. The maximum and minimum power levels, i.e. the range, are also given.

<table>
<thead>
<tr>
<th>488 nm (EXC) laser power while keeping SSC laser at 0.1 mW</th>
<th>785 nm (SSC) laser power while keeping EXC laser at 50 mW</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 mW</td>
<td>0.01 mW</td>
</tr>
<tr>
<td>0.1 mW</td>
<td>0.1 mW</td>
</tr>
<tr>
<td>50 mW</td>
<td>1 mW</td>
</tr>
<tr>
<td>100 mW</td>
<td>2 mW</td>
</tr>
<tr>
<td>200 mW</td>
<td>5 mW</td>
</tr>
<tr>
<td>Range 0-200 mW</td>
<td>Range 0-70 mW</td>
</tr>
</tbody>
</table>

The optimal power settings were identified as 50 mW for the EXC laser, and 2 mW for the SSC laser. These settings gave the best differentiation of the particle types while avoiding saturation of the signal. Thus, the data sets obtained with those particular settings were selected for further data analysis. It was also observed that the autofluorescence emission of the fines were strongest in the green wavelength range (channel 2, see Figure 26). Thus, the total intensity and median intensity in channel 2 (autofluorescence) and channel 6 (SSC) were exported to Matlab for further analysis, as well as the brightfield area, length, and width. The particle differentiation principle is illustrated in Figure 33.

![Diagram](image)

**Figure 33.** Principle of particle differentiation in mixed fines-filler sample, based on reference measurements on pure samples using the ImageStream flow cytometer.

In the analysis of the UKSW and PCC samples, scatterplots of the total autofluorescent intensity (channel 2) vs. the total SSC intensity (channel 6)
were made. In the scatterplots, regions were identified which enclosed 95-99% of all particles, thus giving a fines region from the UKSW sample, see Figure 34, and a PCC region from the PCC sample, see Figure 35. The boundaries of these regions were then copied to the mixed sample. It was found that the two regions did not enclose agglomerates comprising both fines and fillers. Thus, an agglomerate region was also created, see Figure 36. Finally, the area, length, and width of the fines, filler, and agglomerate subsets of particles were exported to Matlab to be visualised as distributions, as well as the same parameters for the whole, un-differentiated sample.

Figure 34. Scatterplots of UKSW fines total fluorescent intensity (channel 2) vs. total SSC intensity (channel 6), showing the density of particles where the colour scale, from blue to red, represents increasing relative occurrence (left) and a defined fines region (right).
Figure 35. Scatterplots of PCC total fluorescent intensity (channel 2) vs. total SSC intensity (channel 6), showing the density of particles where the colour scale, from blue to red, represents increasing relative occurrence (left) and a defined PCC region (right).

Figure 36. Scatterplots of mixed sample total fluorescent intensity (channel 2) vs. total SSC intensity (channel 6), showing the density of particles where the colour scale, from blue to red, represents increasing relative occurrence (left) and defined fines, PCC and agglomerates regions (right).
6. Methods for emittance measurements

6.1. Development of a goniometric setup

Quantitative thermographic measurements require knowledge of the emittance of the material being measured. The type of emittance that is most adapted for infrared cameras is the wavelength-integrated and directional emittance, i.e. the emittance for the specific wavelength range which is detected by the camera (MWIR or LWIR) and for specific observation angles (directions). No established measurement method of the integrated and directional emittance of fibre-based materials existed when this work was started. Thus, a new method was developed, which is described in detail in Paper A. The method development and its applications were also reported in a licentiate thesis [120].

The most convenient way to measure the integrated emittance is to use an infrared camera which operates in the desired wavelength range. Then, the infrared radiation is integrated automatically by the detector material. The two most common methods for camera-based emittance measurements are the temperature-reference and the emittance-reference approaches [121]. In this work, the emittance-reference approach was used. Here, a reference surface with known emittance $\varepsilon_{\text{ref}}$ is simultaneously imaged as the sample and a high-reflectance surface which is used to measure the ambient blackbody radiation of the surroundings. The sample emittance $\varepsilon_{\text{sample}}$ is then calculated according to:

$$\varepsilon_{\text{sample}} = \frac{U_{\text{sample}} - U_{\text{amb}}}{U_{\text{ref}} - U_{\text{amb}}}$$

[Eq. 31]

where $U_{\text{sample}}$ is the signal voltage from the camera detector due to the emitted directional radiance of the sample, $U_{\text{amb}}$ is the signal voltage due to the emitted radiance of ambient surroundings, and $U_{\text{ref}}$ is the signal voltage due to the emitted directional radiance of the emittance reference surface. The reference surface should be kept at the same temperature as the sample, while the high-reflectance surface should be kept at the same temperature as the surroundings. A setup is illustrated in Figure 37.
In the studies made for this thesis, the emittance reference surface comprised an opaque, rectangular piece of metal painted with five layers of a high-emittance coating (Nextel Velvet from Mankiewicz: $\varepsilon_{\text{ref}} = 0.93 \pm 0.01$ at MWIR wavelengths, $\varepsilon_{\text{ref}} = 0.96 \pm 0.01$ at LWIR wavelengths). The surface for measurement of the ambient radiation comprised an opaque, rough, high-reflectance gold surface (Infragold from Labsphere, $\rho = 0.94-0.96$). As the reflectance of the surface was around unity, all radiation scattered from it was assumed to originate from the surroundings. Furthermore, it was assumed that the fibre-based samples, the rough high-reflectance surface, and the reference surface scattered infrared radiation in a similar, diffuse manner.

As previously stated, thermographic measurements have a higher accuracy if the object temperature is high, as the contrast relative to the surrounding increases. To obtain high accuracy and to ensure that the emittance-reference and the samples had the same temperature, the samples were heated in an oven whose temperature could be controlled between 30°C and 100°C [122]. The oven had a sliding horizontal lid to minimise the cooling flow of air when the lid was opened. To allow for variation in the observation angle $\theta$ between the infrared camera and the samples, a goniometric camera mount was designed, see Figure 38. A digital inclinometer was used to measure the observation angle.

To perform an emittance measurement with the developed setup, the fibre-based samples were taped onto a supportive metal surface using heat-resistant tape. Three identical samples were stacked on top of each other to ensure that the sample was opaque. The emittance reference surface was placed by the samples, and the metal surface was placed into the oven and heated to the desired temperature (usually 70°C).
Figure 38. Illustration of the goniometric setup for emittance measurements using an infrared camera, also showing the angle of observation (θ).

The camera with the desired wavelength range (MWIR or LWIR, see Table 11) was attached to the goniometric arm, and fixed at the desired observation angle (usually 0°, i.e. perpendicular to the sample surfaces). The lid was retracted, and a thermographic image sequence was recorded as soon as all samples were in the field of view of the camera. The average signal voltage of the samples, reference surface, and high-reflectance surface were then obtained from the images using a software, ThermaCam Researcher, provided by the camera manufacturer.

Table 11. Specifications of the thermographic cameras used in the studies for this thesis work.

<table>
<thead>
<tr>
<th>Camera</th>
<th>MWIR camera</th>
<th>LWIR camera</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brand</td>
<td>SC6000 (FLIR Systems)</td>
<td>SC640 (FLIR Systems)</td>
</tr>
<tr>
<td>Wavelength range</td>
<td>3.0-5.0 µm (MWIR)</td>
<td>7.5-13.0 µm (LWIR)</td>
</tr>
<tr>
<td>Max. frame rate</td>
<td>120 Hz</td>
<td>30 Hz</td>
</tr>
<tr>
<td>Sensor type</td>
<td>Cooled photometric</td>
<td>Uncooled bolometric</td>
</tr>
<tr>
<td>Accuracy</td>
<td>±2.0°C or ±2.0%</td>
<td>±2.0°C or ±2.0%</td>
</tr>
</tbody>
</table>
The applicability of the developed emittance measurement method was evaluated by measurements on dry TMP paper samples. The following parameters were varied: observation angle $\theta$ (0-80°), wavelength range (MWIR, LWIR) and temperature (30-100°C). An error analysis was made, presented in detail in *Paper D*. The total uncertainty at 1σ level in measurements of normal emittance at 70°C was estimated to be between ±0.03 (at an observation angle of $\theta = 0^\circ$) and ±0.04 ($\theta = 80^\circ$) in the MWIR range, and between ±0.04 ($\theta = 0^\circ$) and ±0.05 ($\theta = 80^\circ$) in the LWIR range.

To validate the results, the emittance of the same samples were measured with a different method: an IR spectrophotometer. Here, the hemispherical reflectance and transmittance was measured over a large range of wavelengths. The values were then integrated over the MWIR and LWIR wavelength ranges, respectively, and the emittance was calculated usingEq. 17.

### 6.2. Measurements of dry and moist samples

A methodology was developed that allowed for emittance measurement under conditions relevant for the paper production process, for example temperature, observation angle, and moisture content of the web. Furthermore, in applications where thermography is used to study the mechanical properties of the material, sheet properties such as fibre orientation and the presence of a coating layer can influence the emittance. A study on the emittance measurement was performed where moisture ratio, pulp properties and sheet properties were varied, see *Table 12*. Additional details are given in *Paper E*.

**Table 12. Parameters varied in the emittance measurements detailed in Paper E.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulp type</td>
<td>TMP, UKSW, BKSW, BKH (birch)</td>
</tr>
<tr>
<td>Pulp drying</td>
<td>Never-dried, dried</td>
</tr>
<tr>
<td>Pulp refining</td>
<td>Unrefined, refined</td>
</tr>
<tr>
<td>Forming procedure</td>
<td>Laboratory sheet, mill-made sack paper</td>
</tr>
<tr>
<td>Fibre orientation in machine-made sheets</td>
<td>MD, CD</td>
</tr>
<tr>
<td>Influence of z-direction in linerboard</td>
<td>Top side, bottom side</td>
</tr>
<tr>
<td>Board coating</td>
<td>Coated (top side), uncoated (bottom side)</td>
</tr>
<tr>
<td>Addition of brightness additives (OBA)</td>
<td>Without OBA, with 0.04% OBA</td>
</tr>
<tr>
<td>Addition of starch</td>
<td>Without starch, with 5 layers of starch</td>
</tr>
<tr>
<td>Moisture ratio</td>
<td>0.05-4.0</td>
</tr>
</tbody>
</table>
The measurements on the dry samples were performed according to the procedure detailed in the previous section. Laboratory handsheets with a range of moisture ratios were prepared and stored in sealed plastic bags. Bleached and unbleached softwood pulp was used, and the moisture ratio of the sheets was determined gravimetrically. It was realised that evaporative cooling could introduce significant errors by lowering the temperature of the samples. To prevent evaporative cooling, the moist samples were covered with a thin plastic film during the measurements, which was taped to the metal surface using heat-resistant tape.

After the measurements, the moist samples were weighed in moist and bone-dry condition. It was noted that some moisture leakage had occurred during the course of sample heating and measurement. In the subsequent analysis, a compensation for the moisture leakage was made. The compensation was based on the observed decrease in the emittance as a function of time during a measurement sequence, and on the interpolation of data from points during the sequence where the moisture ratio was measured.

In Section 5.4, the refractive index of wet fines was estimated using a linear, volume-based mixing rule. A similar, mass-based calculation was made to predict the influence of the moisture ratio on the emittance of a wet sheet:

\[
\varepsilon_{\text{sheet,wet}} = \frac{\text{MR} \cdot \varepsilon_{\text{water}} + \varepsilon_{\text{sheet,\;dry}}}{\text{MR} + 1}
\]

[Eq. 32]

where \( \text{MR} \) is the moisture ratio of the wet sheet, \( \varepsilon_{\text{water}} \) the emittance of water, and \( \varepsilon_{\text{sheet,\;dry}} \) the emittance of the dry sheet. The emittance was calculated using the emittance values given in Table 13, and then compared to the measured emittance of the wet sheet.

Table 13. Emittance values used when applying a mixing rule to predict the emittance of a moist sheet.

<table>
<thead>
<tr>
<th>Source</th>
<th>MWIR (3.0-5.0 µm)</th>
<th>LWIR (7.5-13.0 µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measurements</td>
<td>0.73</td>
<td>0.89</td>
</tr>
<tr>
<td>[123, 124]</td>
<td>0.97</td>
<td>0.99</td>
</tr>
</tbody>
</table>
6.3. Application in a deformation study

The purpose of measuring emittance values (Paper D, Paper E) was to facilitate high-accuracy quantitative thermographic analysis for pulp and paper applications. One such application was demonstrated in Paper F, where precise emittance values and quantitative thermography provided new insights into the rupture of sack paper samples.

During deformation of paper and board, the material is first subjected to an elastic deformation, where the network is stretched. At this stage, the externally applied mechanical energy is stored in the network. With further applied force, bonds between fibres but also the fibres themselves start to break, resulting in irreversible, plastic deformation. During this plastic deformation, energy is released and dissipated as heat. The aim of the study was to use thermography to link the dissipated heat due to irreversible, plastic deformation to the externally applied mechanical forces.

In the experiment, mill-made sack paper was subjected to a uniaxial tensile test, see Figure 39.

![Figure 39. Images of sack paper during a uniaxial tensile test, in the visual wavelength range before the start of the test (left), and in the MWIR wavelength range at the time of rupture (right).](image)

Three independent measurements were made both in the machine direction (MD) and cross direction (CD) of the sheet. The sample was pulled at a constant deformation rate of 0.3 mm/s, and the force-elongation curve was recorded. The sample was simultaneously imaged by a MWIR thermographic
camera, see *Table 11*. The ambient radiation from the surroundings was measured by imaging a gold surface and compensated for. The emittance of the sack paper was measured using the goniometric setup described in earlier sections.

Based on the force-elongation curve, the total mechanical energy was calculated, and the plastic and elastic shares were estimated. The total heat energy dissipated from the paper at the time of rupture was determined based on the infrared image sequence, the measured emittance, and literature values on the specific heat capacity of paper, see *Figure 40*. The values of the total mechanical energy and its plastic and elastic shares were then compared to the value of the thermal energy, as a function of time.

![Diagram](image)

*Figure 40. Conversion to thermal energy, based on the measured emittance of the sample, the emitted infrared radiance recorded by an infrared camera, the area A and grammage w of the sample, and the specific heat capacity c_p of paper.*
7. Results and discussion of fine material characterisation

7.1. Evaluation and comparison of instruments

One laser diffractometer and three flow microscopes with different resolutions and field of views were evaluated by measurements on calibration particles and pure and mixed model stocks. Four different sizes of silica spheres with refractive index similar to that of wet fibres were measured to evaluate performance of the instruments at the resolution limit.

The outcome of the measurements of the silica spheres is summarised in Table 14. As mentioned in the methods section, only certain sizes were measured with a given instrument, as detection was assumed to be improbable if the spheres were much smaller than the spatial resolution of the instrument.


<table>
<thead>
<tr>
<th>Sample Instrument</th>
<th>S20nm</th>
<th>S80nm</th>
<th>S350nm</th>
<th>S2.0µm</th>
<th>S7.0µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS</td>
<td>Red</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IS60X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IS40X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IS20X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FT+</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FT</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The 20 nm spheres were not detected by the Mastersizer, and the 80 nm spheres were oversized. For the other sizes of the silica spheres, the accuracy was good with an average SED close to the size specified by the manufacturers, but the uncertainty was high. The uncertainty was mainly due to poor repeatability. For the image-based instruments, all the silica spheres were oversized, with an average uncertainty of 10-15%. The uncertainty was largely attributed to the random, unrestricted motion of the particles, resulting in the particles being imaged at different distances from the detector; thus appearing either larger or smaller. The random
enlargement due to the particle motion may also explain why the image-based instruments detected a share of the spheres even when their size was smaller than the pixel resolution. When the size of the spheres was close to the pixel resolution of the instrument, the uncertainty was also much larger.

The overestimation of the size by the image-based instruments may be partly due to the random positioning of the particle relative to the pixels, as was illustrated in *Figure 22*. However, for the ImageStream it could be seen that the oversizing of the larger silica spheres was largely due to the segmentation algorithm, which is exemplified in *Figure 41*. The used algorithm, which was adapted for fines, could not override the diffraction halo around the particle, resulting in a systematic uncertainty in the segmentation. This implies that the optical properties of the silica spheres were too dissimilar to those of wet fines to constitute a good calibration material. With a good calibration material, the same algorithms should be usable as for normal samples.

![Figure 41. ImageStream segmentation of a Ø7.0 µm silica sphere, showing the influence of the segmentation algorithm (“mask”) on the measured circle-equivalent diameter (red number) [Paper B].](image)

The performance of the instruments when measuring on pure and mixed fine fractions is summarized in *Table 15*, together with the expected performance on the whole pulp and fibres.


Given the decent performance of the Mastersizer in the measurements of the silica spheres, the performance on the fine fractions was below expectations. Firstly, for the fines and mixed samples, the result was highly sensitive to the refractive index setting, see *Figure 42*. For the PCC, the results were less sensitive. Secondly, the smallest particle in the distribution was surprisingly
large, about 3 µm for the TMP fines, and 6 µm, for the kraft fines, see Table 16.

*Table 16. Smallest and largest particle size (SED for the MS, length for the other instruments) in the measurement results of the UKSW, TMP, and PCC fine fractions, without any upper size limit.*

<table>
<thead>
<tr>
<th>Sample</th>
<th>MS</th>
<th>IS60X</th>
<th>IS40X</th>
<th>IS20X</th>
<th>FT+</th>
<th>FT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smallest size [µm]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UKSW</td>
<td>6.3</td>
<td>0.66</td>
<td>1.0</td>
<td>2.0</td>
<td>4.0</td>
<td>15.0</td>
</tr>
<tr>
<td>TMP</td>
<td>3.5</td>
<td>0.66</td>
<td>1.0</td>
<td>2.0</td>
<td>4.0</td>
<td>15.0</td>
</tr>
<tr>
<td>PCC</td>
<td>1.3</td>
<td>0.66</td>
<td>1.0</td>
<td>2.0</td>
<td>4.0</td>
<td>15.0</td>
</tr>
<tr>
<td>Largest size [µm]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UKSW</td>
<td>800</td>
<td>110</td>
<td>85</td>
<td>83</td>
<td>1141</td>
<td>4131</td>
</tr>
<tr>
<td>TMP</td>
<td>630</td>
<td>89</td>
<td>145</td>
<td>186</td>
<td>5319</td>
<td>4068</td>
</tr>
<tr>
<td>PCC</td>
<td>13</td>
<td>27</td>
<td>29</td>
<td>31</td>
<td>59</td>
<td>3363</td>
</tr>
</tbody>
</table>

By changing the weighting of the distribution, it was ruled out that the absence of sub-micron particles in the MS data was due to the volume-weighting. Instead, it was suggested that the sub-micron fines scattered insufficient light by diffraction to be detected by the instrument. The results allow the conclusion that laser diffractometry is not a suitable method for the size characterisation of fines.

*Figure 42. The influence of the complex refractive index on the Mastersizer measurement results for pure UKSW fines (left), and pure and mixed UKSW fines and PCC (right). Where the extinction coefficient k is not specified, it was zero [Paper B].*

When the image-based instruments were compared with each other, the impact of the resolution became clear, see *Figure 43.*
With increased resolution, more particles were detected. For fines in particular, there is reason to believe that the relative amount of particles continues to increase with decreasing size, down to the size of the elementary fibril. Thus, all improvements in resolution yield additional information.

As the sample in Figure 43 comprises a mixture of fines and fillers, two particle populations would ideally have been distinguishable. That this was not the case may partly be explained by the enriching of PCC particles due to the screening. Even with area-weighting, the small but numerous PCC particles dominate the distribution. However, it also implies that the size and shape of fines and fillers overlap, and that morphology alone is not sufficient to differentiate between the two particle types.

Finally, the results of both the diffraction-based and image-based instruments were compared, see Figure 44. Three ranges in the graph were discerned. Through qualitative inspection of the ImageStream images, typical particles in the size range within each range could be identified, see Figure 45. The first range, between 1 and 3 µm, corresponded to single PCC particles and small fines. Here, the IS60X and IS40X had a significant share of their particles. The second range, between 3 and 10 µm, corresponded mainly to small and large filler agglomerates. Here, the FT+ had its dominant peak. The third range, between 15 and 60 µm, corresponded mainly to large fines and fines-filler agglomerates. Here, the FT and MS peaked. In the raw FT data, single-pixel objects of width 15 µm dominated by number. However, as some large fines and fines-filler agglomerates were present, the volume-weighting caused them to dominate the distribution. The same effect is likely to govern the shape of the MS curve.
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Figure 44. SED distribution (volume-weighted) of the UKSW and PCC mixture, from all instruments. Three size ranges are indicated with arrows on the top of the graph [Paper B].

<table>
<thead>
<tr>
<th>First range: 1-3 µm</th>
<th>Second range: 3-10 µm</th>
<th>Third range: 15-60 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
</tbody>
</table>

Figure 45. Example images from the qualitative analysis of IS60X images for the interpretation of the size ranges in Figure 44.

Based on the qualitative analysis, the FT+ resolved filler agglomerates, but not single filler particles or small fines. It performed similarly as the MS, but has the additional advantage of providing shape information. The ImageStream was best at detecting small particles, but its limited field of view at 40X and 60X magnification prevented it from detecting larger fines. Thus, the ImageStream and the FT+, or other instruments with similar differences in resolution and FOV, can be regarded as complimentary.
7.2. Morphological changes due to refining

Bleached chemical softwood pulp was refined in an industrial-like laboratory refiner with five different refiner segments and sampled at six specific refining energy (SRE) levels. The purpose of the study was to utilize developments in flow microscopy to evaluate the influence of segment design on the morphology of pulp in general and fines in particular. The Schopper-Riegler (SR), fibril perimeter, fibre length, and fines content measured on the whole pulp are shown in Figure 46 and Figure 47. Additional details are given in Paper C.

Figure 46. SR (left) and FT+ fibril perimeter (right) for the various segments, as a function of SRE. As the error bars, based on the reproducibility of the measurements, were smaller than the size of the markers, they are not shown. Labels C1-D3 are defined in Table 9 [Paper C].

Figure 47. FT+ mean length (left) and FT+ fines content (right) for the various segments, as a function of SRE [Paper C].
Despite a large difference in segment design, three segments (C1, D1, and D2) behaved fairly similarly. The C2 segment gave a lower SR than those three segments, but similar fines content. The fibril perimeter of segment C2 was also low, indicating that the lower SR may be due to less external fibrillation. D3, the hardwood segment with very fine design, imposed the least changes on the measured pulp properties.

The content of P-fines (coarse fines) and S-fines (slim fines) was measured both on the whole pulp and on the screened fines fraction, see Figure 48. Before refining, the whole pulp contained 10% P-fines and 10% S-fines, and the fines fraction contained 32% P-fines and 42% S-fines, i.e. some of the P-fines in the whole pulp did not pass the Ø76µm BDDJ mesh.

![Figure 48. Share of total fines (fines content), P-fines, and S-fines in the whole pulp (left) and in the fines fraction (right), as a function of SRE, measured with the FT+. Note the different y-axis scales [Paper C].](image)

In the whole pulp, the amount of P-fines was constant between 0 and 200 kWh/t, and then increased slightly. The amount of S-fines increased monotonically with increased SRE. The trend was the same for all segments, but the D3 pulp had a lower content of both fines classes. In the fines fraction, the amount of P-fines decreased with increased SRE, while the amount of S-fines increased. The difference between the whole pulp and the fines fraction was attributed to coarse fines which were small enough to be classified as fines, but large enough to not pass the BDDJ mesh.

The development of the morphology of the fines was different for the two measurement instruments, see Figure 49. For the FT+, which could measure larger and coarser fines (average length approximately 85 µm), the length
and aspect ratio decreased with increased SRE. The absolute values of the length, width and aspect ratio were similar for the segments, except for D3, which produced longer and slimmer fines. For the ImageStream, which measured smaller and slimmer fines (average length approximately 12 µm), the changes with increasing SRE were minor. Segment C2, which had blunter edges due to wear, produced slightly coarser and shorter fines, and the HW segment with the fine pattern, D3, produced slimmer and more fibrillar fines. For the remaining segments, little change in morphology with increasing SRE was observed.

In summary, segment design had little influence on the measured fines morphology, while the resolution and field of view of the measurement instrument had a very large influence. The FT+ measured surprisingly large fines, while the ImageStream appeared to be capable of resolving macrofibrils.

7.3. Influence on sheet properties

Chemical SW pulp was refined in an industrial-like laboratory refiner and the morphology of the fibres and fines was characterised. The strength properties of laboratory sheets made from the pulp refined to the highest specific refining energy (SRE 400 kWh/t) were measured. The results of the
tensile index (in-plane strength) are plotted against Schopper-Riegler (SR), fibril perimeter, fines content, and bulk in Figure 50 and Figure 51.

![Figure 50](image.png)

**Figure 50.** Tensile index as a function of pulp SR (left) and fibril perimeter (right), measured on laboratory sheets made from softwood pulp refined to 400 kWh/t with different segments. “Unref” stands for unrefined (0 kWh/t), and labels C1-D3 are defined in Table 9 [Paper C].

![Figure 51](image.png)

**Figure 51.** Tensile index as a function of pulp fines content (left) and sheet bulk (right), measured on laboratory sheets made from softwood pulp refined to 400 kWh/t with different segments [Paper C].

In the present study, at the high SRE level that was used, it was difficult to find a correlation between the tensile index and the measured pulp properties. The SR and fibril perimeter showed similar behaviour in their relation to the tensile index. The pulp refined with segment D2 gave the lowest tensile index, while having relatively high SR, fibril perimeter, and fines content. The pulps refined with the other segment gave similar tensile
index, but the D3 pulp had a higher bulk. Usually, bulk decreases with increasing fines content \[15\]. The D2 pulp had highest fines content, while the D1 pulp had the lowest fines content (Figure 47). Thus, the high bulk and high tensile index of the D3 pulp could be partly due to its low fines content. The increase in tensile index compared to the unrefined pulp could be due to internal fibrillation, giving increased flexibility. Internal fibrillation would also make it easier for the fibre to collapse, which creates greater bonding area. It is also possible that segment D3 produced external fibrillation, but that the fibrils were too fine to be resolved by the FT+, and thus contribute to the measured value for fibril area and fibril perimeter.

In this study, none of the refining descriptors (SEL, CEL, MEL, SSL, C-factor) was able to predict the changes in properties of the pulp or the sheet properties. At present, no explanation can be given for that.

7.4. Principle for fines and filler differentiation

In Paper C, it was reported that size and shape alone was not sufficient to differentiate between fines and fillers. Thus, side-scattering (SSC) and fluorescent excitation (EXC) was evaluated as an approach for separating between UKSW fines and PCC fillers in a mixed suspension. Figure 52 compares the results of a differentiation with pure samples, based on their total autofluorescent and SSC intensities.

It can be seen that the differentiated fines and filler subsets of the mixed sample correspond well to the pure fines and filler samples. There is some overlap between the agglomerate subset of the mixed sample and the pure PCC sample. This is likely due to PCC agglomerates, which are present in both samples but not regarded as a separate subset in the pure PCC sample. It can also be seen that the pure PCC sample has higher maximum SSC signal than the PCC subset of the mixed sample. Based on qualitative analysis of the left sides of Figure 35 and Figure 36, the difference is likely due to a higher amount of PCC agglomerates in the pure sample, compared to the mixed sample.
91% of the particles in the mixed sample, by number, were classified as fillers, 8% as fines, and 1% as agglomerates. No other method was available which could quantitatively confirm this concentration. In future studies, the fillers should be added after the BDDJ filtration, so that the concentration, by weight, of both the fines and fillers is well known. Based on the particle density, their volume concentration could then be estimated, which would be more easily compared to the measurement result.

An advantage of the ImageStream system is that the particles cannot only be differentiated and counted; their size and shape can also be characterised. The length and aspect ratio of the differentiated subsets is shown in Figure 53:
Figure 53. Size characterisation of the differentiated particle subsets in the mixed sample. Left: Length distribution (area-weighted). Right: Aspect ratio distribution (area weighted). Mix all: undifferentiated mixed sample. Mix PCC/fines/agglomerates: Differentiated subsets of the mixed sample.

The undifferentiated sample (red curve) appears very similar as the PCC subset, which is not surprising given the high share of PCC. In the undifferentiated sample, the fines and agglomerate subsets of particles cannot be spotted. However, when they are differentiated, it can be seen that they differ significantly in both size and shape from the sample as a whole.
8. Results and discussion of emittance measurements

8.1. Measured emittance values

The results and conclusions of the evaluation of the developed goniometric setup are presented in Paper D. The emittance measurements that were made on the same sample with both the developed setup and a FTIR spectrophotometer were in good agreement, taking into account the methodological differences. This demonstrated the validity of the goniometric method. A summary of the influence of the investigated parameters on the emittance is presented in Table 17. Details can also be found in Paper D, Paper E, and the licentiate thesis [120].

Table 17. Summary of the influence of the varied parameters on the measured emittance of different fibre-based samples. Green: Not significant. Blue: Minor or conditional significance. Red: Significant.

<table>
<thead>
<tr>
<th>Varied parameter</th>
<th>Influence of variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of layers (transmittance)</td>
<td>Not significant</td>
</tr>
<tr>
<td>Temperature</td>
<td>Not significant</td>
</tr>
<tr>
<td>Observation angle</td>
<td>Significant (above a certain value)</td>
</tr>
<tr>
<td>Wavelength range</td>
<td>Significant</td>
</tr>
<tr>
<td>Pulp type (furnish)</td>
<td>Significant (in the MWIR range)</td>
</tr>
<tr>
<td>Pulp drying</td>
<td>Not significant</td>
</tr>
<tr>
<td>Pulp refining</td>
<td>Not significant</td>
</tr>
<tr>
<td>Forming procedure</td>
<td>Not significant</td>
</tr>
<tr>
<td>Fibre orientation in machine-made sheets</td>
<td>Not significant</td>
</tr>
<tr>
<td>Influence of z-direction in linerboard</td>
<td>Not significant</td>
</tr>
<tr>
<td>Board coating</td>
<td>Minor</td>
</tr>
<tr>
<td>Addition of brightness additives (OBA)</td>
<td>Not significant</td>
</tr>
<tr>
<td>Addition of starch</td>
<td>Not significant</td>
</tr>
<tr>
<td>Moisture ratio</td>
<td>Significant</td>
</tr>
</tbody>
</table>
In general, emittance adjustments should be considered when the pulp type, wavelength range, observation angle, and moisture ratio are changed. The influence of these parameters is described in greater detail below. Furthermore, the insignificance of sample temperature deserves a comment. That the emittance does not vary with temperature implies that fibre-based samples can be heated to achieve greater contrast and accuracy in a thermographic experiment, without the need of changing the emittance. In addition, when measuring in different sections of a paper machine, where the temperature may vary significantly, there is also no need to adjust the emittance due to the temperature change.

The emittance was lower in the MWIR range than in the LWIR range, see Figure 54. The average normal emittance, 0.72 in the MWIR range and 0.90 in the LWIR range, correspond well to previously reported values for the normal emittance of dry paper in the respective wavelength range [122, 125]. With the exception of the TMP and the recycled pulp, most sample types had similar emittance, especially in the LWIR range. As mechanical fines are known to have good light scattering properties in the visual wavelength range, it is possible that they contribute to a higher reflectance, and thus lower emittance, in the TMP sheet. Fillers could have a similar effect in the recycled pulp sheet.

![MWIR and LWIR emittance of various fibre-based samples](image)

*Figure 54. MWIR and LWIR emittance of various fibre-based samples: TMP, bleached kraft birch (HW), bleached kraft birch and softwood (SWHW), bleached kraft softwood (BKSW), unbleached kraft softwood (UKSW), bottom-side uncoated linerboard (UCB), top-side coated board (CT), sack paper (SP), and recycled paper (RC), measured at normal incidence angle ($\theta = 0^\circ$) at temperature 70°C [Paper E].*
The sensitivity to observation angle was larger in the MWIR range than in the LWIR range, see Figure 55. The emittance was approximately constant up to an observation angle of approximately 40° in the MWIR range and 60° in the LWIR range; beyond that it dropped. Also, the coated board had slightly higher sensitivity to observation angle than the other samples, possibly due to its smoother surface giving a higher reflectance. Interestingly, the directional behaviour of the emittance was similar to that reported for other natural samples such as soils [123, 126, 127].

![Figure 55. MWIR and LWIR emittance as a function of observation angle for four fibre-based samples: TMP, recycled pulp (RC), bleached kraft softwood (BKSW), and top-side coated board (CT), measured at 70°C [Paper E].](image)

The emittance decreased with decreasing moisture ratio, see Figure 56, and the absolute change in emittance was again larger in the MWIR range than in the LWIR range. Several previous studies suggested a similar influence of moisture on the emittance of paper [92] and other natural samples [128]. A study which reported different trends does not appear to have accounted for the influence of evaporative cooling when measuring the emittance [90], possibly explaining the difference in results.
At low moisture ratio, when the sample was almost dry, a small increase in moisture ratio resulted in a relatively large increase in emittance. At higher moisture ratio, the emittance was less sensitive, implying that it is more important to account for changes in the emittance due to moisture when the sheet is nearly dry. The emittance was well predicted by the mass-based mixing rule (Eq. 32) in both the MWIR and LWIR wavelength ranges.

In summary, in thermographic measurements for pulp and paper applications, a suitable emittance for the wavelength range of the camera should be chosen. In the MWIR range, a lower value should be chosen if TMP or recycled pulp is measured. At most observation angles, the emittance does not need to be accounted for. However, at extreme inclinations, the temperature may be underestimated if the emittance is not adjusted. When measuring a drying process, the emittance should be continuously decreased as the moisture ratio decreases. Here, prediction of the emittance based on the mass-based mixing rule will be very useful.
8.2. Energy assessment in a tensile test

The results of the emittance measurements were applied in quantitative energy calculation of the thermal energy dissipation from sack paper during deformation. The plastic and elastic share of the mechanical energy imparted during the deformation were also calculated as a function of time, and compared to the dissipated thermal energy that was measured using thermography, see Figure 57.

![Figure 57. Calculated mechanical and thermal energy during a uniaxial tensile test of a sack paper in the cross direction (CD) [Paper F].](image)

The value of the thermal energy at the time of rupture was 40-60% of the total imparted mechanical energy. The remaining energy was likely dissipated to the environment during the relatively long experiment. It was found that the increase in thermal energy at the point of rupture corresponded well to the elastic energy stored during the deformation, see Figure 58.
During deformation, elastic energy is built up and stored in the entire sample. However, during rupture, that energy is consumed locally in the rupture zone, leading to a high temperature in this zone. The stored elastic energy appears to provide the energy for the propagation of the rupture. This has been previously proposed [129, 130], but has not been experimentally verified. It should be remembered that the mechanical energy and thermal energy were determined using two completely independent methods. As the results were quantitatively close, and certainly of the right order of magnitude, the approach of comparing the externally applied mechanical load with the dissipated thermal energy seems to be sound and should also be applied in future work, for example in the characterisation of the non-uniformity in mechanical loading.

Figure 58. The thermal energy increase at the time of rupture and the elastic energy stored in the sample until the point of rupture [Paper F].
9. Conclusions and outlook

9.1. Conclusions

Presently, image-based infrared thermography and microparticle characterization for pulp and paper applications are mainly used qualitatively. The purpose of this work was to facilitate the future quantitative use of these methods by applying technological developments and increasing the measurement accuracy.

By employing an imaging flow cytometer, fines and filler suspensions were measured at resolutions (0.33, 0.5, and 1.0 µm/pixel) unprecedented for image-based, quantitative characterization. The same samples were measured with two fibre analysers: one with a resolution of approximately 4 µm/pixel and image analysis routines for fines classification, and the other with a resolution of approximately 10 µm/pixel. The relative amount of small particles increased as the size decreased, i.e. a larger amount of smaller particles were detected with increasing resolution. Using the imaging flow cytometer, it was possible to resolve single particles of the investigated PCC filler; however at the price of a limited field of view. The high-resolution fibre analyser detected only filler agglomerates but could measure the coarser share of the fines fraction. Thus, these two instruments are complimentary.

The flow microscopes were compared to a laser diffractometer with a detection limit of approximately 20 nm. The complex refractive indexes of wet fines and a mixture of fines and fillers were calculated based on mixing rules, as they were required for the laser diffractometry analysis and measured values could not be found. Silica spheres with known size and refractive index similar to that of wet pulp were also measured, to evaluate the measurement accuracy and uncertainty. All the image-based instruments overestimated the size of the calibration spheres. It was suggested that the oversizing was partly due to dissimilar optical properties of the calibration particles, compared to the typical sample, and that better calibration materials for fines need to be developed. The measurement uncertainty due to the unrestricted motion of the particles was also found to be significant.

When measuring on fines and a mixture of fines and fillers, the high-resolution image-based instruments performed better than the laser diffractometer, likely because the wet fines scattered insufficient light by diffraction. An important parameter to consider in both scattering and
imaging measurements was thus pointed out: the contrast, as given by the refractive index differences between water and the particles themselves. The lower the contrast, the larger the particle has to be to overcome the noise of the measurement system. Detection of particles in water solutions is thus not solely a size problem but very much a problem of refractive index decrease as the wood-based particles absorb water.

When measuring on a mixture of fines and fillers, the size and shape of the fines and fillers partly overlapped; thus, it was not possible to tell them apart. Presently, there is no available method which can differentiate between fines and fillers in a suspension. A method based on a combination of side-scattering and autofluorescence was therefore devised. The method was based on the assumption that fillers in the suspension would remain high-scattering but not autofluorescent. In contrast to that, the water-swollen fines would be low scattering, but autofluorescent. A qualitative evaluation of the concept using the imaging flow cytometer showed promising results.

The imaging flow cytometer and the high-resolution fibre analyser were used in quantitative measurements of the morphology changes due to a pulp treatment in a refiner. The changes in morphology were found to be more dependent on the applied specific refining energy than on the design of the refining segment. The size and aspect ratio of the larger fines decreased with increased refining energy, while the smaller fines did not change significantly. Based on the overall performance of the evaluated instruments, it was concluded that the new, image-based instruments provide better and more suitable characterisation of fines and fillers than the previously used techniques.

A method was developed for measurement of the directional and wavelength-integrated emittance of fibre-based samples, both dry and with varying moisture. Thus, a measurement technique that could provide previously lacking emittance data has been established. The emittance of the fibre-based samples was not influenced by the temperature of the sample. However, it varied significantly with pulp type (furnish), infrared wavelength range (MWIR, LWIR), observation angle, and moisture ratio. Thus, variations in these parameters should be accounted for when applying emittance values in thermographic measurements, especially when using an MWIR camera, as the emittance was more sensitive in that wavelength range. This implies that cameras operating in the LWIR range can be considered to be more robust if changes in the emittance over time are expected, for example during continuous web inspection.

The moisture ratio had a large influence on emittance, and was most pronounced when the sheet was nearly dry. The emittance of a sheet with
varying moisture could be predicted by a mass-based mixing rule using the emittances of the dry sheet and water.

Measured emittance values were applied in a thermographic study of the rupture of sack paper samples. The thermal energy emitted during the deformation was determined using quantitative thermography, and related to the applied mechanical energy. It was seen that the increase in thermal energy at the time of rupture corresponded well to the elastic energy invested into the deformation. The result implies that the stored elastic energy fuels the propagation of the rupture.

9.2. Outlook

The characterisation of fines and filler particles can be improved in several ways. For example, to facilitate precise optical measurements of a stock, the refractive index of wet fibres, wet fines and wet fillers should be measured in dedicated experiments. The “holy grail” of quantitative characterisation of cellulose nanofibrils (CNF) cannot be reached using current flow microscopes. However, the efficiency of the CNF manufacturing process could be indirectly assessed by analysis of the coarser residues, after homogenisation. As the low optical contrast of nanofibrils is an issue, it would be beneficial to find a fast, non-toxic cellulose-binding fluorescent stain. Alternatively, non-imaging nanoparticle characterisation techniques such as Tunable Resistive Pulse Sensing (TRPS) \[131\] could be evaluated on CNF.

Much development work can be done based on the proposed method for automatic differentiation between fines and fillers in a suspension. The method should be quantitatively evaluated using suspensions with well-known particle contents. Fillers of smaller sizes and other types should be measured, e.g. ground calcium carbonate (GCC), kaolin, and titanium dioxide. The difference in autofluorescence when illuminating with a red excitation laser could be evaluated for the separation between kaolin and GCC/PCC \[132\]. The difference in autofluorescence due to the lignin content could be used to differentiate between different kinds of pulp fines, e.g. chemical and mechanical pulp fines, or bleached and unbleached chemical pulp fines. Finally, other micron-sized papermaking compounds such as starch, ink and latex should be characterised as pure suspensions. Once a wide range of pure and mixed “model” suspensions have been characterised, the possibility to differentiate different components of the fine fraction of a recycled pulp should be examined.
As the imaging flow cytometer evaluated in this work required the samples to be screened to remove large particles, the technique is difficult to implement in an industrial setting. In on-line applications, flow cells where several particles are imaged at the same time may be more realistic than hydrodynamically focused single-particle measurements. Two approaches for such measurements are darkfield microscopy [133] and the ParticleView instrument [134], which are both based on scattered light. It was seen in this work that side-scattering alone was sufficient to differentiate ~95% of the fines and fillers. However, it was also observed that fines were better characterised through transmission-based measurements than through side- or back-scattering. Thus, a measurement instrument for fines and filler characterisation should utilise both transmitted and side- or back-scattered light.

The measured emittance values provide a good foundation for the implementation of quantitative thermographic analysis in the pulp and paper industry. Several applications can be found in damage mechanics, for example estimation of the amount of energy absorbed by a package, and determining weak spots in a package. A thermographic method for measurements of the heat capacity of paper has been proposed [43], and values of the specific heat of papers containing fillers have been published [135], which will aid in future studies involving calculations of the thermal energy dissipated from a sheet.

Since the emittance measurements in this work were published, they have been used to relate the energy required to evaporate a known amount of moisture to the temperature drop due to evaporative cooling [136]. Many other potential applications of thermography can be found in areas related to moisture, for example in the study of adsorption by tissue paper. While other optical signals may be more directly related to moisture, for example NIR or microwave absorption, methods utilising those signals require the sample to be illuminated. The methods can also be sensitive to multiple scattering in a sheet. As thermography does not require illumination, it is often a more convenient method.

Improvements in uncooled infrared sensors have made thermographic cameras with sufficient frame rates and spatial resolution for web inspection available at a reasonable price. Initiatives have also been taken to integrate infrared cameras with the paper machine QCS system [137]. Here, images of the continuously monitored, moving web could be stitched together, and 2D Fourier analysis could be used to quantify the frequencies of recurring spatial and temporal variations. The frequencies could then be used for troubleshooting and process control by relating them to process variations with the same frequency. Another step forward would be to correlate quantitative temperature variations with quantitative moisture variations.
While such a relationship would likely have to be determined for each product, due to their difference in grammage and thickness, it could provide a significant improvement in quality control. The efficiency of the production processes could then be substantially increased.


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64. ThermoFisher (2015): Physical Properties That Define Fluorescence,


95. Amnis, Personal communication to K. Hyll: *Personal communication*, 2014.


107. Östlund, I., Personal communication to K. Hyll: On the kappa number and SR of the UKSW Frövi pulp, Jul. 02, 2015.


Appendix

Gallery

In this gallery, a selection of images from the high-resolution ImageStream measurements is shown. These images are not solely taken from the studies presented in this thesis. They show the large variety of particles that can be observed in a pulp suspension. These particles are however rather outliers than representative particles as most detected particles were much smaller. Additionally, a high share of the selected images show ray cells, as these have more detailed visual features.

<table>
<thead>
<tr>
<th>Particles in the fine fraction of a chemical hardwood pulp</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Image 1" /></td>
</tr>
<tr>
<td>7 µm</td>
</tr>
<tr>
<td><img src="image5.png" alt="Image 5" /></td>
</tr>
<tr>
<td>7 µm</td>
</tr>
</tbody>
</table>
Particles in the fine fraction of a chemical softwood pulp
Particles in the fine fraction of a chemical softwood pulp (cont.)
Particles in the fine fraction of a softwood TMP

Particles in the fine fraction of a softwood groundwood pulp
Particles in the fine fraction of a softwood CTMP pulp
Particles in the fine fraction of a softwood CTMP pulp (cont.)
Particles in the fine fraction of a softwood CTMP pulp (cont.)
Examples of PCC filler particles

Particles in the fine fraction of a recycled pulp
Examples of multichannel images obtained with the ImageStream

Ray cell with autofluorescent object (possibly bacteria) (bleached softwood kraft pulp)

Ray cell with high-scattering object (bleached softwood kraft pulp)

Primary fines (bleached softwood kraft pulp)

Secondary fines (bleached softwood kraft pulp)

Bordered pit (softwood CTMP)

Bordered pit (softwood CTMP)
Examples of multichannel images obtained with the ImageStream (cont.)

Small autofluorescent particle with low contrast (unbleached softwood kraft pulp)

Fines and filler agglomerate (PCC + bleached softwood kraft pulp)

Fines and filler agglomerate (PCC + bleached softwood kraft pulp)

Fines and filler agglomerate (PCC + bleached softwood kraft pulp)

Agglomerate (recycled pulp)

Agglomerate (recycled pulp)
## Symbols and abbreviations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>2D</td>
<td>Two-dimensional</td>
</tr>
<tr>
<td>α</td>
<td>Absorptance</td>
</tr>
<tr>
<td>A</td>
<td>Area of particle [m²]</td>
</tr>
<tr>
<td>AR</td>
<td>Aspect ratio of particle (length/width)</td>
</tr>
<tr>
<td>BB</td>
<td>Blackbody</td>
</tr>
<tr>
<td>BSC</td>
<td>Back-scattering</td>
</tr>
<tr>
<td>BDDJ</td>
<td>Britt dynamic drainage jar</td>
</tr>
<tr>
<td>BKHW</td>
<td>Bleached kraft hardwood</td>
</tr>
<tr>
<td>BKSW</td>
<td>Bleached kraft softwood</td>
</tr>
<tr>
<td>c</td>
<td>Speed of light [m]</td>
</tr>
<tr>
<td>C_s</td>
<td>Scattering cross-section</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge-coupled device</td>
</tr>
<tr>
<td>CD</td>
<td>Cross direction in the paper machine</td>
</tr>
<tr>
<td>CED</td>
<td>Circle-equivalent diameter of particle [m]</td>
</tr>
<tr>
<td>CNF</td>
<td>Cellulose nanofibrils</td>
</tr>
<tr>
<td>CTMP</td>
<td>Chemi-thermomechanical pulp</td>
</tr>
<tr>
<td>d</td>
<td>Characteristic dimension of particle [m]</td>
</tr>
<tr>
<td>D_{sc}</td>
<td>Directional scattering function</td>
</tr>
<tr>
<td>DOF</td>
<td>Depth of field</td>
</tr>
<tr>
<td>EXC</td>
<td>Excitation</td>
</tr>
<tr>
<td>ε</td>
<td>Emittance (emissivity)</td>
</tr>
<tr>
<td>F_m</td>
<td>Mass fraction</td>
</tr>
<tr>
<td>FC</td>
<td>Fines content</td>
</tr>
<tr>
<td>FOV</td>
<td>Field of view</td>
</tr>
<tr>
<td>FT</td>
<td>L&amp;W Fiber Tester</td>
</tr>
<tr>
<td>FT+</td>
<td>L&amp;W Fiber Tester Plus</td>
</tr>
<tr>
<td>FSC</td>
<td>Forward-scattering</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>h</td>
<td>Planck’s constant [J/s]</td>
</tr>
<tr>
<td>HW</td>
<td>Hardwood</td>
</tr>
<tr>
<td>I</td>
<td>Intensity [W/m²]</td>
</tr>
<tr>
<td>IFOV</td>
<td>Instantaneous field of view</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>IS</td>
<td>ImageStream</td>
</tr>
<tr>
<td>IS_X</td>
<td>ImageStream used at 20X/40X/60X magnification</td>
</tr>
<tr>
<td>J</td>
<td>Bessel function</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>κ</td>
<td>Extinction coefficient</td>
</tr>
<tr>
<td>k</td>
<td>Wave number [m⁻¹]</td>
</tr>
<tr>
<td>k_B</td>
<td>Boltzmann’s constant [J/K]</td>
</tr>
<tr>
<td>λ</td>
<td>Wavelength of electromagnetic radiation [m]</td>
</tr>
<tr>
<td>l</td>
<td>Litre [l]</td>
</tr>
<tr>
<td>L</td>
<td>Length of particle [m]</td>
</tr>
<tr>
<td>LD</td>
<td>Laser diffractometry</td>
</tr>
<tr>
<td>LWIR</td>
<td>Long-wavelength infrared</td>
</tr>
<tr>
<td>m</td>
<td>Relative complex refractive index</td>
</tr>
<tr>
<td>M</td>
<td>Mass of substance [kg]</td>
</tr>
<tr>
<td>MD</td>
<td>Machine direction in the paper machine</td>
</tr>
<tr>
<td>MR</td>
<td>Moisture ratio</td>
</tr>
<tr>
<td>MS</td>
<td>Mastersizer</td>
</tr>
<tr>
<td>MWIR</td>
<td>Mid-wavelength infrared</td>
</tr>
<tr>
<td>n</td>
<td>Real part of the refractive index</td>
</tr>
<tr>
<td>n</td>
<td>Complex refractive index</td>
</tr>
<tr>
<td>N</td>
<td>Number of particles</td>
</tr>
<tr>
<td>NIR</td>
<td>Near-infrared</td>
</tr>
<tr>
<td>OBA</td>
<td>Optical brightness additives</td>
</tr>
<tr>
<td>P_sc</td>
<td>Scattered power [W]</td>
</tr>
<tr>
<td>P</td>
<td>Perimeter of particle [m]</td>
</tr>
<tr>
<td>PCC</td>
<td>Precipitated calcium carbonate</td>
</tr>
<tr>
<td>QCS</td>
<td>Quality control system</td>
</tr>
<tr>
<td>ρ</td>
<td>Reflectance</td>
</tr>
<tr>
<td>R</td>
<td>Distance to object [m]</td>
</tr>
<tr>
<td>RE</td>
<td>Rectangle-equivalent</td>
</tr>
<tr>
<td>S</td>
<td>Shape parameter</td>
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<tr>
<td>SED</td>
<td>Sphere-equivalent diameter of particle [m]</td>
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<tr>
<td>SFSC</td>
<td>Specific forward-scattering</td>
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<tr>
<td>SR</td>
<td>Schopper-Riegler [°SR]</td>
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<tr>
<td>SSC</td>
<td>Side-scattering</td>
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<tr>
<td>SW</td>
<td>Softwood</td>
</tr>
<tr>
<td>τ</td>
<td>Transmittance</td>
</tr>
<tr>
<td>t</td>
<td>Tonne [10³ kg]</td>
</tr>
<tr>
<td>θ</td>
<td>Scattering angle [rad] or observation angle [°]</td>
</tr>
<tr>
<td>TR</td>
<td>Traced</td>
</tr>
<tr>
<td>TMP</td>
<td>Thermomechanical pulp</td>
</tr>
<tr>
<td>U</td>
<td>Signal voltage [V]</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>UKSW</td>
<td>Unbleached kraft softwood</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>V</td>
<td>Volume of particle [m$^3$]</td>
</tr>
<tr>
<td>VIS</td>
<td>Visual</td>
</tr>
<tr>
<td>$x$</td>
<td>Relative size</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>Solid angle [sr]</td>
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