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Fractionated refining and sulphonation as a tool to reduce the energy consumption during refining

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Abstract

Refining is one of the most important processes in a paper mill being the crucial step in stock preparation. It improves fibre-fibre bonding ability, sheet formation and leads to better physical properties of the final product. It is, however, also a highly energy-demanding step. Therefore, different strategies were studied in this thesis aiming at reducing the energy consumption of this process with a focus on the tensile strength-dewatering-porosity relationship of the treated pulp. The main alternatives presented are fractionated refining and chemical pre-treatment. Fractionating the pulp regarding fibre length, i.e. a coarse fraction (long fibre fraction) and a fine fraction (short fibre fraction) beforehand and subsequent separate refining is believed to be a possibility to enhance the final products properties and to reduce energy consumption. Trials using a pressure screen and a PFI mill showed promising results for an unbleached kraft pulp. By refining only the coarse fraction (70% of the material) and adding the fine fraction after refining, comparable results to the reference in terms of tensile strength were obtained, whereas air permeability and dewatering were improved. The results for a bleached kraft pulp show an almost proportional relationship between breaking length and the percentage of coarse fraction refined, meaning that there was no beneficial impact. The influence of fines in the process was also studied. To do so, a novel method that ensured a constant retention of fines in the handsheets formed was developed. Regarding chemical pre-treatment, a sodium sulphite pre-treatment was studied for an unbleached medium kappa kraft pulp. Positive results were found even at low sodium sulphite dosages (0.5% mass related). Sulphonated samples exhibited an enhanced tensile strength-porosity relationship, possibly caused by a higher flexibilization of the treated fibres. Different chemical analyses were performed reporting a yield close to 100%. These results indicate potential energy savings for the studied pulp.

Keywords: fines, refining, fractionated refining, white water recirculation, sulphonation, fines retention

Kurzfassung

Mahlung ist einer der wichtigsten Prozesse in der Stoffaufbereitung einer Papierfabrik. Durch die Mahlung verbessern sich Faser-Faser Bindungen, die Formation des Papiers und die physikalischen Eigenschaften des Endprodukts. Der Nachteil der Mahlung sind die hohen Energiekosten. Deshalb wurden unterschiedliche Methoden untersucht, um den Energieverbrauch des Prozesses zu reduzieren, wobei ein weiterer Fokus auf der Optimierung des Verhältnisses zwischen den Parametern Bruchkraft, Entwässerung, und Luftdurchlässigkeit lag. Die Ansätze, die untersucht wurden, waren die fraktionierte Mahlung und die chemische Modifizierung. Den Zellstoff vor der Mahlung in Bezug auf die Faserlänge zu fraktionieren, d.h. in eine grobe (Langfasern) und eine feine Fraktionen (Kurzfasern und Feinstoffe) zu trennen und getrennt zu behandeln, ist ein bekannter Ansatz, um den Energieverbrauch zu reduzieren. Versuche mit einer PFI Mühle und einem Sortierer ergaben vielversprechende Ergebnisse für einen ungebleichten Kraftzellstoff. Die ausschließliche Mahlung der groben Fraktion (70% des Faserstoffes) und anschließende Beimischung der ungemahlenen feinen Fraktion resultierte in vergleichbarer Bruchkraft bei verbesserter Luftdurchlässigkeit und Entwässerung im Vergleich zur Referenz (Mahlung des gesamten Stoffes). Die Versuche mit gebleichtem Kraftzellstoff zeigten, dass die Reißlänge nahezu proportional zu der Menge an gemahlenem groben Stoff war. Der Einfluss von Feinstoffen auf unterschiedliche physikalische Papiereigenschaften wurde ebenfalls untersucht. Dafür wurde eine neuartige Methode entwickelt, die eine konstante Menge Feinstoff in den Laborblättern garantiert. In Bezug auf die chemische Modifizierung wurde die Vorbehandlung eines ungebleichten Kraftzellstoffes (Kappa 45) durch Sulfonierung untersucht. Die Ergebnisse zeigen, dass die chemische Vorbehandlung des ungebleichten Zellstoffes Energie einsparen kann, da die Reißlänge schneller entwickelt als das bei der unbehandelten Referenz der Fall ist. Darüber hinaus wies der sulfonierte Zellstoff ein verbessertes Verhältnis zwischen Bruchlast, Entwässerung und Porosität auf, was möglicherweise auf eine erhöhte Flexibilität der vorbehandelten Fasern zurückzuführen ist. Verschiede chemische Analysen wurden durchgeführt und zeigten, dass die Ausbeute der chemischen Vorbehandlung bei 100% lag. Ein positiver Effekt dieser Vorbehandlung wurde auch für niedrige Natriumsulfitdosierungen (0.5%) festgestellt.

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List of abbreviations

BDDJ	Britt Dynamic Drainage Jar
DP	Degree of polymerization
SEM	Scanning electron microscope
TMP	Thermomechanical pulp
CTMP	Chemithermomechanical pulp
CMP	Chemimechanical pulp
LW	Length-weighted
SR	Schopper Riegler
MFC	Microfibrillated cellulose
NFC	Nanofibrillated cellulose
O.D.	Oven-dried
WRV	Water retention value
D/IF	Degree of delamination/internal fibrillation
COD	Chemical oxygen demand
TOC	Total organic carbon
ICP-OES	Inductively coupled plasma optical emission spectrometry
LWC	Light weight coated

1. Introduction

1.1 Scope of the thesis

Different unit operations are carried out during the production of paper, from forest harvesting to coating or calendering. Refining is known as one of the key-steps in stock preparation, since the properties of the final product significantly depend on this treatment. The main purpose of refining is to enhance the tensile strength of the product by modifying the properties and structure of the fibres. A poor formation causing low strength due to poor fibre-fibre bonding, high bulk and a rough surface are to be expected, if the pulp is not refined (Chen et al. 2012). However, refining of the pulp is not only a key step in the stock preparation, but also an energy intensive process (Seth 1999). Refining is responsible for a high percentage of the energy consumption during papermaking, since the energy costs of the pulp and paper industry represent around 25-30% of the costs of paper (Shamim et al. 2008). According to some studies, refining could represent up to 60% of the total power consumption (Aldrich 2009).

The scope of the thesis is therefore to identify possible improvements exclusively for chemical pulp refining. These could lead to either a reduction of the energy consumption by keeping final properties invariable, or to achieve a final product with better properties while keeping the refining energy consumption constant. A special focus of the investigations presented in this thesis is on the relationship between tensile strength and dewatering of the pulp, as well as on the tensile strength-porosity relationship. By looking at the available literature dealing with this topic, one can easily see three main approaches to achieve this goal, being

- Enzymatic pre-treatments
- Fractionated refining
- Chemical pre-treatments

Although enzymatic pre-treatments are a very promising method to reduce the energy consumption during refining and some results have been already reported, e.g., by applying cellulases (Lecourt et al. 2010, Singh et al. 2015), laccases (Lian et al. 2012) or beta-glucanases (Gil et al. 2009), the present thesis focuses only on the other presented options, i.e., fractionated refining and chemical pre-treatments. Therefore, the different studies carried out are presented in two separate content blocks. In addition, the influence of fines was also studied, since they affect several pulp and paper properties that are of interest for the present work, such as porosity, dewatering and tensile strength. Besides, removal of fines prior to refining could also lead to an improvement of the refining process. To do so, a novel method based on white water recirculation was developed to ensure a constant retention of

fines in the handsheets formed. This method allows therefore reliable evaluation of the effects of primary as well as secondary fines on handsheet properties.

1.2 Outline

After having defined the scope of the present thesis, the following chapters are presented:

Chapter 2 *The relevance of refining* describes the fundamentals of the refining process, including the different effects caused on the fibres, as well as the different refining equipment available for its study in the laboratory.

Chapter 3 *The role of fines* presents the effect that different types of fines, such as primary and secondary fines, have on several paper properties. It also presents a novel method to ensure a constant retention of fines in the handsheets formed, as well as exemplary results obtained.

Chapter 4 *Fractionated refining* presents different strategies to improve the tensile strength-dewatering-porosity relationships by fractionating the sample into a fine and a coarse fraction, leading to a more efficient use of the raw material in refining.

Chapter 5 *Chemical modification by addition of sodium sulphite* analyses the effect of a sodium sulphite pre-treatment on an unbleached kraft pulp prior to refining, and provides significant information to get a better understanding of the process.

Chapter 6 *Conclusions and outlook* presents the most relevant results and conclusions obtained in the previous chapters. It also gives valuable information and guidelines for future investigations dealing with the improvement of the chemical pulp refining.

1.3 List of publications

Peer Reviewed Articles

Giner, R., Fischer, W., Eckhart, R., and W. Bauer. (2015). White water recirculation method as a means to evaluate the influence of fines on the properties of handsheets. *BioResources*, 10(4):7242–7251

Contribution to conference proceedings

Giner, R., Fischer, W., Eckhart, R., and W. Bauer. (2016). Impact of sodium sulphite treatment on refining of medium kappa chemical pulp. In: *IX Iberoamerican conference on pulp and paper research, CIADICYP*, p. 54, Helsinki, Finland.

Giner, R., Mayr, M., Jagiello, L., Fischer, W., Eckhart, R., and W. Bauer. (2016). Characterization of pulp fines and their technological properties. In: *ACS National meeting Computers in Chemistry*, San Diego, United States.

Giner, R., Fischer, W., Eckhart, R., and W. Bauer. (2015). Fractionated treatment and separate refining of pulp to reduce energy consumption. In: *CEPI-EFPRO ESR Workshop at European Paper Week*, Brussels, Belgium.

Giner, R., Fischer, W., Eckhart, R., and W. Bauer. (2015). White water recirculation as a means to evaluate fines properties. In: *Cellulose materials doctoral students summer conference 2015*, p. 145-149, Autrans, France.

Giner, R., Fischer, W., Eckhart, R., and W. Bauer. (2015). White water recirculation as a means to evaluate fines properties. In: *COST Action FP1105, Understanding wood cell wall structure, biopolymer interaction and composition: implications for current products and new materials: Sixth workshop*, San Sebastian, Spain

Giner, R., Fischer, W., Eckhart, R., and W. Bauer. (2015). Fractionated treatment and separate refining as a way to reduce energy consumption in stock preparation. In: *11. Minisymposium Verfahrenstechnik*, p. 14-18, Vienna, Austria.

2. The relevance of refining

In this section, different effects caused by refining are presented in order to get a better understanding of the process, as well as the equipment used to mimic the process in the laboratory scale. Some fibre parameters such as chemical composition, fibre length distribution and fines content prior to refining cannot be controlled and will affect the properties of the final product. On the other hand, other key properties of the fibres such as fibre flexibility and collapsibility can be modified through refining in order to achieve a product that fulfils certain desired requirements. For both chemical and mechanical pulps the fibres are modified during refining and the properties of the obtained paper are improved, for example developing a higher tensile strength due to an enhanced fibre-fibre bonding, a desired porosity, better optical properties or a smoother surface (Koskenhely 2007). Depending on the refining treatment, a certain deformation of the fibres is achieved. This deformation affects most of the physical and optical properties of the final product. A proper refining treatment should develop the fibres without damaging them, as this would compromise the individual strength of the fibres and therefore the tear strength of the handsheets formed (Bajpaj 2005). It also allows fibres to form a well bonded network, maximizing fibre-fibre bonding. As the fibres become more flexible during refining, the contact area between two single fibres increases, which on the other hand increases the number of bonds that can be formed between them. This deformation of the fibres due to refining affects flexibility, conformability, compactability and collapsibility of lignocellulosic fibres (Lowe et al. 2007). The conformability of fibres during handsheet forming is proportional to the area participating in inter-fibre bonding, which is responsible for the structural strength of the fibre web. An increased bonded area improves the tensile strength of the final product, which is, as previously mentioned, the ultimate goal of refining (Nazhad et al. 2000). The way the fibres are refined dictates to which extent these effects are enhanced, irrespective of the type of fibre used.

Although each pulp responds to refining in a certain way, the treatment conditions (consistency, pH, temperature, pressure, refiner type, fillings and so on) can be customised to a certain pulp and product to achieve the desired result. All these parameters have a different effect on the fibres. Several studies dealing with refining of pulp are available. To mention some, Chen et al. (2012) studied the refining of recycled eucalyptus cellulose fibres. They pointed out that refining caused a fibrillation of the fibre surface, and also an increase in the fines content. The surface of chemical pulp fibres is progressively removed during the refining process. Also, the manipulation of fibres to obtain a desired quality is mainly carried out via refining (Somboon 2011). It was also found by Ljunqvist et al. (2005) that refining increases the strain to failure of spruce fibres. A review article representing a useful summary of knowledge regarding refining and its effects is the one by Gharehkhani et al. (2015). To understand refining it is also necessary to understand the structural modifications induced in the fibres by refining.

These effects are internal and external fibrillation of the fibres, fibre shortening, fibre straightening and formation of fines.

2.1 Internal fibrillation

Internal fibrillation enhances fibre flexibility and collapsibility, essential for inter-fibre bonding (Kang and Paulapuro 2006, Van Hai et al. 2013). The breakage of inner bonds between lignin, cellulose and hemicellulose causes the pore structure inside the cell wall to expand and swell during internal fibrillation, and water penetrates into the fibre cell wall. This phenomenon forms soft and flexible fibres (Maloney and Paulapuro 1999) and can be observed in Fig. 1 (left). This leads to one of the most important effects caused by internal fibrillation of the fibres, which is the enhancement of fibre swelling. An ideally refined pulp will produce swollen fibres that collapse during the drying stage, forming a compact and dense handsheet with little pore space (Bajpai 2005). A high compression ratio of the fibres during refining ensure a maximized flexibility of the treated fibres. The flexibility of the fibres is a crucial parameter and affects most of the physical and optical properties of pulp and paper, including paper formation and paper strength (Fernando et al. 2011). Therefore flexible fibres lead to optimal mechanical properties such as tensile strength of the final product due to the formation of denser sheets with greater bonding area between fibres, proving that refining is indeed a key-step in papermaking (Koskenhely 2007). The fibres flexibility and consequently the relative bonded area of the handsheets can be enhanced by applying compressive forces during refining. The delamination caused by internal fibrillation gives a better conformability of the fibre network during handsheet formation, since flexible fibres are more prone to be redistributed by surface tension forces. A paper formed without refining will have rigid fibres and will not have strong bonds at the points of contact, delivering fibres that are too stiff for paper formation. Stiff fibres form stronger flocs in suspension and therefore poor formation and undesired mechanical properties (Bajpai 2005). An increase of the fibre-fibre contacts and the number of bonds between fibres cause the increase of the relative bonded area. The relative bonded area is defined as the fraction of the available fibre surface in a sheet that is bonded to other fibres (Batchelor and Kibblewhite 2006, Bajpai 2005) and it directly influences the binding and therefore paper strength (Antensteiner 2002). Besides, an increase in the relative bonded area leads to a higher densification of the handsheets formed, reducing the opacity and brightness. As paper density increases due to internal fibrillation, less of the incident energy can be read as reflected light, reducing the brightness value (Bajpai 2005). It is then expected that tensile strength of the handsheets formed increases with improved formation, as shown by Nazhad et al. (2000). Loosening of the fibre wall or a reduction in the bending stiffness of the fibre also takes place during refining due to internal fibrillation (Lammi and Heikkurinen 1997). Internal fibrillation is, according to Bajpai (2005), the most important effect of refining.

2.2 External fibrillation

External fibrillation increases the surface area available for bonding, resulting in a higher tensile and Scott bond strength by further improving handsheet consolidation (Kang and Paulapuro 2006). Fragments of the S2 layer are peeled off and form fibrils that are still attached to the fibre wall, causing the previously mentioned effects (Page 1989). External fibrils could play according to Kang and Paulapuro (2006) a similar role as fines in the fibre network, increasing cohesion between fibre surfaces. This delamination and external fibrillation is mostly caused by shear strain during refining (Antensteiner 2002). As the fibres become more flexible, the cell wall collapses into the lumens, creating ribbon-like elements that improve the conformability of the paper network (Bajpai 2005). The effect is visible in Fig. 1 (right).

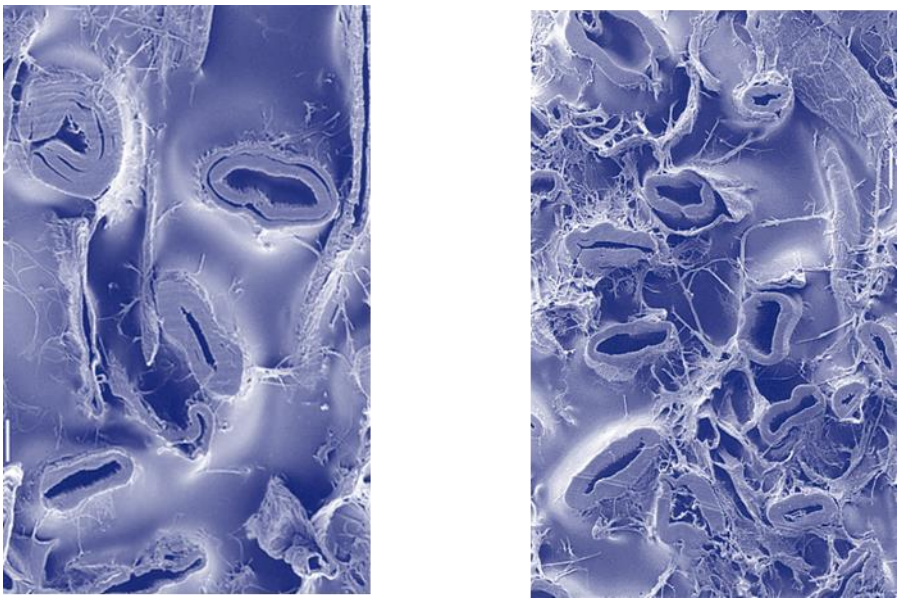

Fig. 1 *Internal (left) and external (right) fibrillation of fibres caused during refining*

2.3 Straightening

During refining, fibres that originally present a curly morphology can be straightened. This straightening of the fibres enhances densification and therefore improves the elastic modulus as well as the tensile strength of the paper, i.e., straight fibres give higher tensile strength than curled ones. Part of the curly morphology caused by cooking and drying of the pulp can be reversed during low consistency refining, which has a positive impact on the tensile strength. This is especially the case with high consistency stages in bleaching, since the fibres do not have available space to be straightened, and therefore some energy is required to get rid of curliness. On the other hand, high-

consistency refining enhances this curly morphology, which can be beneficial for certain purposes as it increases the stretch-to-break of sack papers (Koskenhely 2007).

2.4 Shortening

Fibre cutting and shortening of the fibres can also occur during refining, mainly due to shear action and axial tensile-strain. If a fibre is strained over its limit, it breaks (Koskenhely 2007). Cutting of fibres can produce small fragments of intact cell walls. It is a positive effect regarding paper formation since it causes a decrease in the crowding number, and therefore the flocculation effects are minimized (Kerekes 2005, Bajpai 2005). The crowding number is defined as the number of fibres in a volume swept out by the length of one fibre as it rotates about its centre, and indicates the degree of interaction between fibres in a flowing pulp suspension (Sha et al. 2015). On the other hand, it has a similar effect as fines in terms of dewatering. The small particles generated due to cutting could clog the pores of the paper network, which hinders the drainability of the pulp and limits the speed of the machine during dewatering. This could also increase the costs associated with pulp drying (Koskenhely 2007). Besides, a reduction in the fibre length due to shortening causes a reduction of tear strength (Bajpai 2005), although in low refining intensity of hardwood refining increases tear strength.

2.5 Fines formation and their influence

Refining of chemical pulps also leads to the production of so-called secondary fines, unlike primary fines, which are formed during pulping. Capillary forces created by the fines, together with higher flexibility and a tendency of fibres to collapse, get fibres into closer contact. This leads to an enhanced fibre-fibre bonding (Sirviö 2002, Sirviö et al. 2003) and thus to a denser sheet. As previously mentioned, fines play a key role in pulp and papermaking processes, affecting several properties such as breaking length, porosity or dewatering, which are the main parameters of interest for the present studies. Therefore, their effect is studied thoroughly in Chapter 3.

2.6 Refining equipment

There are a few different methods to mimic the refining of the pulp in the lab scale, being the PFI mill, Valley Beater and Jokro mill as the most common ones. Although all of them lead to the aforementioned effects caused by refining, the treatment of the fibres may differ. Besides, refining methods produce in general less cutting effect compared to industrial refiners, and do not reflect what happens in the industrial operations (Somboon 2011). Different studies were carried out to analyse the differences between different refiner units. For example, Van Hai et al. (2013) studied the effect of PFI and Valley beater on the paper properties. A shortening effect on the fibres was observed for the Valley Beater trials, whereas there were no noticeable fibre length changes by PFI mill refining. No

differences were visible regarding crystallisation or DP. Similar investigations were conducted by Somboon et al. (2011), where they investigated the development of softwood fibres during PFI mill, Valley Beater and industrial pilot refining. As expected, the laboratory refiners were found to give a moderate treatment of the fibres, whereas the treatment provided by the industrial lab refiner was harsher. A pulp with higher amount of fines, lower density and higher light scattering, and lower strength property was produced with the industrial lab refiner. The laboratory refiners caused less damage to the pulp fibres and produced therefore better reinforcement properties. It is believed that the intensity of the impacts on the PFI mill is 1.5% to 15% of the intensity of a disc or conical refiner (Welch and Kerekes 1994). Besides, it is believed that the main effect caused by the PFI mill is internal fibrillation, with almost no external fibrillation or fibre shortening observed. The PFI mill is a low-intensity, high-energy refiner compared to the industrial ones (Kerekes 2005). The major effect of PFI refining is to make the fibres more collapsible due to deformation of the cell wall (Lowe et al. 2007). This can be observed in Fig. 2. Two SEM images of a handsheet surface before (left) and after PFI refining at 8000 revolutions (right) are presented. It is evident that PFI refining forms more compact and homogeneous handsheets. This will also affect the properties of the handsheets, enhancing mechanical properties such as tensile strength.

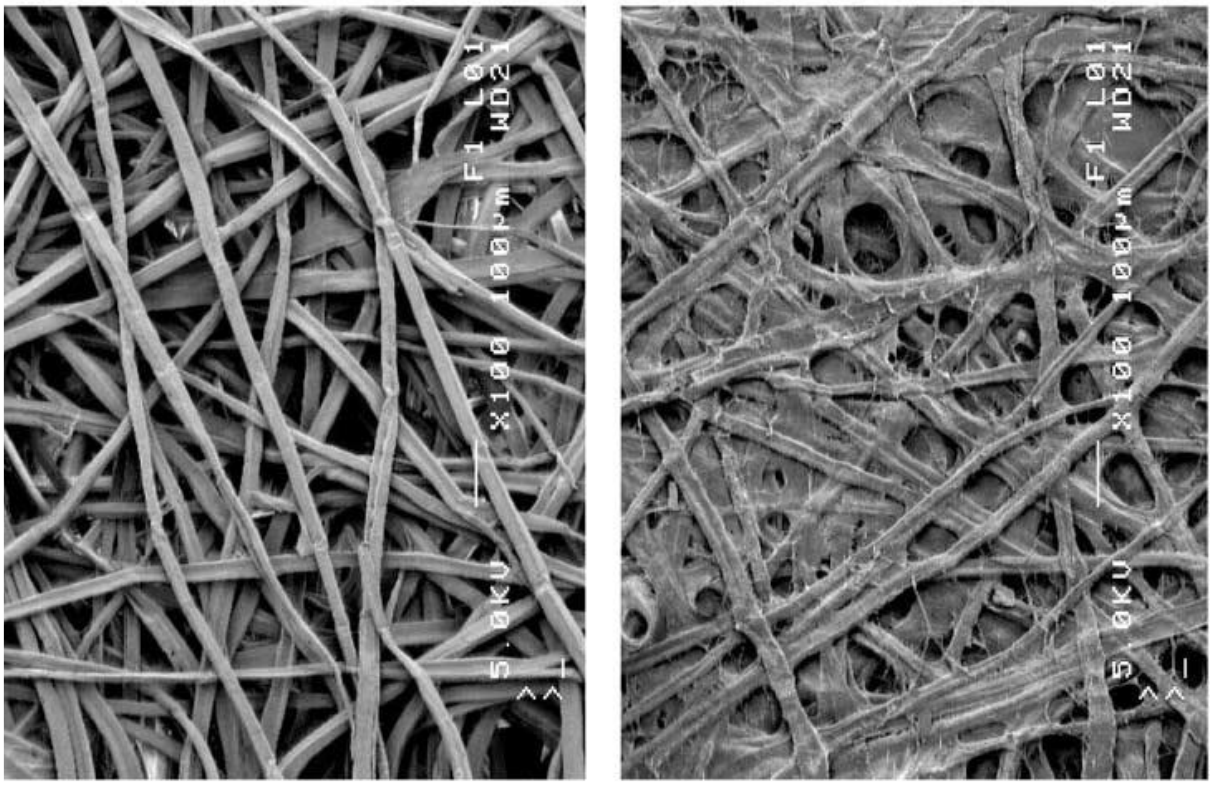

Fig. 2 *SEM image of a handsheet before (left) and after PFI refining at 8000 revolutions (right) (Ljungvist et al. 2005)*

Although PFI refining does not reproduce the shear strain caused by industrial refiners, it allows investigation of pure compression refining since a refining close to zero shear can be achieved (Antensteiner 2002). The PFI refining is therefore based on internal fibrillation, whereas an industrial refiner causes also external fibrillation, damage of the fibre and shortening to a much greater extent (Bajpai 2005). The PFI mill could be therefore not accurate to predict the behaviour of the pulp in an industrial refiner since PFI refining is a much more homogeneous treatment, whereas in an industrial refiner many fibres remain untreated after refining (Seth 1999, Bajpai 2005). In industrial refining there is a certain probability that a single fibre passes through the refining plates, and this does not apply to laboratory refiners. In other words, not all fibres receive the same treatment during industrial refining. Besides, more fines are produced by an industrial refiner (Koskenhely 2007). Regarding the differences between PFI and Valley Beater refiners, the pulp refined with the Valley Beater showed a higher tensile index than the one refined with the PFI mill, which can be explained by a higher degree of external fibrillation. At a given density, the drainability of the pulp refined with the Valley Beater is also worse than that of the PFI refined pulp (Somboon 2011). In the investigations of Eckhart et al. (2006) the fibre wall damage induced by different refiners was evaluated. The results show that the fibres refined by means of a PFI mill show less undamaged fibres compared to the Jokro mill refined fibres. The PFI refiner produces more fibrillation and the friction during refining is higher. On the other hand, the Jokro mill develops the breaking length in a smoother and more time consuming way, imposing less damage on the fibre wall. After analysing these studies it is possible to conclude that the way the pulp is treated during refining hugely influences the final properties of the product. The results obtained in the lab scale will probably differ from the ones obtained at the industrial level, but are a good indicator to assess the pulp development during the refining process.

The previously presented effects of refining on several pulp and paper properties emphasise the relevance of refining and the importance of achieving an optimal refining treatment of the pulp. A poor refining treatment with a short refining time will not improve the properties of the final product to a considerable extent. On the other hand, an overtreatment of the pulp will cause fibre damage, undesirable cutting of the fibres and subsequent increase of the fines content, dewatering time and a higher energy consumption. Therefore it is crucial to determine the refining intensity at which the fibre properties and the energy consumption are optimal.

3. The role of fines

3.1 Effect of fines on papermaking

A special interest of this thesis lies in the influence of fines on different pulp and paper properties. The effect of fines on paper formation and sheet properties has been widely analysed (Retulainen et al. 1993, Seth 2003, Sirviö and Nurminen 2004, Ferreira et al. 2000). Compared to pulp fibres, fines have a large surface area (Peterson et al. 2001), which is also an important parameter affecting various pulp and paper properties. When it comes to the evaluation of their effects on handsheet properties, a defined amount of fines is required to allow accurate extrapolation of the results.

By definition of the Scandinavian Pulp, Paper and Board test committee (SCAN-CM 66:05 (2005)), fines are the fraction of pulp that passes through a screen or a perforated plate with a hole diameter of 76 µm, representing the 200-mesh screen of a fibre length classifier according to TAPPI Test Method T 261 Cm-94 (1994). These particles can be further divided into different categories, including fines from chemical pulps, fines from mechanical pulps, primary fines and secondary fines. Mechanical pulps, for example, contain a large amount of fines (20% to 35% by weight) that have special characteristics and impart the sheet with high opacity and reasonable strength (Retulainen et al. 1993). For mechanical fines, Brecht and Klemm (1953) introduced the classifications 'Mehlstoff' and 'Schleimstoff,' meaning chunky particles of high lignin content and low bonding ability and more fibrillar particles of high bonding capacity, respectively. Sundberg et al. (2003) suggested that the more fibril-like fines in mechanical pulp originate primarily from the primary and secondary fibre wall, while the more flake-like fines originate from the middle lamellae. Chemical pulps contain fewer fines than mechanical pulps. The fines content ranges from a few percent up to 10% to 12%, depending on the level of refining (Paavilainen 1992). The primary fines are formed during pulping, as previously mentioned, and consist primarily of parts of the middle lamellae, ray cells, parenchyma cells, and debris from the fibres (Krogerus and Fagerholm 2002; Bäckström et al. 2008). They exhibit higher extractives and lignin contents compared to those of the rest of the pulp sample (Retulainen et al. 1993, Seth 2003). Once the pulp is refined, the newly formed fine materials produced are categorized as secondary fines. These are primarily parts of the primary and secondary walls of fibres peeled off as a result of mechanical impact. Their effect has been studied by several researchers in the past. Retulainen et al. (2002), for example, pointed out that a higher tensile strength in handsheets (kraft paper) could be obtained via the addition of 15% secondary fines, which were produced by refining the pulp for 2 hours in a Valley beater. They observed changes in the sheet's density and optical properties and a higher anionic charge in the fines fraction compared to that of the long fibre fraction. The addition of secondary fines to the pulp was also shown to negatively affect the dewatering behaviour, prolonging dewatering (Lindqvist et al. 2012).

The effects of secondary fines on parameters such as dewatering, tensile strength, and porosity differ from those of primary fines. Sirviö et al. (2003) and Sirviö and Nurminen (2004) demonstrated that secondary fines are usually of fibrillar nature, which leads to closer fibre contact and enhances fibre-fibre bonding, thereby increasing tensile strength. The positive impact of secondary fines on tensile properties was demonstrated to be higher compared to primary fines (Htun and Ruvo 1978). Another study of the differences between primary and secondary fines was carried out by Xu and Pelton (2005). In their work, primary fines were presented as chunky particles acting as gaskets and increasing the contact area. They showed that the primary fines are less effective than secondary fines for this purpose. Secondary fines, however, yielded stronger adhesion than primary fines. Similar results and conclusions like those mentioned in the work of Xu and Pelton (2005) were presented by Sirviö and Nurminen (2004). In their study, secondary fines were described as particles with a greater specific surface area, reducing thickness and porosity by filling voids between fibres. They also confirmed that there was a positive effect on tensile strength with the addition of fibrillar secondary fines to both chemical and mechanical pulps, as the fines brought fibres closer to each other within the fibre network. When the amount of kraft fines present in the handsheet exceeded 15%, a negative impact on the light scattering coefficient was recorded. Besides, the removal of fines could improve the relationship between breaking length and porosity for sack kraft paper (Olson et al. 2001), which is one of the main targets of the present work. Also, it could be possible to obtain a pulp with improved drainability, reduced bleaching demand and reduced effluent discharges of extractives (Hinck and Wallendahl 1999). Moreover, if fines are of no interest for such processes, it is necessary to understand this fraction in order to further use it for other purposes or applications.

These previous studies show that fines have an important influence on various properties of paper, such as its thickness, tensile strength, dewatering, air permeability, and light scattering. To study the effects of different types of fines at the laboratory scale, the primary challenge is to retain a constant amount of fines in the formed handsheets. This is also necessary to get comparable results during the fractionated refining trials, since a different retention of fines between two trials could influence the properties measured and lead to errors in the interpretation of the results (see Chapter 4). To achieve a constant amount of fines, the following procedures can be applied:

- Forming the handsheets on filter paper using a suction filter, as done in the preparation of laboratory sheets to measure the diffuse blue reflectance factor (ISO 3688 (1999))
- Forming the handsheets on a membrane (Sehaqui et al. 2010)
- Forming the handsheets using a white water recirculation system

Although the first two methods mentioned provide a defined amount of fines in each handsheet formed, based on retention of almost 100%, the third option is preferable because of two major drawbacks with the first two approaches. First, the small pore size of filter papers and membranes slows the dewatering of the pulp. Thus, sedimentation effects may occur during handsheet formation because the fines do not exhibit the same settling behaviour as longer fibres. This behaviour causes a distribution of fine material within the formed sheets that is not expected to occur in a handsheet former unit or in industrial processes. An example was presented by Sehaqui et al. (2010), who analysed the formation of nanopaper structures using a semiautomatic sheet former. The formation of a microfibrillar cellulose (MFC) handsheet over a nitrocellulose ester filter membrane with 0.65-µm pore size required a filtration time of around 45 minutes. This group also pointed out a second drawback: difficulty in separating the formed handsheet from the membrane without damaging the sheet surface. This is also a problem when using filter papers.

Before white water recirculation systems became relevant, other approaches, using a conventional handsheet former unit, were investigated. One of the first reported attempts to study fines' effect on sheet properties was carried out by Htun and Ruvo (1978), in which a 300-mesh wire was used to form the handsheets. Some other studies, such as those presented by Sirviö and Nurminen (2004), have determined the amount of fines retained in a sheet using a Britt dynamic drainage jar (BDDJ). Chen et al. (2013) also studied the effects of adding fines to a high-yield pulp. In this case, 5%, 10%, 15%, or 20% fines were added to the pulp before handsheets were formed using white water recirculation to retain the fines. All of these attempts have one particular problem in common: it is impossible to determine whether each formed handsheet retained the same amount of fines. This makes the evaluation of certain fines effects on paper properties inaccurate.

Using a white water recirculation system can, however, be a solution for the previously mentioned drawbacks. In the industry the white water is recirculated, which ensures a proper retention of fines in the final product. Sedimentation effects are avoided. The fines not retained during sheet formation circulate within the white water system, allowing steady-state fines content to be reached after some handsheets are formed. A method that easily indicates whether the amount of fines in the handsheets has reached this steady-state is of great importance. Once this is accomplished, the handsheet properties can be measured. Bäckström et al. (2008) used a similar approach as the one presented here. They tried to achieve a constant fines content by producing and discarding 10 handsheets before sheets for mechanical testing were formed. In the study conducted by Lindqvist et al. (2012), the method chosen was the one suggested by the Scandinavian Pulp, Paper and Board Committee (SCAN-CM 64:00 (2000)), which also uses a white water recirculation system and links the amount of fines

retained in the handsheets with the dewatering time. In this case, the dewatering time must remain constant even when preparing additional sheets.

In the present study, a method that would ensure a defined amount of fines in each handsheet formed, as well as easy and reliable determination of the fines content, was developed. Determination of the fines content is necessary for each trial, as different fibre and fines properties and furnish recipes can result in a varying number of sheets required to achieve steady-state fines content. The method should also require less effort and only a small amount of fines compared to the other options mentioned. This is crucial, especially if the effects of special types of fines on handsheet properties are to be studied, as their production could be tedious. The fines content is determined by means of L&W Fiber Tester Plus measurements, which are intended to be a substitute for BDDJ tests, as mentioned by Sirviö and Nurminen (2004). Although determination of the fines content using BDDJ tests is rather precise and simple, it is a time-consuming step. Fibre morphology measurements using a flow cell would facilitate the laboratory work and reduce the amount of pulp needed to determine the fines content (5 g when using the BDDJ as compared to 0.15 g when using the L&W Fiber Tester Plus). To reduce the effort required (i.e., the amount of fines needed), a comparison of lab sheets formed with wires of three different mesh sizes (120, 325, and 500) was carried out. The influences of two types of primary and secondary fines and a cellulosic additive on the properties of laboratory handsheets are shown as exemplary results to demonstrate the effectiveness and possible applications of the developed method.

3.2 Materials and methods

3.2.1 Pulps and fines used in the tests

The effect of primary and secondary fines of two pulps were studied:

- a flash-dried bleached softwood kraft pulp, mixture of spruce and pine
- a bleached sulphite pulp, 75% softwood

A third kind of fines material used in these trials was a commercially available cellulosic filler material. To study its effect, it was added to the unrefined, fines-free bleached softwood kraft pulp.

3.2.2 Production of fines

Primary fines were separated from the pulp according to SCAN-CM 66:05 (2005) using the Britt dynamic drainage jar. Originally, this standard was used to determine the amount of fines in the pulp, but it can also be used to separate fines from the pulp. To study the influence of secondary fines, washed pulps (bleached sulphite pulp and bleached kraft pulp, fines free) were refined in the Valley Beater to produce secondary fines. The Valley Beater was chosen for practical reasons since 360 grams

of pulp diluted in 23 litres can be refined per test, compared to 30 grams in PFI or 16 grams in Jokro Mill. In this device, the pulp is recirculated and refined by a beater with a controlled bedplate. The refining intensity is adjusted by extending the time the pulp is recirculated, being in this case 2 hours. The refined pulp was then washed using the pressure screen, and the secondary fines produced during Valley Beater refining were collected and thickened. Afterwards, the dry solids content of the two fines suspension was determined, and the concentrated fines suspension was used on the trials. The standard Tappi T 200 sp-01, which contains the relevant information to perform a test, can be applied for pulp refining.

3.2.3 Characterisation of fines and determination of fines content

All samples were characterised by means of a L&W Fiber Tester Plus (Fig. 3, right). The L&W Fiber Tester Plus was used for different purposes in the present work. It allows the measurement of key fibre morphological parameters (by morphological characterisation) such as fines content, fibre length, fibre width, and coarseness, as well as the fibrillar area of both isolated fines and mixture of fines and unrefined pulp. The fines content was defined as the particles with lengths below 200 µm. A small amount of pulp (typically 0.1 gram dry weight pulp per test) is diluted in distilled water and then evaluated. The device measures the particles diluted until a certain amount of fibres are measured or a certain time elapses. Using this method, the primary and secondary fines of different pulps as well as the fibre fraction can be characterised with little effort (Fig. 3, left). Nevertheless, there is a certain limitation to measure fibrillar material, which can be critical especially for the measurement of secondary fines. The fibrillar material in the swollen state is almost transparent and cannot be always detected by the device, which can lead to an underestimation of the fines content. The standard ISO 16065-2 can be applied. The pulp drainability by means of Schopper-Riegler (ISO 5267-1:1999) was measured prior to handsheet formation.

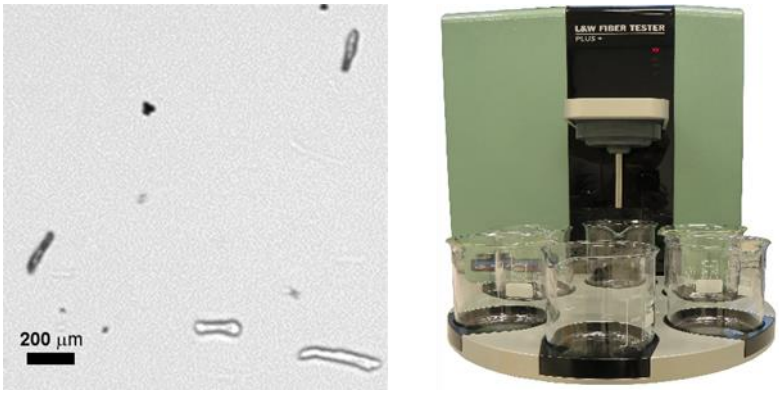

Fig. 3 *L&W Fiber Tester image acquisition of a fines suspension (left) and L&W Fiber Tester device (right)*

3.2.4 Preparation of handsheets using white water recirculation

To get a constant retention of fines in the handsheets formed, a Rapid-Köthen (Germany) sheet former equipped with a white water recirculation system was used to produce handsheets with a grammage of 60 g/m^2 (Fig. 4). The purpose was to have a better reproducibility and comparability of the results, since different fines retention could provide misleading results. As already mentioned, whenever you start thinking about the effect a certain fine fraction has on sheet properties one has to think about the amount of fine material actually present in the formed sheet. Higher or lower retention would yield misleading results not so much representing the properties of the fine material but the retention thereof. By retaining always the same amount of fines, this possibility is ruled out. The mesh chosen in sheet forming was a key parameter, as it determined the amount of fines retained. The bigger the pore size of the mesh used, the higher the amount of the particles passing through, and the lower the retention of fines. Three different mesh sizes were used; 120-mesh (125-µm openings; standard mesh for sheet forming), 325-mesh (44-µm openings), and 500-mesh (25-µm openings). The influence of the chosen mesh on the dewatering time was not an issue, as dewatering in the sheet former lasts only a few seconds and there was no considerable difference between the meshes. In this experimental setup, the white water of each of the formed handsheet was stored in a separate tank and used during the formation of the following sheet. The fines content in the white water increased with every formed handsheet until a 'steady state' value was reached. At this point, every subsequent produced handsheet contained the amount of fines present in the feed suspension. Using this method, handsheets were formed and conditioned for 24 hours. After conditioning, the thickness (DIN EN ISO 534 (2011)), air permeability (ISO 5636-3 (2013)), Gurley (ISO 5636-5:2013) and breaking length (DIN EN ISO 1924-2 (2009)) were determined.

Fig. 4 *Handsheet unit equipped with a white water recirculation system*

3.3 Results

3.3.1 Retention of fines

After handsheet formation with three different meshes and subsequent L&W Fiber Tester Plus analysis, the fines content versus the number of sheets formed using white water recirculation was determined for bleached kraft pulp, and is represented by the arithmetic proportion of particles having lengths below 200 µm (Fig. 5). In this study, it was possible to determine the amount of fines retained in each handsheet formed, whereas in other studies no information is given. Besides, three different meshes were studied in order to evaluate the retention of fine material. As expected, the small pore size screen (500-mesh) retained more fines than the 120-mesh screen. As more handsheets were formed, the fines content increased until levelling out, achieving the so-called “steady-state”. From Fig. 5, it is apparent that steady-state was achieved after three handsheets for the 500-mesh screen, five for the 325-mesh screen, and seven for the 120-mesh screen. Therefore, using a 500-mesh screen would allow for the least number of handsheets to be discarded. In practice, the small openings of this wire make its application very difficult, as the high capillary forces between the sheet and mesh do not allow the sheet to be removed without damaging its surface to some extent, leaving the sheets useless for further evaluation. This was especially true for unrefined pulp samples with wet strengths lower than that of refined samples. For some refined pulp samples, the 500-mesh screen might be applicable in some cases, but one would have to complete respective trials for each sample beforehand, which makes its use impractical. For this reason, the 325-mesh screen was chosen for use in subsequent trials to determine the influence on the handsheet properties of primary fines and secondary fines of both pulps, as well as of a mechanically produced cellulosic filler material.

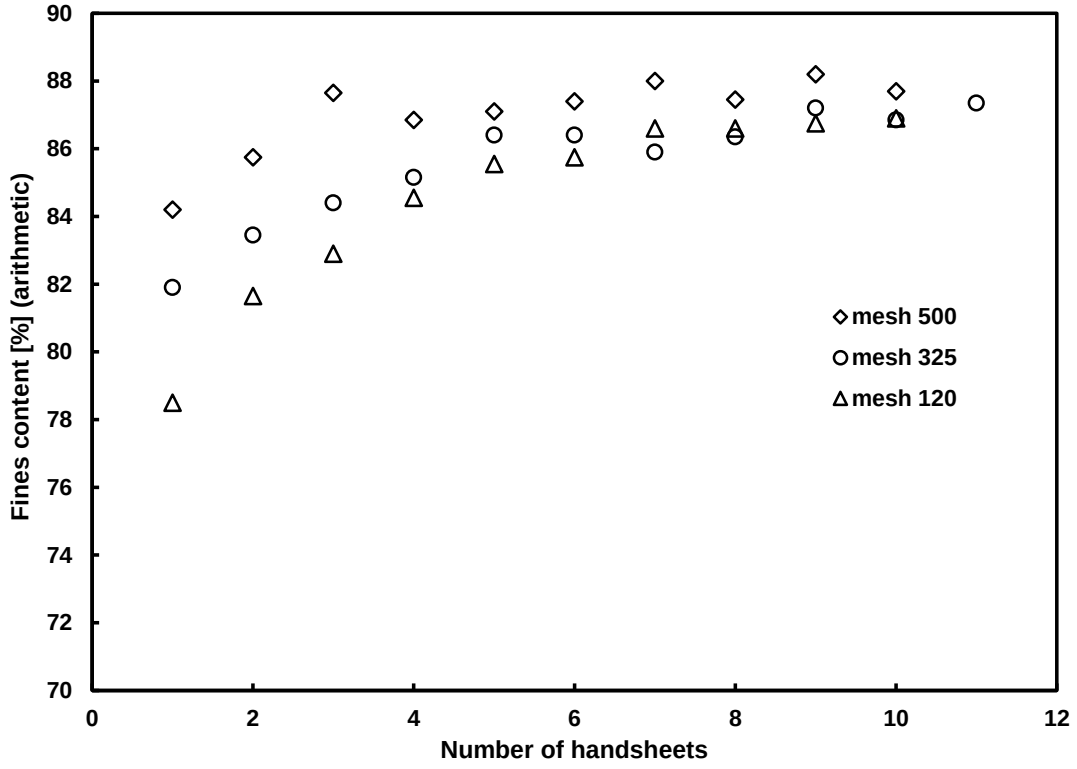

Fig. 5 *Comparison between the fines retention and the mesh size for an unrefined bleached kraft pulp*

The results presented in the following sections are summarized in Table 1.

Table 1 *Properties measured and reported of the different fines and mixtures of fines and unrefined, fines-free pulps studied*

Sample	Physical properties	Fibrillar area	Avg. fibre length	Avg. fibre width
Isolated 1y fines	-	+	+	+
Isolated 2y fines	-	+	+	+
Pulp (A,B) + 1y fines	+	+	-	-
Pulp (A,B) + 2y fines	+	+	-	-
Isolated additive	-	-	-	-
Pulp (A) + additive	+	-	-	-
Pulp (B) + additive	-	-	-	-

being

Pulp A	unrefined, fines-free bleached kraft pulp
Pulp B	unrefined, fines-free bleached sulphite pulp
1y fines	primary fines
2y fines	secondary fines
Isolated additive	the cellulosic additive studied

Physical properties SR, breaking length, air permeability and thickness

3.3.2 Fines morphology

The different fines used in this study were analysed with the L&W Fiber Tester, and the obtained fibre length distributions of the bleached kraft pulp are depicted in Fig. 6. From the figure, it is apparent that both kinds of fines and the cellulosic filler consisted almost exclusively of short particles below 200 µm in size, as defined. Primary fines were larger, on average, whereas secondary fines had a lower average length. The cellulosic filler material had the highest proportion of particles ranging from a few microns to 100 µm in size and was therefore considered the finest material among the presented in Fig. 6.

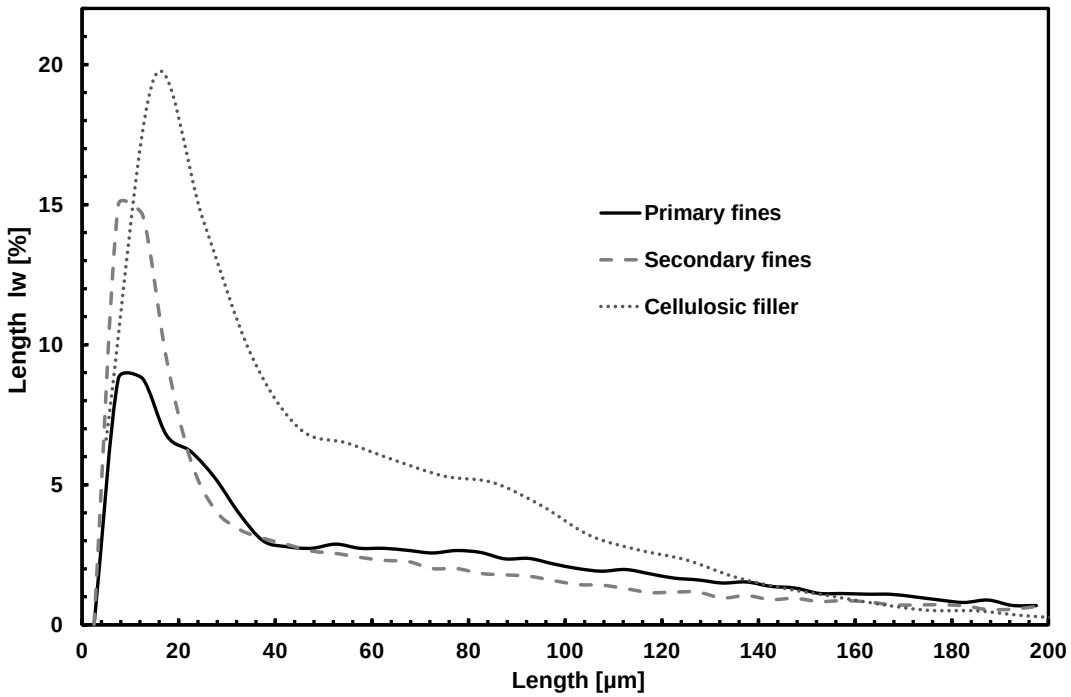

Fig. 6 *Length-weighted length distribution of the fine materials added to unrefined, fines-free bleached kraft pulp*

Regarding the primary and secondary fines of bleached sulphite pulp, the differences in the fibre length distribution are not so pronounced, as seen in Fig. 7. The fibre length distributions of the secondary fines of both pulps studied are comparable as they contain shorter particles than primary fines. The average fibre length of the secondary fines (bleached sulphite pulp) is 72 µm, and contains more particles in the range above 100 µm than secondary fines of bleached kraft pulp (see Table 4). In this case the difference between primary and secondary fines is visibly bigger. The primary fines (bleached sulphite pulp) have an average fibre length of 89 µm, which means that the primary fines are in average longer than the secondary fines. This also correlates well with the results previously

shown for bleached kraft pulp. Primary fines are in both cases longer on average compared to the secondary fines. The secondary fines from the kraft pulp were also shorter on average compared to the secondary fines of the bleached sulphite pulp. These results demonstrate that fines from different pulps can have a completely different morphology and therefore need to be studied individually.

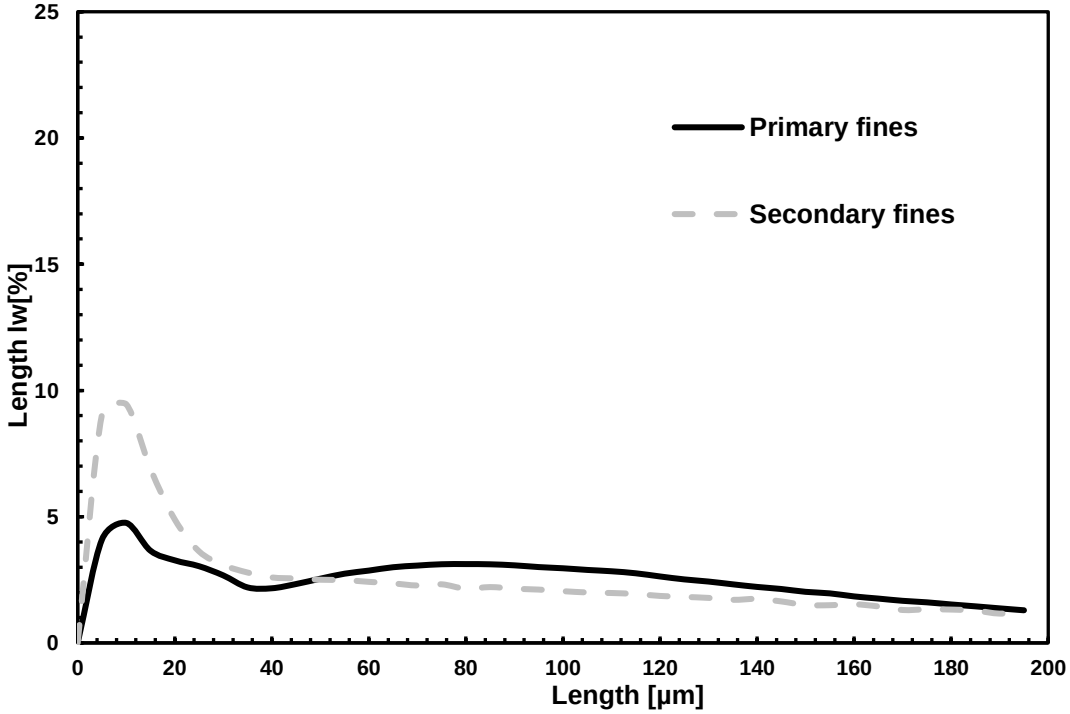

Fig. 7 *Length-weighted length distribution of the fine materials added to unrefined, fines-free bleached sulphite pulp*

3.3.2.1 Influence of bleached kraft pulp fines on handsheet properties

The results obtained using the 325-mesh wire during handsheet forming are presented in Fig. 8. Three trials were performed based on the fines-free bleached kraft pulp (unrefined) and the addition of primary fines, secondary fines, and the cellulosic filler material described above. The amount of fines added to the feed suspension was 4.8%, which corresponds to the amount of primary fines originally present in the pulp sample used (mass related). The physical properties of the fines-free pulp were not measured. Handsheets were formed, and the weight, thickness, air permeability, dewatering, and breaking length were measured. To ensure that the fines content was constant in the sheets evaluated, seven handsheets were discarded, according to the investigations previously presented (see Section 3.3.1). The effects of the primary and secondary fines of the bleached kraft pulp, as determined in this study, were in accordance with data found in literature. The addition of secondary fines resulted in higher sheet density with higher breaking length and therefore tensile

strength, correspondingly lower porosity and slower dewatering (Fig. 8). This effect was explained by Bäckström et al. (2008), who claimed that the creation of higher capillary forces between the fines and the fibre surface improved the paper properties. This is in close association to the findings of Sirviö and Nurminen (2004), the presence of fines brings fibres closer together, decreasing porosity and air permeability. Compared to the primary fines and the cellulosic additive, this effect was more pronounced for secondary fines. Secondary fines are more fibrillar and have a higher charge content than primary fines, thus making them more effective in terms of sheet densification (Xu and Pelton 2005). According to Chen et al. (2013), this increases both the bonded area and the bond strength because they act as binders between long fibres. In a study conducted by Tao et al. (2007), the increase in tensile strength was approximately 5% when primary fines were added. Fines from refined pulp increased the tensile strength by almost 30%. An addition of 8% secondary fines (bleached kraft pulp) into the original pulp increased the tensile strength by 48%, according to the studies of Seth (2003). The increase in tensile strength observed by Bäckström et al. (2008) was up to 30% when 10% secondary fines were added and 15% when primary fines were added, which means that the positive effect of secondary fines on breaking length is 100% higher compared to the primary fines. In the present work, the breaking length was 84% higher when secondary fines were added than when primary fines were added, which is close to the value provided by Bäckström et al. (2008).

Comparison of the effects of primary fines and the cellulosic filler material revealed similar properties with slightly better dewatering achieved using the cellulosic filler. The mechanically produced cellulosic filler material was composed almost exclusively of fine particles, but it did have considerably higher width, according to the L&W morphology measurements. These more spherical particles may lead to higher porosity, which was not determinable for these samples because 5.000 ml/min is the upper limit of the measurement (Fig. 8).

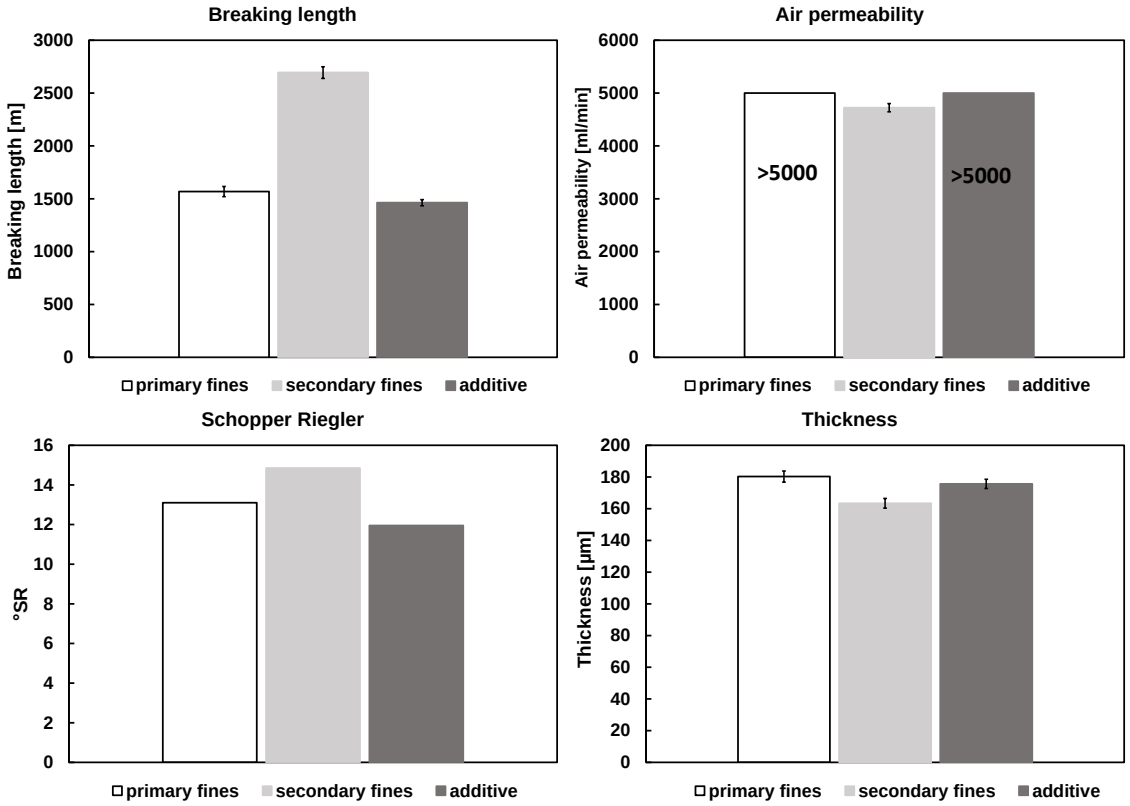

Fig. 8 *Effect of primary fines and secondary fines (bleached kraft pulp), and mechanically produced cellulosic filler material (additive) on unrefined handsheet properties.*

The pores were not plugged by this material as was the case with the primary and, even more so, secondary fines. This also explains the improved dewatering. From these results, one can conclude that the cellulosic filler material acted as a spacer within the sheet. To compare the morphology of primary and secondary fines, the fibrillar area of pure fines (isolated) and of the pulps formed adding primary or secondary fines were also measured by means of L&W Fiber Tester.

Table 2 *Fibrillar area of different samples containing primary and secondary fines (bleached kraft pulp) measured by means of L&W Fiber Tester*

Sample [bleached kraft pulp]	Fibrillar area [%lw]
Pulp containing primary fines	1,27
Pulp containing secondary fines	2,03
Isolated primary fines	7,05
Isolated secondary fines	23,95

As seen in Table 2, Primary fines and secondary fines of the bleached kraft pulp show differences in the fibrillar area. This difference is more obvious in the results of the isolated fines. The fibrillar area of secondary fines is more than three times larger than that of primary fines. This can also explain the

increase in the breaking length previously presented in Fig. 8. The higher fibrillar content of secondary fines implies a better bonding and therefore a better tensile strength, confirming the investigations of Chen et al. (2013). Besides, a difference in the length could also be observed and is presented in Table 3. The primary fines are on average longer than the secondary fines. Regarding the average width, the primary fines had also a higher width than the secondary fines, which could mean that they are formed by chunky particles more than fibrillar material.

Table 3 *Average fibre length and width of isolated primary and secondary fines (bleached kraft pulp) measured by means of L&W Fiber Tester*

Sample [bleached kraft pulp]	Average fibre length [lw%, µm]	Average fibre width [lw%, µm]
Isolated primary fines	86,39	21,05
Isolated secondary fines	59,21	19,30

3.3.2.2 Influence of bleached sulphite pulp fines on handsheet properties

After evaluating the effect of bleached kraft pulp fines, the same procedure was also used on a fines-free sulphite pulp (unrefined), although in this case only primary fines and secondary fines were studied. The amount of fines added to the reference pulp was in this case 5% (original fines content, mass related). The results are presented in Fig. 9. The different behaviour of a sulphite pulp during refining compared to a kraft pulp made the study of fines from sulphite pulp of interest. Unlike secondary fines of bleached kraft pulp, secondary fines of bleached sulphite pulp did not provide such a high increase of the breaking length. As it can be observed in Fig. 9, there is an improvement of the breaking length of the handsheets formed, irrespective of the type of fines added. Nevertheless, the difference between both types of fines is in this case not that accentuated. The breaking length increases by 47.3% when secondary fines are added and 38.2% when primary fines are added. The effect of primary fines of bleached sulphite pulp is much higher than that observed by Asikainen et al. (2010), where they showed a decrease of 12.8% on the tensile strength after removal of primary fines. Comparing directly the effect of fines in the bleached sulphite pulp, secondary fines increased the breaking length 6.7% more than primary fines. As it was shown before, for bleached kraft pulp the increase on breaking length between secondary fines and primary fines was 84%. This means that the primary and secondary fines of the bleached sulphite pulp are much more alike than the fines of bleached kraft pulp regarding their impact on physical properties. The sulphite pulping produces more brittle fibres than kraft pulping. The brittleness of the fibres makes the produced secondary fines more similar to primary fines, i.e., more chunky particles rather than fibrillar material. Besides, they show a

different behaviour during refining. Nevertheless, it is complex to compare results found in literature for different types of fines, since factors like the pulping process, the way fines are separated or the way they are dosed into the pulp may vary, affecting the final values. In addition, the retention can be different according to the method chosen to prepare the handsheets.

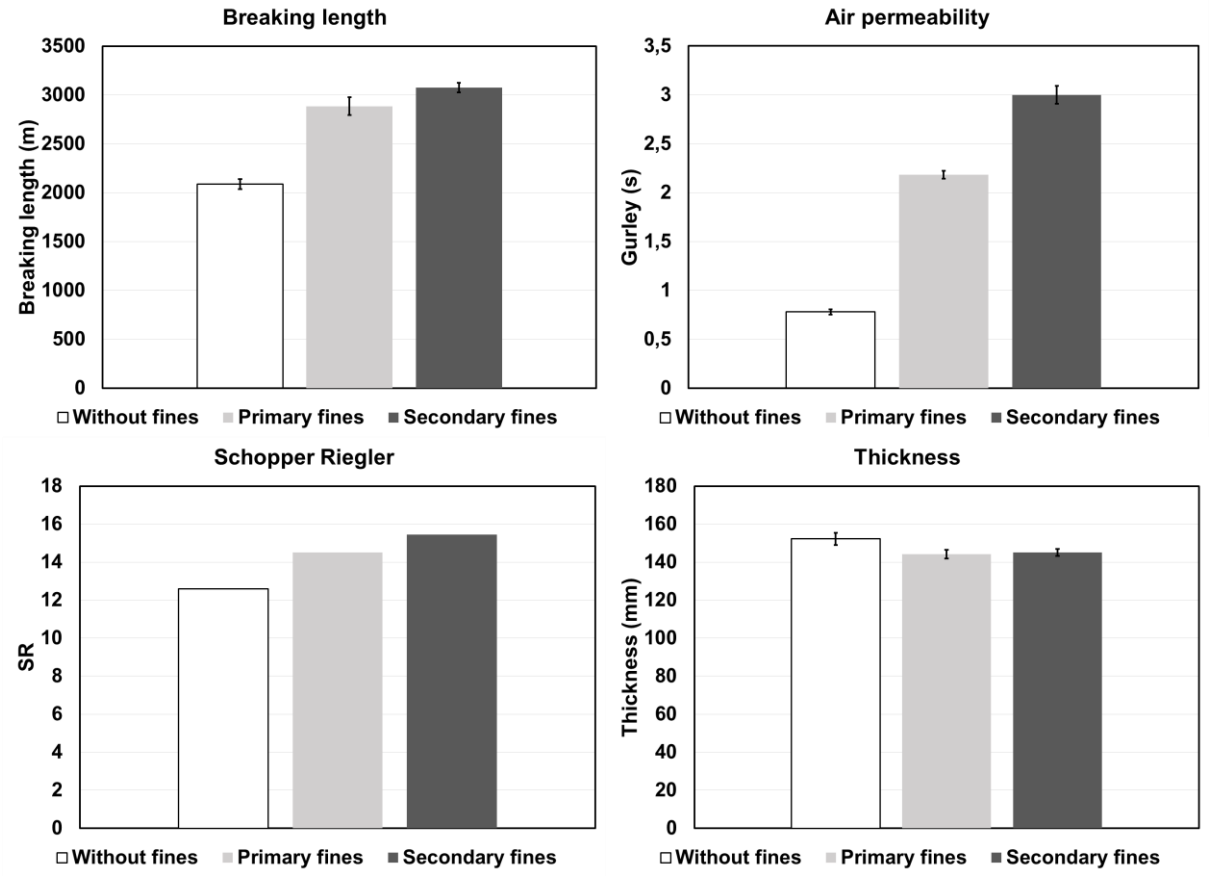

Fig. 9 *Effect of primary fines, secondary fines, and fines-free from bleached sulphite pulp on unrefined handsheet properties.*

The thickness of the handsheets formed with primary and secondary fines (bleached sulphite pulp) were practically identical, whereas a clear difference could be seen for bleached kraft pulp, indicating a higher densification by addition of secondary fines. A confirmation of this can be seen in Table 4, where the fibrillar material in terms of fibrillar area of the pulp is shown. The primary fines contain more fibrillar material than the fines-free pulp. Therefore, the addition of primary fines causes an increase of this value. Due to refining, more fibrillar material is formed and the fibrillar area of the handsheets containing secondary fines is higher (2.17 vs 1.75). By having a look at the fibrillar area of the isolated fines, it is clear that the secondary fines are more fibrillar. Nevertheless, the difference between both pulps is evident. The fibrillar area of primary fines for both pulps is similar (6.77 vs 7.05),

whereas the secondary fines of bleached sulphite pulp have a smaller fibrillar area than bleached kraft pulp (11.5 vs 23.95). Besides, the difference in fibrillar area of the handsheets formed also differ. Secondary fines of bleached sulphite pulp formed handsheets with 0.42 more fibrillar area compared to the primary fines. For bleached kraft pulp this difference was 0.8, almost double. This explains the different impact of secondary fines on the breaking length. A higher fibrillar area of the secondary fines cause a higher increase on the strength properties of the handsheets formed, in relative values.

Table 4 *Fibrillar area of different samples containing primary and secondary fines (bleached sulphite pulp) measured by means of L&W Fiber Tester*

Sample [bleached sulphite pulp]	Fibrillar area [%lw]
Fines-free pulp	1,23
Pulp containing primary fines	1,75
Pulp containing secondary fines	2,17
Isolated primary fines	6,77
Isolated secondary fines	11,5

The average fibre length and width of primary and secondary fines was also studied. The secondary fines were again shorter compared to the primary fines, although the difference is smaller compared to bleached kraft pulp fines. Regarding the width, the results obtained (Table 5) are opposed to the ones for the bleached kraft pulp. In this case, the secondary fines have a higher average fibre width, which could be an indicator that less fibrillar material has been formed during the refining of this pulp. This supports the theory that the brittleness of sulphite fibres induces the production of larger particles during refining. This could be caused by a contrast effect. As explained beforehand, part of the fibrillar material might be undetectable due to its transparency. This can influence the presented results.

Table 5 *Average fibre length and width of isolated primary and secondary fines (bleached sulphite pulp) measured by means of L&W Fiber Tester*

Sample [bleached sulphite pulp]	Average fibre length [lw%, µm]	Average fibre width [lw%, µm]
Isolated primary fines	89,02	20,12
Isolated secondary fines	72,66	22,87

The dewatering effect of the different fines in terms of SR are also comparable with the breaking length. Both primary fines and secondary fines cause an increase of the SR. This difference was expected, since fines carry nearly twice the amount of water per unit dry mass than fibres (Seth 2003). The SR of the handsheets containing primary fines is smaller compared to the ones with secondary

fines. Moreover, the air permeability measured in terms of Gurley also shows a more porous structure when primary fines are added compared to the secondary fines. A smaller Gurley indicates a better air permeability and therefore a more porous structure of the paper. This correlates well with the previously presented values for breaking length. Summing the results up, both types of fines bring fibres into close contact and increase the breaking length of the handsheets, this effect being slightly higher when secondary fines are added. The air permeability decreases, which also indicates a reduction of the porosity (Sirviö and Nurminen 2004). This is also a typical effect observed after secondary fines are formed during refining (Lindvqvist et al. 2012). The differences between primary and secondary fines are not as big as for the previous pulp studied, possibly caused by their differences in terms of fibrillar area. Removal of primary fines prior to refining or fractionation seems to be a good option in the first scenario (bleached kraft pulp). By doing so, a higher tensile strength-dewatering relationship could be achieved without compromising other pulp properties. On the other hand, this procedure does not look suitable for bleached sulphite pulp since the primary fines have a positive impact on the breaking length, comparable and very similar to the one caused by the addition of secondary fines. In this case, removal of primary fines could lead to poor strength properties of the final product. Nevertheless, a separation of the primary fines prior to refining adding them after into the treated pulp could lead to promising results in terms of energy efficiency of refining.

As it has been shown in the previous results, the established method provides a constant amount of fine material in the handsheets and allows for easy determination of the fines content using an L&W Fiber Tester Plus. This procedure enables the evaluation of the effects of fines and other types of additives (i.e., small particles comparable in size to fines) on various pulps and their properties. By having a look at the exemplary results obtained with the method, secondary fines of sulphite pulp behave different than secondary fines of kraft pulp. They contain less fibrillar material, and therefore their ability to increase the tensile strength of the handsheets formed is reduced. These results stress the important role that fines play on pulp and paper properties. Besides, it also emphasises the need to study the different types of fines available in the market (including MFC, NFC and so on), since their properties and impact on handsheets properties probably differ from each other and most of the studies only focus on fines from kraft pulp. The presented procedure could be used in future tests to accurately study different fractions of fines and fine material, such as the cellulosic material presented as an exemplary result. By doing so, important information for further application of fines in pulp and paper could be gathered.

4. Fractionated refining

4.1 Literature

Fractionation of the pulp and subsequent refining has already been reported as a way to reduce the energy consumption. The separation of fibres according to fibre length can lead to a more efficient usage of the raw material, improving the refining step. In fractionation, the pulp is divided into a fine fraction and a coarse fraction, using a pressure screen or a hydrocyclone. The goal is to separate the most suitable fibres for optimum refining and to use them for specific purposes according to their length or coarseness (Koskenhely et al. 2005, Karnis 1997). For example, fractionated refining is a hot topic in recycled paper. The long and strong fibres are refined to improve their properties, whereas the fine material is discarded or added after refining to the treated pulp. By doing so, both refining costs and investment on virgin fibres can be reduced (Bajpai 2005). When the pulp is fractionated with a hydrocyclone, the fine fraction of the pulp is mostly formed by earlywood (thin-walled) fibres and the coarse fraction latewood (thick-walled) fibres, which are denser than the earlywood fibres. The separation is therefore based on the cell wall thickness and on the hydrodynamics of the suspension (Asikainen 2013, El-Sharkawy et al. 2008, Karjalainen et al. 2013). Different studies have been carried out in the area of fractionation and separate refining by means of hydrocyclone. Regarding the separation efficiency of a hydrocyclone, Jokinen et al. (2003) concluded that, for LWC (light weight coated) pulp separation the accept contained more fibrillar fines, whereas the reject contained more flake-like fines and ray cells. Trials on bleached softwood pulp were performed by Vomhoff and Grundström (2003) prior to refining, the fine fraction had 2.5 times the tensile strength of the feed pulp and 3.5 times of the coarse fraction, as well as a better smoothness. Besides, to reach the properties of the fine fraction, considerable refining energy had to be expended on the original pulp and on the coarse fraction. The properties of the fine fraction do not improve much during refining. Therefore it can be separated from the pulp and mixed in again after the refining step. By doing so, the energy consumption could be reduced since there is less material to be treated, whereas the properties of the final mixture should remain unchanged. This would lead to a higher material usage efficiency. The results also showed the convenience of spending energy on fractionation rather than refining. In the studies carried out by Asikainen (2013), the thick-walled fibre fraction had the poorest beatability, with the energy input needed being almost twice compared to the original pulp. Nevertheless, the tear strength was better than for the feed pulp. Besides, the effect of a moderate refining was proven to develop the thick-walled fibre fraction to a higher extent than the thin-walled, causing also a higher flexibility of the fibres. The aforementioned effect could be explained by a softening effect of the thick cell wall (Ljungqvist et al. 2005).

When the pulp is separated by means of a pressure screen, the fine fraction comprises mostly fibres with a short fibre length and fines, whereas the coarse fraction is constituted by long fibres. The separation is performed using a physical barrier and the mechanism is in this case based on fibre length and flexibility of the fibres (Asikainen 2013, Karnis 1997). By using a pressure screen, Koskenhely et al. (2005) performed a fractionation and separate refining to improve the strength and surface properties of softwood handsheets. In these experiments the long fibre fraction consisted of 63% of the total pulp, mass related. Studies carried out by Lin and Lanouette (2012) proved that, for Jack pine chemimechanical pulp, selective refining with pressure screens can reduce the energy consumption and facilitate delamination and peeling-off of fibres. Similar conclusions were found by Pelach et al. (2010), claiming that energy savings by fractionated refining can be achieved for a TMP. The relationship between tear index and porosity also improved due to fractionated refining. The long fibre fraction obtained after fractionation was also studied as a possible reinforcement pulp for mechanical pulp, being easy to refine and showing a good tear index, fracture toughness, freeness and WRV (water retention value) (Asikainen 2013). Lin and Lanouette (2013) also chose for their investigations a fractionation via pressure screen. Selective refining of mechanical pulp from jack pine required less refining energy than the feed pulp (reference) to reach a given freeness without causing undesired shortening of the fibres. Selective refining proved to be an effective and realistic way to reduce the energy consumption during refining. Investigations dealing with fractionation and refining of eucalyptus kraft pulps by El-Sharkawy et al. (2008) also led to the same conclusions. Reject pulp (higher average fibre length and more enriched fibres) produced at a low reject rate consumed less refining energy at a given tensile strength compared to the original pulp. It is again mentioned that this procedure could improve paper quality, as well as reduce the raw materials costs, for example by adding the reject fraction as a furnish component and therefore reducing the softwood needed for the mixture. Another investigation interesting for the scope of the present thesis was published by Olson et al. (2001). In their investigations they studied the beneficial impact of fractionated refining for high porosity sack kraft paper. The pulp used for the aforementioned trials is similar to one of the pulps studied in this thesis. An optimal sack kraft paper has to provide both optimal strength and porosity. By using fractionated refining and removing the fines and short fibres from the feed pulp, a higher strength at a certain porosity can be achieved, i.e., a better tensile strength-porosity relationship can be achieved. The differences within the two fractions can be observed in Fig. 10. Both pictures represent unrefined pulp. On the left, the unrefined short fraction, which contains a high proportion of fines and short fibres, and on the right the unrefined long fraction, formed mainly by long fibres. A difference in the porosity of the handsheets is evident. The handsheets formed with the short fraction have a more compact structure with less porosity, which would hinder air permeability, a critical

parameter for sack kraft paper. On the other hand, the handsheets formed with the unrefined long fraction show a higher porosity.

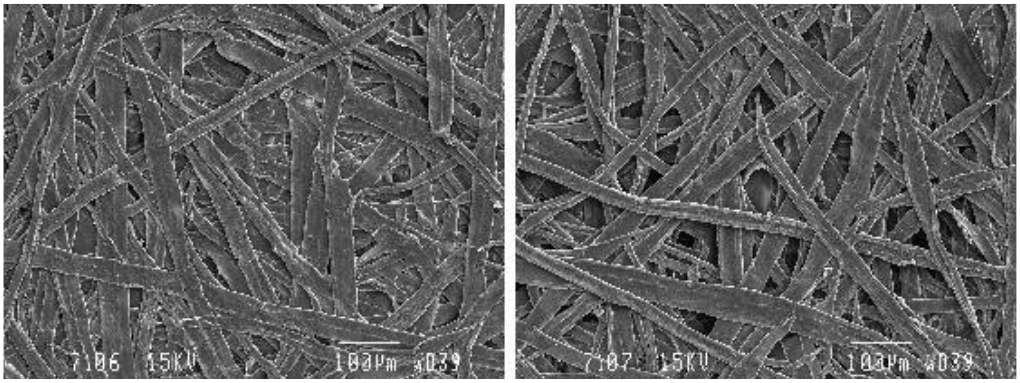

Fig. 10 *Handsheets formed with unrefined short fraction (left) and unrefined long fraction (right) of a kraft pulp (Olson et al. 2001)*

The fine fraction seemed to be more suitable for less demanding products, for example the ones that require smoothness for printing rather than porosity. The highest performance was obtained for the coarse fraction containing the highest amount of long fibres and the lowest amount of short fibres. Fibre fractionation using pressure screens has been also used in sulphite mills as a way to remove extractives and reduce the use of hazardous chemicals during bleaching (Hinck and Wallendahl 1999).

After achieving a constant amount of fines in the system and evaluating the relevance of fines on different handsheet properties (see Chapter 3), the present work studied also the potential of fractionation and separate refining on different pulps, bleached and unbleached to reduce the energy consumption during refining. Although using the white water recirculation previously presented would lead to more precise results, it was not used for practical reasons in the fractionated refining trials. It is therefore assumed that most of the fines will be retained by the fibres that are also present in the system. If any loss of fines took place, it would take place in all tests and therefore would not affect the measurements significantly. A first approach to study the fractionated refining was carried out using a Bauer-McNett fibre classifier, which is another type of mechanical barrier fractionator, and the refining of the different fractions was performed with a Jokro mill, which only requires 16 grams of pulp (o.d.), compared to 30 grams required by the PFI mill. After the first preliminary results were obtained, new trials using a pressure screen and a PFI mill were performed. In these trials, the goal was to obtain a fibre fractionation more similar to what it is obtained in an industrial screen, where the fine fraction still contains a considerable amount of long fibres and vice versa.

4.2 Materials and methods

4.2.1 Pulps used in the different tests

In order to acquire wider knowledge, three different pulps are studied:

- a bleached softwood kraft pulp, which is one of the most common type of pulp used in the industry mainly to increase the tensile strength of the final product
- a bleached sulphite pulp, because the fibres are more brittle and therefore have a totally different behaviour during refining due to lower resistance to refining, which can cause more shortening effects and a higher production of fines
- an unbleached kraft pulp (κ=45, mixture of spruce and pine), since the lignin content is much higher, the fibres are more stiff, showing different behaviour in refining and having also special requirements concerning the tensile strength-porosity relationship as this pulp is typical for sack paper.

The three chosen pulps provide a good scope of the available chemical softwood pulps on the market. Hardwood was not studied in this work. For both trial series using a Bauer-McNett fibre classifier and a pressure screen, all pulps were studied. The results concerning the fractionated refining of the bleached sulphite pulp using a pressure screen and a PFI mill will be presented in the Master´s Thesis of Daniel Mandlez (in progress).

4.2.2 Fractionation devices

Bauer-McNett Fibre Classifier

For the fractionated refining preliminary tests, pulps were fractionated into four different fractions using a Bauer-McNett fibre classifier. A Bauer-McNett unit classifies fibres based on length by selective passage through four different screens, and it is believed to achieve an almost ideal and precise separation, with also a high reproducibility (Gooding and Olson 2001). A typical fibre Bauer-McNett separation would show a Gaussian distribution of the fibres after representing the percentage of fibres (length weighted related) vs the fibre length. Besides, the Bauer-McNett flow is almost steady, whereas a pressure screen has considerable flow reversals (Gooding and Olson 2001). Two different mesh configurations were used. First, the chosen meshes were 30 (pore size 0.595 mm), 50 (pore size 0.297 mm), 100 (pore size 0.149) and 200 (pore size 0.076 mm) according to SCAN M6. The second set of trials was performed using the meshes 16 (pore size 1.19 mm), 30, 50, and 200. The goal was to divide the pulp into two fractions, one comprising mostly long fibres (coarse fraction) and one comprising the short fibres and fines (fine fraction). The screen size using in fractionation is recognized as the most critical variable for the process. In the present study the coarse fraction represents the

pulp retained on the mesh 16. Everything else passing through this mesh is considered to be the fine fraction. A comparison between refining only the coarse fraction and adding the fine fraction after refining, refining only the fine fraction and adding the coarse fraction after refining, and refining the whole pulp as a reference was performed.

Britt-Jar Tester

Originally, this device is used to determine the amount of fines in the pulp (according to SCAN-CM 66:05 (2005)), but it can also be used to separate the fines from the pulp, as seen in Section 3.2.2. In these experiments, it was used to collect fines from the studied pulps for further usage. The mesh used had a pore size of 76 µm. 5 grams of pulp (o.d.) diluted in one litre of distilled water can be washed per trial. For chemical pulps, the pulp has to be washed with 5 litres of distilled water. The fines passing through the mesh were collected and stored.

Pressure Screen

The pressure screen used for the different trials was implemented at the Institute of Paper, Pulp and Fibre Technology at the Graz University of Technology, with the help of the Institute of Paper Technology and Mechanical Process Engineering at the Technical University Darmstadt. The pulp suspension is diluted to a desired consistency and is pumped into the pressure screen body. With the aid of a rotor equipped with foils, the pulp is stirred and accelerated to a certain tangential velocity. Due to the foils shape, a pressure difference is created, which pushes fibres through a perforated plate and at the same time avoids clogging by removing the fibres attached to the plate again (Jagiello et al. 2016). Depending on the hole size of the perforated plate, the pressure screen can be used to wash out fines from the pulp (a hole diameter of 100 µm is used for this purpose, Fig. 11 (right) or to separate the pulp into a coarse fraction (fibres remaining in the body) and a fine fraction (fibres that are able to pass through the screen) using screens with different hole size. After separation, both fractions can be easily collected separately. More information regarding the pressure screen setup, the fundamentals

of pressure screen separation and its characteristics can be found in the work of Jagiello et al. (2016).

Fig. 11 *General view of the pressure screen unit (left) and inlet of the perforated plate used to separate fines (right) (Jagiello et al. 2016)*

Unlike the Bauer Mc-Nett mesh, the pressure screen has a perforated metal plate. The hole diameter of the plate chosen for fractionated refining trials was 1.2 mm. The separation is also based on fibre length, but it is also influenced by fibres flexibility. The probability of long fibres passing through is lower than for short fibres. Besides, during a typical fractionation a fibre mat tends to form over the plate, clogging it to some extent and therefore reducing the effective open area of the screen (Jokinen 2007). It was intended to obtain a fibre fractionation more similar to what it is obtained in an industrial screen. In other words, the separation achieved using a Bauer-McNett fibre classifier is too sharp to be compared to a realistic industrial scenario, where the fine fraction still contains a considerable amount of long fibres and vice versa. By fractionating the sample using a pressure screen with a 1.2 mm hole diameter plate, a scenario more comparable to the industry can be obtained.

4.2.3 Refiners

Two different lab refiners were used for the tests performed: Jokro mill and PFI mill.

Jokro Mill

To confirm that fractionated refining was a suitable method for the different pulps studied, preliminary tests were performed with the Jokro mill according to ISO 5264-3:1979, Pulps - laboratory beating - Part3: Jokro mill method. The Jokro mill allows simultaneous refining of 6 samples of 16 grams each. This makes its use for preliminary tests more suitable than other options when the amount of pulp available is limited. For example, for trials using the Bauer-McNett fibre classifier, as it delivers small amounts of pulp. It uses the principle of centrifugal force. It comprises six different rolls that revolve around their own axes within special housing. At the same time they orbit a central pivot point. The

pulp is therefore placed inside the housing, between the wall and the cylindrical roll. Due to centrifugal forces, the pulp is treated when the roll starts rotating and refining the pulp. The duration of the experiment can be defined beforehand. For all the preliminary trials performed, the pulp was refined for 20 minutes. As indicated previously, tests refining only the coarse fraction adding the unrefined fine fraction afterwards, refining only the fine fraction and adding the unrefined coarse fraction afterwards and refining the whole pulp were carried out using the Jokro mill.

PFI Mill

This device was chosen as it was easier to compare the tensile strength vs dewatering as well as the tensile strength vs porosity relationship. Besides, it is the most common equipment used to mimic pulp refining in the laboratory scale. After pressure screen fractionation, the pulps were refined using a PFI Mill (ISO 5269-1). The number of revolutions of the PFI mill can be adjusted to get different refining intensities. The coarse fraction of the different pulps was refined at different PFI intensities: 0, 2000, 4000 and 6000, whereas the unrefined fine fraction was mixed in after refining, and standard handsheets were formed. This is comparable to the procedure carried out using the Bauer-McNett fibre classifier. A comparison between the different responses during PFI refining and the properties of handsheets comprising only both coarse and fine fractions was also carried out. To do so, the coarse and fine fraction were refined independently, and handsheets were formed and evaluated. The whole pulp was also refined and the obtained values were used as a reference. These trials were intended to show the different development of the fibres according to their size.

4.2.4 Pulp characterisation

All pulps were characterised by means of a L&W Fiber Tester Plus (see Section 3.2.3), with a special focus on the fibre length distribution of the different samples.

4.2.5 Physical testing

The different handsheets formed after fractionated refining were conditioned (23 °C, 50% relative humidity) for 24 hours. After conditioning, the thickness (DIN EN ISO 534 (2011)), air permeability (ISO 5636-3 (2013)), Gurley (ISO 5636-5:2013, Paper and board - Determination of air permeance (medium range) - Part 5: Gurley method), and breaking length (DIN EN ISO 1924-2 (2009)) were determined.

4.3 Fractionated refining trials

4.3.1 Preliminary trials based on Bauer-McNett fractions

In order to evaluate the potential of fractionated refining on the three pulps available in the project, preliminary trials using a Bauer-McNett fibre classifier for fractionation and a Jokro mill for refining were carried out. The Jokro mill was used for these tests as the amount of pulp required was smaller compared to the PFI mill (16 grams instead of 30 grams), and using the Bauer-McNett unit for fractionation purposes is a tedious procedure, allowing only the fractionation of 10 grams of pulp (o.d) per test. A comparison between the refining of the reference (original) pulp and the refining of the coarse fraction adding the unrefined fine fraction afterwards was carried out for all pulps. Besides, refining of the fine fraction and addition of the unrefined coarse fraction afterwards was performed for the unbleached kraft pulp to evaluate the development of the fine fraction during refining. The goal was to acquire basic knowledge that can be applied in further trials, where the pressure screen was to be used to fractionate the pulp. The fractionation in the Bauer-McNett yields fractions that are separated very sharply which is completely unrealistic compared to industrial separation processes where fractionation is more or less an enrichment of coarse or fine fibres instead of a clear separation. By fractionating the pulp using a Bauer-McNett fibre classifier, the coarse fraction comprises only long fibres, whereas the fine fraction comprises all the fines and short fibres. Therefore, the results obtained should be more ideal and easier to interpret. After these trials, the approach will be studied in a more realistic scenario using the pressure screen and the PFI mill.

Regarding the parameters chosen for these preliminary trials, a coarse/fine fraction separation close to 50% (mass related) was the target for all studied pulps. Particles passing through the 200 mesh screen are referred to as fines. They could not be used for further trials as their dilution was too high (less than 0.5 grams in 240 litres) and thickening would have been too tedious. To substitute them, fines were separated from another batch of the original pulp by means of the Britt-Jar Tester, according to SCAN-CM 66:05 standard and the necessary amount was added to the mixture after refining and before handsheet formation. A mass balance was calculated after fractionation based on the pulp retained by each mesh and calculating the dry-weight.

4.3.1.1 Preliminary trials for unbleached kraft pulp

Fig. 12 represents the mass balance obtained after fractionation of unbleached unrefined kraft pulp using the first Bauer-McNett mesh configuration, i.e., meshes 30, 50, 100 and 200, as stated in Section 4.2.2.

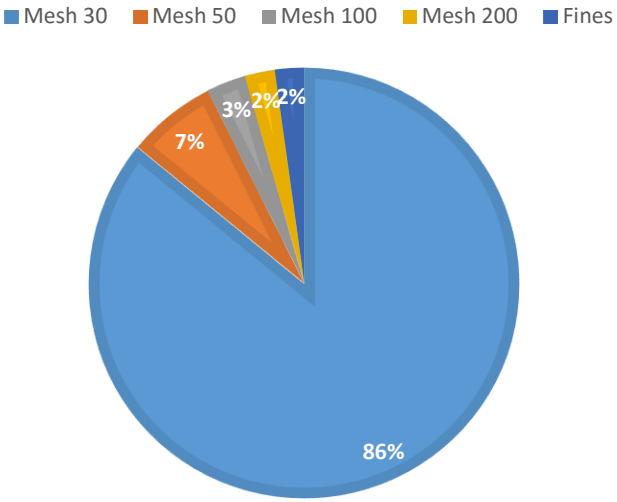

Fig. 12 *Mass balance obtained after fractionation using the meshes 30, 50, 100 and 200 and unbleached, unrefined kraft pulp*

As it was mentioned before, the goal of the fractionation was to have a separation around 50% (mass related). The fibres that remain attached to the mesh 30 represent 86% of the total mass, being the fibres passing through this mesh only 14% of the total mass. The separation with this setup was therefore not suitable for the preliminary tests as a separation around 50% was desired. A second setup using the meshes 16, 30, 50 and 200 and unbleached kraft pulp was evaluated. The mass balance obtained after fractionation is represented in Fig. 13.

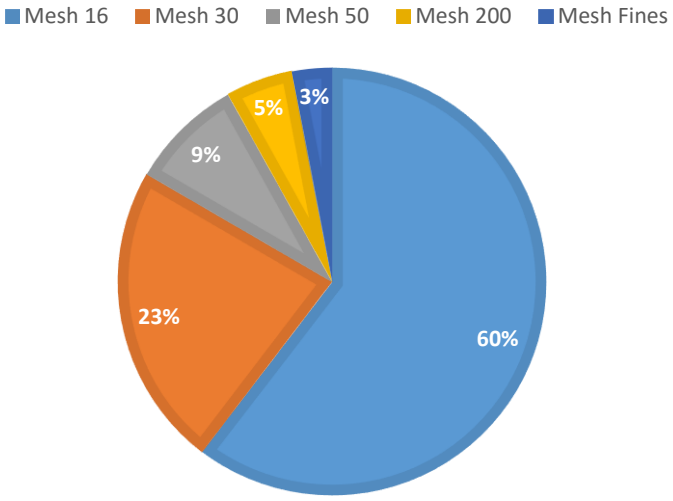

Fig. 13 *Mass balance obtained after fractionation using the meshes 16, 30, 50 and 200 and unbleached, unrefined kraft pulp*

As it can be observed, 60% of the total pulp is represented by the fibres retained on the mesh 16. This result was closer to the desired separation ratio. Therefore, this setup was used to fractionate the pulp,

and the coarse fraction was considered to be the fibres retained by the mesh 16. Everything passing through the mesh 16 is considered to be the fine fraction and represents 40% of the pulp (mesh 30, 50, 200 and fines). The amount of fines present in the sample (3% of the pulp) as well as the fibres retained on meshes 30, 50 and 200 were added to the coarse fraction after refining.

After fractionation with the Bauer Mc-Nett classifier, the different fractions as well as the whole pulp sample were analysed with the L&W Fiber Tester Plus. Fig. 14 shows the length-weighted fibre length distribution of each fraction. The coarse fraction later on used in the refining step (retained on mesh 16) shows fibres with a length of about 1 to 5.5 mm. All other fractions together represent the "fine fraction". The smaller the pore size of the mesh, the lower the average fibre length. For example, most of the fibres retained in the mesh 200 have a fibre length below 500 µm, whereas the fibres retained by the mesh 16 show the highest average fibre length. All curves show an approximatelly Gaussian distribution of the fibre length, indicating an optimal separation, as presented by Gooding and Olson (2001).

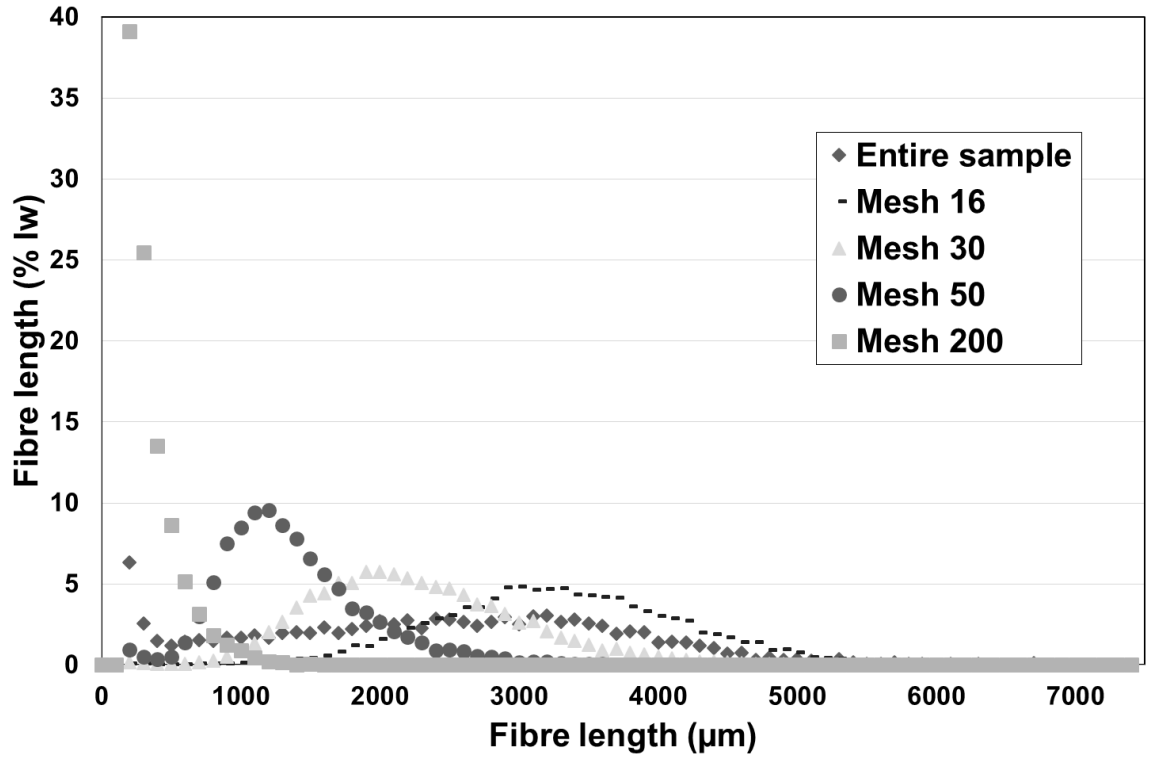

Fig. 14 *Fibre length distribution of the different unrefined fractions (meshes 16, 30, 50 and 200) after Bauer-McNett fractionation (unbleached kraft pulp), as well as the unrefined reference (entire sample)*

The responses of the different fractions after Jokro refining (20 minutes) were studied, and the results obtained in terms of thickness, breaking length, Schopper-Riegler and air permeability are represented in Fig. 15. The entire sample refers to the refined reference pulp. Unrefined refers to the original untreated pulp. Coarse fraction refined refers to the mixture of refined coarse fraction and unrefined

fine fraction. Fine fraction refined refers to the mixture of unrefined coarse fraction and refined fine fraction.

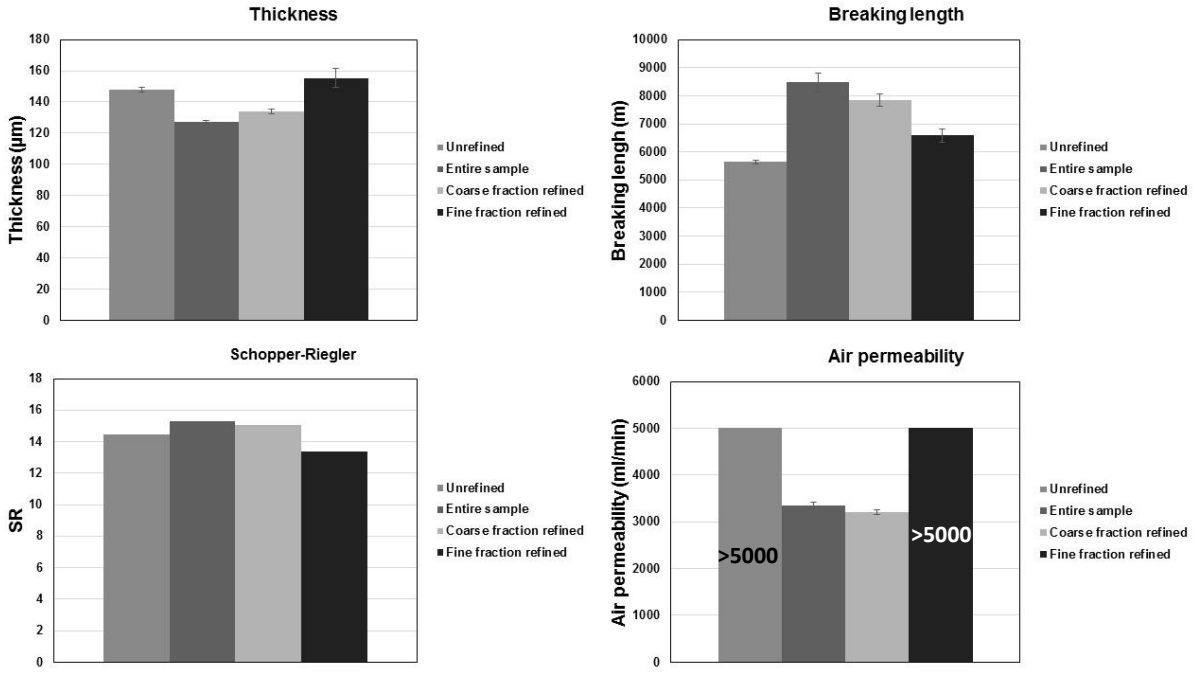

Fig. 15 *Properties of the different handsheets formed during preliminary trials (unbleached kraft pulp)*

It is visible that refining enhances the breaking length and has a negative impact on the air permeability and on the dewatering of the pulp as expected. Due to refining the bonding ability of the fibres is increased and secondary fines are produced, which leads to denser handsheets of higher strength. This in turn reduces the porosity and therefore the air permeability. Looking at the breaking length (which represents the tensile strength potential of the pulp itself, independent of grammage), it is evident that refining approximately 60% of the fibres (coarse fibres) still results in a 79% increase compared to refining the whole pulp. On the other hand, refining of the 40% fine fraction delivers only a 34% increase. The decrease of the breaking length by refining only the fine fraction was 28.5%, whereas refining the coarse fraction gave a breaking length 7.9% lower, both compared to refining the whole pulp. Regarding thickness and air permeability one can see that refining only the fine fraction does not reduce thickness nor air permeability considerably. In fact, the thickness is higher compared to the unrefined pulp, whereas a strong effect is evident when refining only the long fibre fraction. This is due to the fact that the rather stiff coarse fibres in the unrefined state are the ones which deliver the bulk in the sheet. Refining only the fine fractions means keeping the stiff fibres intact and thereby keeping the bulk. The same effect is evident in the dewatering behaviour as the stiff fibres do form a more bulky and porous filter cake during dewatering. One might suggest that the dewatering behaviour also indicates that less fines are produced when refining the fine fibre fraction. However, the L&W length distribution after refining presented in Fig. 16 reveals in the indicated place (which represents all

particles below 200 µm in length) that there are clearly more objects present in the fine fibre classes when the fine fraction is refined, compared to refining the coarse fraction or the whole sample. Less fines are produced during refining when treating only the coarse fraction. This could indicate less fibre cutting due to the absence of short fibres that can be converted into fines.

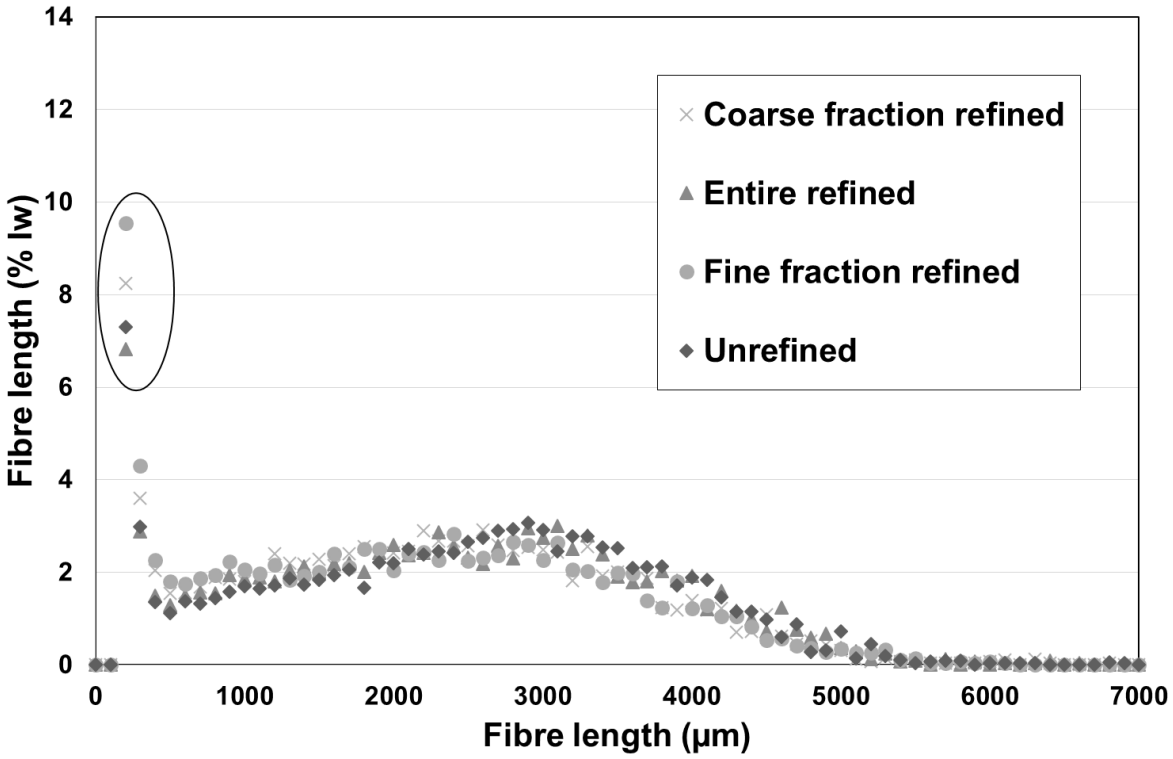

Fig. 16 *Fibre length distribution after refining during the preliminary trials (unbleached kraft pulp)*

The production of fine fibre material during refining is not necessarily a desirable effect and also favours the individual refining of the coarse fraction for most applications. An excess of fine material could lead to a poor dewatering of the pulp and the clogging of the pores, causing a decrease of the air permeability. The aforementioned results present refining of the fine fraction as an unappealing process, as poor properties of the final handsheets are obtained. A poor development of the tensile strength-dewatering properties is to be expected. On the other hand, refining of the coarse fraction which represented 60% of the total of pulp, produced a breaking length increase of 79% compared to the one obtained for the entire refined sample. This would likely lead to energy savings. The possible application of fractionated refining of the coarse fraction using this method was also studied for the other pulps studied in this thesis, i.e., a bleached sulphite pulp and a bleached kraft pulp. Refining of the fine fraction adding the unrefined coarse fraction afterwards was not carried out for these two pulps, since the results obtained using unbleached kraft pulp did not indicate any positive improvement of the refining process.

4.3.1.2 Preliminary trials for bleached sulphite pulp

For the unrefined bleached sulphite pulp, the chosen meshes were again 16, 30, 50 and 200. The amount of fibres retained by each mesh was calculated and is represented in Fig. 17.

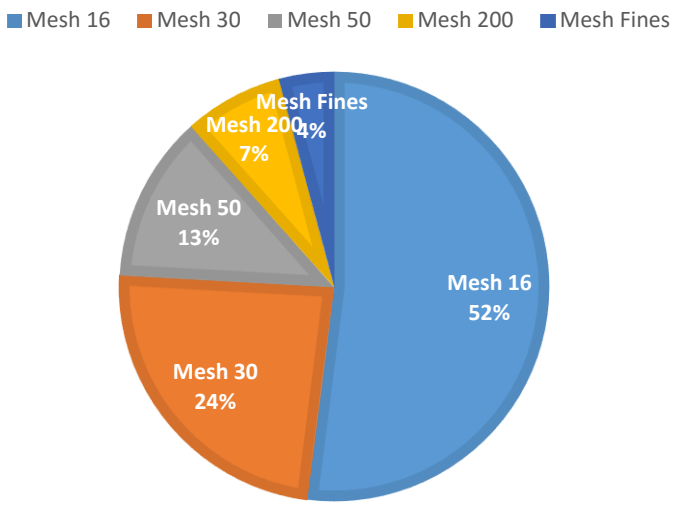

Fig. 17 *Mass balance obtained after fractionation using the meshes 16, 30, 50 and 200 and unrefined, bleached sulphite pulp*

In this case, fractionation of unrefined bleached sulphite pulp is closer to the goal proposed. The mesh 16 is able to retain 52% of the fibres (mass related), very close to the ideal 50% separation. It also shows a higher proportion of short fibres and fines (mesh 200 and mesh fines) compared to the unbleached kraft pulp (11% vs 8%). This configuration was used for further trials and the coarse fraction was considered to be the fibres retained by the mesh 16, i.e., 52% of the total sample. The fine fraction was considered again to be the fibres passing through the mesh 16 (mesh 30, 50, 200, and fines). The entire sample refers to the refined reference pulp. The coarse fraction refined refers to the mixture of refined coarse fraction and unrefined fine fraction. Unrefined refers to the original pulp. The results obtained after measuring the handsheets formed are represented in Fig. 18.

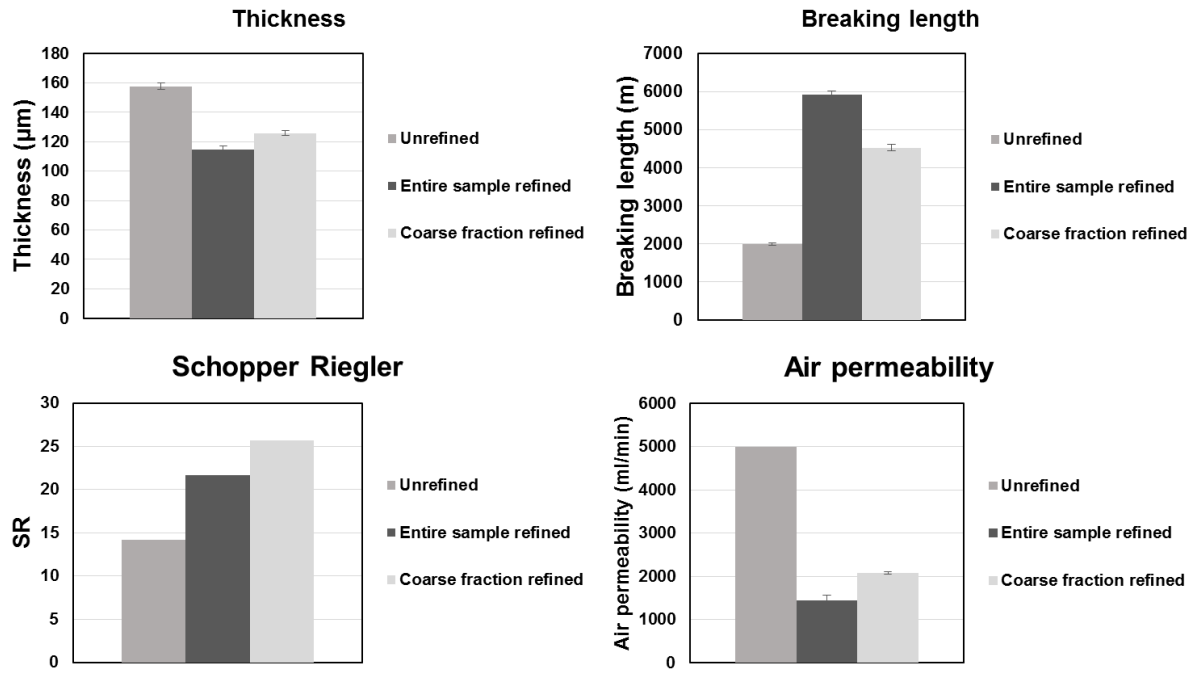

Fig. 18 *Properties of the different handsheets formed during preliminary trials (bleached sulphite pulp)*

As in the previous results obtained for the unbleached kraft pulp (Fig. 15), refining of the pulp causes a decrease in the thickness and air permeability, followed by an increase in the breaking length. These results indicate a more homogeneous mass distribution of the fibres, better fibre-fibre bonding and a subsequent reduction of the porosity. A higher air permeability and thickness are obtained when refining the coarse fraction. Refining the entire sample leads to a higher densification. By refining only the coarse fraction the densification is also lower, which causes the differences observed in air permeability. The dewatering of the sample where only 52% of the pulp was refined is worse than the refined pulp, which was not expected as usually air permeability and Schopper-Riegler are inversely proportional. An explanation for this behaviour was not found at this point. By looking at the length-weighted fibre length distribution in Fig. 19, one can observe that the fibre length distribution refining only the coarse fraction is similar to the obtained for the unrefined pulp. A similar amount of fines should lead to a comparable SR.

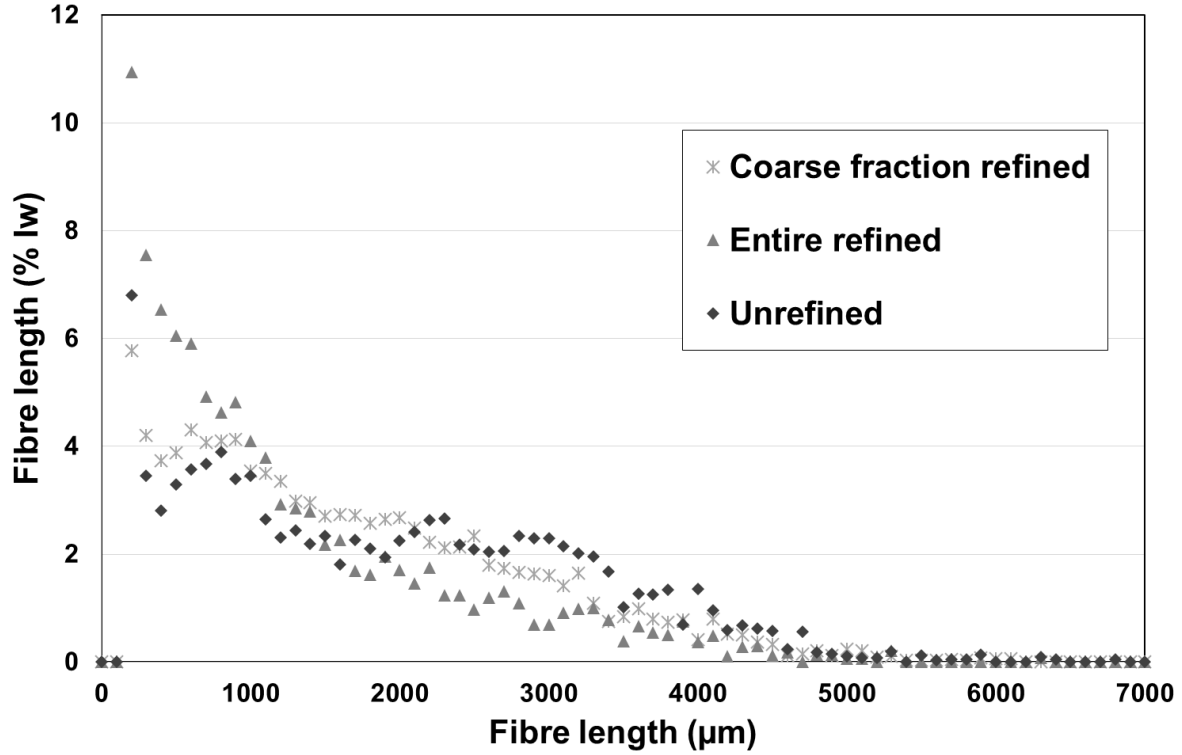

Fig. 19 *Fibre length distribution after refining during the preliminary trials (bleached sulphite pulp)*

Further trials using a pressure screen and a PFI mill will allow to confirm or disprove the present results (see Section 4.3.2). The improvement of the breaking length by refining only the coarse fraction gives poor results compared to the unbleached kraft pulp, although the separation was slightly different: 52% of the pulp forms the coarse fraction of bleached sulphite pulp, whereas coarse fraction of the unbleached kraft pulp represents 60% of the total pulp. Refining of the coarse fraction gave a breaking length only 7.9% smaller compared to refining of the whole pulp for the unbleached kraft pulp (7852 vs 8472). In case of the bleached sulphite pulp, this difference is 30.6% (5907 vs 4521). Besides, the results in terms of Schopper-Riegler and air permeability were similar for coarse and whole refining for the unbleached kraft pulp, but for the bleached sulphite pulp different results are obtained.

4.3.1.3 Preliminary trials for bleached kraft pulp

Regarding the bleached kraft pulp, similar trials with the same mesh configuration (16, 30, 50, 200) were carried out. The obtained mass balance is represented in Fig. 20. Due to technical problems during the L&W Fiber Tester measurements of these tests, the fibre length distribution cannot be presented.

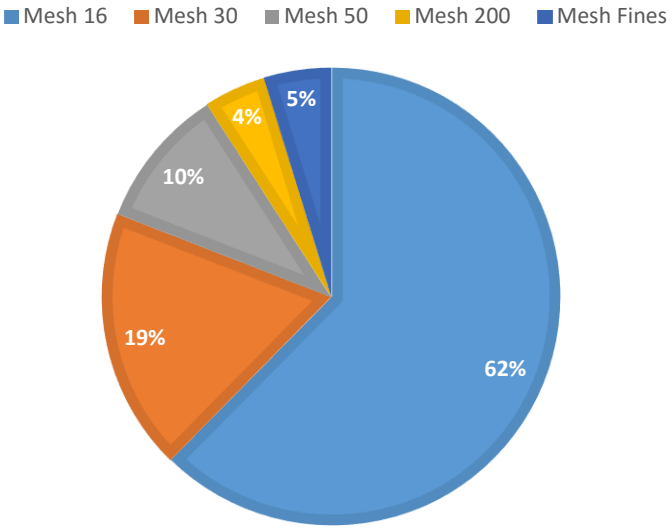

Fig. 20 *Mass balance obtained after fractionation using the meshes 16, 30, 50 and 200 and unrefined, bleached kraft pulp*

The bleached kraft pulp, as seen in Fig. 20, shows similar separation to the unbleached kraft pulp (Fig. 13). The fibres retained by the mesh 16 represent 62% of the total pulp (mass related), and is considered to be the coarse fraction. This is very close to the 60% obtained for the unbleached kraft pulp. The remaining 38% (mesh 30, 50, 200 and fines) is considered to be the fine fraction. By repeating the same procedure as for the other two pulps, the results presented in Fig. 21 were obtained.

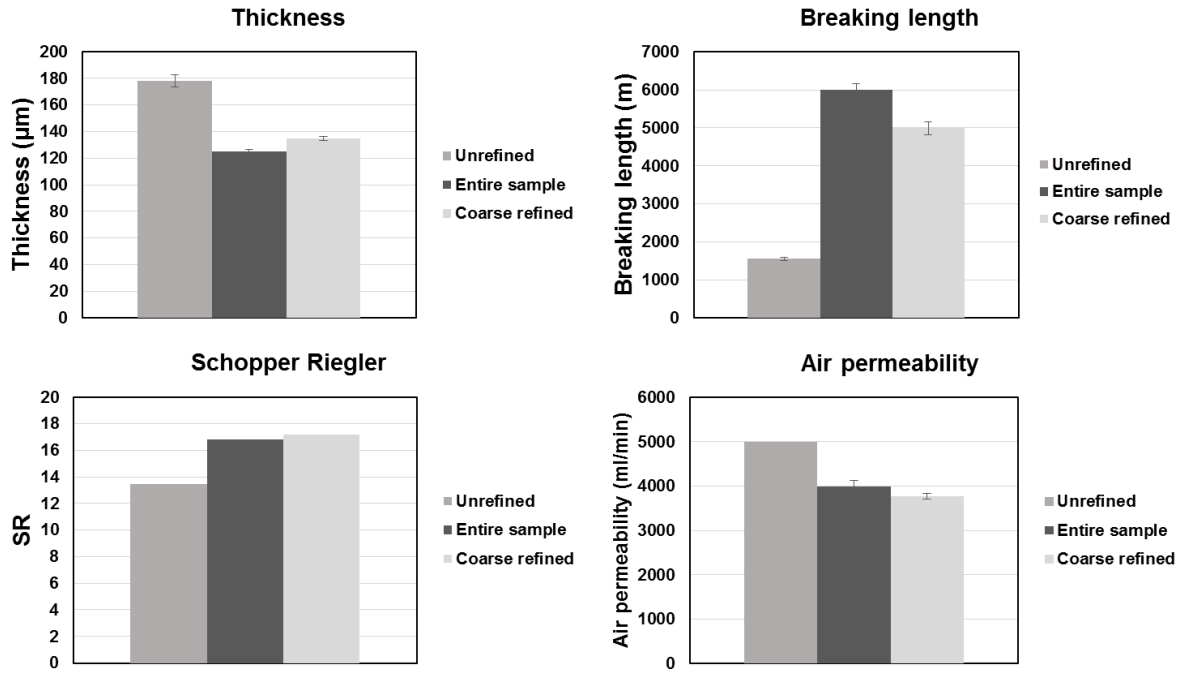

Fig. 21 *Properties of the different handsheets formed during preliminary trials (bleached kraft pulp)*

The comparison between refining the coarse fraction and the entire pulp is for the bleached kraft pulp is more promising, opposed to the bleached sulphite pulp. Similar results in terms of dewatering (SR) were obtained. Moreover, the thickness and the air permeability values that were obtained for the coarse refined pulp are quite close to the reference, indicating a similar formation of the handsheets. Refining only the coarse fraction caused a decrease in the breaking length of 20.3% compared to refining the entire pulp. This value is in-between the previously studied pulps. The results show a better performance on kraft pulp, both bleached and unbleached, whereas sulphite pulp shows a poor development. The presented results also show that the fine fraction of this pulp also develops to a higher extent than the fine fraction of kraft pulps. Therefore, not only is it important to refine the long fibres to achieve an optimal breaking length of a sulphite pulp, but also the short ones. In case of kraft pulps this is not the case and refining the fine fraction might not be necessary. To sum up this preliminary tests, fractionated refining seems to be a promising choice for kraft pulps, whereas the results obtained for a sulphite pulp indicate the contrary.

4.3.2 Trials based on fractionated refining by means of pressure screen and PFI mill

After the positive results obtained during the preliminary tests, it was intended to evaluate a separation of the fibres in a more realistic scenario. To do so, trials using a pressure screen and a PFI mill were performed. The separation of the pulp into a coarse and a fine fraction is expected to be more realistic compared to the one achieved using a Bauer Mc-Nett fibre classifier. A higher proportion of fines and short fibres in the coarse fraction, as well as a higher proportion of long fibres in the fine fraction, was the intention of these fractionation trials. This could allow an easier comparison of the results obtained in the laboratory to the ones obtained in the industry, where a sharp separation according to fibre length is not obtained during fibre fractionation. At the same time, the PFI mill is widely used in pulp and paper laboratories to evaluate pulp refining, whereas the use of Jokro mill is more limited. The procedure is presented separately for two pulps studied in the thesis, i.e., an unbleached kraft pulp and bleached kraft pulp. The results concerning the bleached sulphite pulp will be presented in the Master´s Thesis of Daniel Mandlez, as mentioned previously.

4.3.2.1 Pressure screen adjustment: unbleached kraft pulp

In order to achieve the aforementioned fractionation goal, different parameters were evaluated, such as the amount of pulp to be fractionated, the consistency of the pulp and the residence time of the pulp in the pressure screen. The different fractions obtained during these preliminary trials were measured by means of L&W Fiber Tester to get an understanding of the fibre length distribution. For the first trial, 500 g (o.d.) of pulp were fractionated. The fraction comprising mainly fines and short fibres (fine fraction) were washed out of the pulp and collected, and the reject (coarse fraction) was

recirculated during 45 minutes to achieve a better separation of short fibres. After this period, the coarse fraction was also collected separately. The chosen consistency was 0.2%, and the fine/coarse ratio in terms of volume was 58/42. The pulp was recirculated only once, and after that samples of the fine and coarse fraction were collected separately, corresponding to 0 minutes. After that, samples were collected every 5 minutes and measured with the L&W Fiber Tester. The obtained results are presented in Fig. 22.

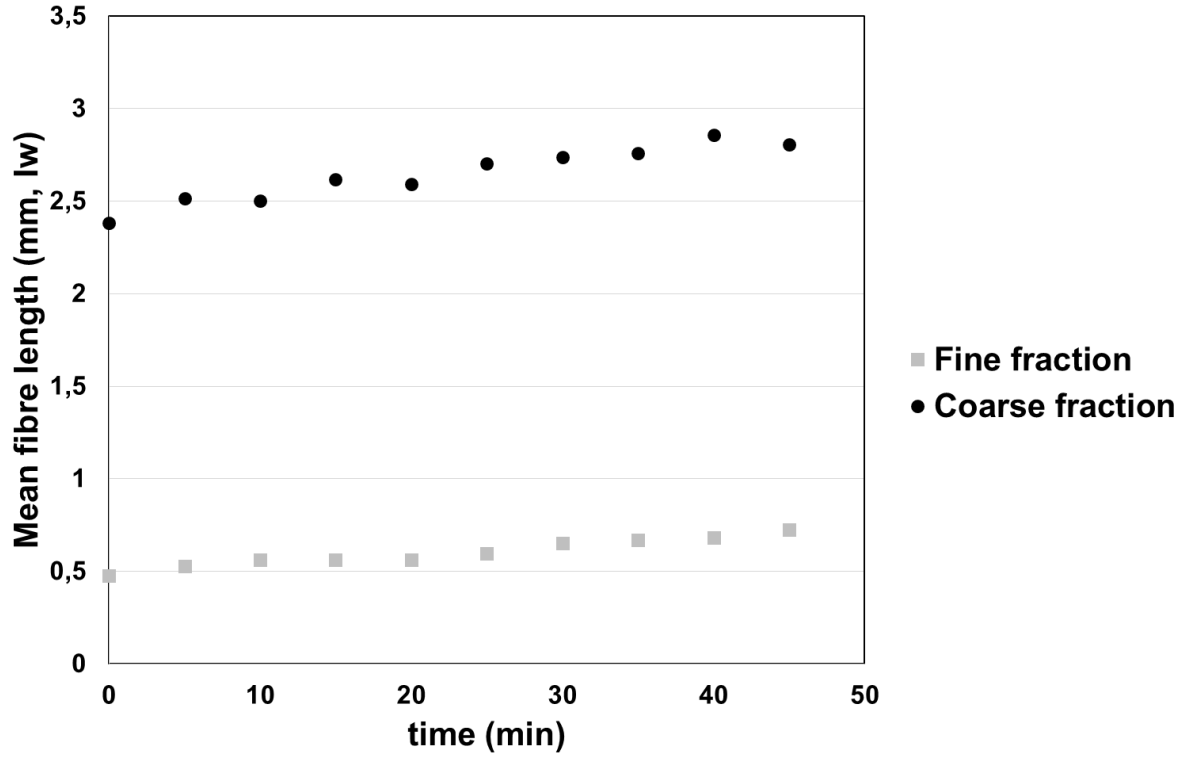

Fig. 22 *Mean fibre length for fine and coarse unrefined fractions during the fractionation process, the fractionation took 45 minutes*

As observed, the measured mean fibre length of both fractions does not seem to vary to a relevant extent, indicating that the desired separation during fractionation was not achieved with the setup used. This can be confirmed by comparing the fibre length distribution of the fine and coarse fraction before and after fractionation, i.e. at 0 and 45 minutes, as presented in Fig. 23. By having a look at these results, it is visible that the fibre length distribution of the fine fraction did not get many long fibres, which was the intention of these trials. The effect observed during this trial is that fine fraction was enriched with short fibres, whereas most of the long fibres were present in the coarse fraction after 45 minutes of fractionation. This is a very positive result if a sharp separation of the pulp into a fine fraction containing only fines and short fibres and a coarse fraction containing only long fibres is intended, similar to what a Bauer-McNett unit can achieve (Gooding and Olson, 2001). However this is not the case, as previously mentioned.

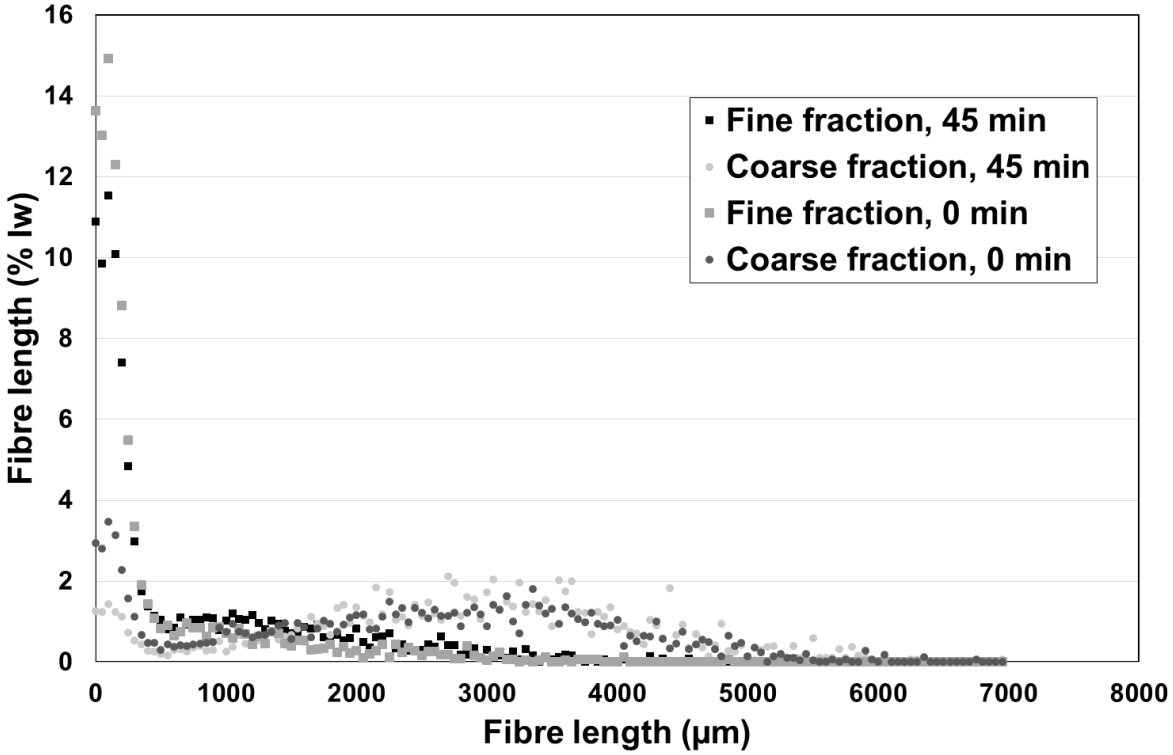

Fig. 23 *Fibre length distribution of both unrefined fractions before (0 minutes) and after fractionation (45 minutes)*

After analysing these results, it is concluded that the separation is not fulfilling the desired requirements. As previously mentioned, the intention of having long fibres in the fine fraction and short fibres in the coarse fraction was not fulfilled. Therefore, a second preliminary trial with different settings was carried out. The consistency was kept at 0.2%, the residence time of the pulp reduced to 30 minutes and the amount of pulp fractionated per test reduced to 100 grams. By reducing the amount of pulp to a fifth part, a better separation was expected. Nevertheless, similar results as the previously presented were obtained. This can be observed in Fig. 24 by representing fibre length distribution before and after fractionation. The fine fraction after 30 minutes contained almost no long fibres, and almost all fines were removed from the coarse fraction after 30 minutes. Therefore, the coarse fraction contained almost exclusively long fibres, and after 30 minutes the fine fraction contained fines and short fibres, but almost no long fibres. This is a behaviour expected after using a Bauer-McNett fibre classifier, as seen in Fig. 25 after comparing the coarse fraction after 30 minutes and the pulp collected from mesh 16 after a Bauer-McNett trial (see Section 4.3.1.1). In both cases, the fibre length distribution shows a Gaussian distribution with a maximum at around 3 mm. It can be concluded that with high residence times and a relatively high amount of pulp (100 grams compared to 10 grams that can be treated using a Bauer-McNett) a separation similar to the ideal one obtained using a Bauer-McNett can be achieved. This may be useful if a high amount of pulp with a comparable

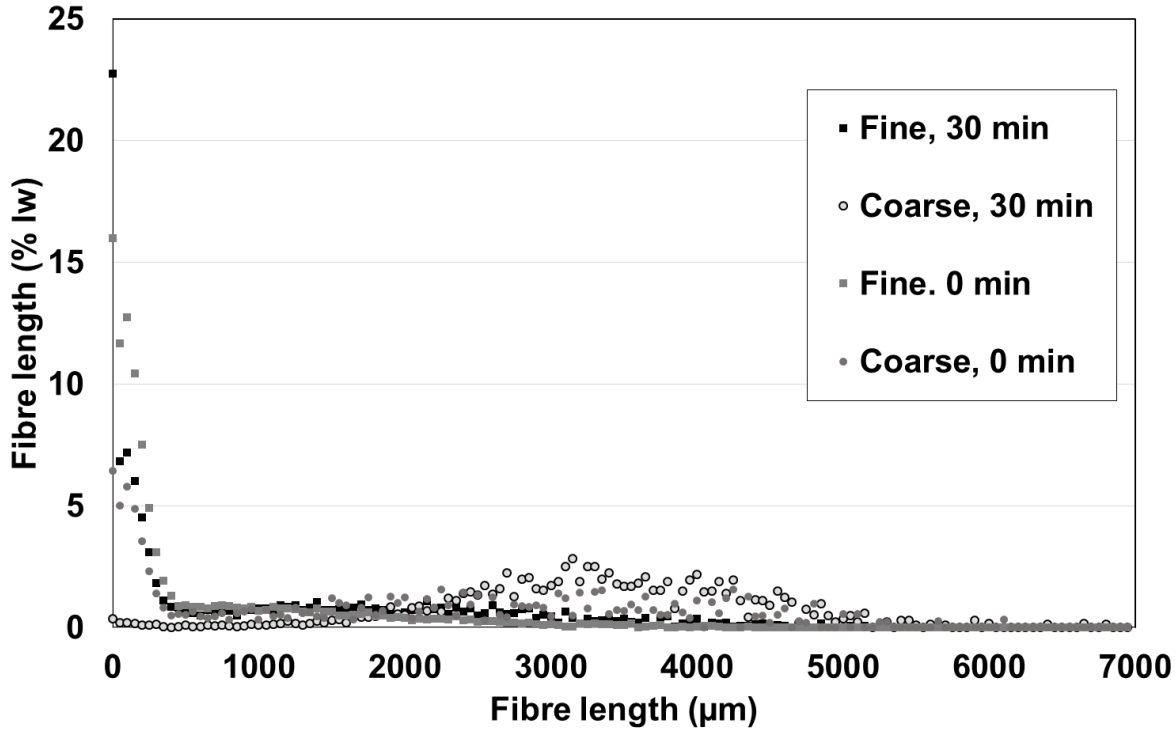

Fig. 24 *Fibre length distribution of fine and coarse unrefined fractions before (0 min) and after (30 min) fractionation*

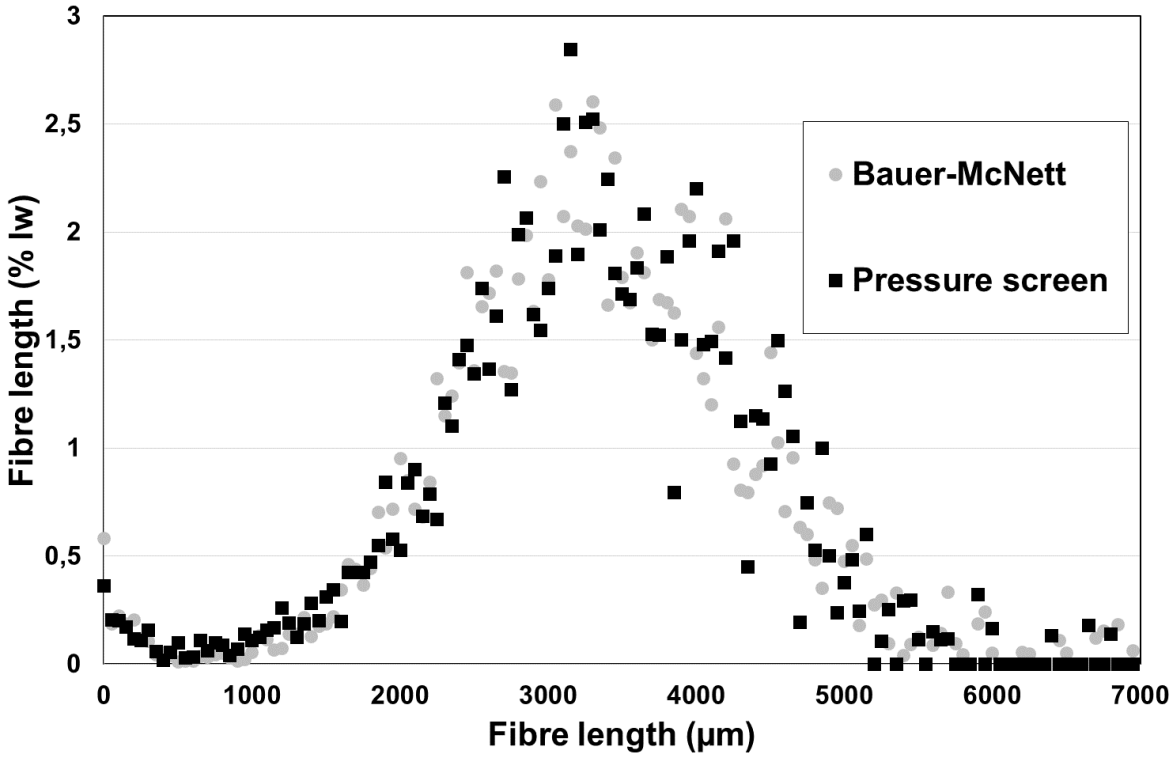

Fig. 25 *Fibre length distribution for a Bauer-McNett 16-mesh and coarse fraction of pressure screen after 30 minutes, both unrefined*

Bauer-McNett separation is required. Nevertheless, the scope of the present investigations is still not accomplished.

After these two preliminary tests, a third set up was investigated. The amount of pulp fractionated per test was reduced to 50 grams. Besides, the consistency was lowered to 0.1% to improve fibre separation during fractionation and avoid clogging of the plate. The pulp was only fractionated in a single loop, in order to resemble a typical industrial fractionation, where the sample passes through the plate once. After that, both fractions were collected separately. Therefore, the probability of fines remaining in the coarse fraction is increased. The dried mass obtained for the two different fractions was also determined. The coarse fraction represented 70% of the pulp (mass related). The fibre length distribution of the different fractions are represented in Fig. 26. The reference represents the fibre length distribution of the unbleached, unrefined kraft pulp used for these fractionated refining preliminary trials.

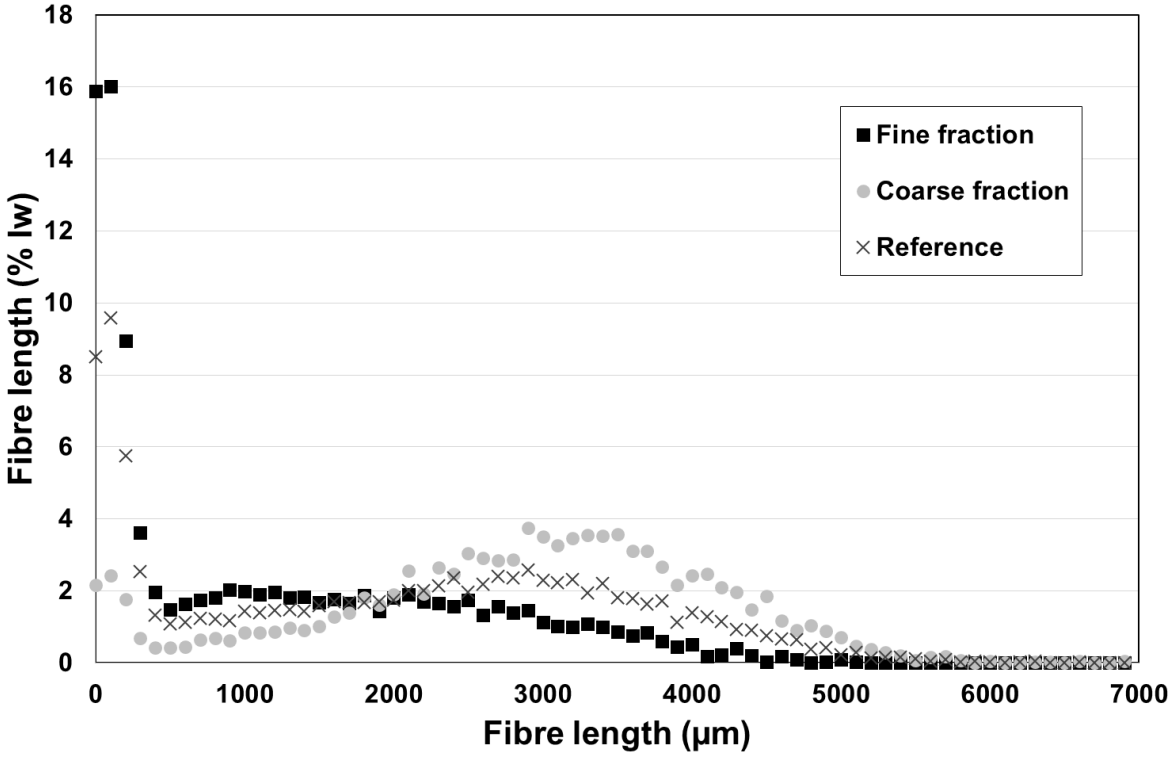

Fig. 26 *Fibre length distribution before and after fractionation using no recirculation of the unrefined coarse fraction, as well as of the unrefined reference*

As it is seen in Fig. 26, the fractionation obtained by reducing the consistency and without recirculation (single loop) suited the purpose of the present investigations better than the first two preliminary trials. The coarse fraction contained on average more long fibres than the fine fraction, but still a considerable amount of fines and short fibres. On the other hand, one can see that a significant amount of fibres with a length ranging between 2 and 4 mm are present in the fine fraction. This was not

observed in other preliminary trials. The average fibre length distribution of the different fractions presented in these trials are presented in Table 6.

Table 6 *Mean fibre length of the different fractions evaluated during the fractionated refining preliminary trials (unbleached kraft pulp)*

Sample	Fractionation time [min]	Mean fibre length [mm]
Reference	-	1.930
Coarse (I)	0 (first loop)	2.381
Coarse (II)	30	3.336
Coarse (III)	45	2.806
Fine (I)	0 (first loop)	0.479
Fine (II)	30	1.010
Fine (III)	45	0.724
Coarse (IV)	1 loop	2.664
Fine (IV)	1 loop	1.284

As observed, when the pulp was fractionated only using 1 loop, the mean fibre length of the fine fraction resulted to be the highest of all performed trials, indicating a higher proportion of long fibres, as intended to obtain results of industrial relevance.

Therefore, this set up was chosen for further fractionation trials for the three studied pulps, i.e., 0.1% consistency, 50 grams (o.d.) of pulp and no recirculation of the coarse fraction. The results obtained for the three studied pulps in terms of fractionated refining are presented below. For all of them, three refining intensities were studied, i.e., 2000, 4000 and 6000 PFI revolutions.

4.3.2.2 Fractionated refining trials using an unbleached kraft pulp

After finding optimal parameters to carry out a fractionation that is comparable to an industrial one, different fractions of the unbleached kraft pulp were prepared to study the effect of fractionated refining. To do so, the coarse/fine fraction flows were adjusted. By opening the valve controlling the coarse fraction flow and therefore increasing it, a higher amount of fibres ended up in the coarse fraction after fractionation. Therefore, a higher coarse/fine ratio (mass related) was obtained. By closing this valve slightly the amount of fine fraction could be increased. At some point the coarse fraction became so thick that it clogged the system and the fractionation could not take place any longer. The sample containing the highest amount of fine fraction (sample 3 in in Table 7) was the highest amount that could be obtained without having this clogging effect. The other two separation ratios (samples 1, 2) were chosen to have a good overview of the effect of the coarse/fine ratio on

fractionated refining. The fractions studied for the unbleached kraft pulp based on mass balance (o.d.) besides the reference sample are presented in Table 7.

Table 7 *Coarse fraction percentage of the fractionated samples (unbleached kraft pulp)*

Sample	Coarse fraction [%]
1	80.8
2	72.4
3	58.6

The fibre length distribution of the reference was compared to the coarse and fine fraction of samples 2 and 3 after fractionation. For convenience, the mass balance was rounded to 80/20, 70/30 and 60/40. The L&W data of the unrefined 80/20 fraction are due to an error during the measurements not available. The results are plotted in Fig. 27.

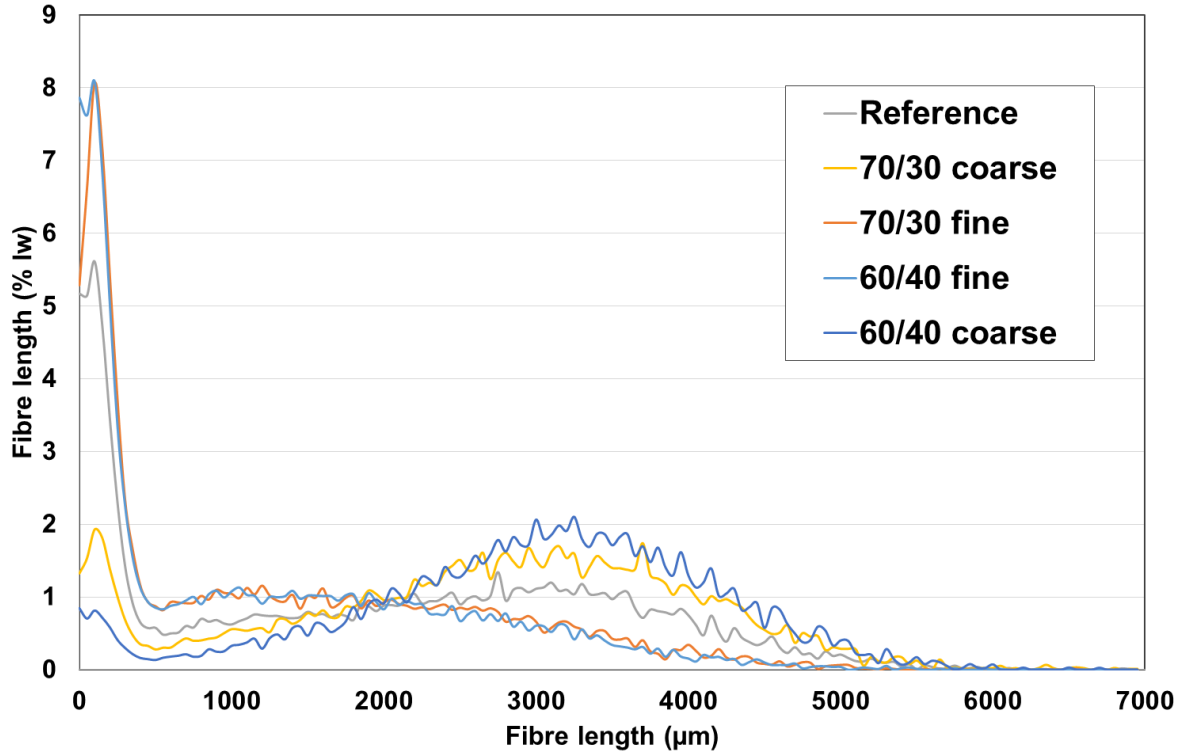

Fig. 27 *Fibre length distribution of the different unrefined fractions and the unrefined reference (unbleached unrefined kraft pulp)*

As it was already observed in Fig. 26, after fractionation two fractions are obtained, a coarse and a fine fration. As it was intended, the fine fraction still contained a relevant amount of long fibres and the coarse fraction contained also short fibres and fines. By comparing the results obtained, it can be observed that the coarse fraction contained a higher amount of fines and short fibres for the 70/30

fraction. This was to be expected, since a higher amount of fines and short fibres should be removed from the coarse fraction to achieve a 60/40 separation. Therefore, the coarse fraction of the 60/40 test contains also more long fibres than the 70/30.

After characterising the different fractions available for fractionated refining, refining trials were performed. The original pulp was refined without any fractionation involved as a reference, i.e., 100% of the pulp was refined. The different coarse fractions were refined at different refining intensities (0, 2000, 4000, 6000 revolutions), and their corresponding unrefined fine fractions were mixed in after refining. Fig. 28 represents the mean fibre length of the obtained mixtures of coarse fractions refined at different refining intensities plus their corresponding fine fraction. The reference showed the lowest mean fibre length, indicating a higher percentage of fines were formed during refining. On the other hand, the fractions 70/30 and 60/40 formed less fines during refining and therefore their mean fibre length was in comparison higher. By comparing only the fines present in the refined pulp at a given refining intensity (in this case at 2000 revolutions), this can be also confirmed. The results are shown in Fig. 29. The reference had the highest fines content, whereas the 70/30 showed the lowest. Similar results were obtained at other refining intensities. After evaluating the fibre length distribution of the different refined samples, handsheets were formed and their properties were measured. The results in terms of breaking length and Gurley are presented in Fig. 30.

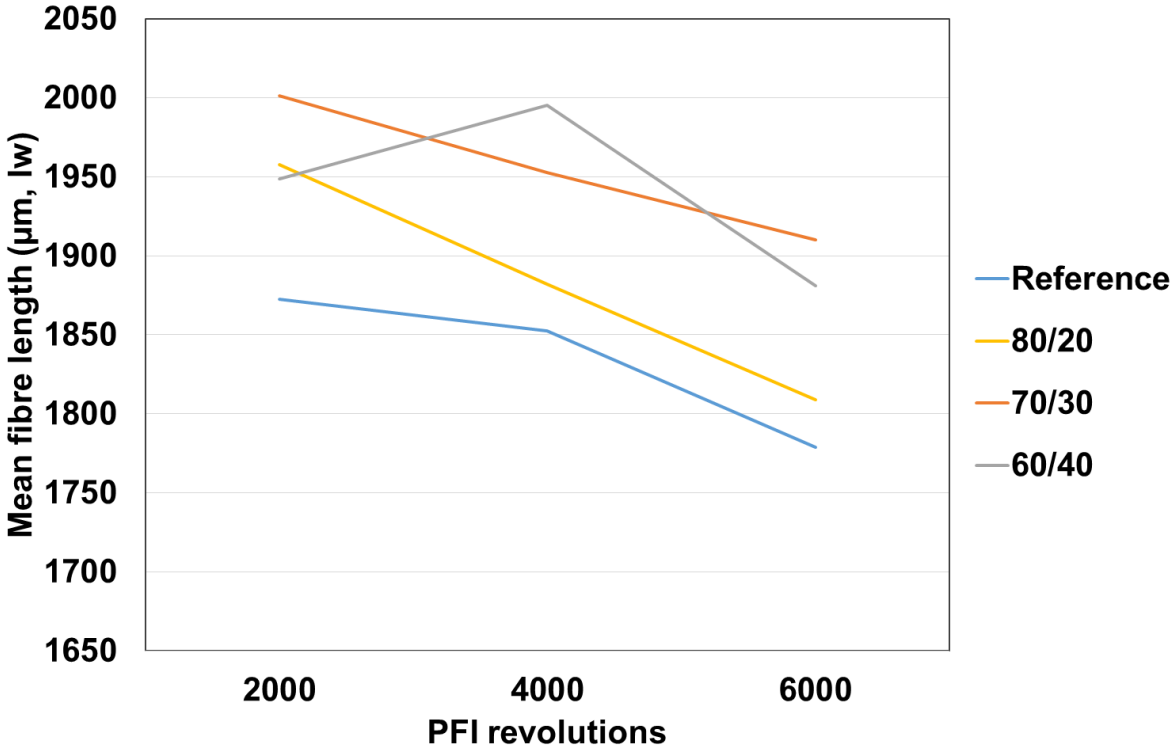

Fig. 28 *Mean fibre length (length-weighted) of the different fractionated samples and the reference after refining (unbleached kraft pulp)*

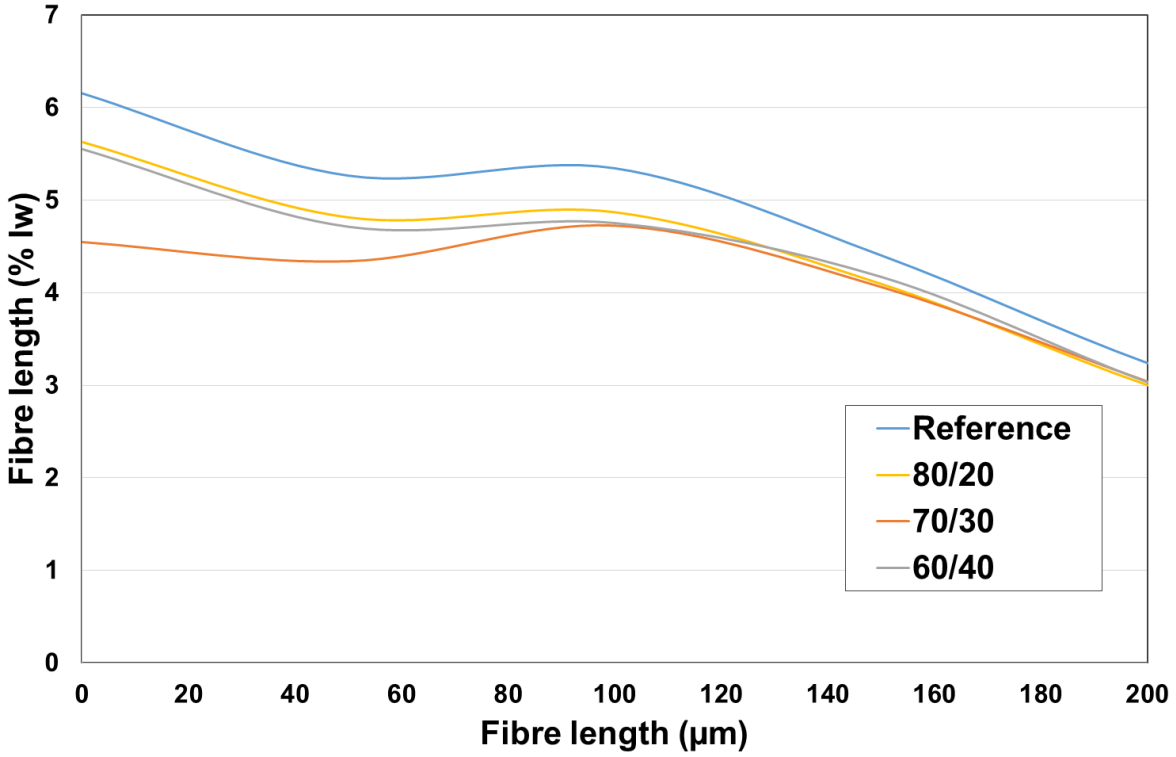

Fig. 29 *Fines content of the different fractionated samples and the reference after refining at 2000 revolutions (unbleached kraft pulp)*

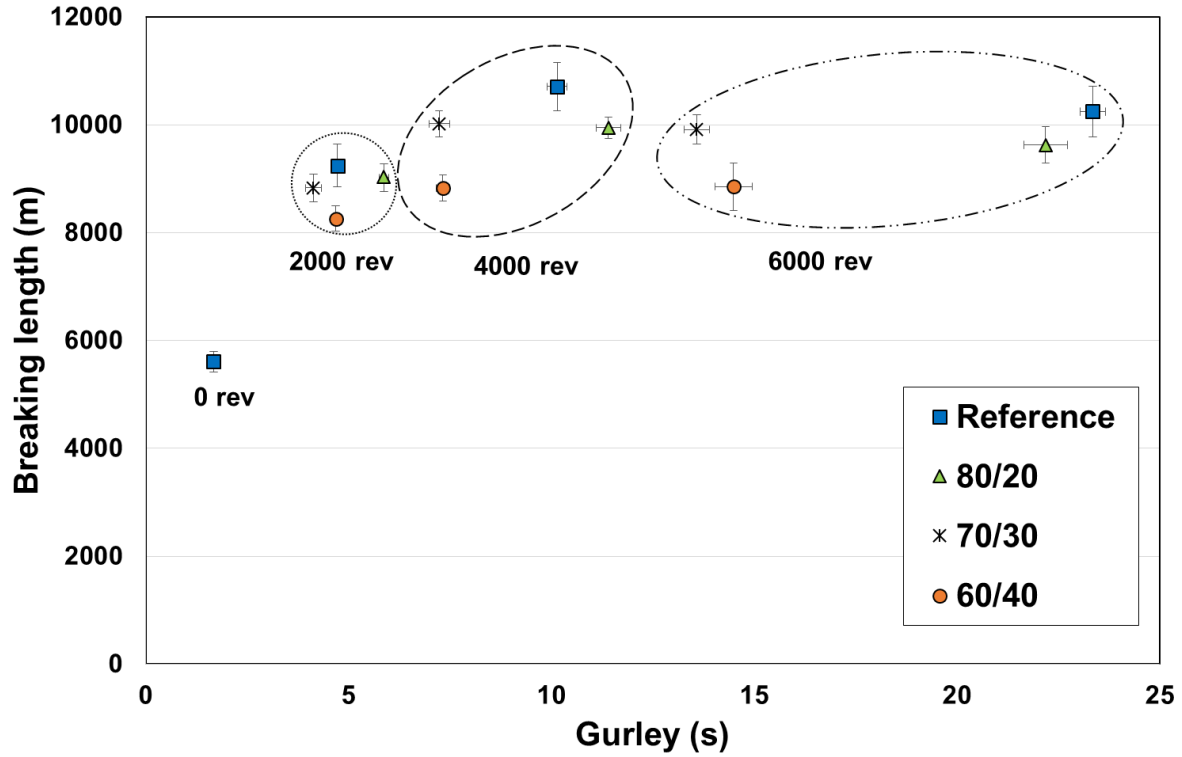

Fig. 30 *Gurley vs breaking length for different fractionated refining samples and the reference (unbleached kraft pulp)*

As expected, the reference had the highest breaking length value, achieving a maximum at 4000 revolutions and levelling off after that. This behaviour was observed for all the studied fractions. It can be also observed that the 80/20 fraction showed a similar behaviour as the reference, having almost the same Gurley but a slightly lower breaking length. On the other hand, the fraction 60/40 showed a poor development of the breaking length, although the Gurley was improved to a higher extent. Regarding the 70/30 fraction, it showed the most promising results. The breaking length achieved at each refining intensity is comparable to the obtained by the fraction 80/20 and only slightly lower than the reference. On the other hand, the Gurley is comparable to the 60/40 fractionation, which means that the air permeability was increased compared to the reference. Therefore, the breaking length-porosity relationship was improved. This may be explained by the amount of fines present in the different fractions after refining. The fraction 80/20 showed a similar fines content as the reference and therefore a similar Gurley, whereas the remaining fractions had a lower amount of fines.

Regarding the effect that fractionated refining has on dewatering, the SR values vs breaking length are plotted in Fig. 31.

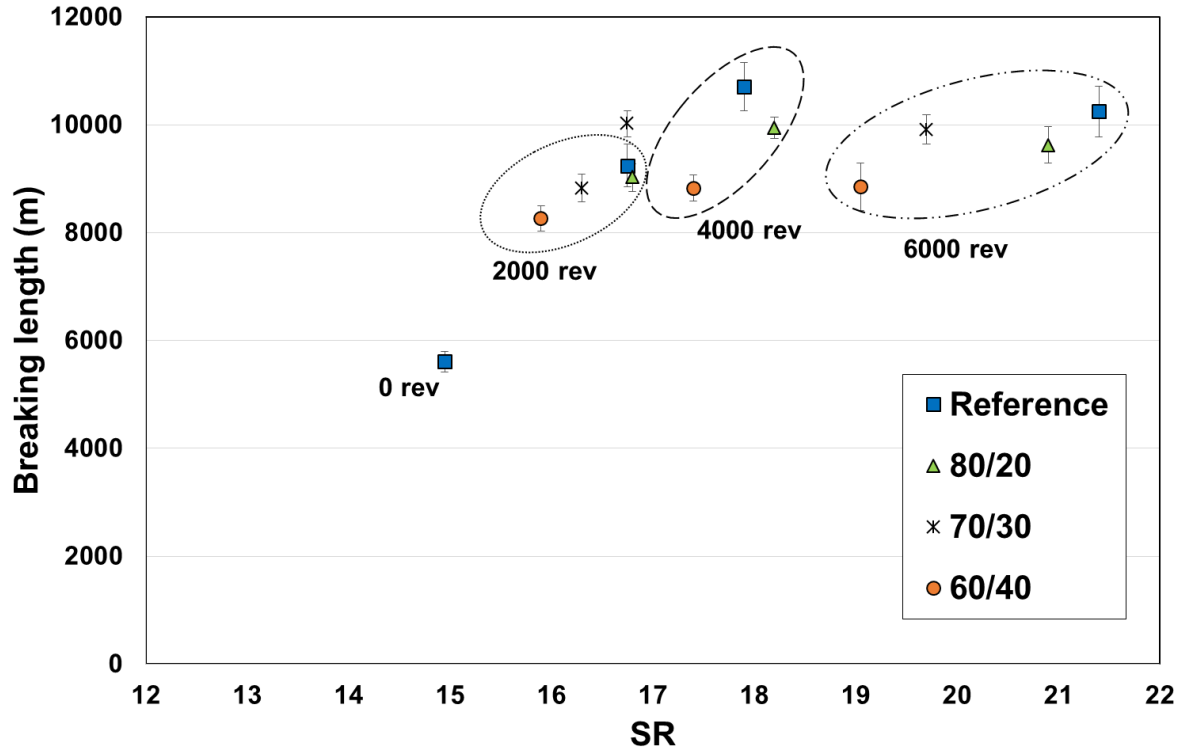

Fig. 31 *Gurley vs SR for different fractionated refining samples and the reference (unbleached kraft pulp)*

The obtained results in terms of breaking length-dewatering provide additional information to understand the development of the different fractions. It also confirms the conclusions presented previously. The 80/20 fraction, which was the one with the highest fines content, also had the highest SR compared to the rest of fractionated trials (70/30 and 60/40). This indicates a poor dewatering of the pulp and corroborates the impact of fines on dewatering. On the other hand, the 70/30 and 60/40 fractions, which had a lower amount of fines, also had a lower SR. Therefore, the dewatering of these two fractions was improved. It can be again stated that the 70/30 showed the most promising results, not only in terms of breaking length-porosity, but also in terms of breaking length-dewatering. A similar breaking length as the reference is obtained, but the Gurley is improved to a high extent as well as the SR. This could lead to potential energy savings, since 30% of the material was spared during refining.

To see the development that both fine and coarse fraction are having during refining, a similar procedure based on 70/30 fractionation was carried out. For these trials, the sample was fractionated using the same procedure into two fractions, which were refined separately. The coarse fraction represented 70% of the pulp (mass related). After that, handsheets with only coarse fibres as well as handsheets with only fine fibres were formed. The results obtained are presented in the same way as the ones shown for fraction 70/30. The main difference between the “Coarse” and “70/30” trials is that for the trial labelled as “Coarse”, the 30% of the fine fraction is not added after refining. To get a better understanding of the fractions obtained after fractionation, the average fibre length (length-

weighted) of both samples is represented at different refining intensities in Fig. 32. The mean fibre length of the fine fraction lies below 1 mm even in the unrefined state, whereas the coarse fraction shows a mean fibre length close to 3 mm. It is also observable that the fine fraction shows an almost constant mean fibre length at 2000 and 4000 revolutions, indicating that no fines are formed during refining. On the other hand, the mean fibre length of the coarse fraction is decaying over refining, indicating fibre shortening and fines formation. The breaking length-porosity relationship is represented in Fig. 33. It can be clearly observed that the fine fraction, which contained a high amount of fines and short fibres, had a much higher Gurley number compared to the other studied fractions. Even in the unrefined state, the Gurley is much higher than any of the other fractions refined at 6000 revolutions. This value even increases during refining, leading to values close to 350 seconds after 4000 revolutions. This would make the use of this fraction problematic if a certain porosity needs to be achieved.

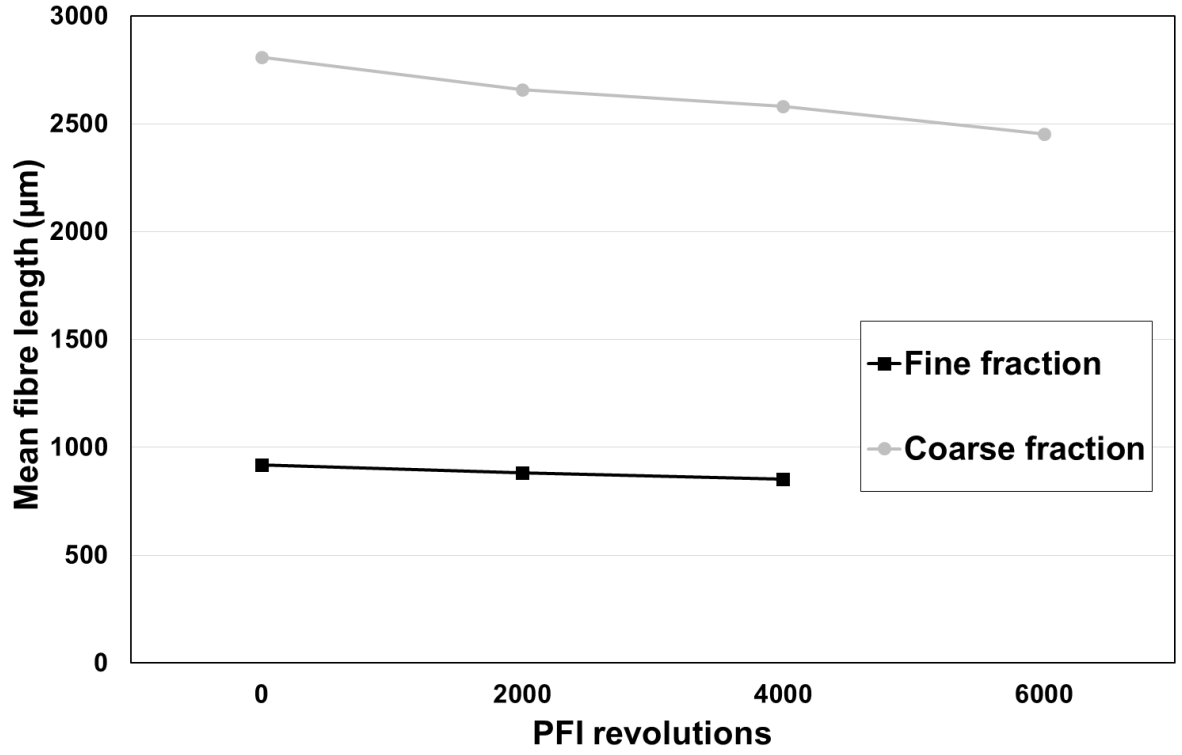

Fig. 32 *Mean fibre length represented at different refining intensities for separate refining of fine and coarse fractions (unbleached kraft pulp, 70/30 separation)*

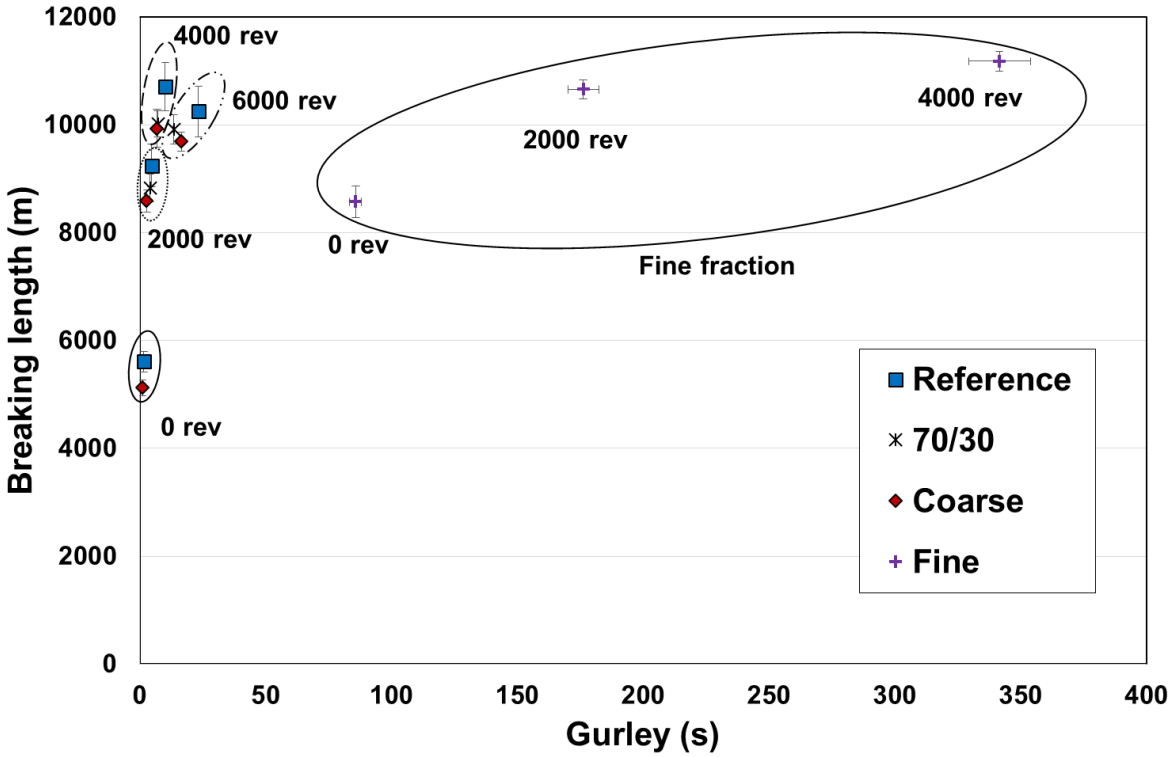

Fig. 33 *Gurley vs breaking length for handsheets formed exclusively with either fine or coarse fractions, as well as the reference and the 70/30 trial previously presented (unbleached kraft pulp)*

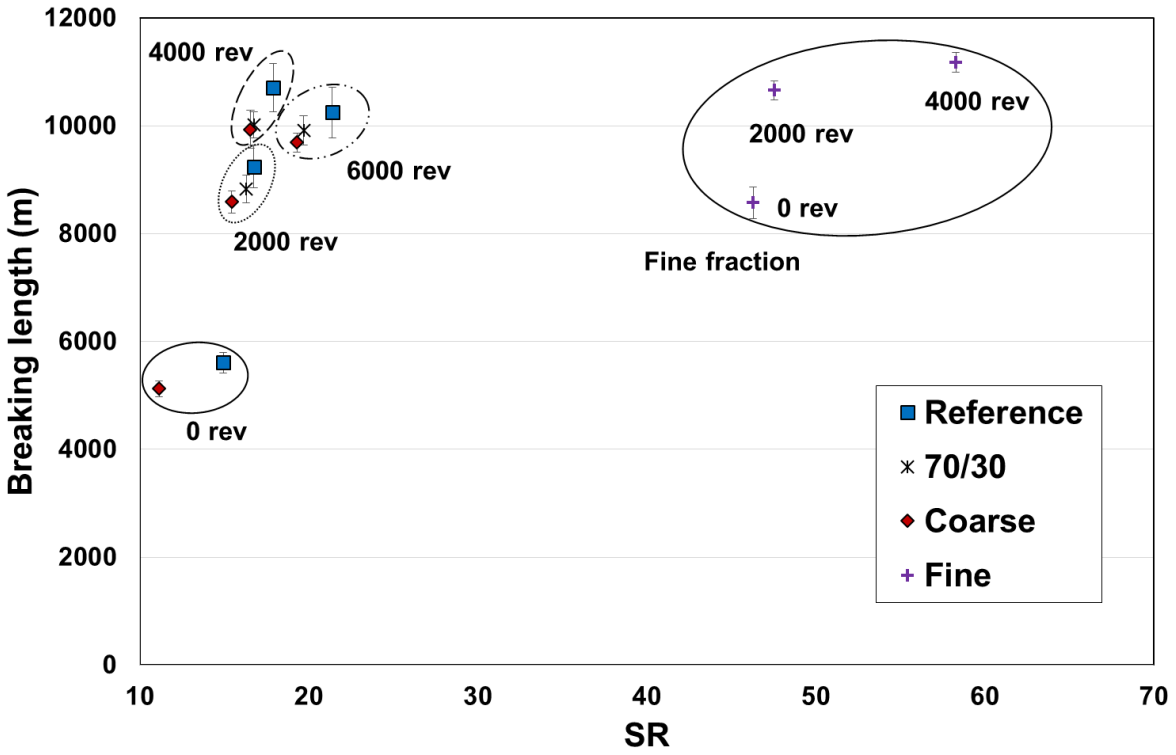

Fig. 34 *SR vs breaking length for handsheets formed exclusively with either fine or coarse fractions, as well as the reference and the 70/30 trial previously presented (unbleached kraft pulp)*

Regarding the dewatering behaviour of the fine fraction, the breaking length vs SR relationship was also studied and can be found in Fig. 34. It is noticeable that the fine fraction show a poor dewatering behaviour, besides the aforementioned poor air permeability, i.e., higher SR and Gurley values. Even in the unrefined state, the fine fraction has a SR of 46.3, much higher than any of the other refined samples. This value increases also with refining, being 58.3 at 4000 revolutions. These two figures provide useful information to assess possible applications for the fine fraction, in case it is not added to the pulp after refining. Regarding the breaking length of the fine fraction, it shows higher values compared to any of the other possibilities, even without refining. For example, the unrefined fine fraction shows a breaking length of 8573 m, compared to 5609 m obtained for the reference or 5123 m obtained for the coarse fraction. This confirms that the fine fraction shows a considerably higher breaking length compared to the coarse fraction, as claimed by Vomhoff and Grundström (2003). Nevertheless, this value also increases with refining, which contradicts their theory that the fine fraction does not develop to a relevant extent during refining. After 2000 revolutions, the fine fraction shows a breaking length of 10657, representing an increase of the breaking length of 24.3%. From the unrefined state to 2000 revolutions refined, the breaking length of the coarse fraction increases by 67.7%, which is almost three times the increase of the fine fraction. This confirms that the coarse fraction needs to be refined to improve their properties. According to these results, the use of the fine fraction may suit certain applications where a high breaking length is expected and neither air permeability nor dewatering are limiting factors. On the other hand, in applications where a high air permeability of the final product is crucial, such as sack paper, removal of the fine fraction may be beneficial, since handsheets formed only with the coarse fraction show comparable results in terms of breaking length with the reference, but due to the lack of fines and short fibres, an enhanced air permeability is obtained (e.g. 2.94 s for the coarse fraction vs 4.23 s for the reference at 2000 revolutions). In order to compare the results obtained for the coarse fraction refined, the reference and the 70/30 trial, the same figures are presented without showing the fine fraction. The breaking length-porosity relationship is presented in Fig. 35. The breaking length-dewatering relationship is presented in Fig. 36.

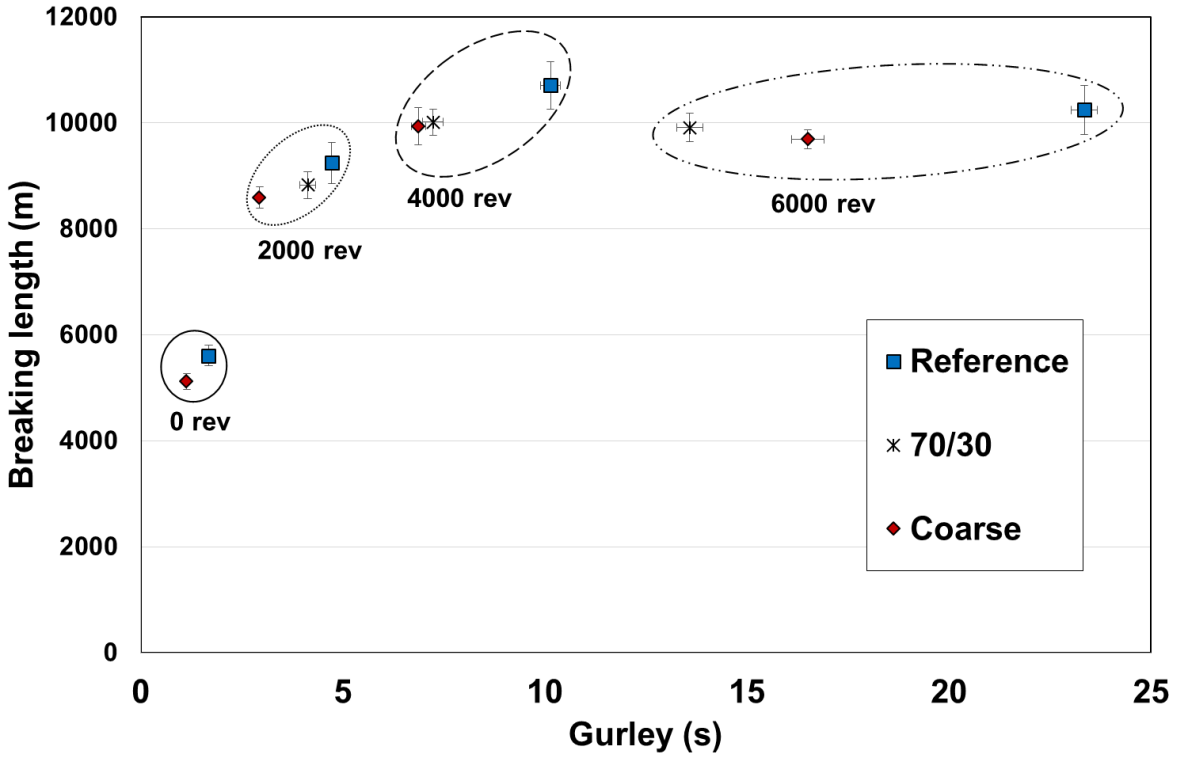

Fig. 35 *Gurley vs breaking length comparison between reference, 70/30 and coarse fraction trials (unbleached kraft pulp)*

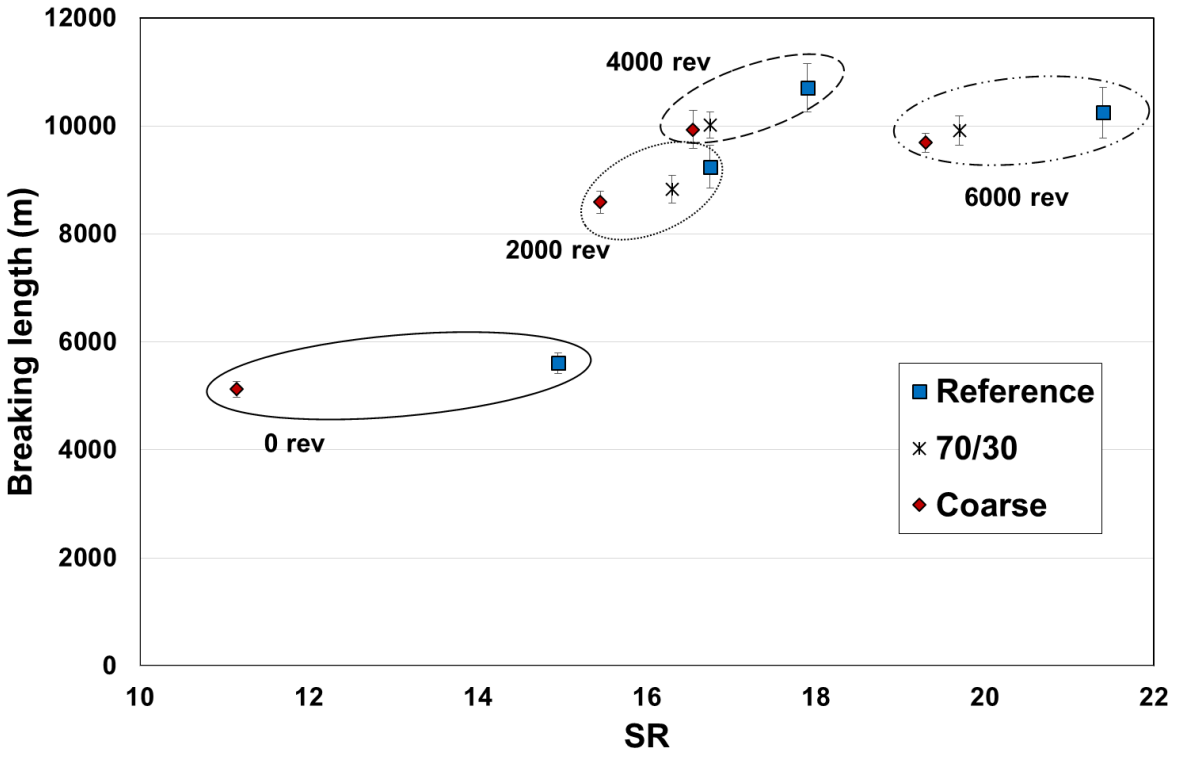

Fig. 36 *SR vs breaking length comparison between reference, 70/30 and coarse fraction trials (unbleached kraft pulp)*

In Fig. 35, the Gurley vs breaking length relationship is represented. At first sight, it is evident that the reference achieves the highest breaking length value, whereas both 70/30 and coarse fraction present a slightly smaller breaking length. It is also interesting to observe that these two trials show a quite similar behaviour during refining. In both cases almost identical values of breaking length-Gurley are obtained, especially at 4000 revolutions. It seems that the development of the pure coarse fraction takes a bit longer than the 70/30 trial, but still a similar breaking length is obtained at 6000 revolutions. This is also confirmed by the results represented in Fig. 36. The results concerning breaking length-SR are quite close at each refining intensity, and the SR is reduced compared to the reference. This may indicate that the unrefined fine fraction (30% oven-dried mass) added after refining has almost no impact on the pulp and paper properties, although it has been shown in Fig. xx that in the unrefined state the fine fraction showed a higher breaking length compared to the coarse fraction. It has to be mentioned once again that this 30% is not added to the sample labelled as “coarse”, and yet similar results are obtained. Therefore, it could be possible to fractionate the sample into 70% coarse fraction and 30% fine fraction, refine and form handsheets only with the coarse fraction and use the fine fraction in other applications where its properties (high breaking length but low porosity) are required. By doing so, 30% of the material is spared during refining, which could reduce the energy consumption of the refining step to a certain extent, and achieve an optimal breaking length. For example, for the coarse sample a breaking length 7.2% smaller compared to the reference was obtained at 4000 revolutions. At the same time, both SR and Gurley are reduced leading to enhanced properties of the final product in terms of dewatering and porosity. The SR is reduced from 16.8 to 15.4, and Gurley is reduced from 10.1 to 6.9. This makes fractionated refining an attractive procedure to enhance the porosity-dewatering relationship of unbleached kraft pulp, and confirms the positive results observed in the preliminary trials (see Section 4.3.1.1)

4.3.2.3 Fractionated refining trials using a bleached kraft pulp

The fractions studied for a bleached kraft pulp based on mass balance (o.d.) besides the reference sample are presented in Table 8. The same procedure as presented in Section 4.3.2.2 was used, and sample 3 represents the highest amount of fine fraction that could be obtained without clogging the system.

Table 8 *Coarse fraction percentage of the fractionated samples (bleached kraft pulp)*

Sample	Coarse fraction [%]
1	90.7
2	78.8
3	72.3

The differences in coarse fraction percentage were achieved in a similar way as it was done for a bleached kraft pulp: by changing the coarse/fine fraction flow relationship. The separation achieved in terms of fibre length distribution for the different fractions is represented in Fig. 37. The coarse fraction percentage was rounded to 90, 80 and 70% to facilitate description of the results.

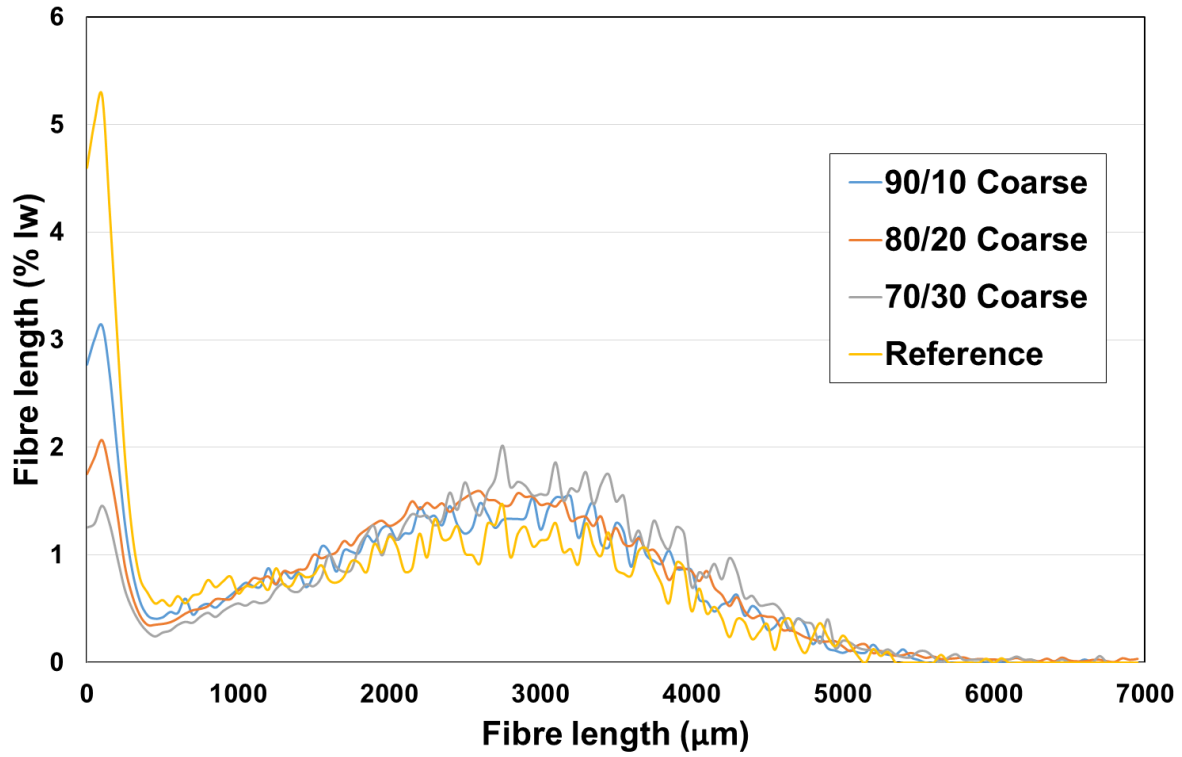

Fig. 37 *Fibre length distribution of the unrefined reference and the different unrefined fractions (bleached kraft pulp)*

As observed in Fig. 37, the reference fraction contained the highest amount of fines and short fibres. This was to be expected, since no fractionation was performed and therefore no fines or short fibres were removed from the pulp. The results obtained for the fractionated samples correlate well. A 90/10 fractionation separates a limited amount of fines and short fibres, and therefore still 3% of the total amount of fibres and fines have a length between 50 and 100 µm (length-weighted related). The higher the percentage of the fine fraction separated from the original pulp, the lower the amount of fines and short fibres. Therefore, the 70/30 fraction showed the lowest amount of fines and short fibres. For example, only 1.5% of the fibres have a length between 50 and 100 µm. This is easy to observe by representing only the fines fraction present in the coarse fraction of the different samples as well as in the reference, as shown in Fig. 38 .

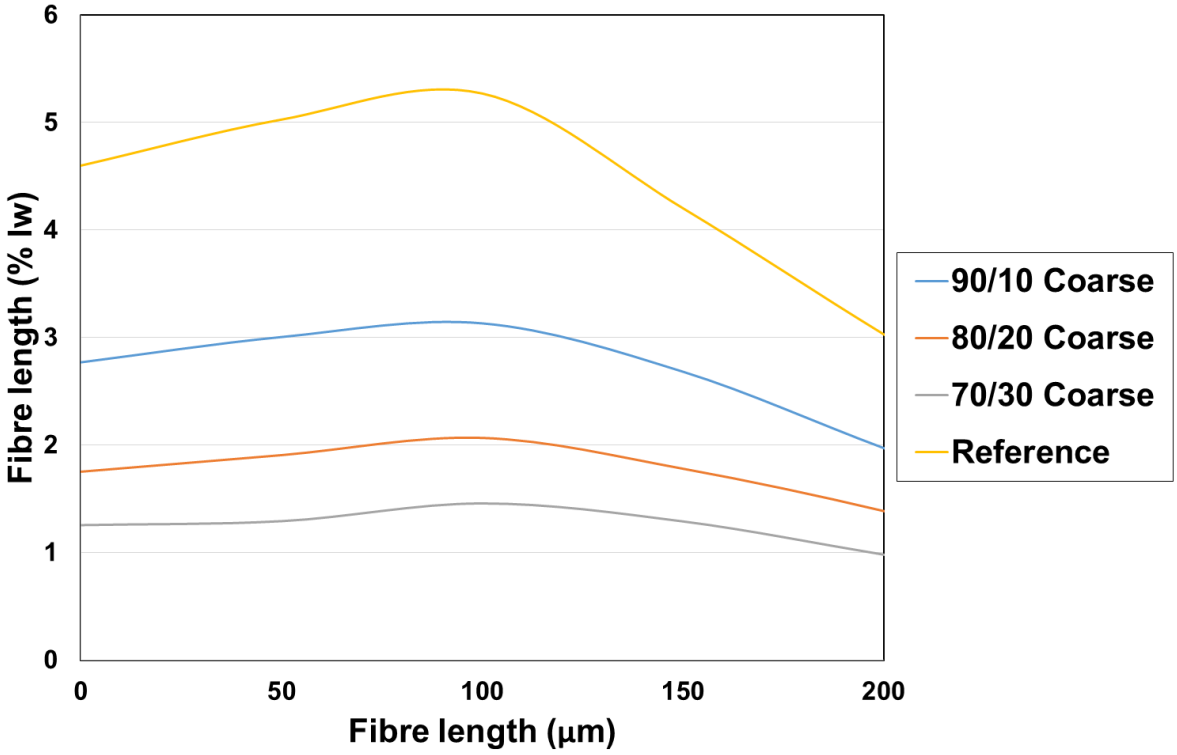

Fig. 38 *Fines fraction present in reference and in the different coarse fractions studied (bleached kraft pulp) in the unrefined state*

Nevertheless, this clear difference in fines content is no longer visible after the different samples are refined. In Fig. 39 the mean fibre length of the different samples are represented after refining at different PFI intensities (2000, 4000 and 6000 revolutions). It is observed that no clear differences are obtained, irrespective of the fractionation of the pulp. The studied bleached kraft pulp behaves in this respect in a different way as the unbleached kraft pulp, where differences in the mean fibre length of around 0.1 mm were observed. In the present figure, the highest difference obtained is below 0.05 mm. Besides, the fines content levels off to the same value, irrespective of the fractionated refining, as observed in Fig. 40. The only remarkable difference is observed at 6000 revolutions for the reference. The proportion of fines increases with refining, but it is not affected by the amount of coarse fibres refined. Therefore, identical results are obtained when the whole sample or only 70% of the pulp is refined. This is also observed at all refining intensities. These data explain to a certain extent the results obtained in terms of physical properties of the pulp and handsheets formed.

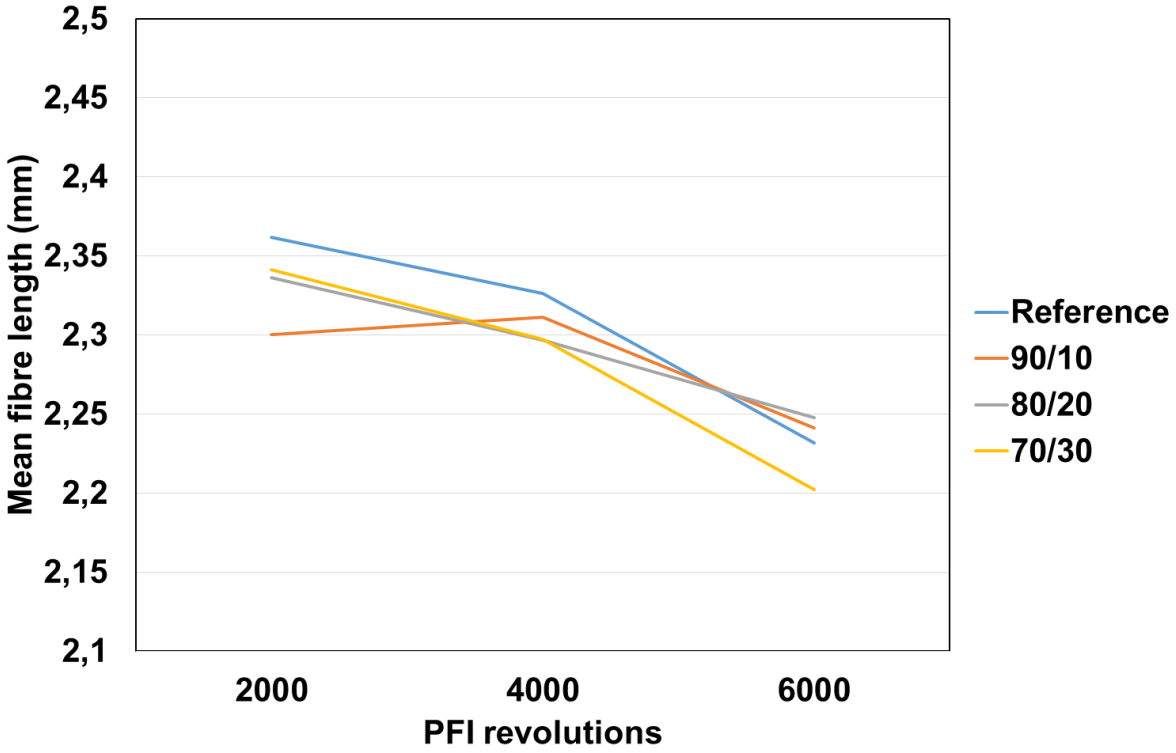

Fig. 39 *Mean fibre length (length-weighted) of the different fractionated samples and the reference after refining (bleached kraft pulp)*

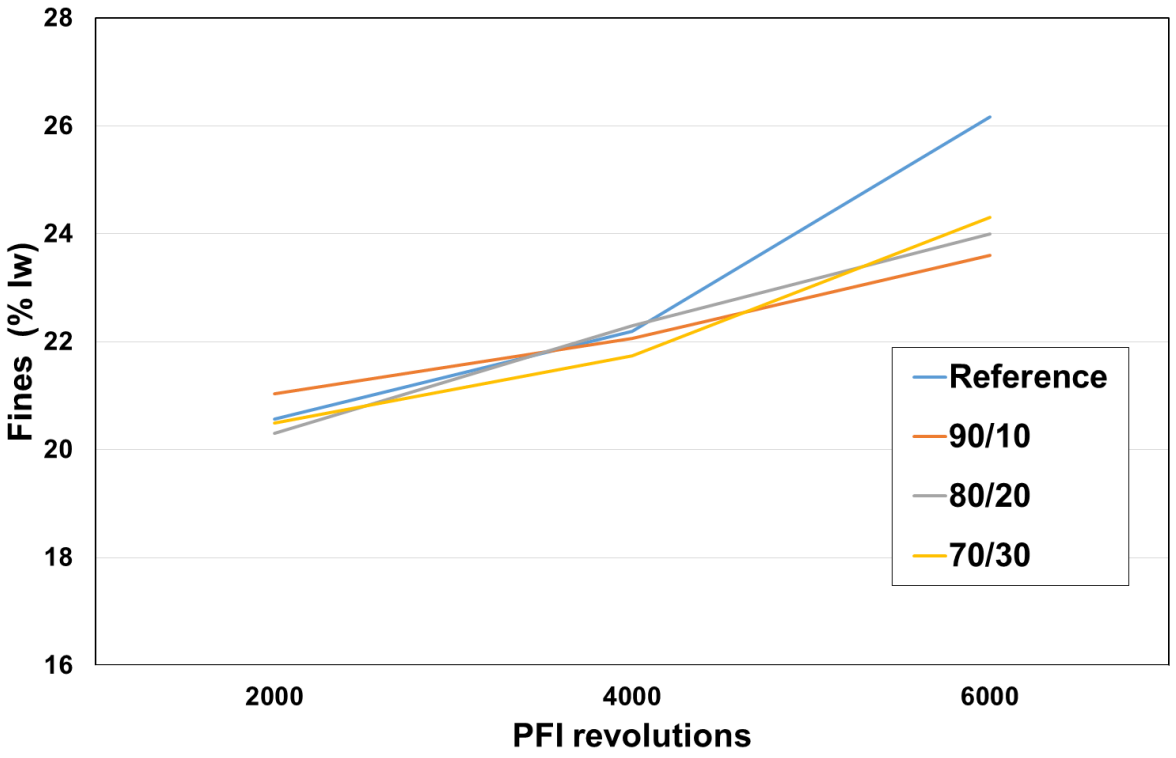

Fig. 40 *Fines content of the different fractionated samples and the reference after refining at different refining intensities (bleached kraft pulp)*

After evaluating the fibre and fines length distribution before and after refining, the properties of the pulp and handsheets formed with the fractionated samples were evaluated. The results in terms of breaking length-porosity are represented in Fig. 41.

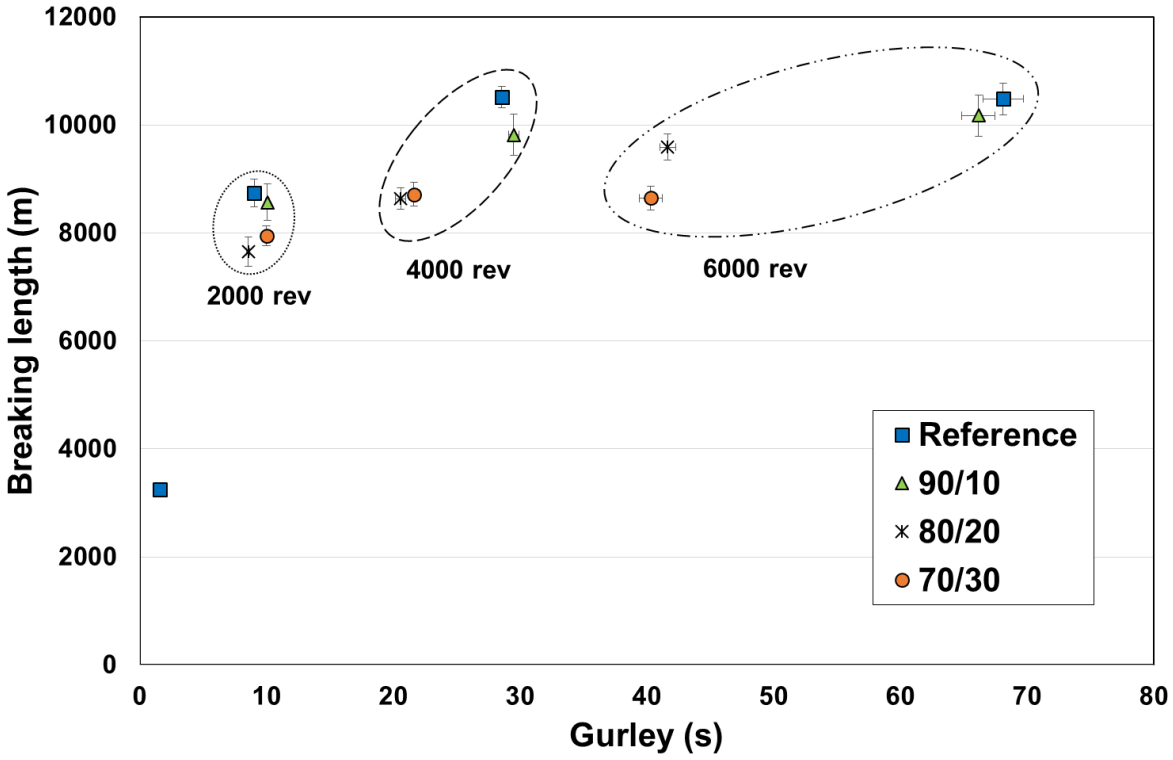

Fig. 41 *Breaking length vs Gurley results for the different fractionated samples and the reference (bleached kraft pulp)*

In this case, the results show an almost proportional relationship between breaking length and the percentage of coarse fraction refined. The higher the proportion of the coarse fraction refined, the higher the breaking length, i.e., the highest breaking length value was obtained for the reference, followed by 90/10, 80/20 and 70/30. This was not the case for the unbleached kraft pulp, as comparable results were obtained by only refining 70% of the total amount of pulp. In Fig. 41, one can observe that the 90/10 sample achieves slightly lower results than the reference at different refining intensities, but also very similar in terms of Gurley. On the other hand, refining 70% of the material provided poor results in terms of breaking length, although the Gurley was improved noticeably. Interesting results were obtained for the 80/20 trial, especially at 6000 revolutions. The breaking length was lower compared to the 90/10 and reference samples, but a similar improvement of Gurley as the one obtained for the 70/30 trial was achieved, indicating a higher porosity of the handsheet. In terms of breaking length-dewatering, the results are shown in Fig. 42. The results clearly show that fractionated refining does not improve to a relevant extent the dewatering of the pulp. This correlates

well with the findings related to fines content. Since a similar fines content was obtained after refining for all samples, also similar SR of the different pulps were obtained. The SR at 2000 and 4000 revolutions is almost constant for all the samples, whereas the 70/30 pulp showed a slightly better dewatering at 6000 revolutions compared to the other pulps. This would make fractionated refining less attractive for the bleached kraft pulp, since it does not lead to a better dewatering of the fractionated pulps, which could lead to a better runnability of a paper machine. This was already observed during the preliminary trials performed using a Bauer-McNett fibre classifier. During these tests, the whole refined pulp and the mixture formed by the refined coarse fraction and the unrefined fine fraction showed almost identical values in both SR and air permeability (see Fig. 21). Therefore, fractionated refining of bleached kraft pulp seems to be only interesting if a higher air permeability is required for a certain process, and a reduction of the breaking length is not critical. In this case, a fractionation 80/20 showed the most promising results. By performing such a fractionation, the Gurley could be improved from 68.1 to 41.7 seconds at 6000 revolutions, although the breaking length was 16.1% lower compared to the reference. This behaviour was also observed in the preliminary trials, where the air permeability of the trial performed refining only the coarse fraction and adding the fine fraction afterwards did not show a significant increase of the air permeability or dewatering compared to the reference (see Section 4.3.1.3).

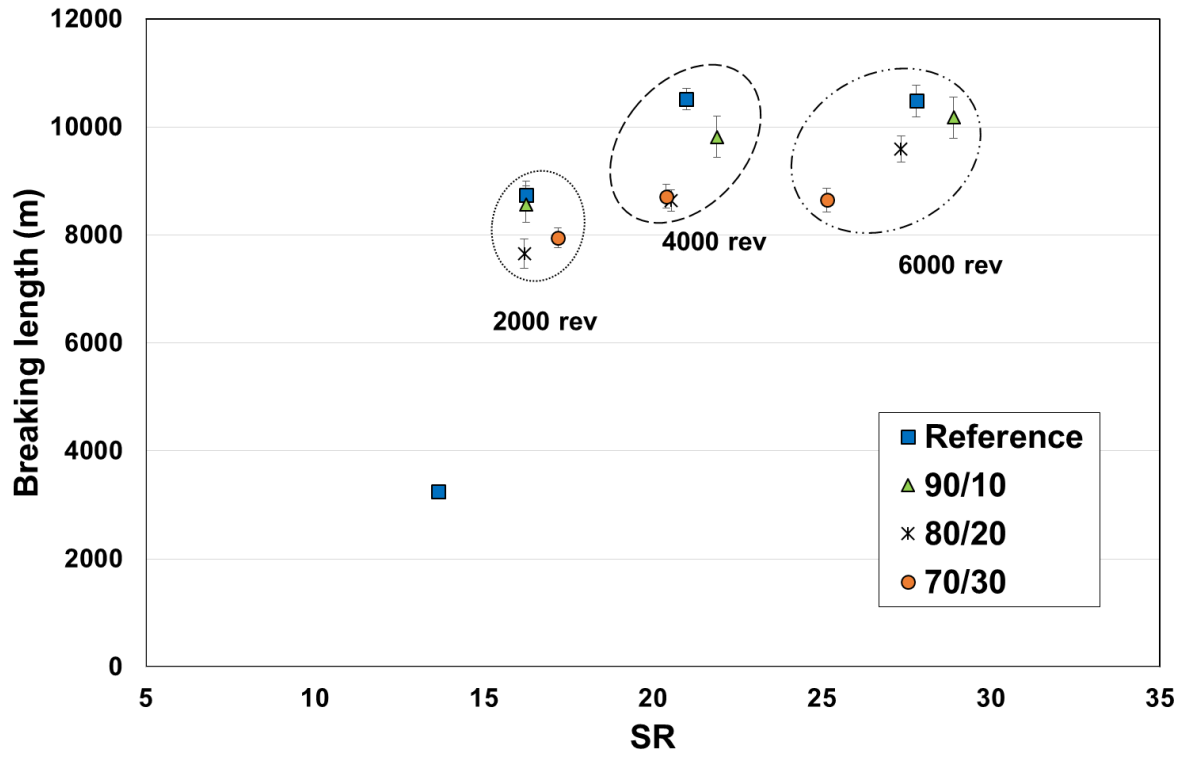

Fig. 42 *Breaking length vs Gurley results for the different fractionated samples and the reference (bleached kraft pulp*

5. Chemical modification by addition of sodium sulphite

5.1 Literature

5.1.1 Possible chemical pre-treatments suitable for the studied pulps

The following section deals with chemical modification methods available to reduce the refining energy consumption. The main idea is to apply a chemical pre-treatment to the pulp that allows either a reduction in energy consumption and/or an improvement of any of both interesting relationships studied in this thesis: tensile strength-dewatering and tensile strength-porosity. Different approaches applying chemical pre-treatments to different pulps (chemical and mechanical pulps) were found in literature. Some of them, such as APMP (alkaline peroxide mechanical pulp) and SCMP (sulfonated chemimechanical pulp) are common types of CMP (chemimechanical pulps) already produced in the industry. Nevertheless, these methods are not comparable to the pulps available in the project, since mechanical pulping treats chips and it has little in common with chemical pulping. Regarding new methods to improve pulp properties available in literature, Sun et al. (2014) studied the effect of adding ozone into a thermomechanical pulp. By adding 1.5% ozone, 21% of the total refining energy could be saved. This investigation was carried out with TMP and therefore cannot be taken into consideration. Nevertheless, the investigations of Kobayashi et al. (2016) dealing with chemical pulps are in close relation to this findings, as it also increased the number of carboxylic groups by oxidizing the pulp. They formed handsheets containing TEMPO-oxidized pulp (2,2,6,6-tetramethyl-piperidine-l-oxy radical). Different contents of TEMPO-oxidized pulp (0-40%) were added into a hardwood bleached kraft pulp, increasing both wet and dry tensile strength of handsheets after refining. Duarte et al. (2006) also reported that the amount of carboxylic groups in a chemical pulp was increased by a catalytic oxidation using TEMPO and therefore the swelling properties of the fibres were improved. Due to this, treated pulp exhibited a 33% increase in the tensile strength in the unrefined state. In these three investigations the fibres are treated with a powerful oxidizing agent, either TEMPO or ozone, which modifies the lignin and cellulose present in the lignocellulosic matrix, forming more carboxylic groups and reducing the energy consumption during refining. Samples with high content of carboxylic groups are characterized by a higher swelling ability that leads to significantly lower specific refining energy consumption (Katz et al. 1984, Sun et al. 2014, Duarte et al. 2006, Vendula and Miloslav 2013). Changes in swelling could be also induced by modifying the pH or the conductivity of the pulp. Two investigations were using chemical pulps, and therefore would be suitable for the pulps studied in the present thesis (Duarte et al. 2006, Kobayashi et al. 2016). Nevertheless, treating the sample with ozone leads to weakened fibres, decrease of tear index and undesired dewatering behaviour of the

pulp. On the other hand, the high costs of TEMPO and the increase of the water retention value make its application in the industry unfeasible. It could then be possible to evaluate the introduction of acidic groups into the pulp to obtain similar effects in terms of reduced energy consumption by other methods that would not damage the treated fibres. Comparable effects as the ones observed in the aforementioned studies by the introduction of carboxylic groups into the cellulose fraction were also reported for sulphonic groups introduced in the lignin fraction of the fibres by treating the pulp with sodium sulphite. The increase of acidic groups (carboxylic and sulphonic) within the pulp causes an increase in the strength and in the swelling of fibres (Katz et al. 1981). Phenolic and hydroxyl groups can also have a similar influence, although under normal pulping conditions carboxylic and sulphonic groups are the major contributors. Carboxylic groups can be already present in the pulp before pulping, whereas sulphonic groups can be introduced by treating the pulp with sodium sulphite. The reactions taking place during sodium sulphite pre-treatment depend on the pH. Under acidic conditions, a substitution at benzylic carbon atoms takes place, whereas at neutral conditions only phenolic units react (Lindström 1992). Sulphonation under alkali conditions causes a cleavage of α-hydroxyl or α-ether to form a quinone methide. The α-carbon then, by nucleophilic attack by the sulphite ion, forms a α-sulphonic acid group (Heazel 1988).

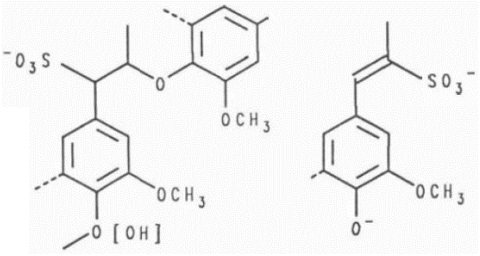

Fig. 43 *Some major sulphonated lignin structures formed during the treatment of chemical pulps (Lindström 1992)*

The degree of sulphonation and carboxylation of the lignin present in the fibres reduces the lignin softening temperature, since most of the sulphonated groups are present in the lignin fraction. This causes a higher swelling potential of the pulp and forms more flexible fibres. Besides, it is also important the counter-ion used in the pre-treatment, since it also influences the swelling of the pulp. The higher the valence of the counter-ion, the lower the swelling of the pulp. According to the studies of Scallan et al. (1983), sodium is the counter-ion that causes the most positive effect on pulp swelling, followed by calcium, hydrogen and aluminium. In their investigations, Bäckström and Haimnar (2010) proved that hardwood and softwood fibres in the Na^+ -form had the highest degree of swelling compared to the original or the Ca^{2+} forms, being also more efficient in terms of energy consumption during refining. This better refinability (in terms of dewatering-tensile strength relationship), was

followed by a higher WRV or tensile index per unit energy input. The reason may be a higher osmotic pressure in the fibre wall. The electrostatic repulsion forces due to the ionization act as an additional aid to increase the swelling of the pulp. This effect could be additional to the introduction of sulphonic groups into the pulp caused by the addition of sodium sulphite. However, this is not feasible in the industrial level, as the pulp is refined using tap water and the counter-ion will always be calcium. A higher swelling ability was believed to be the reason of the energy consumption decrease using TEMPO or ozone as a chemical pulp pre-treatment (Sun et al. 2014, Duarte et al. 2006). Fibre swelling enhances bonding and cell wall cohesion, and the improved flexibility of the fibres lead to a better conformability of the paper network. The combination of both effects induced by sulphonation of unbleached chemical pulps can enhance the internal fibrillation and therefore the strength of the formed handsheets (Eriksson et al. 1991, Bäckström and Haimnar 2010, Lindström 1992). Internal and external fibrillation caused by refining are hugely influenced by the swelling properties of the fibre wall. At the same time, internal fibrillation influences the flexibility of the fibres to a high extent. Introducing charged groups into the lignin polymer by sulphonation enhanced the swelling of mechanical pulps (Fjellström et al. 2013). Although the lignin content of the chemical pulps is much lower compared to mechanical pulps, similar effects could be achieved. Additional acid groups such as carboxylic or sulphonic groups on fibre surfaces increase specific fibre-fibre bond strength, being intermolecular diffusion the mechanism believed to cause this effect (Barzyk et al. 1997). Bäckström and Haimnar (2010) claimed that the lower refining efficiency showed by bleached softwood fibres compared to bleached hardwood fibres lies in their lower charged groups content. Lin and Lanouette (2010) tried to find a suitable chemical agent that could increase the utility of the Jack pine in CTMP, by increasing the strength properties of the pulp to some extent. The mechanism chosen was the enhancement of the hydrophilicity of the fibres, i.e., the swelling ability of the pulp. In addition to, the flexibility of the fibres, which would reduce the cutting effect during refining, could be also increased. They tested the effect of different chemicals before the primary refining step, analysing the increase of fibre swelling and the increase of fibres flexibility. The chemicals studied were alkaline peroxide, sodium borohydride, peracetic acid, and sodium sulphite. The treatment with alkali increased the amount of carboxylic groups. The treatment with peroxide caused an oxidation of the lignin, similar to the use of ozone. Peracetic acid caused a hydroxylation, which attaches new hydroxyl groups to the lignin structure. The treatment with sodium borohydride reduced the carbonyl groups to alcohol groups. Last but not least, a sodium sulphite pre-treatment added sulphonic groups onto the lignin structure, which as seen before, improved the refining of the pulp. A pre-treatment with sodium sulphite resulted in the most promising results, followed by the pre-treatment with alkaline peroxide. Both chemicals were increasing the total charge of the pulp, which caused also an increase of the WRV. This resulted in a higher tensile strength of the handsheets formed after refining. It is possible to observe the same

effects in chemical pulps, since this was also reported by Öster et al. (1988), proving that sulphonic groups were introduced into a softwood kraft lignin after treating it with sodium sulphite and an oxidant agent, increasing the sorption of water. Therefore, a pre-treatment with sodium sulphite was chosen as the most promising method in terms of reducing the energy consumption during refining of a lignin containing unbleached kraft pulp. The effectiveness of this pre-treatment is related to the amount of lignin available, which is much higher in TMP compared to chemical pulps. The lignin fraction in a typical TMP can be around 30-40%, whereas the unbleached kraft pulp studied in the present thesis has around 7%. Since the sulphonated groups are included into the lignin structure, a reduction of the lignin content would hinder the process (Lindström 1992). Therefore, the unbleached kraft pulp, which is the pulp with the highest amount of lignin available in the project (κ=45), was chosen for the tests. The κ-number is an indicator of the lignin present in chemical pulp fibres. A higher κ-number indicates a higher lignin content in the fibres. The lignin content of a pulp in % is defined as 0.15 times the κ-number.

5.1.2 Chemical pre-treatment with sodium sulphite in chemical and mechanical pulps

The addition of sodium sulphite to the pulp prior to refining has already been reported in previous investigations (Axelson and Simonson 1983, Kringstad and Olausson 1974) as a possible way to reduce the energy consumption during refining. Sulphonation is a common procedure used to produce pulps having a high lignin content, specifically thermomechanical (TMP) as well as chemi-thermomechanical (CTMP) pulps (lignin content usually around 30-40%). For both TMP and CTMP, the lignin is softened rather than dissolved as in chemical pulping, and yields are usually close to 100%. This means that more lignin remains in the fibres and the lignin percentage is much higher compared to chemical pulps (Lönnberg 2009).In TMP, sodium sulphite is added to the chips prior to refining as an impregnation pre-treatment. As stated by Heazel (1988), a sulphite pre-treatment modifies the lignin that remains in the fibre walls. Studies dealing with this treatment were already carried out in the 80´s by Axelson and Simonson (1983), and the topic is still of interest nowadays (Fernando et al. 2015). Positive results on TMP were reported in various publications, achieving a higher tensile strength compared to the unsulphonated pulp (Fernando et al. 2015, Lin and Lanouette 2013). For instance, Stevanic et al. (2008) suggested that a low charge of sodium sulphite to the chips could lead to surface fibrillation in the fibre rupture zone, which facilitates the fibre separation during the refining step. Therefore, energy savings of approximately 200 kWh/t were achieved and reported. They claimed that a low sulphonation pre-treatment could cause a weakening of the lignin pectin and lignin protein bonds, which would lead to a higher swelling ability and viscoelasticity of the fibres. After treating the lignin with sodium sulphite it becomes more hydrophilic and its structure looser, increasing the fibre swelling and decreasing damage of the fibres during refining (Heazel 1988). Mao et al. (2004) also observed a softening effect

on both early- and latewood fibres. Sulphonation decreases the compression stress of the primary and secondary plastic zones, as well as the toughness of wood. The softening of the primary cell wall would also be the reason for an easier fibre separation and therefore a better refining, reducing the energy consumption required compared to unsulphonated chips (Eriksson et al. 1991). The improved fibre separation during refining minimize cutting and breaking of fibres (Mao et al. 2004). Similar findings were found by Axelson and Simonson (1983), and also by Heazel (1988), who found sulphonated CMP fibres more intact and less damaged after refining due to easier fibre separation. A softening of the pulp, caused by sulphonation, is related to the transition of lignin from brittle glass-like to an elastic rubber form (Nelsson et al. 2015). This transition takes place at approximately 74°C, according to the studies of Salmen (1984). The higher the operating temperature of the process, the higher the probability of lignin leaching and yield loss (Eriksson et al. 1991). By reducing this temperature, a higher swelling and flexibility of the fibres and therefore a better refining of the pulp could be achieved (Heazel 1988). This was later on confirmed by Nelsson et al. (2015). They also investigated the effect of a low sulphonation pre-treatment combined with a modern high consistency double disc refiner. Due to this pre-treatment, the tensile index, density, elongation and brightness of the final product were enhanced. The increase of the tensile index was proportional to the sodium sulphite dosage. By adding 1.2% sodium sulphite, the energy consumption was reduced by 15%. They proved by means of Simons´ staining that a higher degree of delamination/internal fibrillation, which influences flexibility of the fibres to a high extent, was obtained with the addition of sulphite, indicating a higher swelling ability of the treated pulp. This can be seen in Fig. 44.

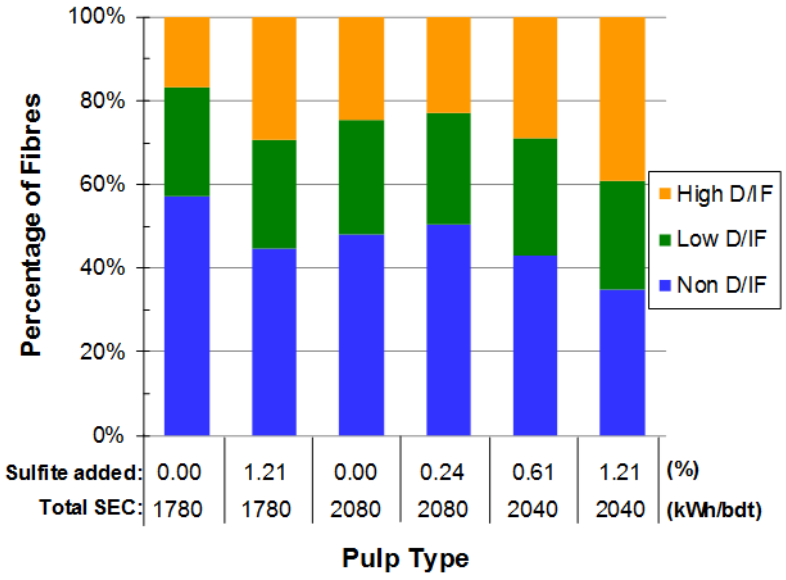

Fig. 44 *Degree of delamination/internal fibrillation (D/IF) for pulps with different sulphite addition (Nelsson et al. 2015)*

The Simons stain is formed by a mixture of orange and blue dyes and is used to evaluate the degree of delamination and internal fibrillation of the fibres. The unrefined fibres will stain blue, whereas the refined ones will stain orange in regions where internal delamination, fibrillation or fibre damage has occurred (Yu et al. 1995). During the tests, Fernando and Daniel (2010) examined the dyed fibres using a light microscope. The obtained data provided useful information regarding fibre development due to sulphonation. The addition of sodium sulphite increased the degree of delamination and internal fibrillation. This correlates well with the improvement of the mechanical properties of the final product, such as flexibility of the fibres and tensile strength. This is also reported by Nelsson et al. (2015). Lin et al. (2010) also pointed out that the positive effect of sodium sulphite could be attributed to a higher surface charge of the pulp, as well as to a higher internal fibrillation. The generation of new acidic groups could also lead to an improved water retention value (WRV). Katz et al. (1981) studied the effect of a sodium hydroxide treatment on a mechanical pulp. They concluded that the increase in strength was caused by a higher swelling of the fibre walls. The swelling was directly related to the number of acidic groups in the pulp, since the content of acidic groups in the pulp is increased by means of sulphonation (Fjellström et al. 2013). Scallan (1983) proposed that the acidic groups within the fibre wall increase the swelling of pulp in water. Therefore, a treatment with sodium sulphite could increase the amount of acidic groups present in the pulp, and thus lead to an upgrading of the pulp. The same approach was applied by Kringstad and Olausson (1974). They concluded that the introduction of sulphonic acid groups in the pulp is responsible for the higher mechanical properties. These sulphonic groups are very hydrophilic, and have a big impact on the solubility of lignin fragments. Therefore, sulphonation of the pulp contributes to easier refining at a given SR (Annergren and Germgard 2014). The aforementioned studies claimed that a pre-treatment with sodium sulphite increases the fibres flexibility and swelling. Both effects lead to a better conformability of the handsheets and therefore better fibre-fibre bonding, producing handsheets with a better tensile strength and increased density (Lin and Lanouette 2013, Kringstad and Olausson 1974, Heazel 1988, Fernando et al. 2015). The treatment of the TMP chips with sodium sulphite exhibited the best results compared to any other chemicals studied (Lin and Lanouette 2010).

Regarding chemical pulps, less studies can be found. Kringstad and Olausson (1974) performed a sulphonation of a high yield kraft pulp to produce sack paper. The treatment showed a positive effect of some mechanical properties, such as tear strength as well as the relationship tear factor vs breaking length. This effect seems to be independent of the temperature and of the sodium sulphite charge. Johakimu and Bush (2011) also demonstrated that a treatment with sodium sulphite was of importance for kraft pulps produced having a κ-number of 85. By adding 10% of sodium sulphite to the coarse fraction, 17% less refining energy was required in comparison with the untreated pulp to achieve a certain freeness. These studies claimed that the lignin present in the fibres was modified

rather than dissolved. This would explain the high yields (close to 100%) reported in previous studies. This was also shown by Kringstad and Olausson (1974), although in both studies this yield was measured by means of κ-number, which is only related to the lignin present in the pulp and not to the cellulose and hemicelluloses. Therefore, an eventual loss of cellulose or hemicelluloses during the pre-treatment was not taken into account.

The main reasons defended by the aforementioned authors after treating chemical and mechanical pulps with sodium sulphite are the softening of the lignin and reduction of the softening temperature (Nelsson et al. 2015, Mao et al. 2004), a higher swelling ability of the pulp by addition of acidic groups into the pulp in the sulphonated form (Stevanic and Salmen 2008, Bäckström and Haimnar 2010, Bäckström et al. 2009, Lin and Lanouette 2013, Heazel 1988), and a higher internal fibrillation during refining, which enhances the flexibility of the fibres (Stevanic and Salmen 2008, Axelson and Simonson 1983, Fernando et al. 2015). Therefore, the scope of the present work was to study the effect of a sodium sulphite pre-treatment on an unbleached kraft pulp with a κ-number of ~45 in order to achieve a similar beneficial impact as reported for Johakimu and Bush (2011) for a κ-number of 85 In terms of tensile strength-dewatering relationship. It was intended to operate with the lowest temperature and sodium sulphite dosage possible, since higher temperatures and dosages may cause delignification and a consequent reduction of the Kappa number, implying a yield reduction (Hanhikoski et al. 2016). It was also within the scope of this study to get a better understanding of the sulphonation process on an unbleached chemical pulp by measuring the sulphonic groups present in the pulp, the yield of the process and the formation of secondary fines during refining as a flexibility indicator. The same procedure was applied also to a bleached pulp to show eventual positive effects on even lower κ-number pulps.

5.2 Materials and methods

5.2.1 Sample preparation and sulphonation pre-treatment

Pulp

All investigations have been performed using a never-dried, unbleached softwood (mixture of spruce and pine) kraft pulp having a κ-number of 45. Classified (fines-free pulp) and non-classified pulps were studied to determine the effect of the fines fraction on sulphonation.

Fines removal

To evaluate whether the presence of primary fines influences the effect of sodium sulphite and the improvement of the mechanical properties, two different sets of trials with and without primary fines (classified and non-classified pulp) have been performed. To do so, the primary fines were removed from the sample prior to sulphonation by means of a custom built pressure screen. This device is equipped with a perforated strainer having holes with a diameter of 100 µm, which is close to the one of a 200-mesh screen of a fibre length classifier according to TAPPI Test Method T 261 Cm-94 (1994). The washed samples are therefore comparable to the samples washed by means of Britt Dynamic Drainage Jar. The amount of pulp that can be washed per trial is nevertheless significantly higher when the pressure screen is used.

Chemicals

For the sulphonation trials a sodium sulphite anhydrous (Na_2SO_3, 96% purity, produced by MERCK) was used and the dosage ranged between 0.5% and 10% related to pulp oven-dried mass.

Treatment of the pulp

For each trial a certain amount of sodium sulphite (0.5%, 1%, 2%, 5% or 10%) was dissolved in water. For convenience, the amount of sodium sulphite added will be represented in the results as Na instead of Na_2SO_3. The mixture was added to 150 grams (o.d.) of pulp. Then, water was added until a 10% consistency pulp suspension was obtained. The suspension was hand-mixed and heated up to a certain temperature (105°, 90° and 75°C) and sulphonated in a digester for a certain time (20 minutes or 2 hours). The digester rotates automatically to ensure a homogeneous treatment.

Washing of the pulp

After sulphonation, the pulp was washed using a centrifuge unit. The first filtrate obtained was stored and used for COD and TOC analyses. The pulp was afterwards washed with distilled water and centrifuged again to remove any remaining sodium sulphite present in the suspension. The non-sulphonated sample used as a reference was also heated up in the digester and washed in the same way as the treated pulp to rule out any possible effect caused by heating or washing.

5.2.2 Refining of the pulp and evaluation of technological effects

Refining

The pulp was refined using a PFI Mill (ISO 5269-1, see Section 4.2.3) at different refining intensities (0, 2000, 4000, and 6000 revolutions).

Preparation of handsheets

Handsheets with a grammage of 80 g/m^2 were formed using a Rapid-Köthen handsheet former unit (DIN 54358). The sheets were stored in a conditioning chamber at 23°C and 50% relative humidity for 24 hours before testing.

Tests performed on the handsheets

Prior to sheet forming the pulp drainability by means of Schopper Riegler was determined according to ISO 5267-1. After conditioning, the thickness (DIN EN ISO 534 (2011)), air permeability (ISO 5636-3 (2013)), Gurley (ISO 5636-5:2013, Paper and board - Determination of air permeance (medium range) - Part 5: Gurley method), whiteness (ISO 11476:2010), zero-span breaking strength (T 231 cm-96) and breaking length (DIN EN ISO 1924-2 (2009)) were determined.

Fibre length distribution

The fibre length distribution as well as the fines content (based on morphological characterization) were measured with the L&W Fibre Tester Plus (Sweden) (ISO 16065-2).

5.2.3 Chemical analyses

Determination of the sulphur content

The amount of total sulphur present in the sample was determined by means of ICP-OES (inductively coupled plasma optical emission spectrometry). The sulfonated groups present in the pulp were measured by conductometric titration, following the procedure described by Beatson (1992). In this procedure, the electrical conductivity of the solution is measured after successive additions of reagent (in this case NaOH), and the values are plotted against the volume of reagent added (Kolthoff 1944). After plotting conductance vs volume, two end points are determined, which correspond to the titration of the sulphonic acid groups and of the sulphonic and carboxylic acid groups. These end points are found at the intersection of the extrapolated linear portions of the titration curves (Beatson 1992).

Yield determination

To examine whether there was any loss in pulp due to the sulphonation treatment the pulp yield was determined. For this purpose carbohydrates present in the filtrate after cooking were measured. This was indirectly done by measuring the COD (DIN 38409-H41-44) and TOC (DIN 38409-H3). A COD test measures in a direct way the amount of oxygen required to oxidize a waste sample, i.e., indirectly measures the organic matter present in the filtrate in milligrams per litre. The TOC measures the amount of carbon found in an organic compound. Constant COD and TOC values before and after

sulphonation would indicate no carbohydrates loss by leaching and therefore high yield of the process. The lignin content was also determined indirectly by measuring the κ number (ISO 302:2004) of the different samples. The κ number is an indicator of the residual lignin content in the sample. By measuring the κ-number, one could easily see when the lignin was dissolved rather than modified. Besides, a determination of structural carbohydrates was carried out for both sulphonated and non-sulphonated samples, according to a standard called "Determination of structural carbohydrates and lignin in biomass", technical report NREL TP-510-42618. By using this method it was possible to check whether the pulp composition changed during the chemical pre-treatment or remained constant in a more precise way. Thus, these measurements were intended to validate the results obtained by means of COD, TOC and κ number.

5.3 Results

5.3.1 Preliminary trials

The first preliminary trials were intended to evaluate the suitability of a sodium sulphite pre-treatment. It was intended to study the effect on the physical properties of the final product. Similar conditions as the ones investigated by Johakimu and Bush (2011) were chosen to observe if the method was suitable for the unbleached kraft pulp chosen for the trials. Besides, different temperatures were tested to analyse their influence during the treatment process. To study the influence of the temperature a 10% sodium sulphite dosage was added to the pulp at two different temperatures (90°C and 105°C). The pulp was cooked for 20 minutes. The first results regarding the tensile strength-dewatering relationship are plotted in Fig. 45. The breaking length and the SR of the pulp were the two parameters studied. A low SR corresponds to a better drainage of the pulp.

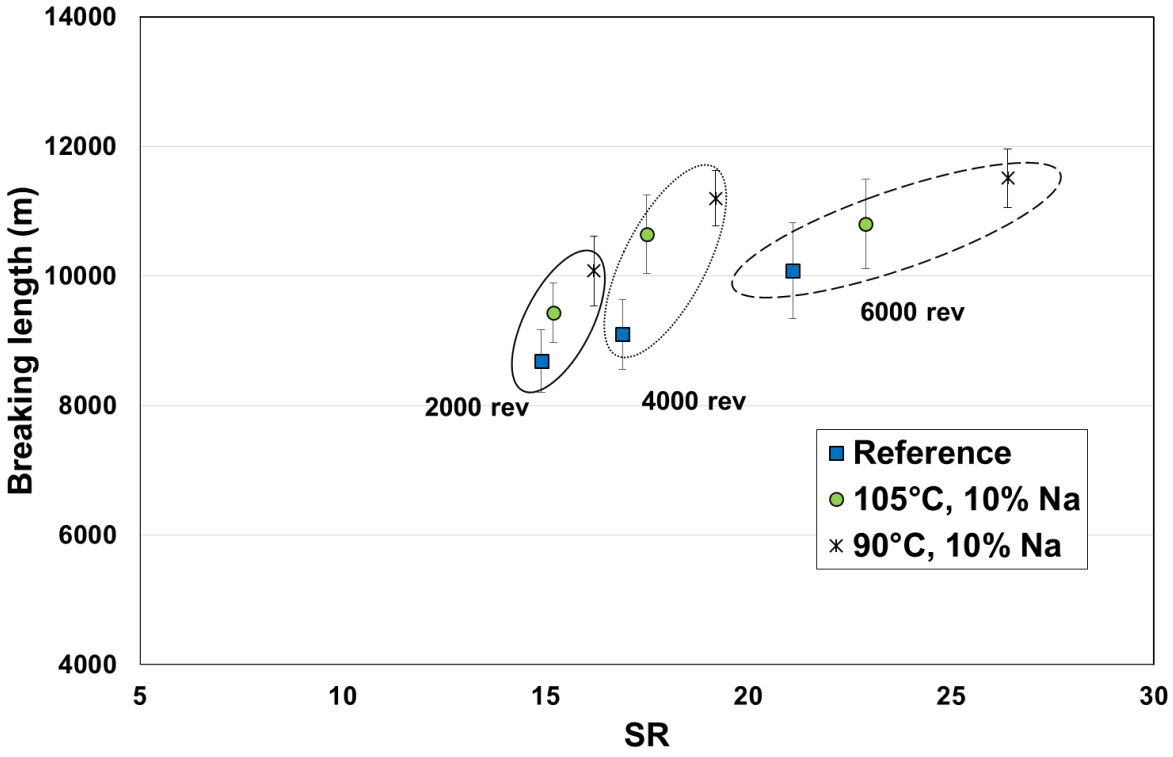

Fig. 45 *Breaking length-SR relationship of the preliminary trials*

It is evident that a higher breaking length is obtained for the sulphonated samples. There is a faster development during refining for the sulphonated samples and a better tensile strength-porosity relationship. A higher SR is obtained at given revolutions, but with a much better tensile development. The final tensile strength seems to be higher for the sulphonated pulps. This can clearly lead to a reduction in the energy used during refining. In terms of dewatering, the SR difference between the sulphonated and non-sulphonated samples is small at 2000 revolutions, whereas it starts to be evident at 4000 and especially 6000 revolutions. Positive results are obtained for the trial carried out at 105°C. Comparable SR values are obtained at 2000 and 4000 revolutions, indicating that a better breaking length is not related to a poor dewatering of the pulp. The trials performed at 90° show a slightly higher SR at 2000 revolutions. This difference between sulphonated and non-sulphonated samples increases at 4000 revolutions and is significant at 6000 revolutions.

The relationship tensile strength-porosity can be studied by representing the breaking length vs air permeability (Gurley), as in Fig. 46.

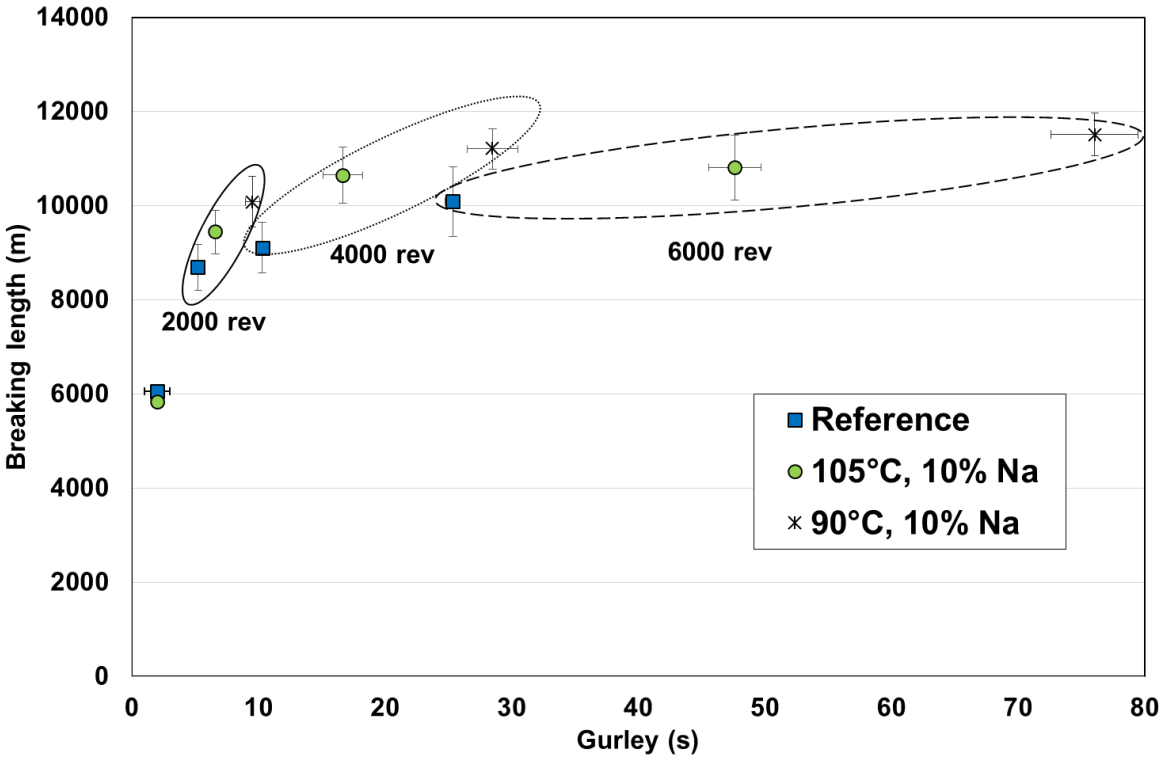

Fig. 46 *Breaking length-Gurley relationship of the preliminary trials*

It can be observed also in this diagram that refining the pulp after pre-treating it with Na_2SO_3 led to a higher breaking length of the formed handsheets, i.e., a faster development of the strength properties. This effect was noticeable for both sulphonated samples. It seems that a pre-treatment with sodium sulphite enhanced the breaking length of the final handsheets, and at the same time increased the Gurley, indicating a lower porosity of the handsheets. The increase in the Gurley number was more pronounced for the highest refining intensity (6000 revolutions). The breaking length of the sulphonated fibres reaches a maximum at 4000 revolutions, and then it levels off. From 4000 to 6000 revolutions, only the Gurley increases. At this point it can be concluded that fibres are over-treated, which causes shortening and fines formation. Both can clog the pores of the paper network and therefore cause a decrease of the air permeability and further densification without additional increase of strength. On the other hand, the non-sulphonated fibres still increase their breaking length from 4000 to 6000 revolutions. This is an indicator of a faster development of the fibres during refining after pre-treating them. Less refining intensity is needed to achieve a certain breaking length. As it can be seen, the breaking length of the sulphonated sample at 105° and 4000 revolutions is similar to the breaking length obtained for the reference at 6000 revolutions. Regarding the different temperatures studied for sulphonated samples, better results are obtained by using a lower temperature, i.e., 90° delivers better results than 105°C. A lower temperature was also associated with a high yield of the process, since lignin is less likely to leach at low temperatures (Eriksson et al. 1991). The pre-treatment can be used at low temperatures, which saves heating energy and also preserves the carbohydrates

present in the sample, leading to a higher yield of the process. The previously mentioned over-treatment of the fibres sulphonated at 90°C causes an increase in Gurley and for the same reasons an increase in the SR. A porous structure facilitates the dewatering of the pulp, enabling water to exit easily, as stated by Joutsimo and Asikainen (2013). Thus, a reduction in the porosity of the handsheets hinders the dewatering process, leading to higher SR values. According to the results presented in Fig. 45 and Fig. 46, a pre-treatment with sodium sulphite was seen as a promising method to reduce the energy needed to refine unbleached kraft pulp. By adding 10% sodium sulphite, 2000 revolutions could be spared and comparable results in terms of breaking length could be obtained. Hence, the process was studied more in detail, with the main focus on evaluating the effect of the sodium sulphite dosage, and to study the process even at lower temperatures. From now on, all trials were carried out being 75°C the temperature of the treatment. Besides, the reaction time was increased from 20 minutes to 2 hours to make sure that all dosed chemical has enough time to react.

5.3.2 Effect of sodium sulphite dosage on a fines-free unbleached kraft pulp

To evaluate the process in a simplified way, the primary fines were removed from the pulp using a pressure screen (see Section 4.2.2). By doing so it was possible to observe the effect of the pre-treatment on the long fibres. Moreover, it is also known that primary fines may cause a higher consumption of chemicals. For example, the consumption of hydrogen peroxide during bleaching can be reduced to 7 kg/t pulp for a given brightness (Bäckström and Brännvall 1999). After removing the primary fines from the pulp, the remaining sample was sulphonated and treated. Four different trials using non-sulphonated pulp (reference) as well as sulphonated pulps with a 2%, 5% and 10% dosage of sodium sulphite were performed.

The obtained breaking length at a given PFI refining intensity (0, 2000, 4000, and 6000) is shown in Fig. 47.

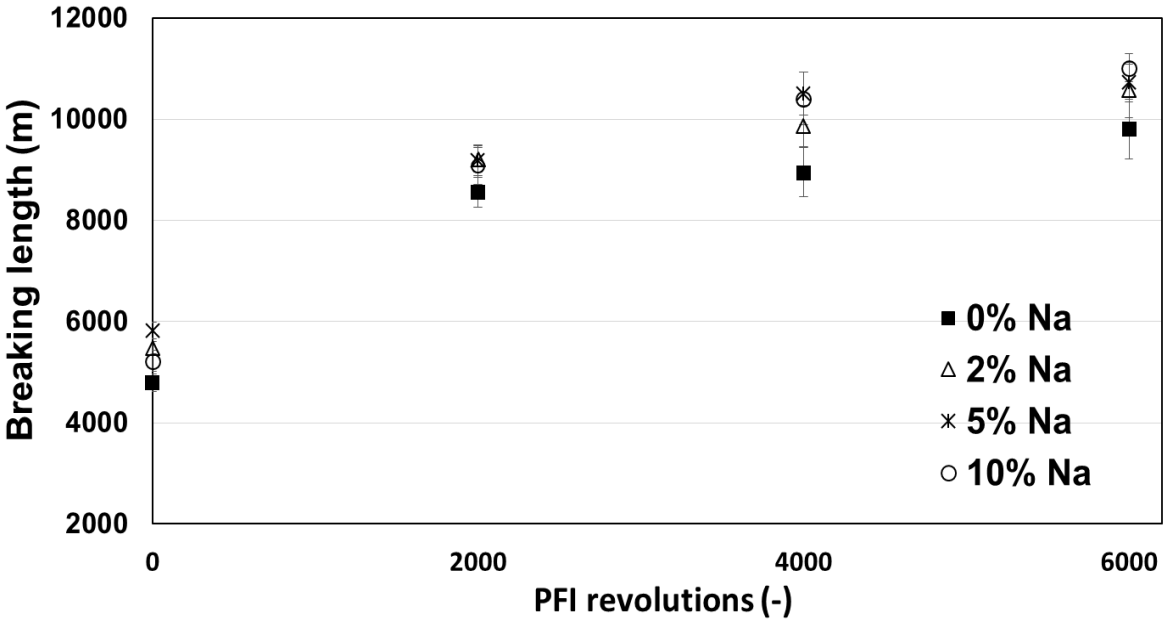

Fig. 47 *Breaking length development during refining of the fines-free pulps (unbleached kraft pulp)*

From the results it is noticeable that even in the unrefined state a higher breaking length for the sulphonated samples was achieved. The increase in breaking length is also visible for the different refining intensities (2000, 4000, and 6000). The development of the breaking length seems to be almost independent from the sodium sulphite dosage. The increase levels out from 4000 to 6000 revolutions. Besides, the increase in breaking length is not that pronounced for non-sulphonated samples. This is an indication that the sodium sulphite is positively influencing the breaking length development during refining also at lower temperatures (75°C). It is then possible to achieve a higher breaking length by adding 2% of sodium sulphite. To observe the effect of the pre-treatment, the density is plotted vs the breaking length in Fig. 48. It can be seen that in the unrefined state the sulphonated samples show a higher density, irrespective of the sodium sulphite dosage. This could indicate a higher flexibility of the fibres leading to a higher relative bonded area and therefore to a better breaking length. This effect is no longer visible after refining the pulp. At 6000 revolutions the density is almost identical for all samples.

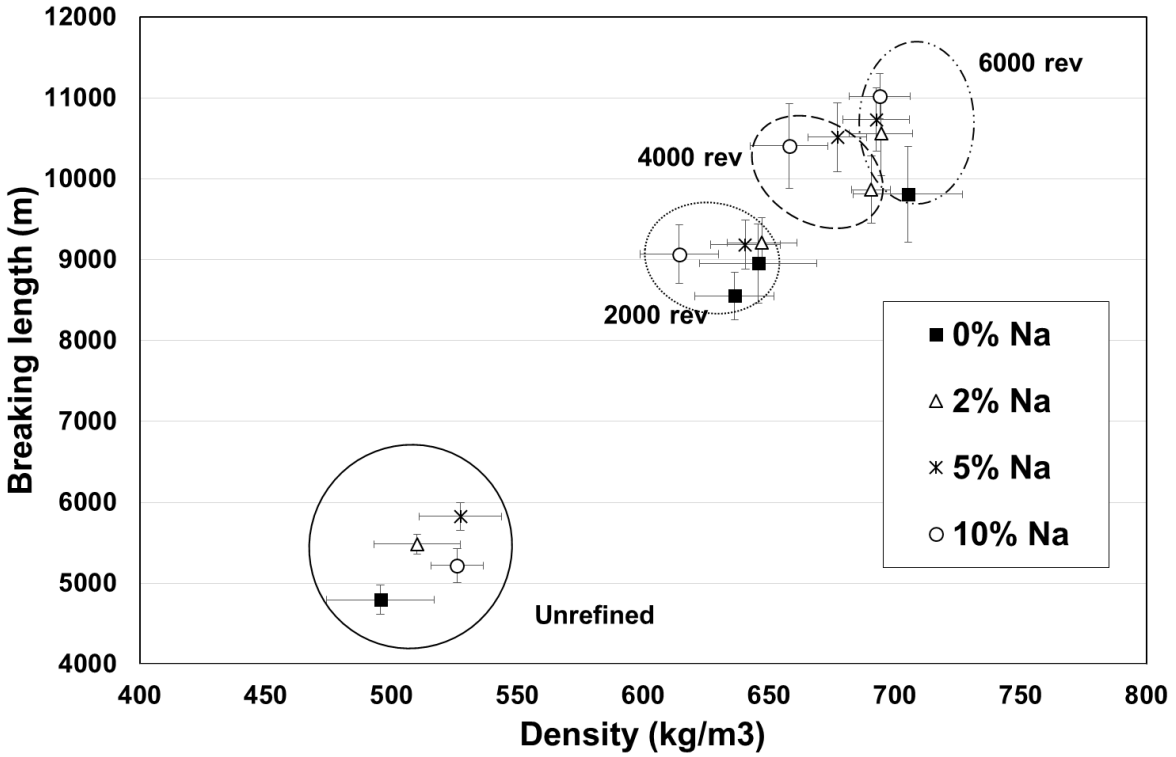

Fig. 48 *Breaking length-density relationship of the fines-free pulps (unbleached kraft pulp)*

Similar conclusions can be obtained by representing the breaking length vs Gurley, as in Fig. 49. Here the enhancement of the breaking length for the sulphonated samples is evident. The best results are obtained at 4000 revolutions, where a higher breaking length at a comparable Gurley is obtained for the sulphonated sample. In these trials, the sodium sulphite dosage (2%, 5% or 10%) does not seem to play a role in the process since the increase in the breaking length seems to be almost constant, irrespective of the dosage. Almost identical results are obtained for the three studied dosages, which indicates that the sodium sulphite is added in excess and does not further react with the pulp. Also, it indicates that 2 hours is enough time for the chemicals to react. Again, the breaking length development of the sulphonated samples seem to level out at 6000 revolutions. At this point only the porosity is reduced, which increases the Gurley number. Nevertheless, the breaking length still increases from 4000 revolutions to 6000 revolutions, unlike previous trials. This is probably due to the separation of the fines prior to refining.

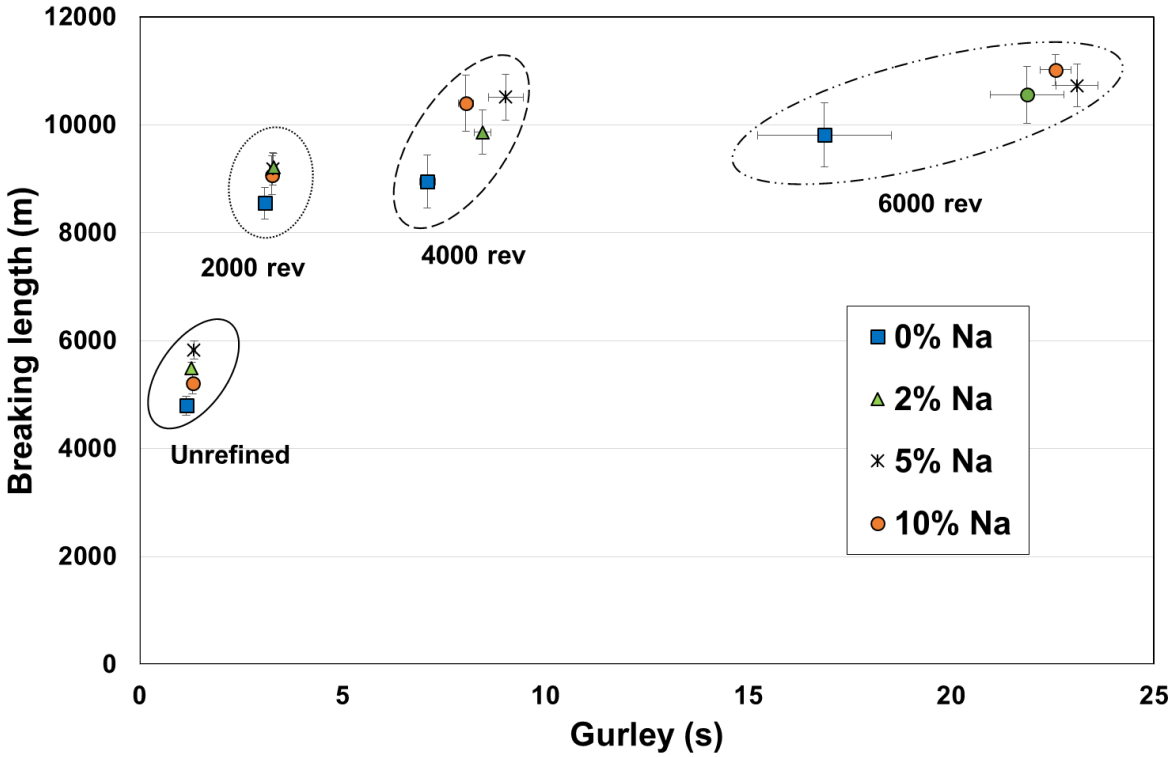

Fig. 49 *Breaking length-Gurley relationship of the fines-free pulps (unbleached kraft pulp)*

The effect on the dewatering was also studied. The breaking length vs SR of this set of trials is plotted in Fig. 50.

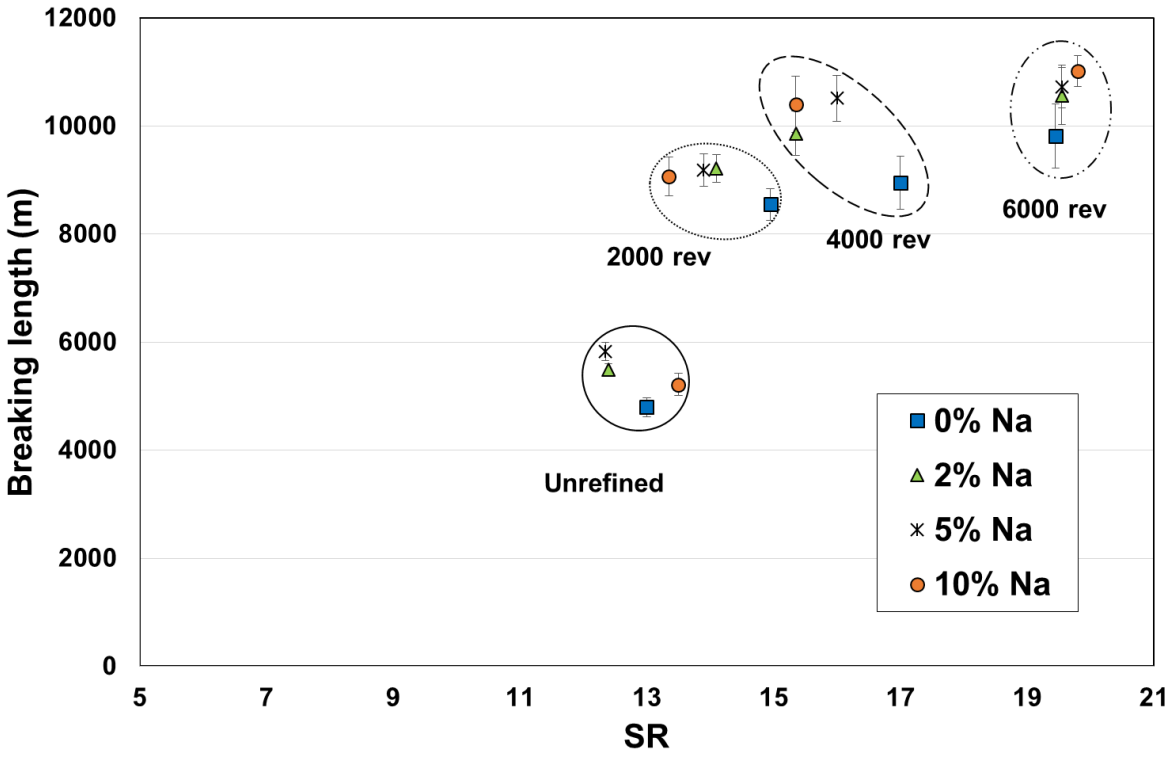

Fig. 50 *Breaking length-SR relationship of the fines-free pulps (unbleached kraft pulp)*

There are no big differences between the SR of the different sulphonated samples, according to Fig. 50. Regarding the reference pulp, it seems that the sulphonated pulps show a slightly lower SR. This may indicate a higher flexibility of the fibres, which reduced the fines formation. The fines formation seems to be stronger than the effect of densification due to flexibilization at 2000 and 4000 revolutions. At 6000 revolutions the SR is identical for the four different trials. This confirms that the results obtained with 2% dosage are as good as adding 10%, and also that it does not hinder the dewatering of the pulp. A special interest was to study the thickness of the formed handsheets, as an indicator of the flexibility and conformability of the fibres. The results obtained for the non-sulphonated pulp and the sulphonated pulp using 10% sodium sulphite are represented in Fig. 51.

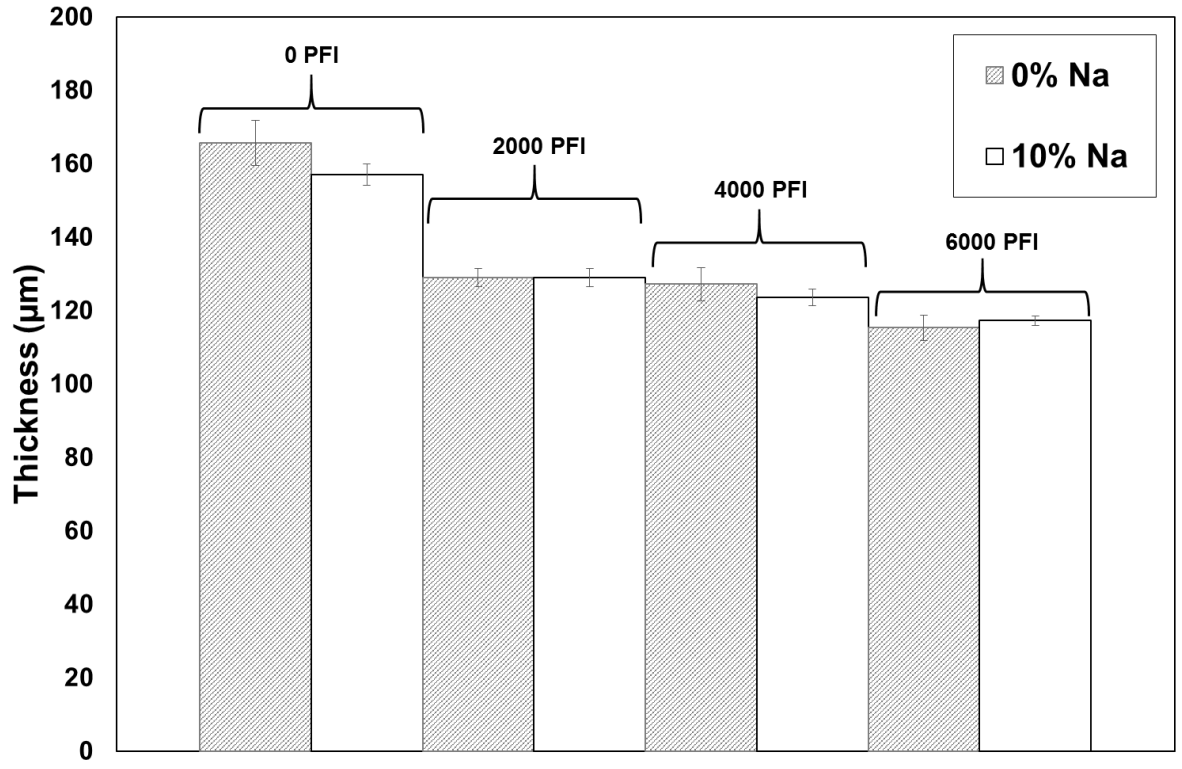

Fig. 51 *Thickness difference caused by sulphonation on the fines-free pulps ((unbleached kraft pulp, 10% sodium sulphite)*

It is apparent that the handsheets formed using a sulphonation pre-treatment show a lower thickness in the unrefined state. This could confirm the claim of a higher flexibility of the sulphonated fibres seen in the density-breaking length diagram (Fig. 48). The fibres are more flexible after sulphonation, which leads to a better conformability of the fibre network and therefore cause a reduction of the thickness. This effect is no longer visible after refining the handsheets at either 2000, 4000 or 6000 PFI revolutions. The higher flexibility of the unrefined sulphonated fibres is minimized by the effects induced through refining. Similar effects are obtained when the sodium sulphite dosage is reduced to

2%. The obtained results are plotted in Fig. 52. In this case, the effect is visible even at 4000 revolutions, which proves that the fibres are modified during sulphonation and their flexibility is enhanced, causing a reduction of the thickness at 0, 2000 and 4000 revolutions. At 6000 revolutions the effect vanishes. Another significant result to point out is the reduction of the standard deviation for the sulphonated samples. As observed in both figures, the values of the sulphonated samples are closer and therefore the standard deviations of the measurements are smaller compared to the reference. This could mean that due to sulphonation the fibres are refined in a more homogeneous way, forming also more uniform handsheets, where the thickness differences between different points of the handsheets are minimized.

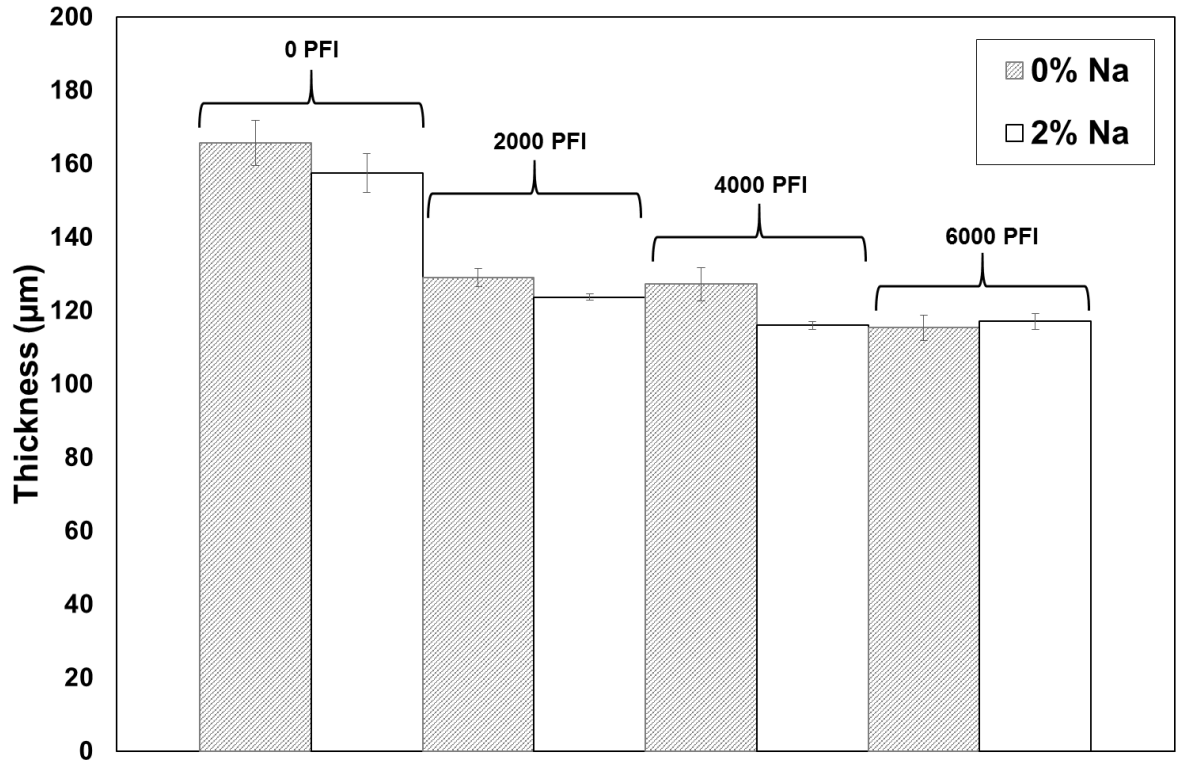

Fig. 52 *Thickness difference caused by sulphonation on the fines-free pulps (unbleached kraft pulp, 2% sodium sulphite)*

5.3.3 Effect of sodium sulphite dosage on an unbleached kraft pulp containing primary fines

After studying the sodium sulphite pre-treatment on a fines-free pulp, the same procedure was applied to the original pulp containing primary fines. It was of interest to study the alkali dosage needed to achieve the same increase on the breaking length, as shown in Fig. 47 for the fines-free pulp. The trials were performed with 0.5%, 1% and 2% sodium sulphite dosage, as 5% and 10% seemed to be in excess. The obtained results were then compared to the pulp free of primary fines.

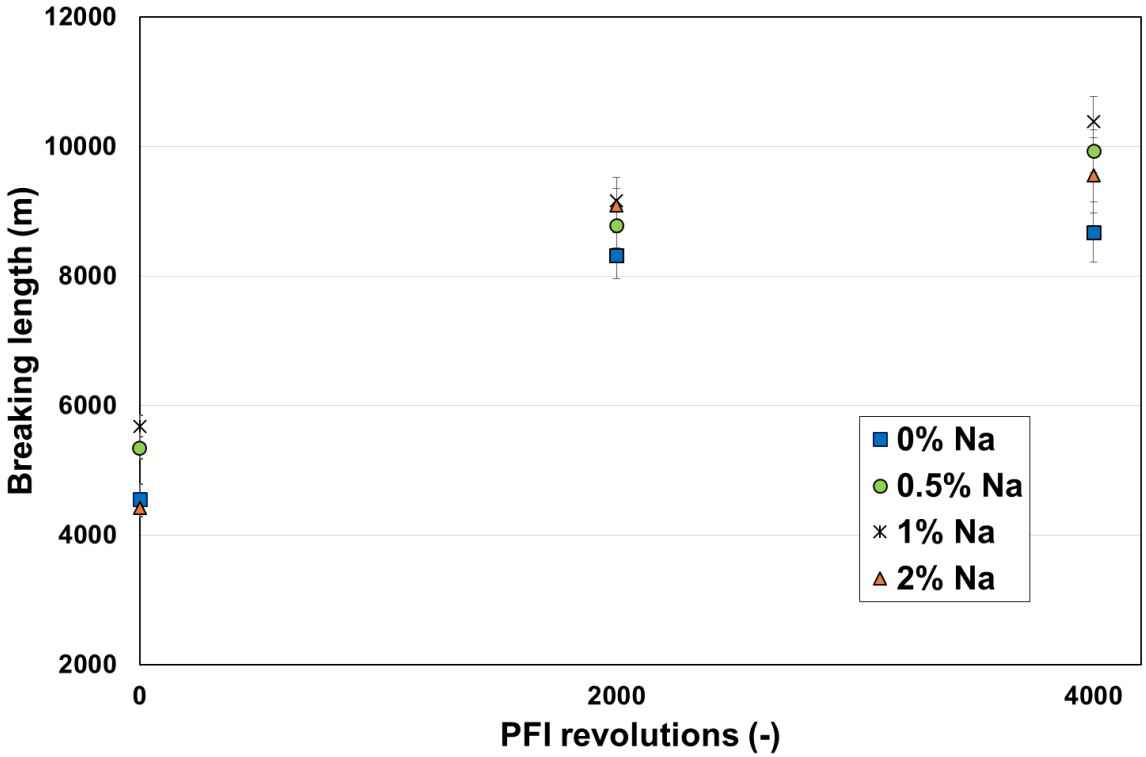

Fig. 53 *Breaking length development during refining of the pulps containing primary fines (unbleached kraft pulp)*

In Fig. 53 the breaking length of the handsheets containing primary fines is plotted at different PFI refining intensities. It is noticeable that the development of the breaking length is faster for the sulphonated samples. A higher breaking length is obtained for the sulphonated samples compared to the reference at a given refining intensity. The results are similar to the ones obtained for the fines-free pulp (Fig. 47). Therefore, it is clear that the pre-treatment with sodium sulphite is suitable even if primary fines are originally present in the pulp. The fines material does not seem to consume sodium sulphite to a relevant extent, and therefore the pre-treatment effect is not reduced by the presence of fines. The density of the handsheets formed is also plotted vs the breaking length in Fig. 54. It is noticeable in the unrefined state that the sample containing 2% of sodium sulphite gave a higher density compared to the other three samples. Nevertheless, a higher breaking length compared to the non-sulphonated pulp is observed for the pulps containing 0.5 and 1% sodium sulphite. The effect is, as observed for the fines-free pulp, no longer observed after refining. There are almost no differences in terms of density at 2000 or 4000 revolutions. The breaking length-porosity relationship for the pulp containing primary fines is plotted in Fig. 56.

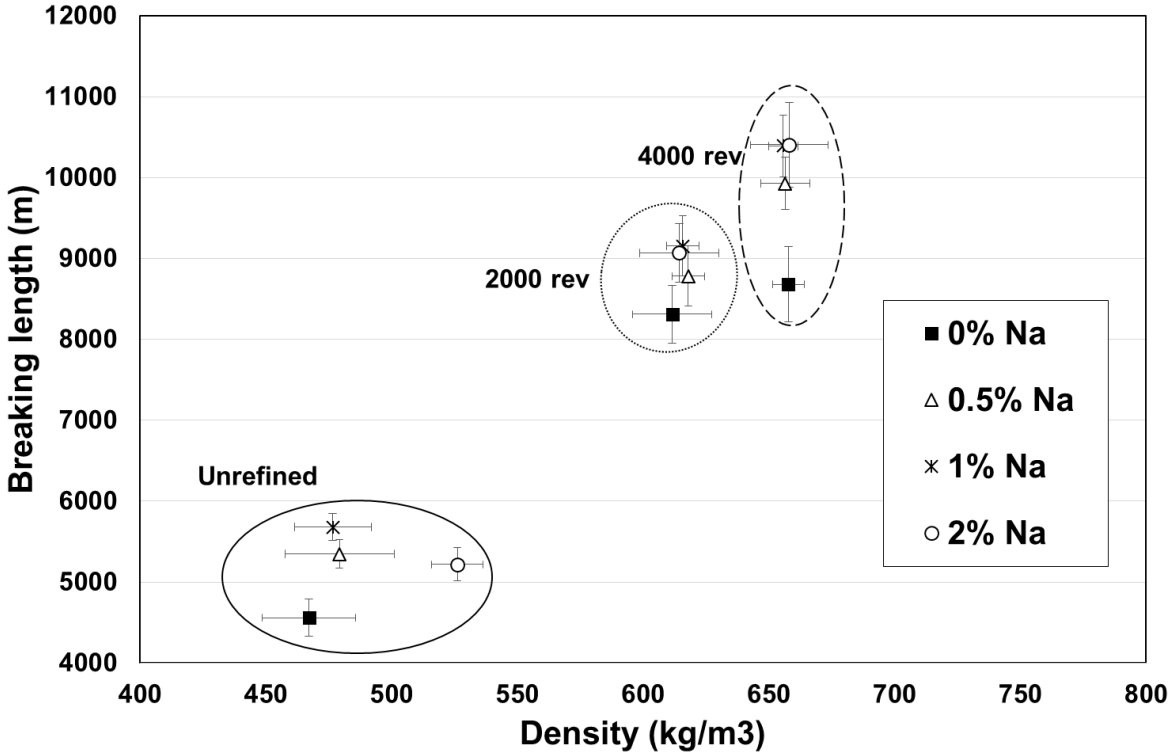

Fig. 54 *Breaking length-density relationship of pulps containing primary fines (unbleached kraft pulp)*

As a confirmation of the faster development of the breaking length due to sulphonation irrespective of the presence of primary fines, the results obtained for samples containing 2% sodium sulphite with and without primary fines are plotted in Fig. 55. Here, it can be observed a similar development of the breaking length-Gurley number for both trials. The sulphonated samples show a higher breaking length at a comparable air permeability, as shown in a previous figure (Fig. 49). The difference between the sulphonated sample and the reference was comparable at each refining intensity, irrespective of the presence of primary fines.

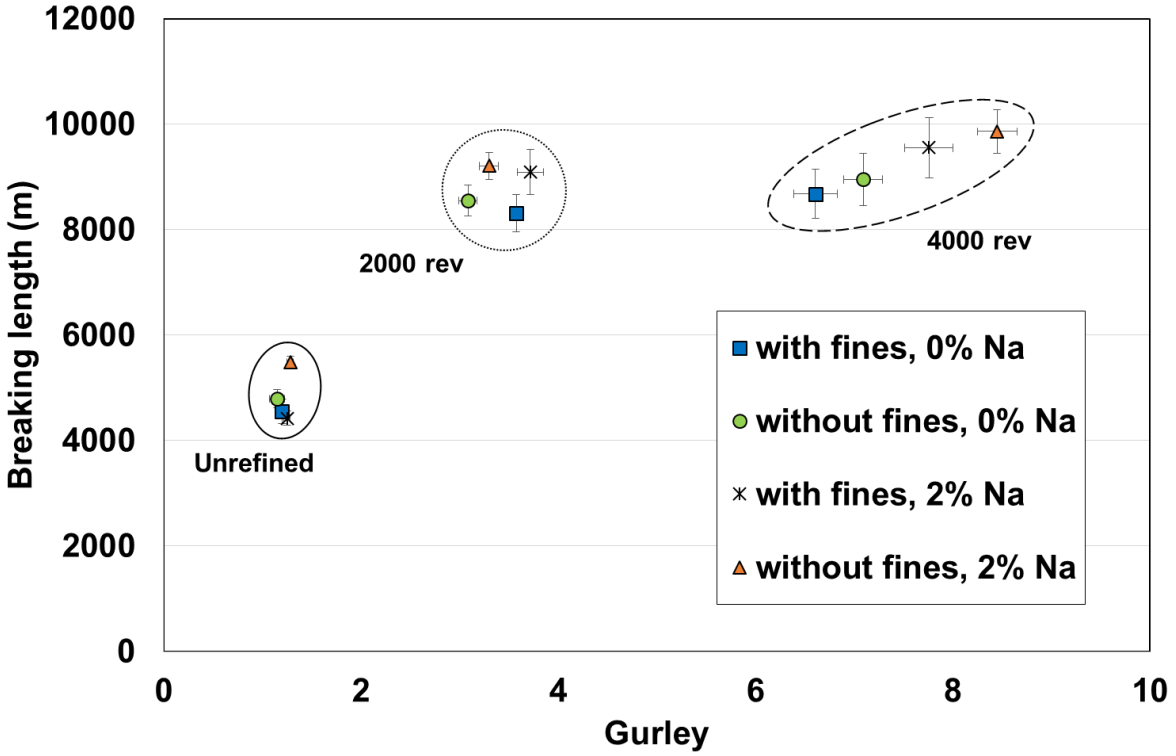

Fig. 55 *Influence of primary fines on the Breaking length-Gurley relationship (unbleached kraft pulp)*

Table 9 shows the increase in the breaking length for the tests performed, with and without primary fines. This increase in % is related to the non-sulphonated sample, which was used as a reference.

Table 9 *Breaking length improvement (in %) for different samples with and without primary fines at 2000 and 4000 PFI revolutions (unbleached kraft pulp)*

Na_2SO_3 dosage [%]	Primary fines	Breaking length improvement[%] 2000 rev. PFI	Breaking length improvement[%] 4000 rev. PFI
0.5	yes	5,69	14,4
1	yes	10,2	19,7
2	yes	7,14	10,09
2	no	7,69	10,16
5	no	6,05	16,21
10	no	7,41	17,40

The results show that there is always a positive effect on the breaking length for every sulphonation trial performed, even for a low alkali dosage (0.5%). When comparing the results for a 2% sodium sulphite dosage with and without fines, it is apparent that there is no significant difference (7.14%

higher breaking length with primary fines and 7.69% without primary fines at 2000 revolutions), as already seen in Fig. 55. This indicates that the presence of fines does not seem to play a role on the sulphonation process as well as on the development of the breaking length during refining. Besides, it also confirms that primary fines do not increase the chemical consumption of the process. The pre-treatment with sodium sulphite is effective regardless of the presence of primary fines in the pulp. There are some variations in the results when using different sodium sulphate dosages, but the increase in breaking length is similar. Therefore, one can conclude that a pre-treatment with a 0.5% dosage yields almost the same effect as adding 2% of sodium sulphite if the primary fines are present. Thus, it looks quite promising for an industrial implementation. For the primary fines-free pulp, the effect is quite similar, irrespective of the alkali dosage. The improvement of the breaking length is almost the same for the 2%, 5% and 10% sulphonated samples. It is possible to compare these results with those obtained in previous studies. For instance, Kringstad and Olausson (1974) achieved an 8.33% breaking length increase (compared to the non-sulphonated pulp) at 3000 PFI revolutions, 100°C and 10% sodium sulphite dosage. This improvement is close to the one obtained in the present study at 2000 PFI revolutions (10% sodium sulphite dosage, 7.41% increase, without primary fines). Besides, a comparable increase in the breaking length was achieved using a lower sodium sulphite dosage (2% sodium sulphite dosage, 7.69% increase, without primary fines). Johakimu and Bush (2011) were able to reduce 1000 revolutions during PFI mill refining and still achieve a similar tensile strength. The results with sulphonated pulp and PFI refining at 5000 revolutions and non-sulphonated pulp and PFI refining at 6000 revolutions were in the same range. In this case the sodium sulphite dosage was 10%. In the present study, similar results were observed. The breaking length of sulphonated pulp (10% dosage) refined at 2000 PFI revolutions was 9068 m, whereas for the non-sulphonated pulp refined at 4000 revolutions was 8954 m. Therefore, 2000 PFI revolutions could be spared while maintaining a similar breaking length.

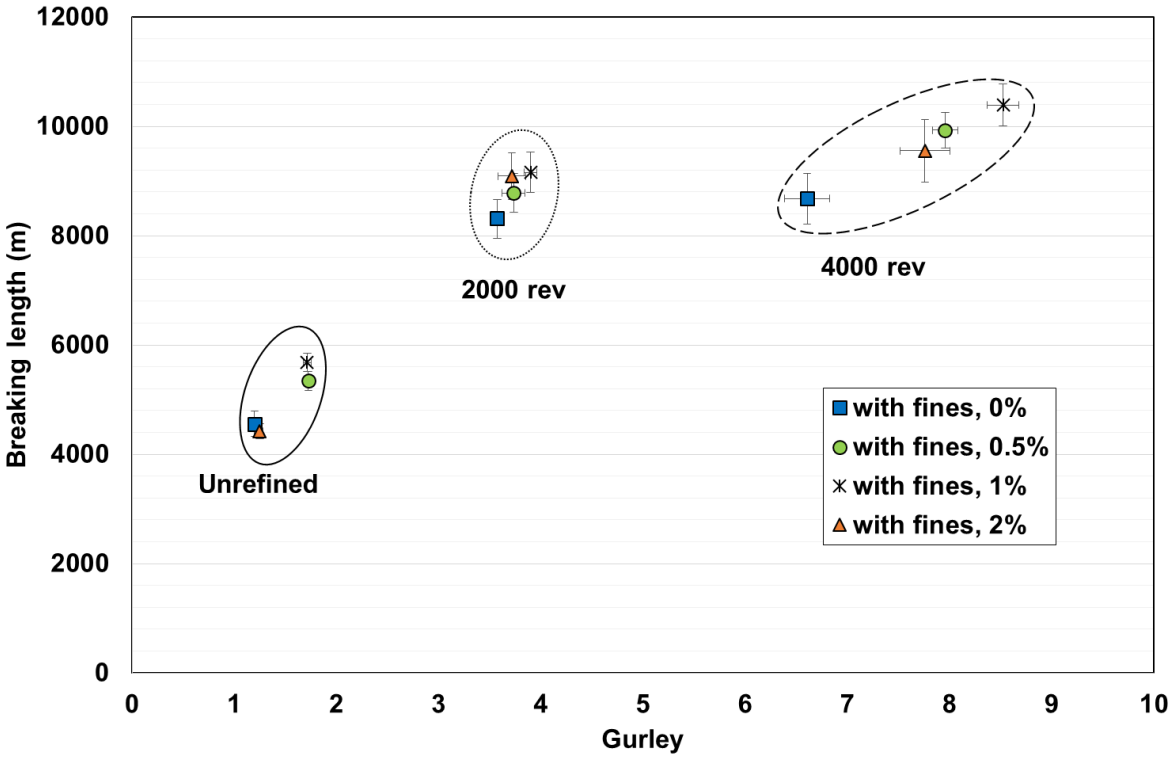

Fig. 56 *Breaking length-Gurley relationship of the pulps containing primary fines (unbleached kraft pulp)*

To evaluate the influence of sulphonation on the dewatering behaviour of the pulp, the SR number was also determined. The obtained results are shown in Fig. 57.

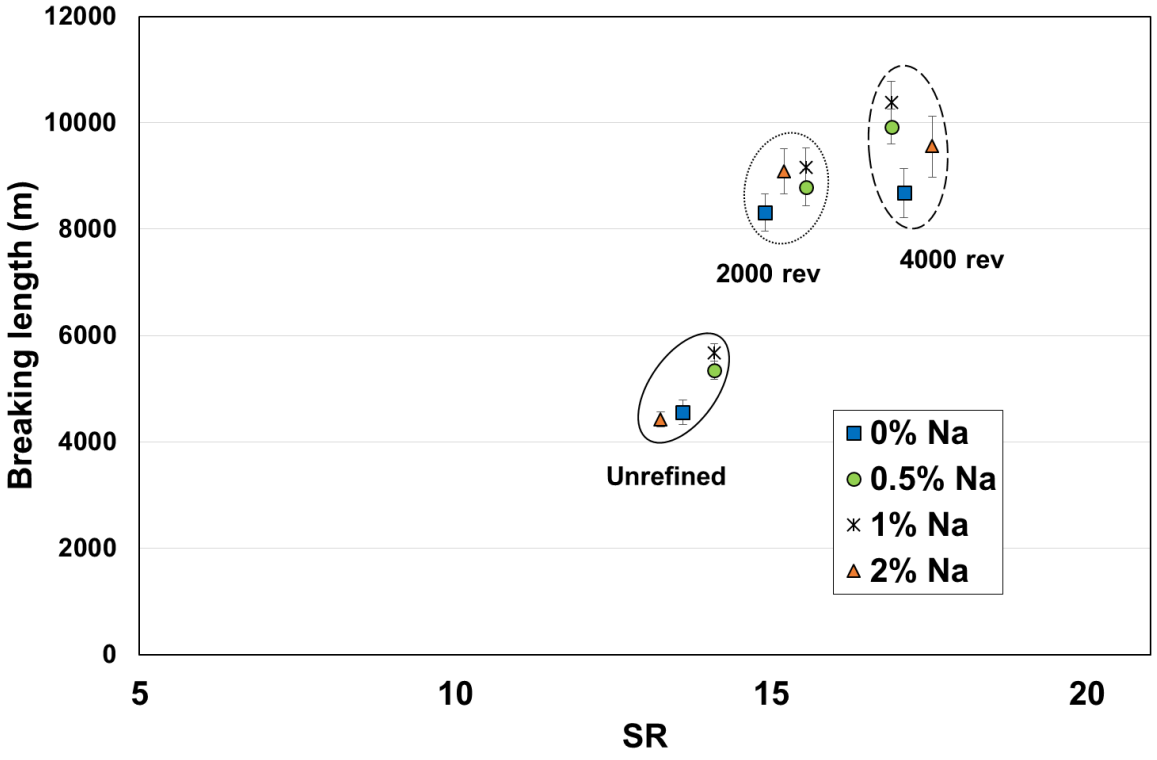

Fig. 57 *Breaking length-SR relationship of the pulps containing primary fines (unbleached kraft pulp)*

From Fig. 57 it can be seen that there is not a significant difference in the SR at a certain refining intensity. A higher breaking length was obtained after refining (2000, 4000) for the different sulphonated samples. The SR increased slightly at 2000 PFI revolutions, although the effect is not visible at 4000 revolutions. At this refining intensity, the SR of the different samples are almost identical, irrespective of the sodium sulphite dosage. It can be concluded that the addition of sodium sulphite does not affect the pulp drainage to a relevant extent. The SR is only affected by the refining intensity, i.e., the higher the refining intensity, the higher the SR. Similar results were obtained for the fines-free pulp (Fig. 50). Regarding the thickness variation observed for the fines-free pulp, the same measurements were carried out for the pulps containing primary fines. The results for the 1% sodium sulphite pulp (containing primary fines) as well as the reference are plotted in Fig. 58.

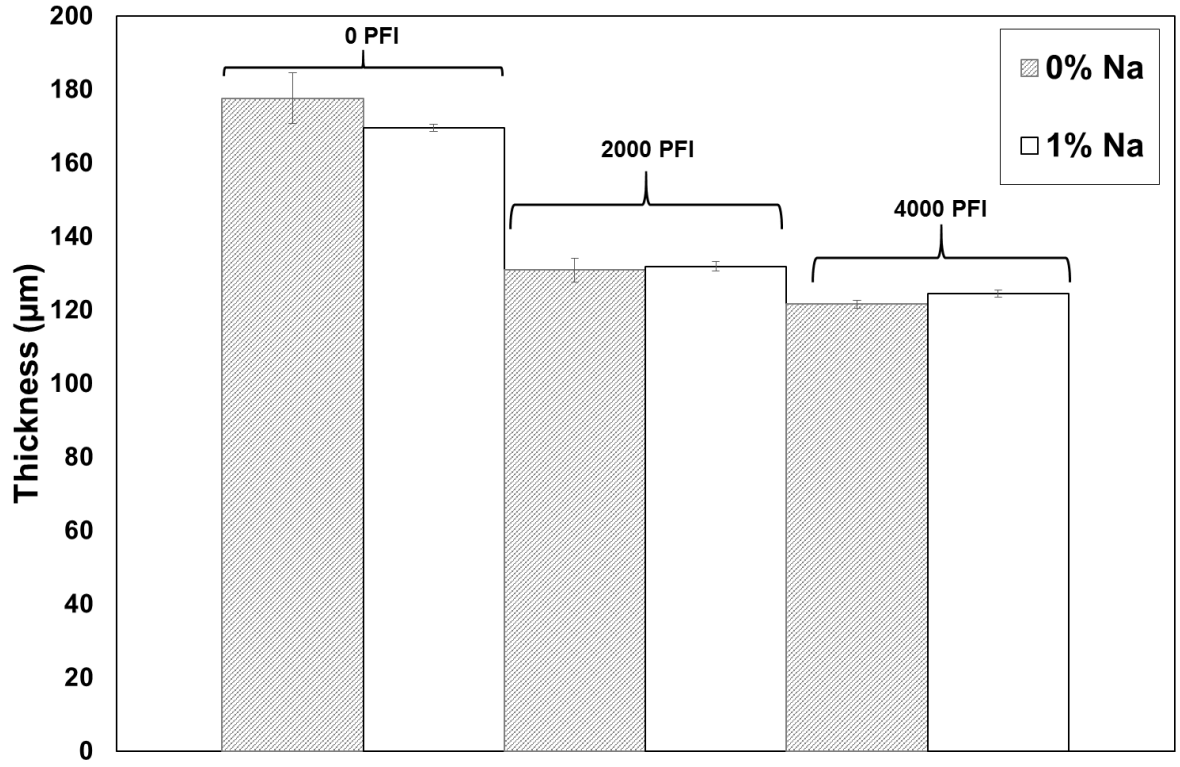

Fig. 58 *Thickness difference caused by sulphonation on pulps containing primary fines (unbleached kraft pulp, 1% sodium sulphite)*

These results provide similar information as the ones obtained for the fines-free pulp. A lower thickness value was obtained for the sulphonated handsheets, indicating that the sulphonated samples lead to more compact and denser handsheets. The density, as observed in Fig. 54, was also slightly higher compared to the reference. This effect disappears after refining at 2000 or 4000 revolutions. Moreover, the standard deviation is once again smaller for the sulphonated samples compared to the reference, indicating more homogeneous handsheets in terms of thickness. The presence of primary fines prior to treatment does not influence the behaviour of the fibres before and during refining. This

correlates well with the obtained results in terms of tensile strength-dewatering. Thus, primary fines do not seem to play a role in the process, as previously stated. Same results were obtained even for the lowest dosage of sodium sulphite evaluated (0.5%), and are represented in Fig. 59.

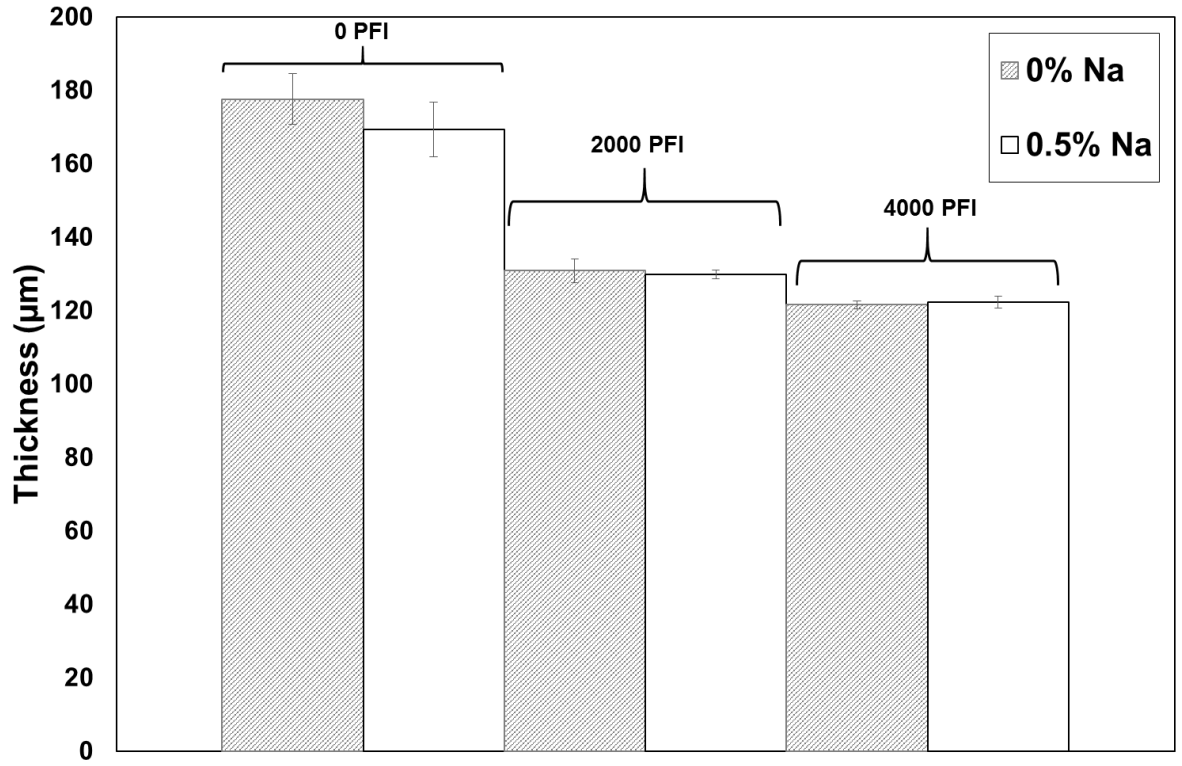

Fig. 59 *Thickness difference caused by sulphonation on pulps containing primary fines (unbleached kraft pulp, 0.5% sodium sulphite)*

5.3.4 Effect of sodium sulphite dosage on a bleached sulphite pulp

A similar procedure was carried out for bleached sulphite pulp, which has a much lower lignin content compared to the unbleached kraft pulp. The intention was to see whether positive effects reported previously could be observed even at a lower lignin content. A higher flexibilization of the fibres would be of utmost importance for sulphite pulps as they are more brittle on a fibre level and show a lower refining resistance. In these trials, the pulp was treated at 75°C and the sodium sulphite dosage was 10%. The non-treated pulp was handled in the same way. The density-breaking length relationship is plotted in Fig. 60. As it can be observed, there were not noticeable differences between the sulphonated and the non-sulphonated pulps, neither in terms of breaking length nor in density. The effect observed during the pre-treatment of the unbleached kraft pulp was no longer observed, i.e., the sulphonated pulp did not show an increase of the density in the unrefined state. Besides, the breaking length was even lower for the sulphonated pulp. This result was not observed in the previous trials. The obtained results in terms of breaking length-Gurley are plotted in Fig. 61.

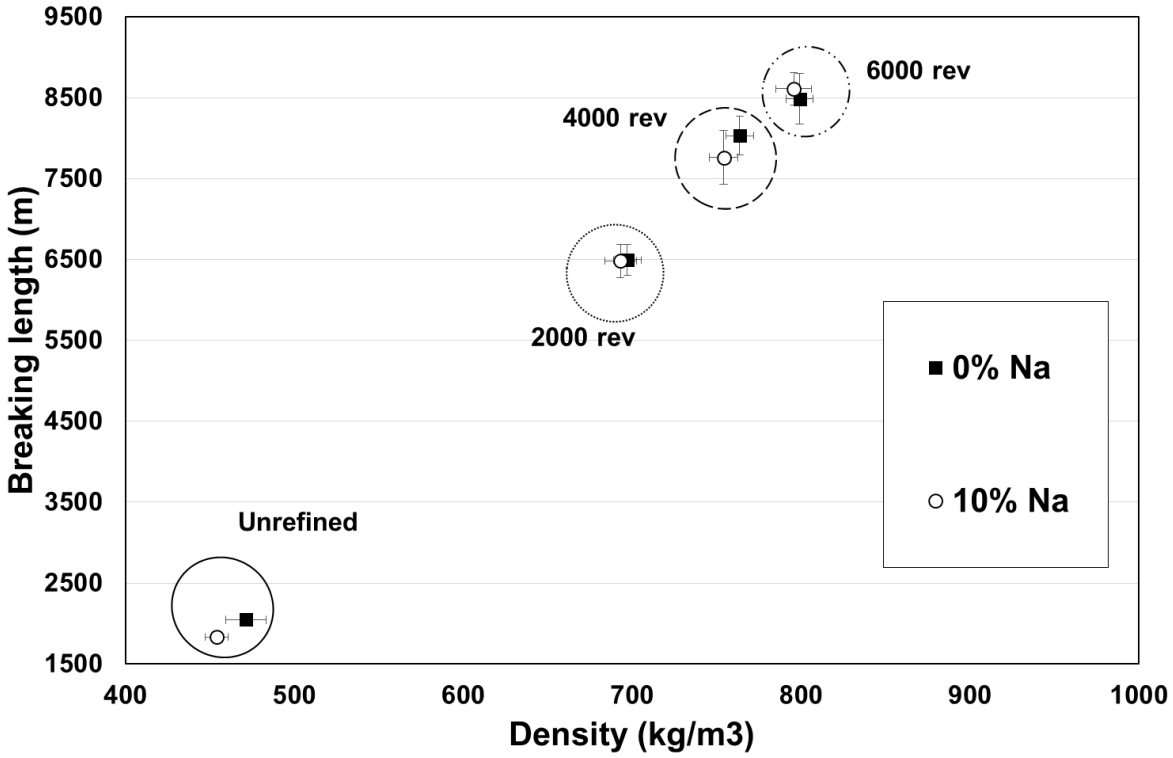

Fig. 60 *Breaking length-density relationship of a bleached sulphite pulp before and after sulphonation*

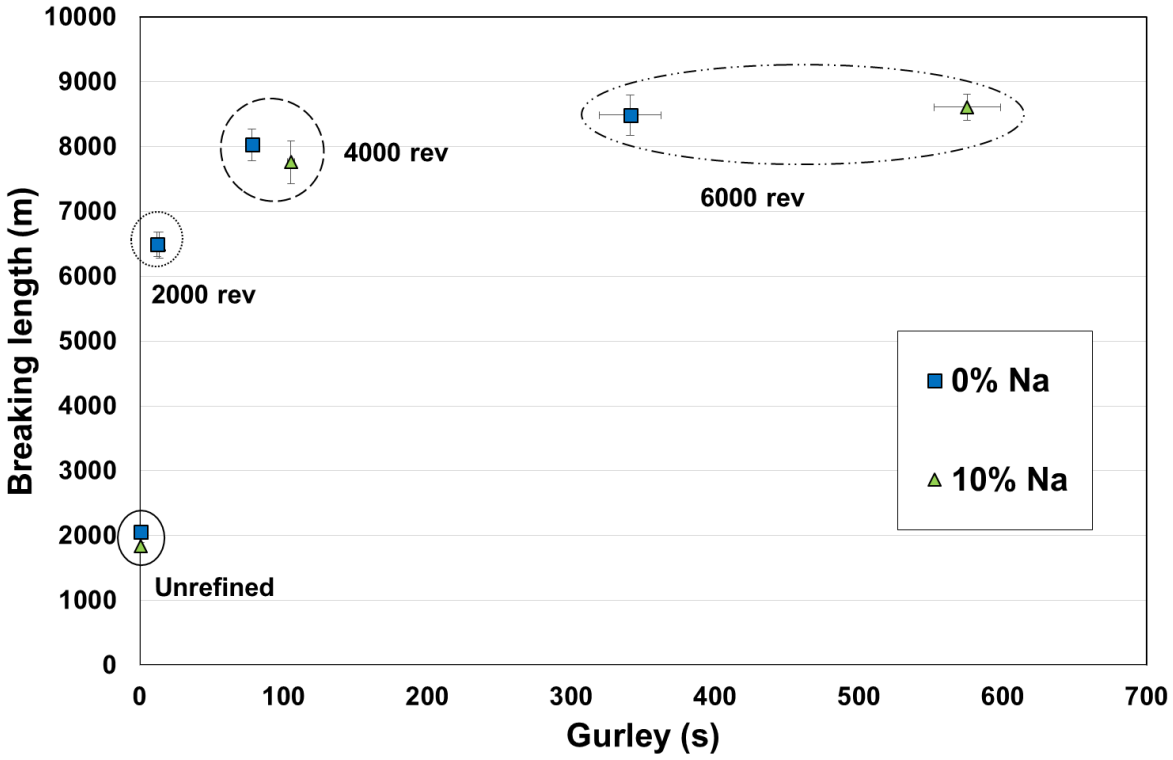

Fig. 61 *Breaking length-Gurley relationship of a bleached sulphite pulp before and after sulphonation*

After observing the results, it can be concluded that the pre-treatment does not enhance the breaking length of bleached sulphite pulp. The effect was noticeable already in the unrefined state for unbleached kraft pulp. In case of bleached sulphite pulp, the sulphonated pulp has even a lower breaking length compared to the reference pulp. At 2000 revolutions the results are identical in terms of breaking length and Gurley, which proves that no positive effect is visible. At 4000 and 6000 revolutions, the sulphonated sample exhibit a higher Gurley number, whereas the breaking length remains similar to the reference. A higher porosity of the handsheets is obtained for the reference, although the fines content and fines length distribution is similar for both samples, as seen in Fig. 63. In this diagram the fibre length of the fines and short fibre fraction (below 400 µm) is plotted versus the percentage of fibres related to length. By doing so it is possible to observe whether sulphonated pulps produce a different amount of fines during refining or even in the unrefined state. No differences in terms of thickness were found, as seen in Fig. 62, which would have explained a different mass distribution of the handsheets. The thickness in the unrefined state is even higher for the sulphonated sample. Besides, the observed reduction of the standard deviation after sulphonation is not observed in this case. A comparable standard deviation was obtained for both samples at each refining intensity. This visible effect on the Gurley number is therefore hard to explain. Regarding the dewatering effect of this sulphonated pulp, the results are given in Fig. 64.

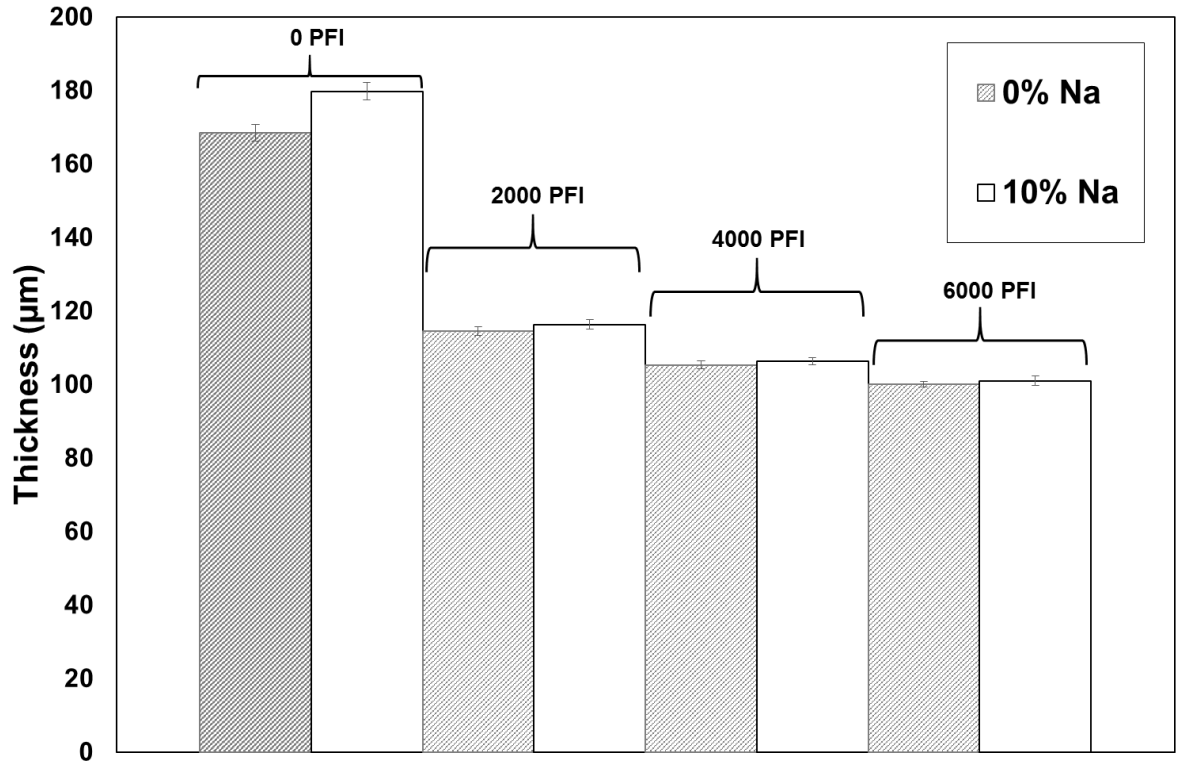

Fig. 62 *Thickness difference caused by sulphonation on a bleached sulphite pulp (10%)*

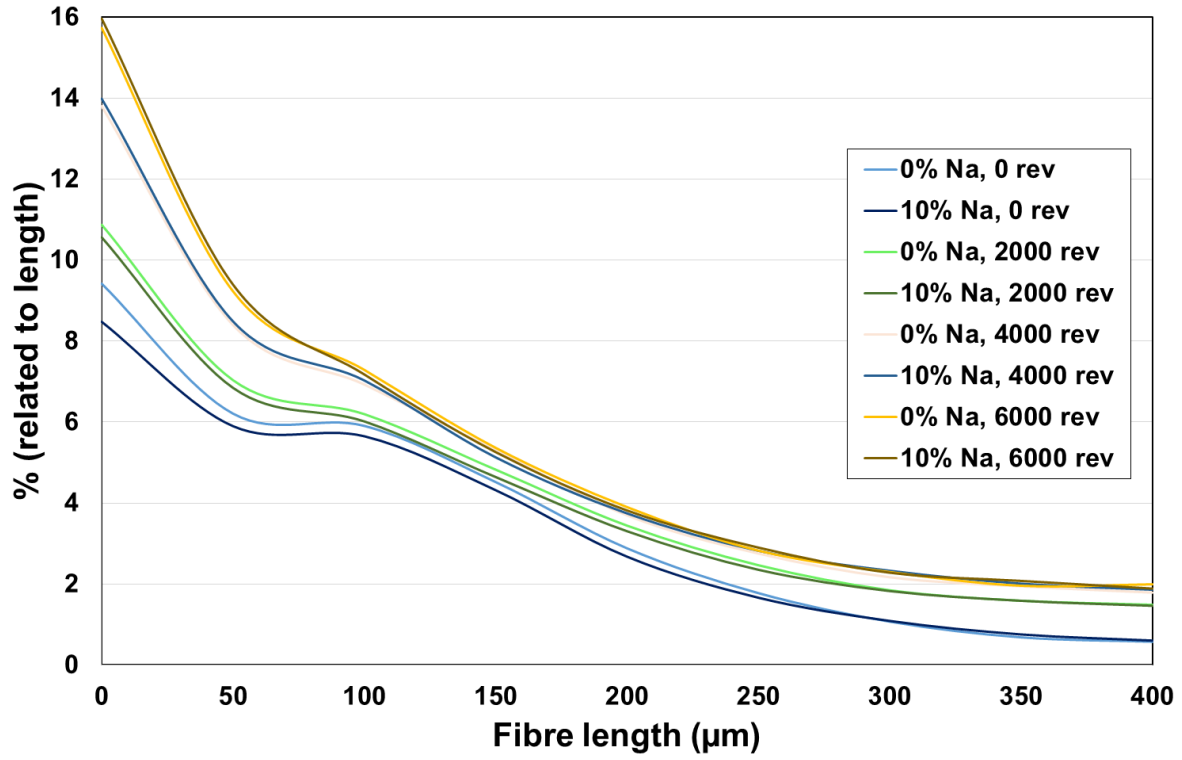

Fig. 63 *Effect of sulphonation (10% sodium sulphite) on fines and short fibres range during refining for a bleached sulphite pulp at different refining PFI intensities (0, 2000, 4000 and 6000 revolutions)*

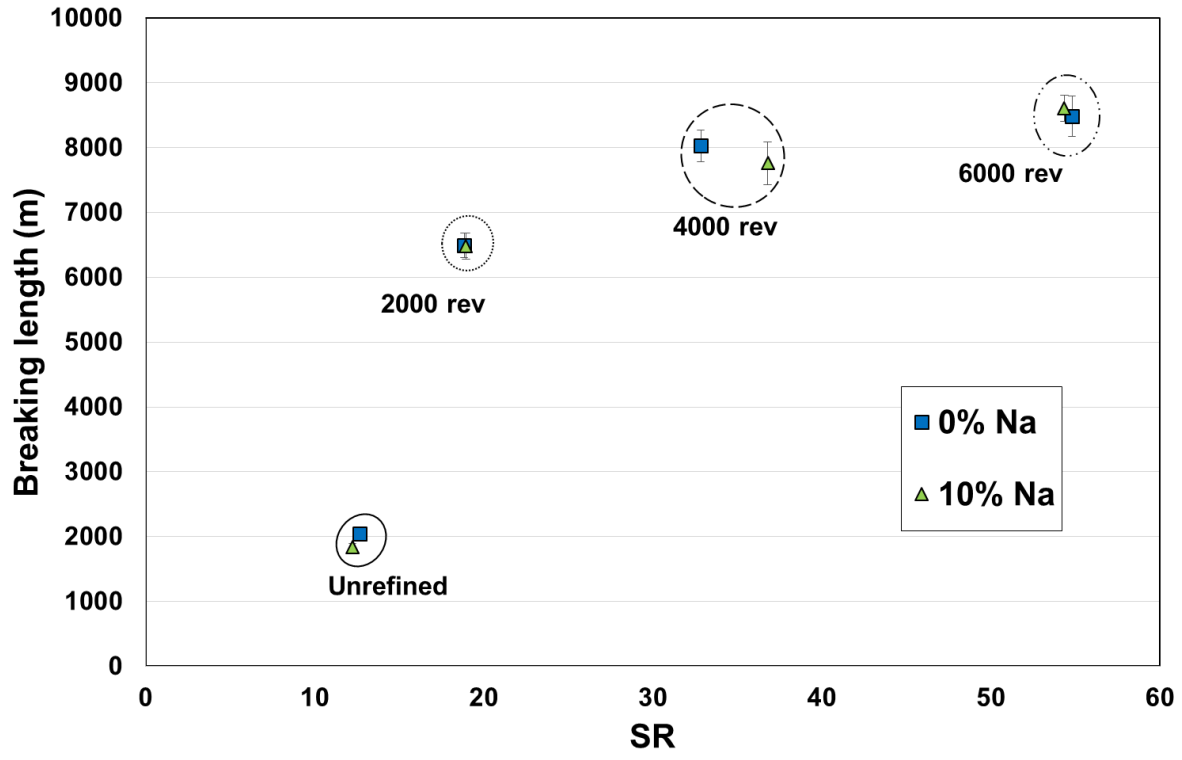

Fig. 64 *Breaking length-SR relationship of a bleached sulphite pulp before and after sulphonation*

It is evident that the sulphonation pre-treatment does not influence neither breaking length (as already shown) nor the dewatering in terms of SR. There is a discrepancy at 4000 revolutions, but this is believed to be an outlier of the measurements. There is no possible reason of why the SR should be different only a 4000 revolutions. One may have expected a difference on the SR from 4000 revolutions, which would fit the results in terms of Gurley. Nevertheless, no effect is observed and the differences in Gurley number remain incomprehensible.

According to the previous results, the sulphonation pre-treatment looks like a promising method to reduce the energy consumption during refining for a pulp with a relevant lignin content (Kappa 45), but not for a bleached pulp with a low kappa number. An absence of lignin in the pulp inhibit the positive effect on the tensile strength-dewatering relationship observed for unbleached kraft pulp. Similar results were expected for a bleached kraft pulp as it also has a low Kappa number.

To sum up the results already presented, the possibility of sulphonating the sample with a 0.5% dosage without hindering the dewatering has been demonstrated to be beneficial for unbleached kraft pulp. At the same time, it has been also demonstrated that the pre-treatment properly works only if some lignin is still present in the sample. To get a better understanding of the reaction, different measurements using unbleached kraft pulp were carried out. There is an indication in previous studies that the fibres are more flexible after sulphonation (Lin and Lanouette 2013, Fernando et al. 2015). During refining, secondary fines are formed via external fibrillation and fibre cutting. If the fibres are more flexible due to sulphonation, less cutting should be caused during refining, which would reduce the amount of secondary fines formed. In Fig. 65 one can see the fibre length distribution (analysed using L&W Fibre Tester PLUS) of fines and short fibres (in the range below 400 µm) that are present in the sample after refining at different PFI intensities, for both sulphonated (10% sodium sulphite dosage) and non-sulphonated samples. When comparing the sulphonated and non-sulphonated samples it is evident that the pre-treated sample generate less secondary fines through refining. This is an indication of the higher flexibility of the sulphonated fibres, already observed by comparing the breaking length-density relationship. They are more flexible, having a higher viscoelasticity that facilitates fibre separation (Stevanic and Salmen 2008). Therefore, the fibres are more prone to pass through the refining gap without any cutting effect, forming less secondary fines. The difference between the secondary fines formed is also proportional to the refining intensity, being almost inexistent for 0 revolutions and the highest at 6000 revolutions, where more secondary fines are formed for the non-treated pulp (the particles ranging below 50 µm rise from approximately 6% to 9%).

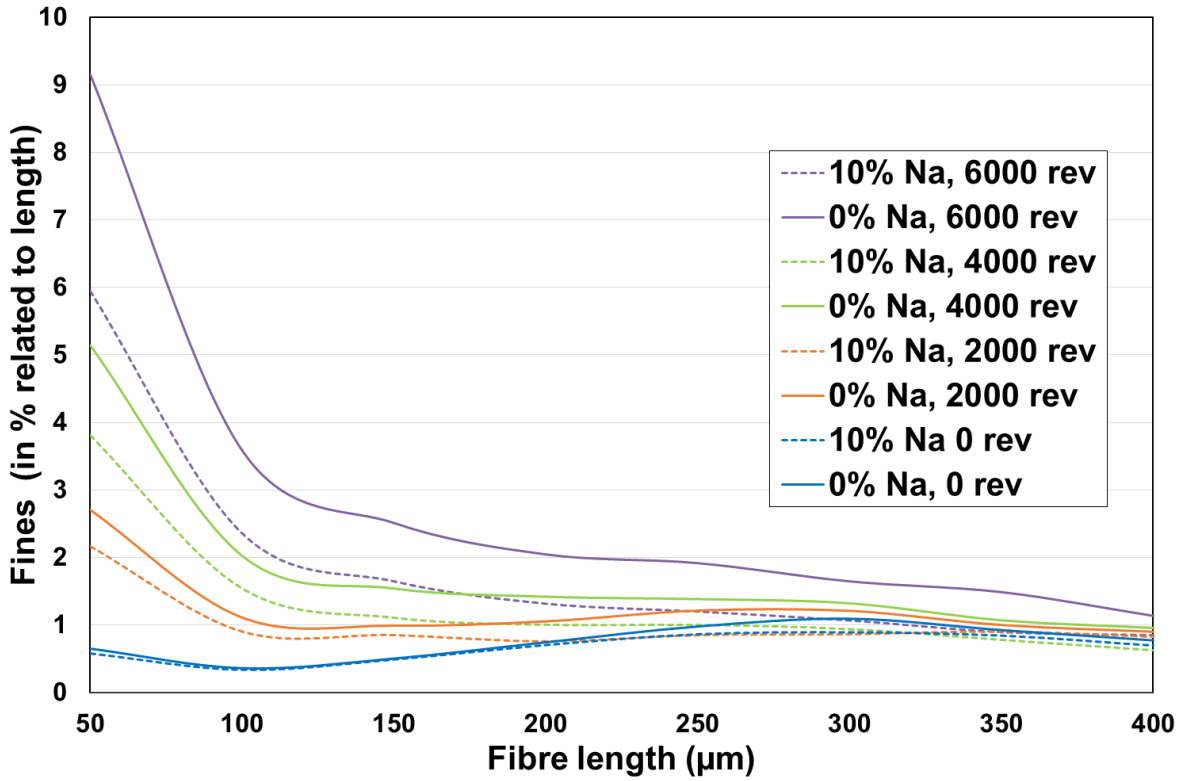

Fig. 65 *Effect of sulphonation (10% sodium sulphite) on fines and short fibres range during refining for an unbleached kraft pulp at different refining PFI intensities (0, 2000, 4000 and 6000 revolutions)*

This is also observed for the sample treated with 2% sodium sulphite, as seen in Fig. 66. Fewer fines are formed during refining for the sulphonated sample, although the effect is not visible below 4000 revolutions. This may indicate that a higher sodium sulphite dosage could lead to a better flexibility of the fibres. Nevertheless, this difference does not affect the improvement of the breaking length. As observed in Table 9, the breaking length improvement at 2000 revolutions is almost identical for the samples treated with 10% and 2% sodium sulphite.

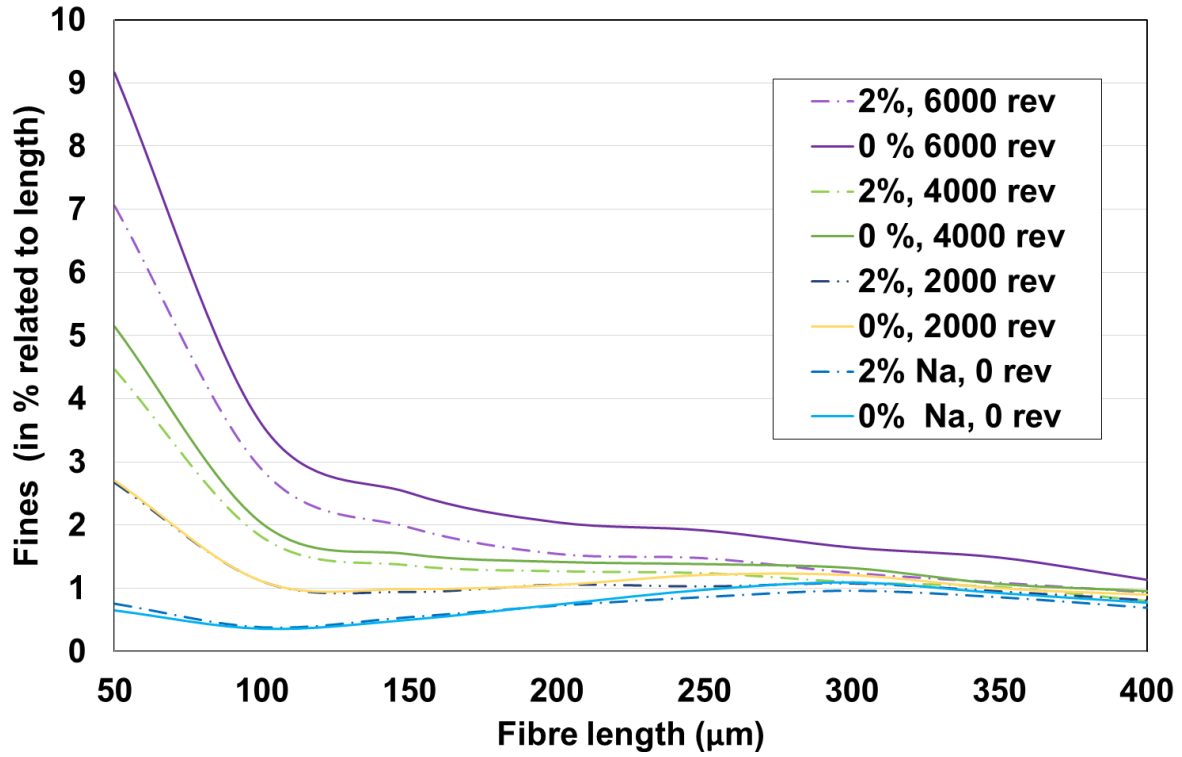

Fig. 66 *Effect of sulphonation (2% sodium sulphite) on fines and short fibres range during refining for an unbleached kraft pulp at different refining PFI intensities (0, 2000, 4000 and 6000 revolutions)*

5.3.5 Determination of sulphur content, yield and zero-span

The mechanism behind the sulphonation was also of interest for the present work. Different analyses such as conductometric titration, COD (chemical oxygen demand), TOC (total organic carbon), carbohydrate composition, κ-number, and ICP-OES (inductively coupled plasma optical emission spectrometry) were conducted for both sulphonated and unsulphonated unbleached kraft pulps to get a better understanding of the process. Such analyses gave also useful information to see whether the sulphonation effect is caused by a softening effect of the lignin or due to structural changes within the fibre, implying a yield loss. Some authors (Annergren and Germgard 2014, Kringstad and Olausson 1974) that previously studied the process claimed that the effect is caused due to the introduction of sulphonic groups. In order to proof this theory, the amount of total sulphur present in the sample before and after sulphonation was analysed. Three different samples were measured: non-sulphonated sample, and sulphonated samples treated with 1% and 2% sodium sulphite dosage. All samples contained primary fines. The total sulphur content present in the sample was determined by means of ICP-OES. The results are shown in Table 10.

Table 10 *Total sulphur content of unbleached kraft pulps containing primary fines*

Na_2SO_3 dosage [%]	Total sulphur content [mg S/g]
0	0,29
1	0,29
2	0,28

As one can easily see, the sulphur content in the sample remained the same with and without sodium sulphite pre-treatment. This contradicts the preceding theory, since there is no proof that the amount of sulphur increases after treating the sample with sodium sulphite. In order to verify this, the sulphonic acid content was also determined by conductometric titration of pulp (Beatson 1992). The pulps studied were a non-sulphonated sample and a sulphonated sample treated with 2% sodium sulphite (same as for the previous tests). Fig. 67 show the results obtained in these investigations.

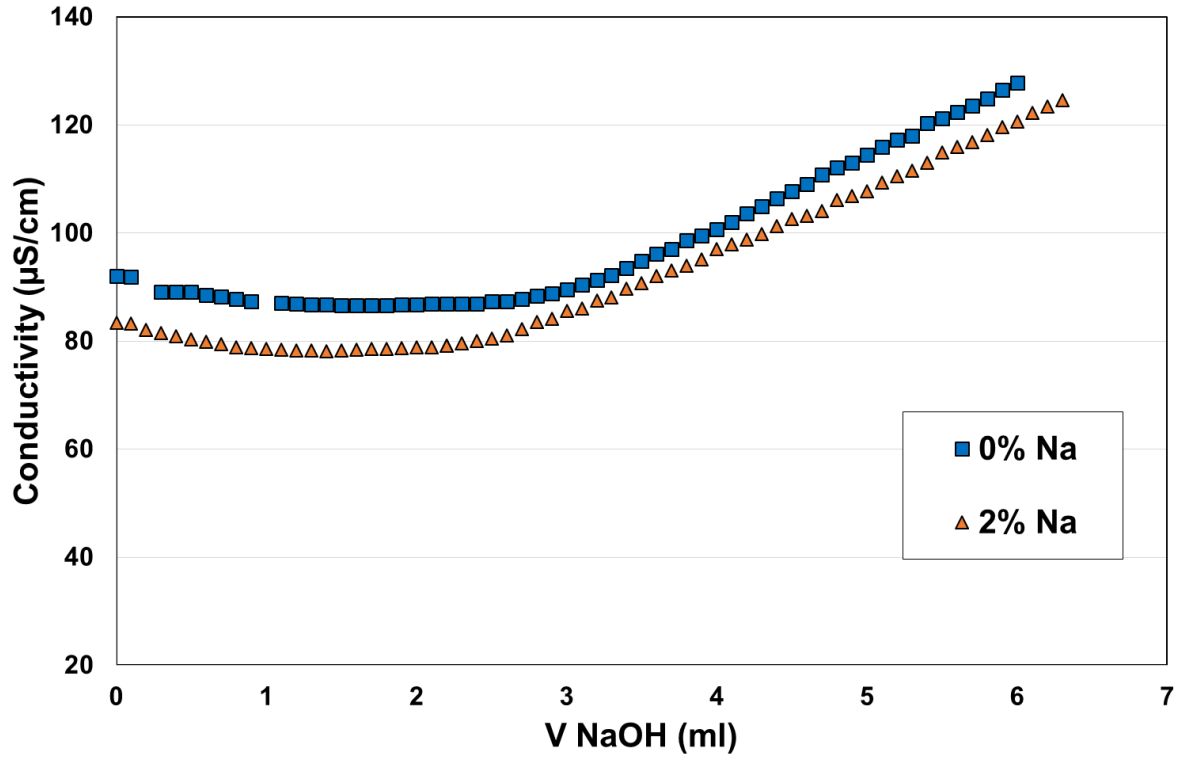

Fig. 67 *Conductometic titration results of sulphonated (2% sodium sulphite) and non-sulphonated pulps (unbleached kraft pulps), both containing primary fines*

As shown in Fig. 67 the conductivity vs the volume of NaOH added to the sample are plotted. The addition of NaOH is related to the sulphonic acid groups (for both cases approximately 1 ml NaOH). The horizontal portion (1 to 3 ml) corresponds to the titration of weaker carboxylic acid groups. The final slope of the curve is merely due to an excess of NaOH (Beatson 1992). It is not possible to conclude that the sulphonated sample contains a higher amount of sulphonic acid groups, since both curves are

almost identical. However, by calculating the total acidic group content according to SCAN-CM 65:02 one can see a higher total acidic content in the sulphonated sample. This acidic content measures both carboxylic and sulphonic groups. This could mean that the sulphonation is introducing a limited amount of carboxylic and sulphonic groups into the pulp. The results are shown in Table 11.

Table 11 *Total sulphur content of unbleached kraft pulps containing primary fines calculated after conductometric titration*

Sodium sulphite added to the sample	Total acidic content [µmol/g]
0%	106,3
2%	117,0

Nevertheless, there is no confirmation that better development of the breaking length during refining is produced by a higher content of sulphur or sulphonic groups and the difference observed might not be significant. Results reported by Lin and Lanouette (2010) showed a reasonably higher acidic content of the sulphonated fibres of a TMP, although a higher temperature and sodium sulphite dosage was used (130°C, 10% Na_2SO_3). Similar results treating TMP with sodium sulphite were reported by Fernando et al. (2015). This could not be clearly observed in the present work.

Another explanation taken into account was a possible modification of the fibres due to sulphonation, producing more resilient fibres. To study this, zero-span measurements were conducted in a 10% sulphonated sample as well as in a non-sulphonated sample, according to ISO 15361:2000(en). As stated in the standard, tensile strength data at a span length of zero may be used to assess the retention of fibre strength through the entire fibre-processing chain. In other words, the tensile strength of the individual fibres can be measured and compared with the breaking length data obtained for the handsheets formed. If the individual fibres are damaged through sulphonation, a lower fibre strength and a lower zero-span tensile strength is expected for the sulphonated fibres. The results obtained are represented in Fig. 68. The individual strength of the fibres does not develop during refining and it is independent of the paper strength.

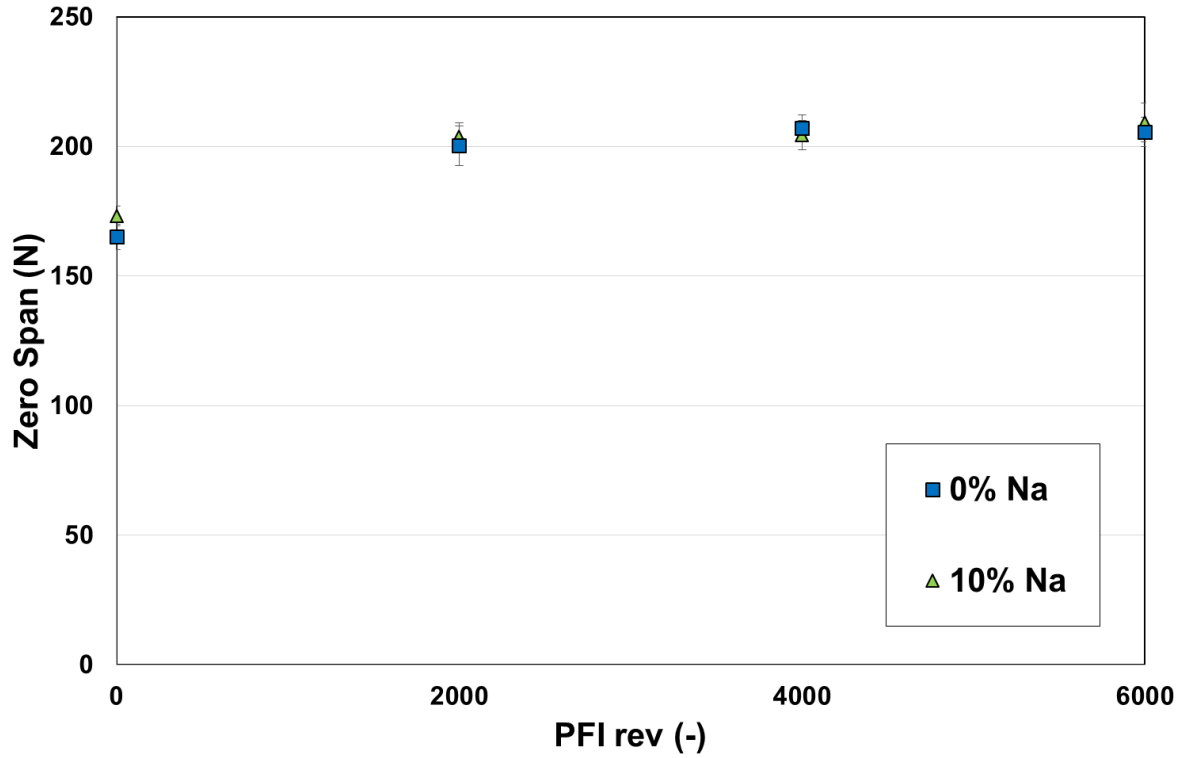

Fig. 68 *Zero-span development during refining for sulphonated and non-sulphonated fines-free pulps (unbleached kraft pulps)*

It is clearly observed that both results are almost identical at each refining intensity. The zero-span seems to be independent of the sulphonation pre-treatment. This can be interpreted as fibres remaining undamaged after sulphonation. The individual strength of fibres does not increase due to the pre-treatment, but it also does not decrease. Thus, sulphonation does not interfere with the strength of individual fibres. Nevertheless, some issues related with the device used to measure the zero span (specifically a problem with the clamps of the device) may have caused some errors during the tests. Due to this the strength measured might be a combination between individual fibres strength and paper strength. This problems have not been solved to date. Thus, the present results may not be trustworthy and need to be confirmed by future investigations. However, this relative comparison should give a difference related to the individual fibres if there were any.

The possibility of structural changes within the fibres implying a yield loss was also considered. Firstly, the approach was similar to the studies carried out by Johakimu and Bush (2011). A possible leaching of lignin and subsequent yield reduction was evaluated by measuring the kappa number of the pulp before and after sulphonation. The sulphonated sample chosen for the study contained 10% of sodium sulphite. It was compared with a non-sulphonated sample. Both samples contained primary fines. The premise was that the lignin loss (if existing) should be proportional to the sodium sulphite dosage, and therefore the maximum should be seen at 10%. This difference on the lignin content should be also

observable by having a look at the kappa number. The results obtained for both samples are plotted in Fig. 69.

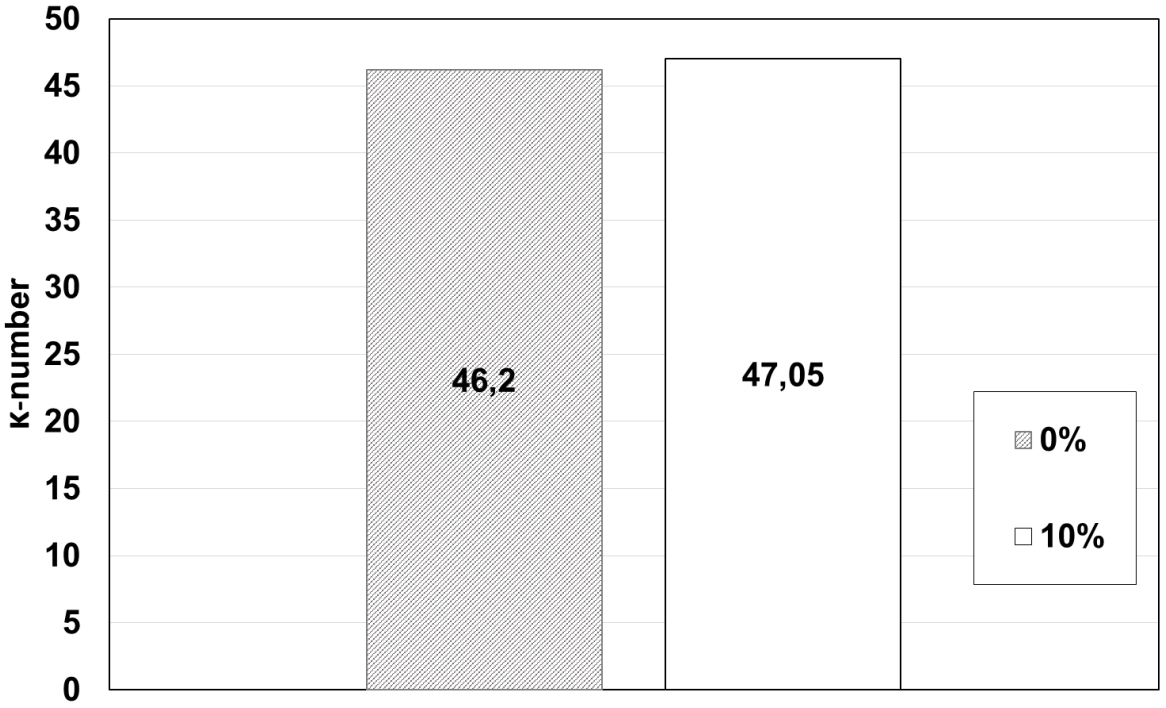

Fig. 69 *Kappa number measurements for sulphonated and non-sulphonated pulps (unbleached kraft pulps) containing primary fines*

It is noticeable that the kappa number remain constant even after treating the pulp with 10% sodium sulphite. Therefore, it can be assumed that no lignin loss takes place at with 10% dosage neither at lower dosages. The difference observed between both measurements is attributed to a low precision of the method, since it is impossible to have a higher lignin content in the pre-treated pulp. Therefore, the results are considered to be identical. Nevertheless, further trials with a pulp treated with 2% sodium sulphite and a reference pulp (both free of primary fines) were performed to confirm this. These samples were washed before and have a different starting Kappa number. The results are shown in Fig. 70.

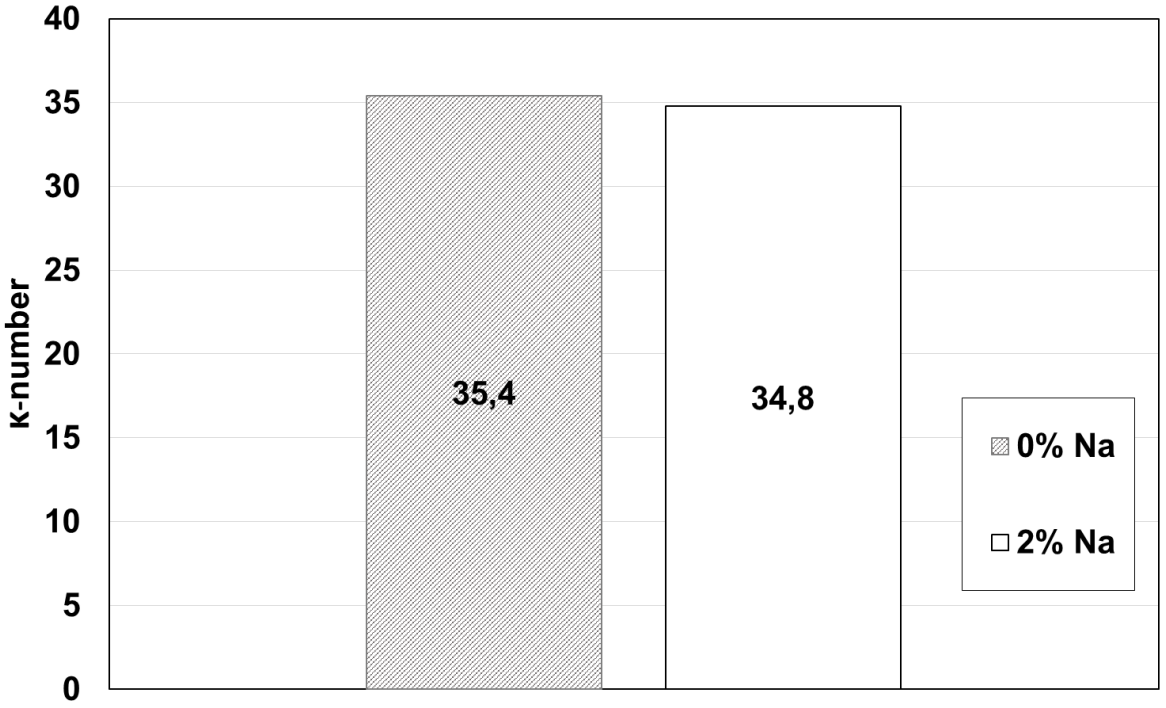

Fig. 70 *Kappa number measurements for sulphonated and non-sulphonated fines-free pulps (unbleached kraft pulps)*

Similar conclusions are obtained in this case: no lignin loss (or at least no significant losses that can be detected by measuring the Kappa number) caused by a sodium sulphite pre-treatment. The observable differences are too small and this method may not be that precise to measure small lignin losses. The main difference in the kappa number compared to the previous results lies in the lack of primary fines, which in general contain a higher amount of lignin compared to kraft pulp fibres (Bäckström et al. 2008). This causes an increase of about 10 units in the Kappa number.

It was also the intention of the following measurements to evaluate the pre-treatment effect on the cellulose and hemicelluloses. A possible leaching of these two fractions was not evaluated in other studies that only measured the yield by means of kappa number and therefore only considered lignin. The possible losses of cellulose, hemicellulose or lignin caused by sulphonation were evaluated by analysing the carbohydrates present in the filtrate obtained after pre-treatment. The samples chosen for these measurements were treated with 1% and 2% sodium sulphite, all contained primary fines. This was determined indirectly by measuring both COD and TOC. The results are shown in Table 12.

Table 12 *COD and TOC measurements for different filtrates collected after pre-treatment from pulps (unbleached kraft pulps) containing primary fines*

Filtrate sample	COD [mg/l]	TOC [mg/l]
2%	1,124	3,173
1%	1,078	3,060
0%	1,289	3,523

The amount of organic matter dissolved in the filtrate is moderately low. It seems that the sulphonation pre-treatment does not dissolve organic matter, i.e., cellulose, hemicellulose and lignin. A higher value of either COD or TOC would be expected for the sulphonated samples, if some carbohydrates were getting dissolved. This is in this case not observable, indicating no noticeable losses during the pre-treatment. In order to validate these results, the chemical composition of both sulphonated and non-sulphonated samples were directly determined with a more precise method (NREL/TP-510-42618). The samples are the same chosen for COD and TOC analyses. The lignin, cellulose and hemicelluloses (galactoglucomannan and xylan) content were measured. The obtained results are shown in Fig. 71.

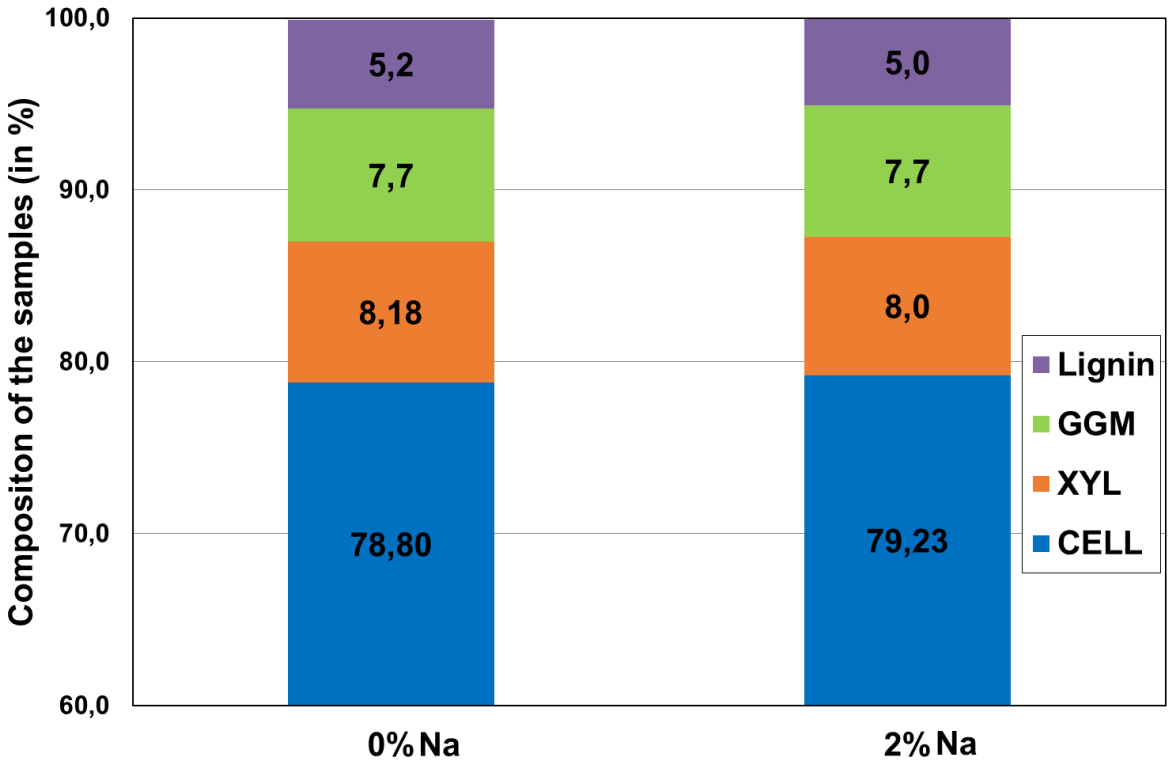

Fig. 71 *Chemical composition of sulphonated and non-sulphonated pulps (unbleached kraft pulps) containing primary fines*

There is no evidence of cellulose, hemicelluloses (galactoglucomannan and xylan) or lignin losses due to sulphonation. The differences are within the measurement uncertainty of the method (±0.5%). This correlates well with the results reported by Kringstad and Olausson (1974), where a maximum yield loss of 0.5% was obtained. This confirms the results obtained from Kappa number and filtrate measurements. From all these results (Kappa number, COD, TOC and chemical composition), it can be concluded that a yield close to 100% was obtained during the presented experiments. It also supports the idea that sulphonation is modifying the lignin rather than dissolving it, as stated by Johakimu and Bush (2011). Therefore, a possible explanation of this phenomenon could be the enhanced flexibility of the fibres, caused by lignin and cell wall softening. This would lead to a higher conformability of the cell wall and to fibres more prone to collapse, as suggested by Heazel (1988).

The presented results indicate potential energy savings when sulphonating a medium kappa chemical pulp prior to refining. Sulphonation of a κ-number 45 kraft pulp seems to be beneficial, in contrast to the studies conducted by Worster and Pudek (1975), as they claimed that a κ-number above 100 was required. It is possible to achieve an energy reduction of the refining process by using a sodium sulphite pre-treatment, but it was also important to study the impact on the porosity of the handsheets produced. For the application of the final product (sack paper), a high porosity is required. The target was to achieve an improved tensile strength-porosity relationship. This indicates that a sodium sulphite pre-treatment of an unbleached kraft pulp led to better tensile strength-porosity and tensile strength-dewatering relationships. This is visible even at low sodium sulphite dosages, and it is also not affected by the presence of primary fines in the pulp. Besides, no carbohydrates losses were reported by any of the conducted analyses. It can be then concluded that the yield of the pre-treatment was 100%.

6. Conclusions and outlook

6.1 Overview of the results obtained

The main scope of the present thesis was to find and evaluate different alternatives that would lead to an improved refining at reduced energy demand. To achieve this, different approaches were studied, with the main focus on fractionated refining and chemical modification. Besides, the influence of fines in the pulp and paper properties and their retention in the handsheets was also of interest to have a better reproducibility and comparability of the results. By retaining always the same amount of fines, this possibility is ruled out. To do so, a novel method was developed. By using the recirculation of the white water and a 325-mesh, a constant amount of fine material in the handsheets can be obtained. Besides, it allows an easy determination of the fines content using an L&W Fiber Tester Plus. This procedure enables the evaluation of the effects of fines and other types of additives (i.e., small particles comparable in size to fines) on various pulps and their properties. This determination of fines content can substitute the determination by means of Britt-Jar, which is a tedious procedure and requires 5 grams of pulp (o.d.), whereas the L&W Fiber Tester requires only 0.15 grams per measurement. Primary and secondary fines of two pulps (bleached sulphite pulp, and bleached kraft pulp) were evaluated as exemplary results using this method. Secondary fines of bleached kraft pulp showed a much higher impact on the breaking length, dewatering and air permeability compared to the primary fines. The breaking length was 84% higher when secondary fines were added than when primary fines were added. Besides, the air permeability was reduced, as an indicator of a better formation and bonding of the fibres. The pulp containing secondary fines also showed a higher fibrillar content and a lower average fibre length compared to the pulp containing primary fines, which could mean that the primary fines are formed by chunky particles more than fibrillar material. Regarding fines from bleached sulphite pulp, the obtained results show that some fibrillar material is present in the primary fines and therefore their properties are similar. The brittle nature of softwood sulphite fibres causes more similar results in terms of fibrillar area as well as average fibre length. The breaking length increases 47.3% when secondary fines are added and 38.2% when primary fines are added. The air permeability of the handsheets is also reduced when primary fines are added, but the difference is not as large as for bleached kraft pulp. Besides, both show a similar impact on dewatering. These exemplary results intend to show the relevance of fines and their impact on pulp and paper properties, especially in terms of tensile strength, dewatering and porosity. Two types of primary fines can lead to totally different results, and therefore it is important to evaluate the fines of different pulps to understand the behaviour of a certain pulp.

These findings are in close relation with the fractionated refining trials, where the pulp is separated into two fractions: the fine fraction, which comprises a high percentage of fines and short fibres, and the coarse fraction, which contains a higher number of long fibres. Ideally, refining of the coarse fraction and addition of the unrefined fine fraction would provide comparable results to the refined reference, since the long fibres develop to a higher extent. By doing so, the amount of pulp that need to be treated during refining could be reduced. A preliminary set of trials using a Bauer-McNett fibre classifier and a Jokro mill were performed to evaluate the potential of the procedure, obtaining promising results in terms of tensile strength-dewatering, especially for unbleached kraft pulp and bleached kraft pulp. Two of the pulps available in the project, i.e., an unbleached kraft pulp and a bleached kraft pulp, were studied more in detail using a pressure screen and a PFI mill and different coarse/fine fraction ratios. The results obtained for unbleached kraft pulp show that by refining only 70% of the pulp (o.d., coarse fraction) similar results in terms of breaking length are obtained. Besides, improved tensile strength-dewatering and tensile strength-porosity relationships are observed. Less fines are produced for the fractionated samples, which leads to lower SR values and therefore better dewatering of the pulp. This could lead to potential energy savings, since 30% of the material is spared of being refined, and both porosity and dewatering are improved. Another set of trials was carried out to observe the development of both fine and coarse fraction of unbleached kraft pulp have independently during refining. The fine fraction show a high breaking length even in the unrefined state. The breaking length is increasing with refining, achieving at 4000 revolutions a higher breaking length as the refined reference at 6000 revolution. Nevertheless, poor results in terms of dewatering and porosity are obtained. This could make its usage suitable for products that require a high strength and where porosity and dewatering are not of interest. Regarding the coarse fraction, the results show that comparable results are obtained, irrespective of adding the fine material after refining (30% of the whole pulp, mass related). Therefore, it may be beneficial to use only the coarse fraction during refining, and either add the fine fraction afterwards or find another application for it. This would reduce the amount of pulp to be treated, leading to energy savings during refining. Besides, the removal of the fine fraction would also lead to better tensile strength-dewatering and tensile strength-porosity relationships.

Concerning bleached kraft pulp, the obtained results show a different behaviour of the pulp during fractionated refining. The breaking length is proportional to the amount of pulp refined, being the highest for the reference and the lowest for the 70/30 test. Besides, the dewatering of the pulp does not improve to a relevant extent. This is mainly caused by the presence of fines, which is almost constant, irrespective of the fractionation performed. In this case, fractionated refining does not reduce the fines present in the pulp after refining. The brittleness of the fibres can provoke effects like delamination or breakage of the fibres merely by fractionating the pulp. This could explain that no

difference is observed after refining. Fractionated refining of bleached kraft pulp seems to be only interesting if a lower Gurley is required for a certain process, and a reduction of the breaking length is not critical. In this case, a fractionation 80/20 showed the most promising results. By performing such a fractionation, the Gurley could be improved from 68.1 to 41.7 seconds at 6000 revolutions, although the breaking length was 16.1% lower compared to the reference.

The main alternative to fractionated refining that is studied to improve refining is a chemical modification. The studied procedure is a pre-treatment with sodium sulphite, performed with unbleached kraft pulp (Kappa number 45) and bleached sulphite pulp (low lignin content). Trials on bleached sulphite pulp did not show any positive results on breaking length, and the air permeability of the handsheets decreased. This confirmed previous studies that claimed that sulphonation affects the lignin present in the fibres. On the other hand, the sulphonation of unbleached kraft pulp led to an increase of the breaking length, even at rather low dosages of sodium sulphite (0.5%) and low temperatures (75°C) at a given refining intensity. The positive effect observed at different sodium sulphite dosages (ranging from 0.5% to 10%) is almost constant. On the other hand, this pre-treatment does not affect negatively the dewatering of the pulp. Sulphonated pulps show a higher breaking length at a given Schopper-Riegler (SR). This can lead to potential energy savings in the refining step. Besides, the influence of primary fines in the process was studied by treating pulps containing primary fines and washed pulps free of primary fines. The results with and without primary fines are almost identical in terms of breaking length and dewatering development. Therefore, it was concluded that primary fines did not play a role in the process and did not increase the chemical consumption as they do in the bleaching process. Additional costs associated with the equipment needed to separate primary fines before sulphonation can be neglected. The measurements on the chemical composition of the pulp and the filtrate after treatment indicated that no noticeable yield loss takes place during the procedure, indicating that lignin is modified rather than dissolved. Therefore, yield is assumed to be 100%. There was no confirmation of sulphonic group addition to the pulp due to sulphonation. Indeed, a higher flexibility of the fibres after sulphonation is believed to cause the improvement on the breaking length. The fibres are more flexible, producing fewer secondary fines during refining and improving the conformability of the fibre network, as it can be seen by analysing the different fibre length distribution of the samples. This leads to a higher breaking length of the handsheets formed at a given refining intensity. By treating an unbleached kraft pulp with 0.5% sodium sulphite, an improved tensile strength-porosity relationship after refining can be achieved, which was one of the most important goals of the present thesis.

6.2 Future work

The presented studies have completed a thorough evaluation of the aforementioned methods. Nevertheless, there is always room for improvement and several trials could be conducted in order to complete these investigations. The sulphonation pre-treatment has been proven to be a suitable method to improve refining of unbleached kraft pulp, whereas fractionated refining also provided some interesting results. It would be then logical to combine both methods, by fractionating the sample and conducting sulphonation only for the coarse fraction. By doing so, the chemical consumption of the pre-treatment would be reduced and similar results in terms of tensile strength-porosity could be achieved. Fractionated refining may lead to an improved porosity and dewatering, whereas sulphonation may enhance tensile strength reducing the gap observed between the refined reference and the 70/30 trial, which was the coarse/fraction rate that provided the best results. Besides, a proper determination of the lignin softening temperature in the fibre would be of great importance to understand the mechanism behind sulphonation and confirm the hypothesis of a higher flexibility of the fibres due to lignin softening. Regarding fractionated refining, the separation achieved in terms of fibre length distribution is much more realistic than the obtained by a Bauer-McNett fibre classifier, but is still far from an industrial pressure screen. To get more comparable results to the industrial level, a fine fraction containing a higher amount of long fibres and vice versa would be required. This could be achieved by replacing the 1.2 mm hole plate for a slot mesh, which would provide a different fibre separation. Similar trials as the ones conducted in this thesis could then be performed and compared with the obtained results. Last but not least, the important role that fines play in pulp and paper properties has been demonstrated with some exemplary results. Therefore, it is highly suggested that the importance and role of fines is evaluated for each procedure intended to improve refining, such as their influence on dewatering or chemical consumption. Altogether, the knowledge acquired during the present investigations together with possible tests performed in the future could allow a better understanding of refining, improving the process and therefore reducing the energy of one of the most demanding steps in terms of total power consumption.

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Appendix I: Main results presented in Chapter 3

Table 13 *Main results obtained for bleached sulphite pulp fines and bleached kraft pulp fines*

Sample	**Bleached sulphite pulp**			
Fines	**SR**	**Gurley (s)**	**Breaking length (m)**	**Thickness (µm)**
Without	12,6	0,8	2088	152
Primary	14,5	2,2	2885	144
Secondary	15,5	3,0	3076	145
Sample	**Bleached kraft pulp**			
Fines	**SR**	**Air permeability (ml/min)**	**Breaking length (m)**	**Thickness (µm)**
Primary	13,1	over 5000	1568	180
Secondary	14,9	4724	2694	163
Additive	12,0	over 5000	1463	176

Appendix II: Main results presented in Chapter 4

Table 14 *Main results obtained in fractionated refining of a bleached kraft pulp*

Bleached kraft pulp				
Sample	**PFI rev.**	**SR**	**Gurley (s)**	**Breaking length (m)**
Reference	0	13,7	1,6	3247
	2000	16,3	9,0	8743
	4000	21,0	28,6	10520
	6000	27,8	68,1	10484
90/10	0	-	-	-
	2000	16,3	10,1	8571
	4000	21,9	29,5	9818
	6000	28,9	66,2	10174
80/20	0	-	-	-
	2000	16,2	8,6	7652
	4000	20,6	20,6	8632
	6000	27,4	41,7	9591
70/30	0	-	-	-
	2000	17,2	10,0	7952
	4000	20,4	21,6	8715
	6000	25,2	40,3	8647

Table 15 *Main results obtained in fractionated refining of an unbleached kraft pulp*

Unbleached kraft pulp				
Sample	**PFI rev.**	**SR**	**Gurley (s)**	**Breaking length (m)**
Reference	0	15,0	1,7	5610
	2000	16,8	4,7	9244
	4000	17,9	10,1	10711
	6000	21,4	23,4	10247
80/20	0	-	-	-
	2000	16,8	5,9	9021
	4000	18,2	11,4	9948
	6000	20,9	22,2	9628
70/30	0	-	-	-
	2000	16,3	4,1	8830
	4000	16,8	7,2	10020
	6000	19,7	13,6	9915
60/40	0	-	-	-
	2000	15,9	4,7	8263
	4000	17,4	7,3	8829
	6000	19,1	14,5	8854
Only coarse	0	11,2	1,1	5123
	2000	15,5	2,9	8593
	4000	16,6	6,9	9935
	6000	19,3	16,5	9694
Only fine	0	46,3	85,8	8574
	2000	47,6	176,2	10657
	4000	58,3	341,7	11178
	6000	-	-	-

Table 16 *Main results obtained in fractionated refining of a bleached sulphite pulp*

Bleached sulphite pulp				
Sample	**Jokro mill**	**SR**	**Air permeability (ml/min)**	**Breaking length (m)**
Unrefined	-	14,2	over 5000	1997
Entire sample	20 min	21,7	1444	5908
Coarse fraction	20 min	25,7	2074	4522

Appendix III: Main results presented in Chapter 5

Table 17 *Main results obtained in sulphonation of an unbleached kraft pulp*

Sample	Unbleached kraft pulp					
Dosage	**Fines**	**PFI rev.**	**SR**	**Gurley (s)**	**Breaking length (m)**	**Density (kg/m³)**
0%	yes	0	13,6	1,2	4558	467
	yes	2000	14,9	3,6	8310	612
	yes	4000	17,1	6,6	8679	658
0.5%	yes	0	14,1	1,7	5347	479
	yes	2000	15,6	3,7	8782	618
	yes	4000	16,9	8	9929	656
1%	yes	0	14,1	1,7	5681	477
	yes	2000	15,6	3,9	9156	616
	yes	4000	16,9	8,5	10389	656
2%	yes	0	13,3	1,3	5219	526
	yes	2000	15,2	3,7	9069	614
	yes	4000	17,6	7,8	10406	658
0%	no	0	13,0	1,2	4795	496
	no	2000	15,0	3,1	8551	636
	no	4000	17,0	7,1	8954	646
	no	6000	19,5	16,9	9809	705
2%	no	0	12,4	1,3	5484	510
	no	2000	14,1	3,3	9209	647
	no	4000	15,4	8,5	9864	691
	no	6000	19,6	21,9	10561	695
5%	no	0	12,4	1,3	5826	527
	no	2000	13,9	3,3	9185	641
	no	4000	16,0	9	10513	677
	no	6000	19,6	23,1	10731	693
10%	no	0	13,5	1,3	5219	526
	no	2000	13,4	3,3	9069	614
	no	4000	15,4	8	10406	658
	no	6000	19,8	22,6	11019	694

Table 18 *Main results obtained in sulphonation of a bleached sulphite pulp*

Sample	Bleached sulphite pulp					
Dosage	**Fines**	**PFI rev.**	**SR**	**Gurley (s)**	**Breaking length (m)**	**Density (kg/m³)**
0%	yes	0	12,7	1,0	2047	471
	yes	2000	18,9	12,2	6496	697
	yes	4000	32,9	78,1	8028	764
	yes	6000	54,8	341,2	8485	799
10%	yes	0	12,3	0,9	1833	454
	yes	2000	19,0	13,9	6484	693
	yes	4000	36,8	105,2	7761	754
	yes	6000	54,4	575,3	8611	796