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Ultrasonic refining of chemical pulp fibres

Master of Science Thesis in Innovative and Sustainable Chemical Engineering

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The master thesis was performed in cooperation with Södra Innovation, Väröbacka Sweden.

Cover:
The picture shows the ultrasonic equipment which was used in the experiments of this thesis, see pages 5 and 6 for information. Photographed by Anna Josefsson.

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Abstract

In the pulp and paper industry there is a constant need of development in terms of process efficiency as well as new products and innovations. A large energy consumer in the production of paper is the mechanical refining and therefore alternative refining techniques are highly interesting. In this context ultrasonic refining has emerged as a method with potential to achieve energy reductions meanwhile developing desirable fibre properties. The aim of this study was thus to investigate the method of ultrasonic refining in order to determine the possibilities of achieving the above mentioned results.

The project was carried out at the pulp producing company Södra in Väröbacka, Sweden. A piezoelectric ultrasonic equipment with a recirculation system was used to ultrasonicate pulp samples of differing qualities at different consistencies and duration times. The pulp samples were in dried and never-dried forms and both softwood and hardwood pulps were included in the study. After ultrasonication of fibres, subsequent analyses of fibre properties and physical properties were performed and the energy consumption was evaluated.

It was shown that the dried pulps were little affected by the ultrasonic treatment, in contrast to the never-dried samples which showed significant increases in inner and outer fibrillation of fibres with interconnected increases in tensile index. No fibre cutting action or creation of fines was identified. In terms of energy consumption the equipment was highly energy demanding in comparison to conventional refining and very undesirable in this aspect. However this result should be regarded as specific for the particular lab scale equipment used in these experiments. Perhaps there are, or will be in future, other types of equipment which are more energy effective.

Keywords: ultrasound, pulp fibres, refining, fibre properties, strength properties

Preface

This master thesis was performed in the spring 2010 at the pulp producing company Södra´s unit for research and development, Södra Innovation, in Väröbacka Sweden. The supervisors for the project were Karin Sjöström and Jon Tore Eriksen at Södra Innovation and Harald Brelid at Chalmers Forest Products and Chemical Engineering.

First of all I would like to thank Södra and the people there who accepted me as a master thesis worker in the company. I really enjoyed my time at Södra and it was a very instructive experience to get in touch with the world outside university. The work with ultrasonic refining of pulp fibres was sometimes a big challenge but even though difficulties occurred it was always interesting and exciting to be within the project and its open-ended nature was highly stimulating.

I am very thankful to all of my supervisors who helped me to complete this project and contributed with their expertise. Especially Karin Sjöström, main supervisor at Södra, who always had time for my questions and discussion of results, owes to be thanked a lot. I would also like to thank all the people at the Södra Innovation pulp lab who helped me with various matters and kindly responded to my questions.

I am grateful to Malgorzata at the Innovation pulp lab, who taught me how to perform the different analyses on pulp fibres, and the mechanics Mats and Sten-Gunnar, whom helped me with questions related to the ultrasonic equipment. In addition I would also like to thank Fredrik at Chalmers Forest Products and Chemical Engineering, who taught me how to use electron microscopy.

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1. Introduction

Paper is an important product in the industrial society and it is used every day in many different applications. Ever since the first paper was produced in China, in 100 AD, the paper has come to increase its importance in our lives and world overall paper usage is still increasing. To exemplify, the most widely used wrapping and packaging material is paper and paper also has an invaluable role in terms of information handling. [1]

Paper is made from pulp, which is usually of vegetable origin in the form of wood. [1] In Sweden, the forest resource is of major importance in many aspects and it has both ecological and economical values. Focusing on the industrial use of the forest resource, wood can be used in many different applications among which the pulp and paper industry is a large consumer.

One actor in the Swedish forest market is Södra Skogsägarna, an economical association for forest owners in the south of Sweden. In addition to forest resources, the association owns a group of companies producing forest products within four different business areas. The business areas are sawn and planed timber goods, interior products, paper pulp and biofuel. Besides the forest products Södra is also a producer of green electricity. [2]

The production of pulp and paper is a large energy consumer. One energy consuming step in the production of paper is the refining, which is used to develop desirable fibre properties in pulp before it is used in the paper machine for production of paper. Methods for achievement of either energy reductions in the refining process or development of suitable fibre properties are therefore highly interesting. Due to this fact, Södra Innovation, which is the division for research and development within the Södra group, are interested in investigation of alternatives to conventional refining.

An alternative to conventional refining is ultrasonic refining, which is a method not yet taken into use in industry. The technique has showed potential in the refining process as the ultra waves are relatively gentle to the fibres and do result in increased fibrillation without fibre cutting action [e.g. 3]. However, even though promising results have been recorded, previous research studies are non-consistent, showing mixed results on pulp properties after ultrasonication. In addition, inefficient usage of energy and the method's uncommonness has so far contributed to the absence of success for ultrasonics in industrial refining. [4] Therefore many questions about ultrasonic refining are still without answer and further research studies are of interest.

This master thesis was run in cooperation with Södra Innovation in Väröbacka, Sweden. The overall purpose of the thesis was to investigate the method of ultrasonic refining to give the possibility of providing pulp customers with up to date information in the refining area. The project consisted of a literature study as well as experimental trials on sonication of pulp with lab scale ultrasonic equipment.

2. Theoretical background

To give a fundamental understanding of the method of ultrasonic refining the basic principles of ultrasound technology and equipment were studied. The aim of conventional refining and its effects on the cellulosic fibres was also studied. Another important part of the project was a literature study which aimed to give an overview of what has been done in previous research studies on ultrasonic refining of pulp fibres. The literature study provided an opportunity to evaluate and support the results obtained in this project in a proper way.

2.1. Refining of pulp

The main target of refining of pulp is to improve the bonding ability of fibres. The reason why this is desirable is that an improved bonding ability between fibres results in a paper product with a good strength, smooth surface and good printing properties. Another aim of refining, depending on the specific type of product to be produced from the pulp, can sometimes be to shorten the fibres through fibre cutting. But even though short fibres are suitable in some applications fibre cutting is not always desirable. [5]

Mechanical refining usually takes place at a consistency of about 3-5%. The refining action is achieved in the gap between a stator and a rotor with bars and grooves. More specifically the refining takes place at the so called leading edges of the refiner where fibre flocs, to a large extent consisting of water, are assembled. When the leading edge of the rotor approaches the leading edge of the stator the fibre flocs are compressed and water is pressed out of them. What happens then is that the shorter fibres will flow into the grooves between the bars and the longer fibres will get refined by the metallic bars. After refining the fibres have collapsed and are made more flexible, having an improved bonding ability. However not all fibres will be subjected to the refining action. In addition it should be noted that in the context of refining action the exact procedure of the refining process is still until this day unknown. [5]

The most important effects of refining on the fibre are as follows [5]:
- Cutting and shortening of fibres
- Fines production, complete removal of parts from fibre walls
- External fibrillation, partial removal of fibre wall
- Internal changes in fibre wall structure (fibrillation, swelling…)
- Curling or straightening of fibres
- Creation of nodes, kinks, slip planes, microcompressions
- Dissolving/leaching of colloidal material
- Redistribution of hemicelluloses
- Abrasion of fibre surface at molecular level

The effect of refining on paper properties are as follows [5]:
- Increased drainage resistance
- Increased tensile strength, tensile stiffness, burst strength, internal bonding strength and fracture toughness
- Tear strength softwood: slightly improved first, then decreased
- Tear strength hardwood: significantly improved first, then decreased
- Air permeability, bulk, absorbency, opacity, light scattering decreases
- Brightness slightly decreases

2.2. Ultrasound

Ultrasound has a broad range of applications and is used in several businesses and sectors. Perhaps one of the most widely recognized applications is that of ultrasonic imaging in medicine. Another well known application is in the echo technique SONAR. [6] Other applications are for example in the food industry for emulsification and disinfection and in inks and paints production for particle size reduction and dispersion [7]. Ultrasound has also showed potential for utilisation in various applications in the pulp and paper industry, for example in the refining of pulp fibres [4].

2.2.1. Principles

Ultrasound is defined as sound of a higher frequency than that to which the human ear can respond. The range of human hearing is restricted from 20 Hz to 20 kHz, which implies that ultrasound is sound of a frequency higher than 20 kHz. The upper limit of ultrasound is not sharply defined but it is often taken as 5 MHz for gases and 500 MHz in liquids and solids respectively. [8]

To further define the range of ultrasonic frequencies, ultrasound can be divided into two different categories; diagnostic ultrasound and power ultrasound. Diagnostic ultrasound is sound of the lower power and higher frequency, 2-10 MHz, which is the non-destructive form of ultrasound. The diagnostic ultrasound is used in for example ultrasonic imaging. The other category of ultrasound, power ultrasound, is sound of higher energy or lower frequency, constricted to the interval 20-100 kHz. Power ultrasound is used in applications such as cleaning, plastic welding and sonochemistry and it is this kind of ultrasound that is used in the experiments of this study. [9]

2.2.2. Characteristics

Ultrasound has the properties of a wave. It is transmitted through all media possessing elastic properties by setting molecules into motion, making them vibrate around their original position. The sound wave propagates through the medium as the vibratory motion is transferred from one molecule to another adjacent molecule. When a molecule has transferred its kinetic energy to another molecule it will return to the original position. [10]

In liquids and gases the propagation of sound waves takes place only in the longitudinal direction, in contrast to solids where transversal waves can emerge due to shear elasticity. When a sound wave is followed by another sound wave this will result in an oscillation, which means that the molecules of the medium move forwards and backwards around their original position. This phenomenon gives rise to alternating regions of compression and rarefaction in the medium. In one moment there will be an excess (compression) of particles in a specific region meanwhile in another moment there is a deficiency (rarefaction) in the same place due to oscillation. As a result of these effects the pressure varies with time over the sound wave propagation area; in compression areas the pressure is higher than normal and in the rarefaction regions it is lower than normal. These regions of alternating pressures give rise to a phenomenon called cavitation, which is taken advantage of in many industrial applications of ultrasound. [10]

2.2.3. Cavitation

Cavitation is a phenomenon created by high intensity sound waves in liquids when the attractive forces of liquid molecules are overcome. The phenomenon takes place in regions of rarefaction, where low pressure emerges. At sufficiently high intensities of the sound wave the pressure in rarefaction regions is low enough to overcome the attractive forces of the liquid molecules and formation of gas-filled cavities takes place. [11]

Depending on the purity of the liquid the magnitude of the low pressure needed to overcome the attractive forces of the liquid and form cavities varies. It is claimed that in a completely pure liquid it is impossible to achieve cavitation with the transducers available today. However real liquids are not completely pure and therefore cavitation takes place more easily. This is due to existing impurities in a real liquid, e.g. dissolved gas and impurities, which act as weak spots and starting points for bubble formation. [11]

When a cavity is formed it will absorb energy from the oscillation cycles, resulting in contraction and growing of the bubble. Some cavities are stable and last for many cycles meanwhile they oscillate in size; other cavities are referred to as transient and grow in size for each compression cycle until they finally implode. Implosion takes place at very high temperatures, around 5500 K, and pressures, about 1000 atm, which result in the generation of a jet stream moving at a velocity of 400 km/hr. The implosion proceeds in a spherical, symmetrical, way in liquids if it does not take place close to a surface. When a cavitation is imploding close to a surface it will in contrast be directed at the surface, which is the reason why ultrasound is very powerful in applications such as cleaning surfaces. [11] This is also a property which gives potential for ultrasound in the refining of pulp fibres.

2.2.4. Factors affecting cavitation

The factors affecting the cavitation process are physical properties of the cavitating medium and the ultrasonic field [11].

The properties of the medium exposed to ultrasonication affects cavitation in several different ways. An important property is the *viscosity* of the medium, which is preferably low to simplify cavitation. Another parameter which should be kept at a low level to promote cavitation is the *surface tension*. This is due to the fact that low surface tension means lower cohesive forces, which is positive for bubble formation. Other properties of interest are *vapour pressure* and the presence of *impurities* in the liquid. Due to the fact that cavities consist of gas and that impurities act as nuclei for cavitation, it is positive to have a relatively high liquid pressure and concentration of impurities in the medium. To mention one last important property of the liquid medium, increasing the *temperature* corresponds to a reduction in cavitation intensity. This implication originates from the increasing cushioning effect of reduced bubble collapse upon increase in temperature, even though the increasing vapour pressure of cavities should suggest an increased cavitation intensity that is not the overall result. [11]

Considering the ultrasonic field its frequency and amplitude are affecting the cavitation formation. Altering the *frequency* means that the time intervals between compressions and rarefactions will be either shorter or longer. If the frequency is increased it will be harder to pull the molecules apart before they are compressed again. Consequently the

generation of cavities is reduced with an increasing frequency until the range of MHz is reached, then there will be no bubble formation at all. For the *amplitude* the effect is the opposite, meaning that an increasing amplitude increases cavitation. But this is only true until a certain level, depending on the equipment design, is reached. Another effect of an increase in amplitude is the increase in number of bubbles, something that results in a possible coalesce of bubbles with associated reduction in bubble collapse. [11]

2.2.5. Equipment

In the experiments of this thesis a piezoelectric transducer was used to create sound waves of ultrasonic frequency in the medium. A piezoelectric transducer consists of a piezoelectric material, which functions based on the piezoelectric effect. The piezoelectric effect implies two different things:

1. *The direct effect*: If a mechanical pressure is applied to a piezoelectric material, this will give rise to electrical charges on both sides of the plate. Opposite charges, equal in size, are generated on the sides and if tension is applied the polarity will be reversed. [12]

2. *The inverse effect*: A piezoelectric material under influence of an electric field will respond to this by deformation of the material. The material will contract or expand depending on the polarity of the applied charge. [12]

The inverse piezoelectric effect has the consequence that an alternating voltage across the material results in fluctuations in material dimensions. This effect is taken advantage of in the transfer of ultrasound by piezoelectric transducers. The transducer will vibrate at a specific frequency, resulting in formation/transfer of ultrasound through the medium applied to. Depending on the size of the transducer crystal it will have its own specific optimal performance frequency (its natural resonance frequency). Therefore piezoelectric transducers are designed for a specific frequency generation and that is why studies of ultrasonication at differing frequencies can not be performed using the same transducer equipment. [11]

In addition to the piezoelectric *transducer* an ultrasonic system consists of a *generator* which is needed to supply power to the transducer where it is converted into mechanical energy. Another part of the equipment is the *booster* which is mounted onto the transducer. Depending on the direction of the booster it reduces or increases the amplitude of the ultrasound. In direct connection to the booster is the *sonotrode* which transfers the mechanical oscillations into the medium to be sonicated in the *flow cell*. The pulp suspension is added to the *sample container* and recirculated in the system by a *pump*. See figures 1 and 2 for pictures of the ultrasonic equipment used in the experiments of this project.

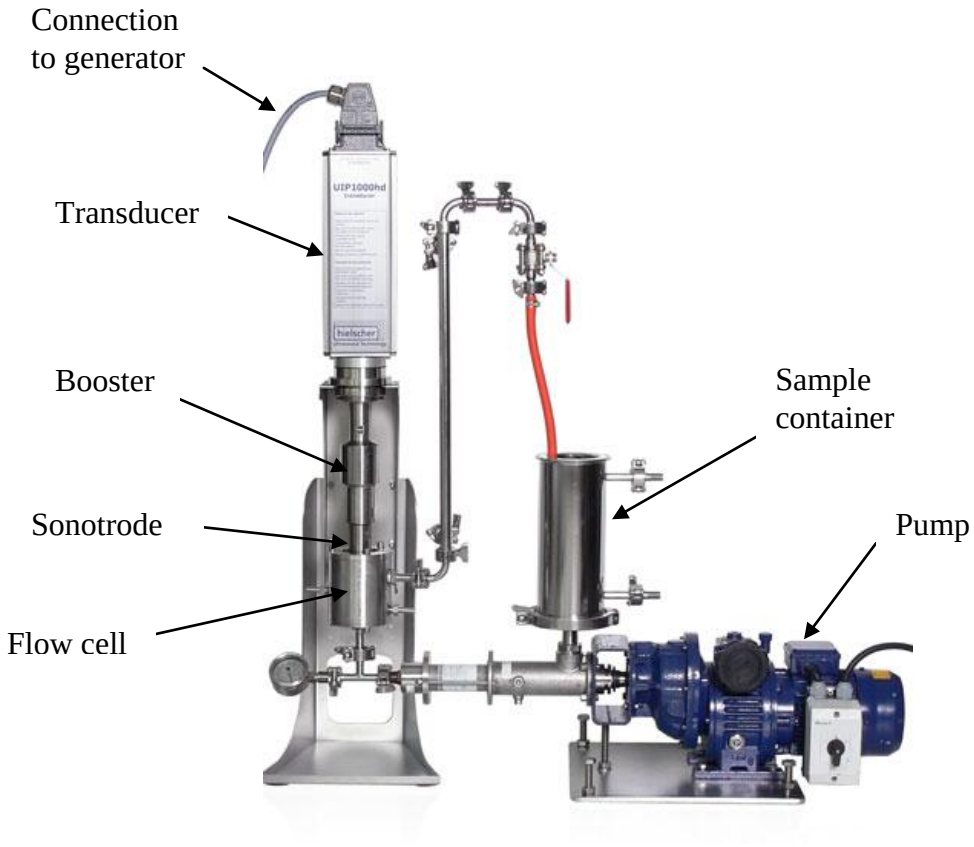

Figure 1. The ultrasonic equipment, UIP1000hd, which was used in the experiments [13].

Figure 2. The ultrasonic generator used in the experiments [14].

2.3. Analyses

In order to determine the properties of fibres subjected to ultrasonic treatment a number of different analysing methods were used. For characterisation of physical pulp properties the water retention value, Schopper-Riegler number and tensile index were measured. Furthermore fibre properties were analysed in a FiberMaster equipment and scanning electron microscopy was applied for imaging of pulp samples.

2.3.1. Water retention value

Water retention value (WRV) is a measure of how much water a fibre is able to hold under certain, standardised, conditions. Normally WRV increases with increased beating as a result of the creation of deformations in the fibre wall, which increase the capacity of water uptake. [15] For analysis of WRV a specific amount of fibres suspended in water are filtered and put into a centrifuge for a certain duration time. The centrifuged fibre samples are weighed (m_1) and left overnight for drying in a cabinet drier. Afterwards the dried pulp sample is weighed once again (m_2) and the WRV, measured in g H_2O/g dry fibres, can be calculated from eq. 1, see below. [16]

$$WRV = \frac{m_1}{m_2} - 1 \quad \text{(eq. 1)}$$

2.3.2. Schopper-Riegler number

An analysis of the Schopper-Riegler number of a pulp sample gives an indication of the de-watering properties. Schopper-Riegler is measured in terms of °SR and depends on some different properties of the fibres, such as the amount of fines and fibre flexibility. The degree of fibrillation also affects the de-watering properties. For measuring of the Schopper-Riegler number a specific volume of pulp, in suspension, is dewatered on a mesh in the testing equipment. When the pulp sample is poured into the testing equipment a fibre web will be created on the mesh. Some of the sample water will go through this fibre web and is collected for weighing meanwhile some water leaves the equipment in a side effluent. If the pulp is hard to dewater a smaller part will pass the fibre web and be collected in the beaker, resulting in a high °SR. After weighing the collected water the volume is correlated to a specific Schopper-Riegler number at standardised conditions. [17]

Sometimes the de-watering properties of a pulp sample are specified in terms of freeness with a Canadian Standard Freeness (CSF) value. The experimental procedure for determination of the CSF value is identical to the method for measuring of the Schopper-Riegler number. The difference between the CSF value and the Schopper-Riegler number lies in the scales for specification of the de-watering property, which are oppositely graded. Basically this implies that a high Schopper-Riegler number corresponds to a low CSF value.

2.3.3. Tensile index

One important paper property is the tensile strength, which is a measure of the greatest stress a piece of paper can withstand before it breaks. The property depends on fibre length and strength as well as specific bonding strength and bonded area. [18] To compare between laboratory sheets of differing surface weights a tensile index can be calculated. The tensile index of a pulp is analysed in laboratory handsheets produced at standardised conditions. The sheets are being pressed and conditioned before testing can take place. After completed conditioning the sheets are weighed and divided into slips of specific width. The sheet thickness is tested to give possibility for later tensile index determination. Then the paper slips are put into the tensile tester which locks the slip with clamps at two places whereupon the clamps are pulled apart until the strain results in a break. [19]

Tensile strength, X_1, (kN/m) is calculated as: $X_1 = \frac{a}{b}$ (eq. 2) where

a = strain at break (N)
b = width of paper strip (mm)

Tensile index, X_2, (kNm/kg) is calculated as: $X_2 = 1000 \cdot \frac{X_1}{W}$ (eq. 3) where

W = surface weight (g/m^2)

2.3.4. Fibre properties

Fibre properties such as dimensions, shape, fines material and kink angle can be measured in a piece of equipment called FiberMaster. A highly diluted sample of pulp is placed in the sample input of the equipment which then uses image analysis to determine the fibre properties.

2.3.5. Scanning electron microscopy

Scanning electron microscopy (SEM) is a technique for visualisation of very fine surface structures. The sample surface is bombarded with a beam of electrons from an electron gun. When they reach the surface, some electrons will be emitted from the material meanwhile others will be backscattered. These electrons are detected. The incoming electron beam is scanned across the sample and the current from the emitted and backscattered electrons is detected. As the amount of scattered electrons depend on the angle of the surface in relation to the beam, the intensity of the emitted electrons will vary and a picture of the sample surface can be constructed, showing the topography and structure of the sample. [20]

When performing SEM analysis on a non-conducting material, it must be covered with a conducting surface (e.g. gold) to prevent build-up of negative charge in the sample. In the case of aqueous samples the water also has to be removed before analysing the sample. To perform this, freeze drying can be used, putting the sample under vacuum to make the water undergo sublimation.

2.4. Literature study

Ultrasonic refining of pulp fibres is a relatively unexplored research area. However, studies ranging from primarily the middle of the 20th century until present do exist and provide some information even though they have not shown consistent results, as reported by Brodeur et al. [4] and Poniatowski and Walkinshaw [21]. Another drawback is that experiments are not directly comparable as different apparatus and parameters have been used. These implications obstruct the understanding of the topic. [4]

Iwasaki et al. studied the effect of ultrasonic treatment of 20 kHz frequency on individual softwood fibres, from spruce, without mechanical pre-treatment [22]. The fibres were from springwood and summerwood holocellulose, sulphite and sulphate pulps. Both never-dried and dried fibres were analysed. The studying of sonicated fibres showed a general pattern of four stages in the beating process, which could be divided into deformation (dislocations formed in the cell wall), removal of the S1 layer, swelling and fibrillation. Other observations were that summerwood fibres were harder to beat than springwood fibres and dried fibres were harder to beat than never-dried. In

the case of never-dried holocellulose and sulphite springwood fibres no fibrillation was obtained.

In a study by Manning and Thompson [3] it was concluded that no fibre cutting action occurred in the case of previously unrefined as well as previously mechanically refined ultrasonicated fibres. Both chemical hardwood and softwood Kraft fibres were included in this study, in which sonication took place at 20 kHz frequency. It was noted that the pulps which were not previously refined upon sonication did not fibrillate, this was true for the hardwood as well as the softwood pulps. When the pulp was mechanically refined before sonication, a significant decrease in CSF values could be noted and an increase in fibrillation was also verified. In this case the decrease in CSF value was somewhat more pronounced for the hardwood pulp than for the softwood. In a comparison of strength values for the softwood pulps the burst index was not altered in the unrefined sonicated pulp meanwhile the pre-treated pulps showed an increase in burst index in the interval of medium degree of refining.

In accordance with the results from Manning and Thompson, Poniatowski and Walkinshaw [21] also observed that ultrasonic treatment without mechanical pre-treatment has no significant effect on fibrillation. This study used an ultrasonic equipment of 31 to 35 kHz frequency and bleached softwood Kraft fibres. Besides the results on fibrillation it was shown that ultrasonic treatment resulted in smaller reductions in CSF values for ultrasonically refined recycled pulp than for mechanically refined. Another observation was that the breaking length of the ultrasonically recycled pulp was lower than for refiner recycled pulp.

In a study on hardwood Kraft fibres, Poniatowski and Walkinshaw [23] looked into ultrasonication in the recycling of pulp fibres. They used the same frequency of ultrasound as in the previous mentioned study on softwood fibres, 31 to 35 kHz. It was observed that the CSF values were lower for ultrasonically refined pulp than for refiner recycled pulp. Another observation was that the fibrillation was greater in ultrasonicated recycled fibres than in refiner recycled pulp. However, they also noted that if the pulp was not mechanically pre-treated, there was little or no effect on fibrillation by sonication. Considering the breaking length, it was only little affected in recycled-refined and recycled-sonicated pulp but both of these pulps showed better strength than recycled-untreated pulp.

Mohlin [24] studied cellulose fibre bonding in sulphite and Kraft pulps of different yields. All the samples were treated ultrasonically at 20 kHz for the same sonication duration times and compared to unbeaten and PFI-beaten fibres respectively. Depending on the type of pulp and the yield the mean bond strength of fibres varied.

It was observed that the ultrasonically refined fibres had lower mean bond strengths than the unbeaten and PFI-refined pulps in the Kraft pulp tested. In the case of sulphite pulp two pulps of different yields were tested. It was shown that the pulp of the higher yield had a lower mean bond strength for ultrasonically refined fibres than the PFI-beaten (which had a lower mean bond strength than the unbeaten pulp). However, in the case of the lower yield sulphite pulp the PFI-refined and ultrasonically refined fibres had relatively similar mean bond strengths, both of them higher than for the unbeaten pulp. These results show that the chemical composition of a pulp is important to mean bond strength. Mohlin points out that the mechanism behind mean bond strength values is the creation of new surfaces by beating and these surfaces bonding ability.

The surface modification of lignocellulosic fibres with ultrasound was studied by Gadhe et al. [25]. They used TMP from pine and sonicated the fibres at 610 kHz. The experiments showed an increase in non-conjugated carbonyl groups, which was explained by the assumption that phenolic hydroxyl groups in lignin are oxidised. It was also shown that the surface energy of fibres increased when they were sonicated, probably due to that the sonicated fibres are more active than unsonicated fibres. Another result was the finding that the extent of surface oxidation increases linearly with an increase in ultrasonic power but it is not significantly affected by an increase in sonication time.

The effects on fibre structure by ultrasonication were studied by Laine and Goring [26], who sonicated dried sulphate pulp fibres from spruce at 23 kHz. They noted a marked effect on fibre surfaces (ruptures in the S1 layer) and showed that the porous structure was altered and that the fibre saturation point increased. The median pore width increased and so did overall water uptake too. As the volume of smaller pores decreased with a simultaneous increase in the volume of larger pores, it was concluded that ultrasonication results in a transformation of smaller pores into larger pores.

Another conclusion from the experiments by Laine and Goring was that the carbohydrate composition does not change by ultrasonic treatment and neither does the cellulose molecular weight. Therefore, the increase in porosity may be due to disruptive effects of the ultrasonic waves rather than removal of material from the fibre wall. It was also shown that the crystalline structure does not change by ultrasonication. Regarding chemical composition, it was noted that the amount of carboxyl groups in fibres did not change by ultrasonication meanwhile the carbonyl groups increased. Laine and Goring suggest that this is due to the production of H_2O_2 in water by ultrasound. H_2O_2 can then react with the carbohydrates, which causes oxidation. Finally it was noted that sonication has the most pronounced effect at lower consistencies and longer duration times.

A study on the effect of ultrasonication on recycled pulp fibres was performed by Tatsumi et al. [27]. In addition to the recycled fibres, samples of a virgin bleached softwood Kraft pulp were also included in the study which was performed at a sonication frequency of 20 kHz. For the virgin fibres it was observed that the initial sedimentation rate decreased with increasing sonication time, something that indicates an increase in specific surface area. The results imply that fibres are made bulky and flexible by the ultrasonic treatment. In accordance with many other studies on ultrasonication of pulp fibres it was also reported that the sonication caused increased fibrillation of the fibres. This conclusion originated from SEM pictures taken of ultrasonically treated and untreated recycled fibres, which showed an increased external fibrillation on the fibres subjected to ultrasound.

According to Tatsumi et al. the WRVs could be significantly increased by the ultrasonic treatment, i.e. it was higher than for the untreated fibres compared with. As microphotographs showed that few fines were produced from ultrasonic treatment, the increase in WRV could not be due to the formation of fines. It was also observed that ultrasonic treatment results in decreased CSF values. Finally, considering strength properties, the ultrasonic treatment improved the strength of recycled paper which means that the tensile index was higher in ultrasonically treated recycled fibres than in untreated recycled fibres.

3. Experimental

The experiments in this project involved both softwood and hardwood fibres, in never-dried or dried form. Among the dried samples some received mechanical pretreatment prior to exposure to ultrasound, in contrast to the never-dried pulps which did not receive any pretreatment except defibration. After ultrasonication the samples were analysed in terms of different analyses regarding fibre properties and the energy aspects of the sonication were evaluated. To distinguish between all the experiments performed and simplify for the reader they are divided into *Experiment 1* and *Experiment 2*.

3.1. Pulp qualities

In the experiments performed in this project four different pulp qualities were used. The pulps were industrially produced softwood and hardwood pulps in dried or never-dried form. The never-dried pulps were withdrawn in the end of the bleaching process, where a large sample of each pulp quality was collected at a specific occasion to ensure that there would be enough pulp for all experiments. The pulp was thereafter stored in a cooling room. All different pulp qualities used in the experiments are described below.

Softwood 1 (SW1): softwood pulp (spruce and pine), produced from a mixture of pulpwood logs and sawmill chips, TCF, mid-length (2.15-2.35 mm) and medium-coarse fibres

Softwood 2 (SW2): softwood pulp (mostly spruce), produced from 75-100% pulpwood and wood from thinnings, TCF, short (2.05-2.25 mm) and thin-walled fibres

Softwood 3 (SW3): softwood pulp (spruce and pine) produced from 75-100% sawmill chips, TCF, long (2.35-2.65 mm) and coarse fibres

Hardwood 1 (HW): hardwood pulp (birch), TCF, very short fibres (ca 0.9 mm) [28]

3.2. Experiment 1

The first experiments (hereafter referred to as Experiment 1) were performed in Teltow, Berlin at the company Hielscher [29] which is a supplier of ultrasonic devices. Four different samples of SW1 pulp were treated ultrasonically. One sample consisted of never-dried defibrated pulp and the others were dried pulps among which one was defibrated at 0 kWh/t and the others were mechanically refined at 50 kWh/t and 100 kWh/t respectively prior to ultrasonication. The pre-treated dried pulps were refined in a laboratory refining equipment, Voith LR40. See table 1 below for a summary of experiments.

Table 1. Summary of the trials performed in Experiment 1.

Sample	Sonication time (min)				
	0	**1**	**2**	**3**	**5**
Never-dried pulp, 0 kWh/t defibration	x	x	x	x	
Dried pulp, 0 kWh/t defibration	x	x	x	x	x
Dried pulp, 50 kWh/t mechanical pre-treatment	x	x	x	x	x
Dried pulp, 100 kWh/t mechanical pre-treatment	x	x	x	x	x

As stated in table 1, all pulps except the never-dried were tested for all sonication times. The reason for not running the never-dried pulp for 5 minutes was a breakdown in the pump of the equipment used and lack of time to perform more trials.

The pulp was treated in the ultrasonic equipment UIP1000hd with associated cooling by tap water. The pump used was a Seepex mono pump and the process parameters in experiment 1 were as summarised below.

Fibre consistency: 1% (10 g/l)
Pump flow: 1 l/min (100%)
Frequency: 20 kHz (fixed)
Amplitude: 35 μm (100%)
Power: 500 W (1 bar counter pressure)

The power was regulated by closing a valve, setting a counter pressure of about 1 bar into the flow cell, thereby resulting in a power of 500 W. (Higher counter pressures than 1 bar could not be used due to the risk of plugging in the pump.) The power input was controlled by a power meter showing the actual input into the system. After adding 1 litre of pulp suspension to the sample container, the pump was started and the power of the generator turned on. Then the pressure was adjusted to 1 bar and timekeeping started. After circulating the fibre suspension for appropriate trial time the generator was turned off and the pressure released. The sample was pumped out of the system and cleaning of the system was performed by the addition of water until all fibres seemed to have been removed from the system.

The sonicated pulp samples were analysed at the Värö plant in accordance with the procedures described in Analysis, section 3.4. Due to limited amounts of pulp no analysis of Schopper-Riegler number was performed.

3.3. Experiment 2

After complete analysis of the first experiments it was decided to rent the equipment used in Experiment 1 in order to do more experiments. The equipment rented was of the same model as that used in Experiment 1 and the process parameters were kept identical to those used in the first trial besides a lower consistency of the pulp suspension in this experiment. This time the pulp was sonicated at 0.5% consistency, i.e. 5 g/l, and for

longer duration times. The reason for the choice of larger energy input was a lack of significant results when using the same consistency and sonication times as in Experiment 1.

Four different qualities of never-dried pulp fibres were used in these trials; three softwood pulps and one hardwood (see section 3.1, Pulp qualities, for information). The pulps did not receive any mechanical treatment prior to sonication, they were only defibrated. The trials performed in Experiment 2 are summarised below in table 2.

Table 2. Summary of the trials performed in Experiment 2.

Sample	Sonication time (min)			
	0	**5**	**10**	**15**
Never-dried pulp, SW1	x	x	x	x
Never-dried pulp, SW2	x	x	x	x
Never-dried pulp, SW3	x	x	x	
Never-dried pulp, HW	x	x	x	x

The reason why there is no sample of SW3 pulp sonicated for 15 min was a plugging of the pump during performance of that experiment.

3.4. Analysis

Analysis of the sonicated pulp samples was performed in terms of WRV determination, FiberMaster analysis and sheet forming with associated tensile testing. The samples in Experiment 2 were also analysed by determination of the Schopper-Riegler number due to sufficient amounts of pulp fibres in this case. A number of pulp samples from both Experiment 1 and 2 were selected for image analysis with SEM.

3.4.1. Physical testing

As a result of that the pulp samples were suspended during the ultrasonic treatment and some material usually could not be collected in each trial the concentration had to be determined. Therefore the method for preparation of samples in the SCAN and ISO standards for physical testing of pulps could not be followed in this respect. Otherwise the standards mentioned below were followed.

WRV determination was performed in accordance with the SCAN-C 62:00 standard.

The *Schopper-Riegler number* analysis was performed in accordance with the EN ISO 5267-1 standard.

Sheet formation and pressing, for final determination of tensile index, was performed mainly in accordance with the EN ISO 5269-1 standard. The exception was the fact that due to limited amounts of pulp only one sheet was formed of each sample. After pressing, the sheets were subjected to *conditioning* according to EN ISO 20187 standards. Then the sheets were weighed and divided into standard strips of paper (165·15 mm).

Testing of *sheet thickness* was performed according to EN 20534 standards in a L&W Micrometer with one exception. Instead of measuring the thickness of four sheets, one standard paper strip was divided into four parts and the thickness of these was measured.

The *tensile index* analysis was performed in accordance with the ISO 1924-3 standard but with the exception that seven or eight strips of paper were tested instead of ten as normally used in the standard. This was due to the only sheet available. The tensile tester was a L&W Tensile Tester with Fracture Toughness.

3.4.2. Fibre properties

The fibre properties analysis was performed in a L&W STFI FiberMaster (FM) equipment. The pulp samples from Experiment 1 were analysed in a process FM equipment in the Värö Mill meanwhile the samples from Experiment 2 were analysed in an equipment at the Innovation pulp lab. The reason why two different equipments were used was a breakdown in the FM at lab at the time for analysis of Experiment 1.

3.4.3. SEM

Before analysing the fibres in an electron microscope the samples needed some preparation. Some millilitres of the aqueous fibre samples, all of a concentration about 2 g/l, were poured into a beaker and freeze-dried overnight until the water had disappeared. A small piece of the freeze-dried fibre web was attached to a "stub" with the help of silver glue. The stub was put into an ion sputter for coating with gold atoms. Finally the prepared samples were examined in a scanning electron microscope, model JEOL JSM-820 at 60 μA. Pictures of the fibre web were taken at some different magnification levels ranging from 50x to 1000x. The pictures taken of the sample surface were handled in the computer software SemAfore.

As a consequence of limitations in available time for analysis, only some of the total amount of samples were being analysed with SEM. For Experiment 1 one sample of each type of fibres was analysed meanwhile in Experiment 2 it was chosen to only analyse the HW pulp in order to see the effect on hardwood fibres. Softwood fibres hade in comparison already been analysed in Experiment 1.

3.5. Energy aspects

The energy output of the ultrasonic equipment was calculated for both experiments. To give values comparable to those of conventional refining, energy consumption was defined in kWh/t pulp. For a comparison in the opposite direction, from mechanical refining to ultrasonic refining, the equivalent sonication times for some different conventional refining degrees were also calculated.

4. Results and discussion

4.1 Physical properties

To determine the physical properties of the sonicated fibres, pulp samples were analysed in terms of WRV, tensile index and Schopper-Riegler number. The results are visualised in the following sections and all experimental values are also summarised in tables in Appendix A1.

4.1.1. WRV

The results obtained from the analysis of WRVs in Experiment 1 and 2 are shown below in figure 3 and 4 respectively.

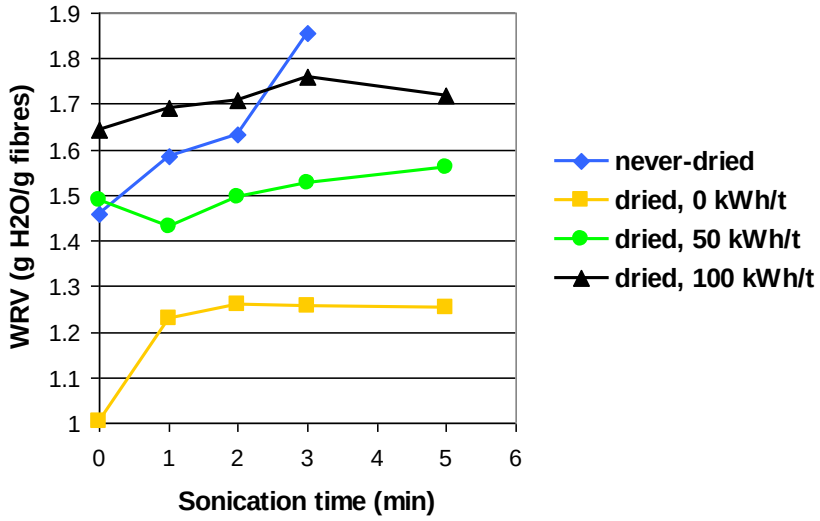

Figure 3. WRV as a function of sonication time for samples of SW1 pulp, ultrasonicated at 1% consistency in Experiment 1, without and with preceding mechanical refining at different energy levels.

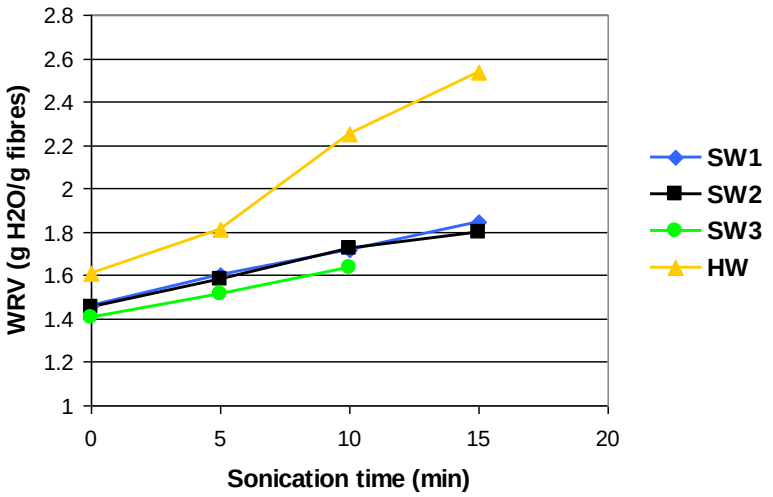

Figure 4. WRV as a function of sonication time for samples of never-dried pulps, ultrasonicated at 0.5% consistency in Experiment 2 without any preceding mechanical refining.

From the results of Experiment 1, visualised in figure 3, it can be noted that the never-dried SW1 pulp was more easily ultrasonically refined than the dried pulps. This is in accordance with the observations by e.g. Iwasaki et al. [22]. Most of the previous lab scale studies of ultrasonic refining had shown that samples of dried pulp, which had not been refined prior to sonication did not fibrillate or undergo any changes when sonicated. It is therefore strange that the dried pulp which is only defibrated (0 kWh/t) prior to sonication shows an increase in WRV. However there is no increase for different sonication times, only from reference to sonication for 1 min. It could therefore be suspected that the increase in WRV in some way has to do with different treatments of the reference and sonicated pulps.

Considering the results from Experiment 2, shown in figure 4, it can be concluded that there is an increase in swelling for all pulp qualities sonicated at 0.5% consistency. The results also show evidence that the hardwood pulp, HW, is more easily beaten than the other pulps as this is undergoing the largest change in WRV. Among the softwood pulps the SW2 and SW1 qualities show identical evolutions of WRVs, a significant improvement in water retention, even though not at the same magnitude as that of the hardwood pulp. The SW3 quality shows the same trend as the other pulps but is slightly less easily beaten than the other softwood qualities. Probably this is due to the fact that this pulp consists of coarser fibres which are harder to beat.

According to the results on WRVs it seems reasonable to assume an increased inner fibrillation of the never-dried fibres subjected to ultrasonic treatment. The results on never-dried fibres obtained in Experiment 1 and 2 are in accordance with each others as well as with the ones stated in literature studies on WRV (e.g. Tatsumi et al. [27]).

4.1.2. Tensile index

The results obtained from the analysis of tensile index in Experiment 1 and 2 are visualised below in figures 5 to 8. In figures 5 and 6 the results on tensile index are shown as a function of the duration time of ultrasonic treatment meanwhile in figures 7 and 8 it is shown as a function of the sheet density.

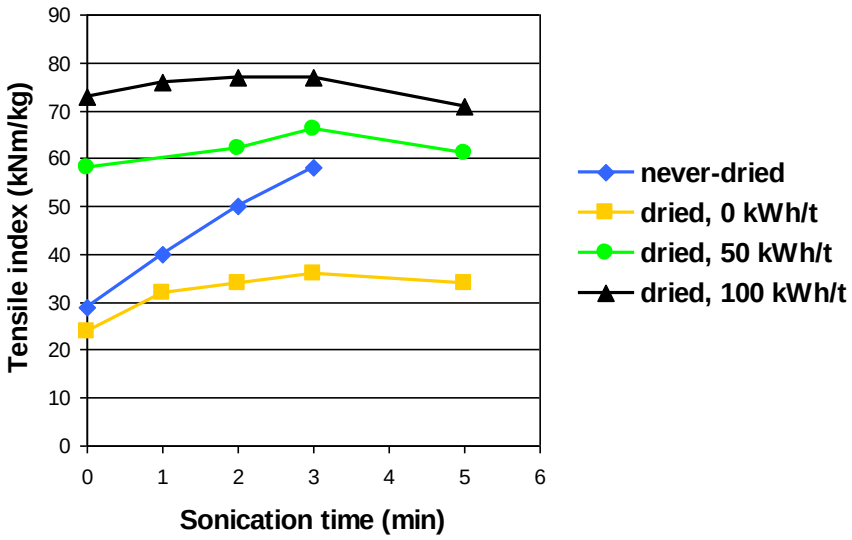

Figure 5. Tensile index as a function of sonication time for handsheets produced from samples of SW1, ultrasonicated at 1% consistency in Experiment 1, without and with preceding mechanical refining at different energy levels.

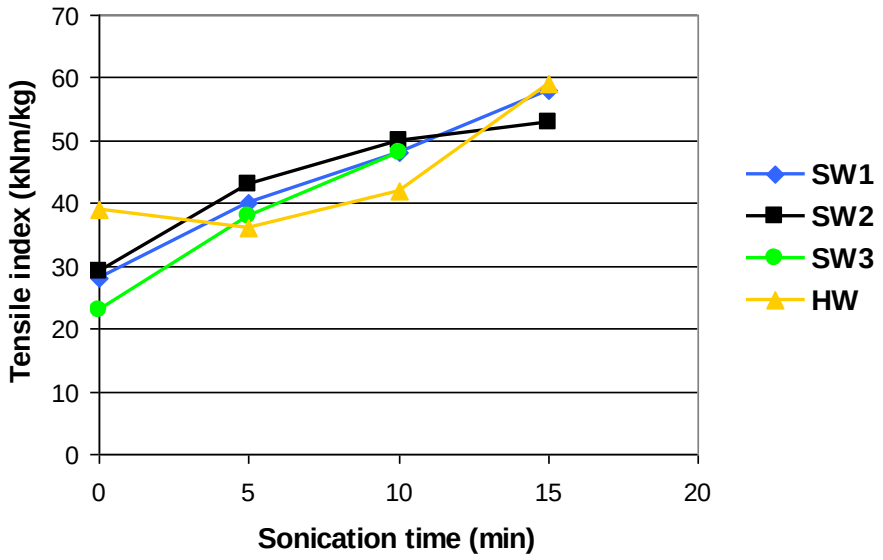

Figure 6. Tensile index as a function of sonication time for handsheets produced from never-dried pulp samples, ultrasonicated at 0.5% consistency in Experiment 2 without any preceding mechanical treatment.

In figures 7 and 8 the values of the reference samples, which did not receive any ultrasonic treatment, are marked with circles in the figures.

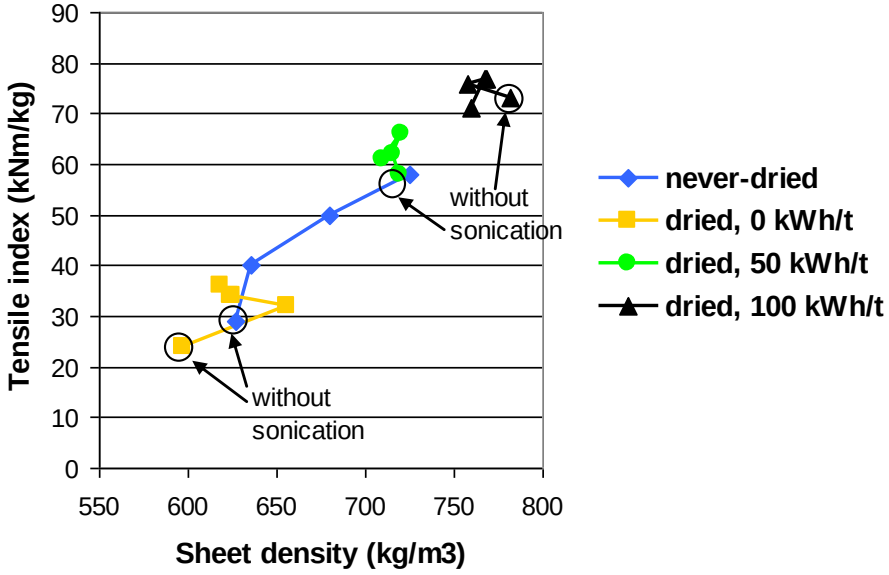

Figure 7. Tensile index as a function of sheet density for handsheets produced from samples of SW1, ultrasonicated at 1% consistency in Experiment 1, without and with preceding mechanical refining at different energy levels.

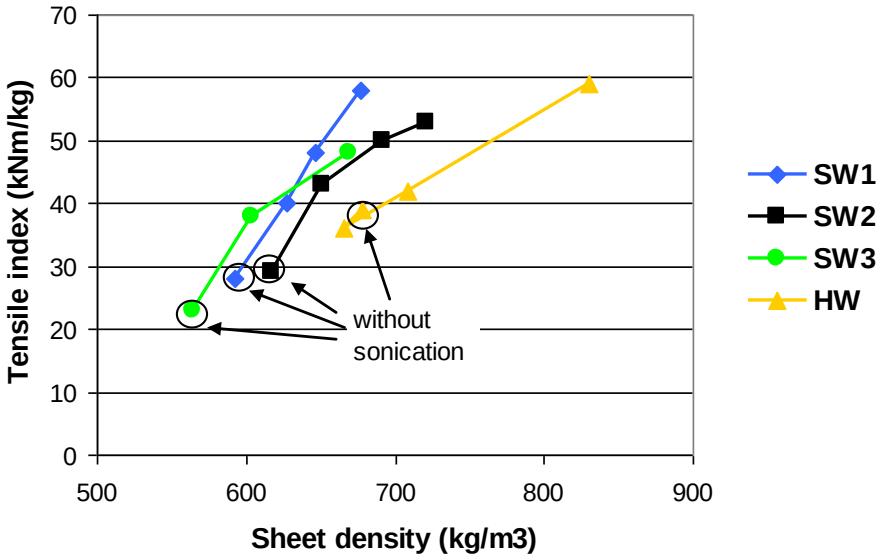

Figure 8. Tensile index as a function of sheet density for handsheets produced from never-dried pulp samples, sonicated at 0.5% consistency in Experiment 2 without any preceding mechanical treatment.

In accordance with the results on WRVs, it can also in the analysis of tensile index be concluded that the dried pulps in Experiment 1 are largely unchanged by

ultrasonication. This is relatively clear in both figures 5 and 7, even though the dried pulp which was only defibrated (0 kWh/t) prior to sonication seems to develop tensile index somewhat. In contrast to the dried fibres, the never-dried SW1 pulp in Experiment 1 and all the never-dried pulp qualities in Experiment 2 showed significant development of tensile index with related increase in sheet density. It is therefore most likely that poor evolution of physical properties of the dried pulps is due to the fact that they are dried. Drying makes the fibre cell wall more rigid and swelling of the fibres is prohibited due to hornification. Probably this is the reason why the dried fibres were little affected by the ultrasound.

Also in the case of Experiment 2 the evolution of the tensile index is relatively similar to that of the WRVs. At 0.5% consistency the hardwood pulp however shows a smaller evolution of the tensile index than the WRV in comparison to other qualities. This can be explained by the fact that hardwood pulps consist of shorter fibres than softwood pulps and therefore result in paper with a lower strength due to the fact that each fibre has got fewer bonds to other fibres. However it should be added to the discussion that the HW pulp shows a bit of a strange trend as the tensile index, compared to the reference, is reduced at a sonication time of 5 min and then increasing remarkably from 10 up to 15 min (in figure 6). These results are probably due to unavoidable fluctuations in pulp quality and experimental variance.

Regarding the softwood pulps in figures 6 and 8 it can be concluded that they show a similar trend to that of the WRV analysis. The SW1 and SW2 qualities are following each other closely in strength development at the different sonication times and compared to the SW3 pulp the other softwood pulps are a bit higher in tensile strength. In spite of this the SW3 pulp shows the most pronounced increase in tensile index among the pulp qualities, i.e. an increase of 25 kNm/kg, when comparing the sample which was sonicated for 10 min with the untreated reference sample. The SW1 and SW2 qualities showed in comparison increases of 20 and 21 kNm/kg respectively in tensile index for the same duration times of ultrasonication.

The results on tensile index indicate more or stronger bonds between fibres in the ultrasonicated handsheets compared to the untreated reference pulp. It is therefore most probable to suspect that the fibres have been increasingly fibrillated, resulting in a larger area of fibre surface available for bondings between fibres and therefore a stronger fibre network. The deviating results can most probably be explained by an unavoidable experimental error and variance between trials. A replication of the experiments would make it possible to get more certain results but the trends are still trends and conclusions can be drawn thereby even though the results should be treated as indications and not statistically true values. However the results on increased tensile values were in accordance with literature studies such as that by Tatsumi et al. [27].

4.1.3. Schopper-Riegler number

The results obtained from the analysis of Schopper-Riegler number in Experiment 2 are visualised below in figure 9.

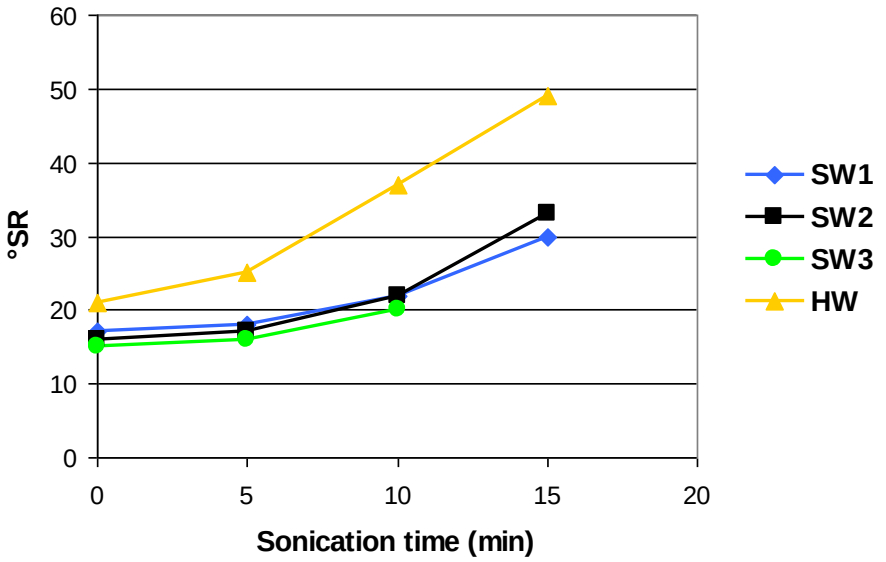

Figure 9. De-watering measured in terms of °SR as a function of sonication time for samples of never-dried pulps, ultrasonicated at 0.5% consistency in Experiment 2 without any preceding mechanical refining.

The results from the Schopper-Riegler number analysis in figure 9 show the same trend as the WRV and tensile index results with clearly visible increases for all pulp qualities at 0.5% consistency. The HW pulp shows the largest increase and the highest °SR numbers, which is consistent with the WRVs and tensile index. Among the softwoods the SW1 and SW2 qualities are once again relatively similar to each other, both a bit lower in °SR than the hardwood pulp. As valid for the other pulp qualities, the SW3 pulp is a bit lower than the others but still shows a significant increase in °SR.

The results in °SR can theoretically be interpreted in many ways. One reason for an increase in Schopper-Riegler number can be an increased amount of fines material, which reduces the de-watering capacity of the pulp. But as will be concluded in the next section of the report, see section 4.2, this is not likely to be the explanation in this case. It seems much more likely that the increase in °SR is due to an increased fibrillation of the fibres.

An increased flexibility of fibres upon ultrasonication is implied by the study performed by Tatsumi et al. [27]. Besides, many articles report on decreased CSF values as a result of sonication, something that indicates decreased de-watering capacity and is transferable to a comparison with increases in the Schopper-Riegler number. Therefore the results obtained in this investigation are supported by the studies of e.g. Thompson and Manning [3], Poniatowski and Walkinshaw [21] and Tatsumi et al. [27].

4.2. Fibre properties

The results obtained on fibre properties from FiberMaster analysis of the sonicated pulp samples in Experiment 1 and 2 respectively are summarised below in table 3 and 4. All results in the tables are average values of the sample analysis. It should be kept in mind that different equipments were used for evaluation of results from Experiment 1 and

Experiment 2, see section 3.4.2. A difference between the equipments used is that one of them measured the kink angle meanwhile the other did not. The equipments are however of the same type.

Table 3. Fibre properties of SW1 pulp, ultrasonicated at 1% consistency in Experiment 1, without and with preceding mechanical refining at different energy levels.

Pulp	Sonication time (min)	Fibre length (mm)	Fibre width (µm)	Fibre shape (%)	Fines content (%)
Never-dried 0 kWh/t	0	2.32	28.3	82.1	8.8
	1	2.30	28.2	82.7	8.7
	2	2.35	28.3	82.2	8.7
	3	2.28	28.3	83.1	9.8
Dried pulp 0 kWh/t	0	2.27	26.2	83.9	10.0
	1	2.30	26.6	82.5	9.1
	2	2.28	26.5	82.6	9.2
	3	2.29	26.6	82.6	9.1
	5	2.25	26.6	82.8	9.5
Dried pulp 50 kWh/t	0	2.24	27.4	83.1	11.4
	1	2.40	27.5	82.6	9.0
	2	2.32	27.5	83.7	8.8
	3	2.35	27.6	83.6	9.1
	5	2.33	27.5	83.9	8.8
Dried pulp 100 kWh/t	0	2.27	28.2	83.1	10.7
	1	2.28	28.3	83.8	9.6
	2	2.29	28.5	83.7	9.3
	3	2.26	28.4	84.4	9.4
	5	2.29	28.2	83.8	9.5

Table 4. Fibre properties of different never-dried pulps ultrasonicated at 0.5% consistency in Experiment 2 without any preceding mechanical refining.

Pulp	Sonication time (min)	Fibre length (mm)	Fibre width (µm)	Fibre shape (%)	Fines content (%)	Kink angle (°)
SW1	0	2.26	31.4	82.4	8.38	57.1
	5	2.30	32.0	82.2	8.50	57.4
	10	2.30	32.2	82.1	8.35	57.5
	15	2.26	32.3	82.1	8.53	59.4
SW2	0	2.20	30.3	81.8	8.23	57.0
	5	2.20	30.3	82.5	9.00	57.6
	10	2.21	30.6	82.2	8.55	58.8
	15	2.24	31.1	82.1	7.67	59.5
SW3	0	2.51	32.9	81.2	8.40	57.1
	5	2.54	33.0	82.0	7.93	57.1
	10	2.54	33.4	81.8	7.58	56.9
HW	0	0.919	23.0	88.5	6.98	51.7
	5	0.963	23.1	88.7	7.15	51.4
	10	0.932	22.8	88.9	7.35	51.6
	15	0.940	22.8	88.7	7.03	51.3

Fibre length
According to tables 3 and 4 it seems likely that sonication does not affect the fibre length, i.e. there is no cutting of fibres. In the case of Experiment 1 there are some fluctuations in values but these can be due to statistical variance and it does not at all seem probable that there is any shortening of the fibres. For the different pulps tested in Experiment 2 the fibre length also keeps relatively constant. These results are supported by the literature study e.g. Manning and Thompson [3].

Fibre width
For the samples sonicated in Experiment 1, it is hard to conclude if there is an increase or a decrease in fibre width from the results in table 3. The average fibre width seems to keep relatively constant for all different samples tested even though the results could also be interpreted as if there is a small increase in fibre width for the dried pulps which were defibrated at 0 kWh/t and mechanically pre-treated before sonication at 50 kWh/t respectively. The softwood pulps in Experiment 2, see table 4, show indications on a small increase in fibre width but it is difficult to tell if there really is an increase without any replications of experiment. However it seems likely that there is an increase in fibre width as this would be consistent with the identification of increased swelling/fibrillation of fibres, which should result in an increased fibre width.

Fibre shape
The pulps of different refining degrees in Experiment 1, table 3, show relatively inconsistent trends in fibre shape. The dried pulps which were previously refined at 50 and 100 kWh/t respectively before sonication seem to have been straightened by the ultrasonic treatment. This is also the trend identified for the never-dried pulp despite one confusing/non-consistent value. In contrast, the sample of dried pulp defibrated at 0 kWh/t showed what could be identified as a decrease in fibre shape, i.e. the fibre was more curled than before the treatment. This is probably due to the fact that the reference sample was defibrated in another piece of equipment than the sonicated pulp.

In the case of never-dried pulps in Experiment 2, table 4, it is most easily to interpret the results as that there is no effect of ultrasonic treatment on the fibre shape. There is little evidence that the fibres are neither straightened nor curled upon sonication even though a replication of experiments would be needed to get more actual evidence for the conclusion that fibres are unaffected in the sense of shape.

It seems therefore like there is more fibre straightening effect in conventional mechanical refining but perhaps the results from ultrasonic refining could show more of a straightening effect under other conditions than the ones used here. What is not known in this case is if the pump in the sonication equipment has any effect on the fibre shape for example. See Appendices, section A2, for a small investigation of possible pump refining action. Perhaps other flow conditions would be able to straighten the fibres i.e. it is not possible to say if it is the pump that curls the fibres or the ultrasonic treatment, if they are curled at all.

Fines content
According to table 3 and 4 respectively it seems most likely that the fines content is not increasing due to ultrasonic treatment. This is also in accordance with the observation of constant fibre length. The results are strange in the sense that the fines amount is decreasing in several cases in Experiment 1 as well as in Experiment 2. This is perhaps

due to that only a part of the total pulp amount from sonication was brought back to the Värö plant for analysis in Experiment 1 and therefore some fines probably were lost. In Experiment 2 the differences are probably due to experimental variance/lack of replication of experiments (even though the values are averages from duplicates) and the fact that it was not possible to get ideal mixing of the samples before taking out samples for FM analysis. However the results on no fines formation imply that ultrasonic refining is much gentler to the fibres than conventional mechanical refining. These results are supported by Tatsumi et al. [27] and Manning and Thompson [3] for example.

Kink angle

According to table 4 the average fibre kink angle is increased for some pulp qualities meanwhile others remain unaffected. The hardwood pulp HW is not increasing its average kink angle, which could be related to the fact that these fibres are shorter than the softwood fibres. Among the softwoods the SW3 pulp, which consists of fibres with higher coarseness than the other softwood pulps, remains at constant kink angle. This is perhaps because of the coarser structure which makes the fibres more resistant to the ultrasonic treatment. In contrast, both other softwood pulps; SW1 and SW2 reach larger average kink angles with increased duration times of ultrasonic treatment. Perhaps this is a result of the flow properties of the pulp in the recirculation system and pump. At longer circulation times the pulp fibres showed an increasing tendency to plug the system and the fibres still circulated in the system can have been affected by this. Probably the flow of the hardwood pulp in the system was more ideal and less affected by fibre flocculation and this fact can be the explanation to the constant kink angle for these fibres.

4.3. SEM microphotographs

Some selected samples of the sonicated pulps were analysed with SEM. In Experiment 1 one sample of each pulp was analysed meanwhile in Experiment 2 only the hardwood sample was subjected to this analysis. The results from the analysis with SEM are summarised in the following sections in figures 10 to 45. In order to make the results section a bit less dense, the sample of dried pulp, which was mechanically refined at 50 kWh/t prior to sonication, in Experiment 1, is placed in Appendices, section A3.

For the microphotographs visualised in the following sections it should be noted that the magnitudes are ranging from 50 times up to 1000 times enlargement. The magnitudes are denoted with an x in the text below the figures; e.g. 50x corresponds to 50 times.

SW1 never-dried pulp

In the figures 10 to 19 below are samples of SW1 never-dried pulp from Experiment 1 visualised. One sample is an untreated reference sample meanwhile the other is ultrasonicated for 3 min at 1% consistency without any mechanical pre-treatment.

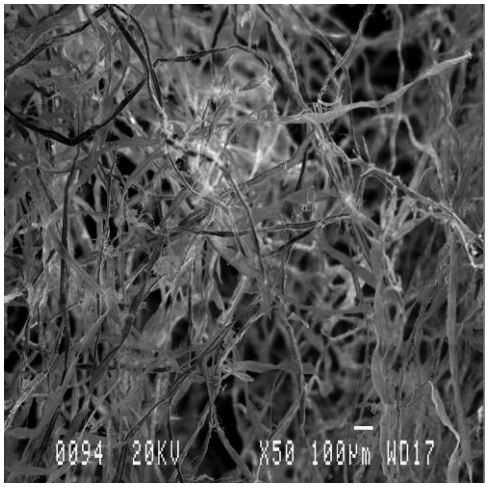

Figure 10. Reference, 50x

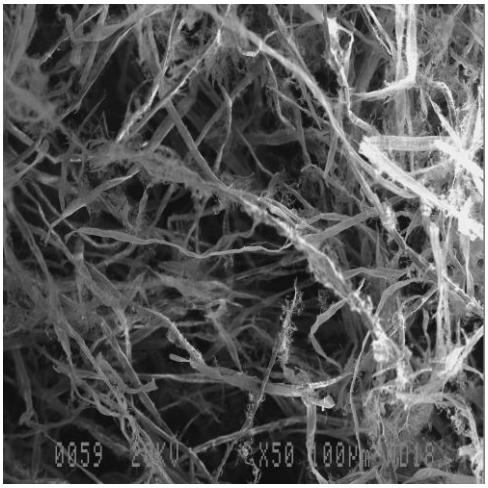

Figure 11. Ultrasonicated, 50x

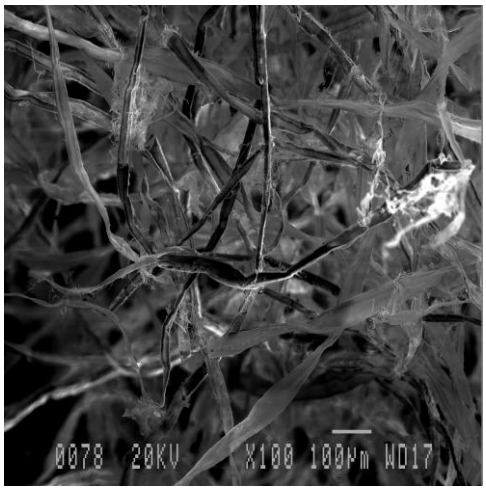

Figure 12. Reference, 100x

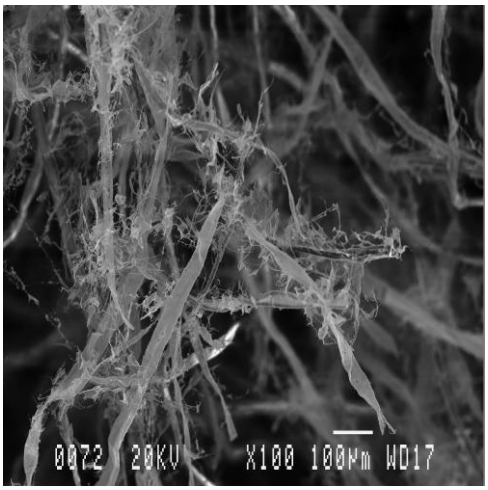

Figure 13. Ultrasonicated, 100x

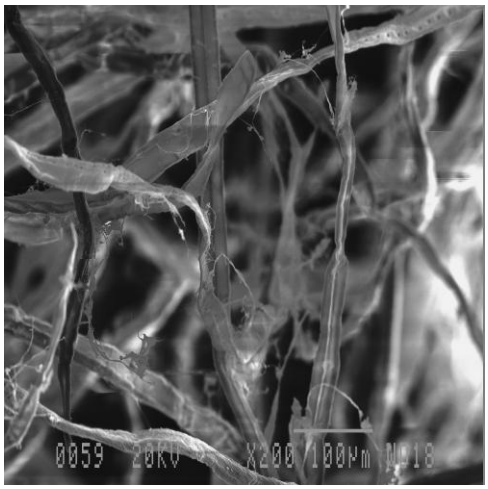

Figure 14. Reference, 200x

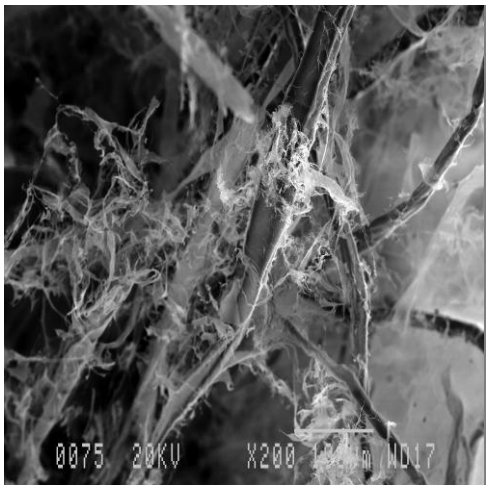

Figure 15. Ultrasonicated, 200x

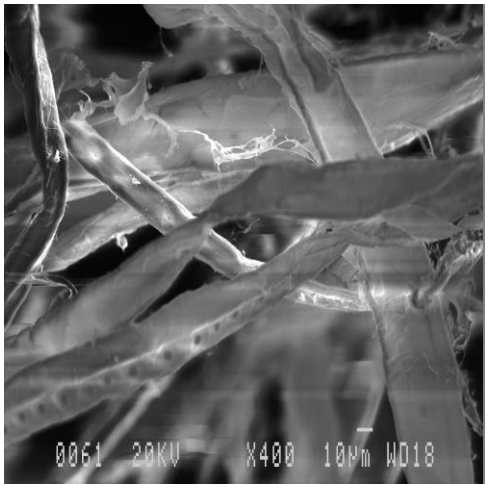

Figure 16. Reference, 400x

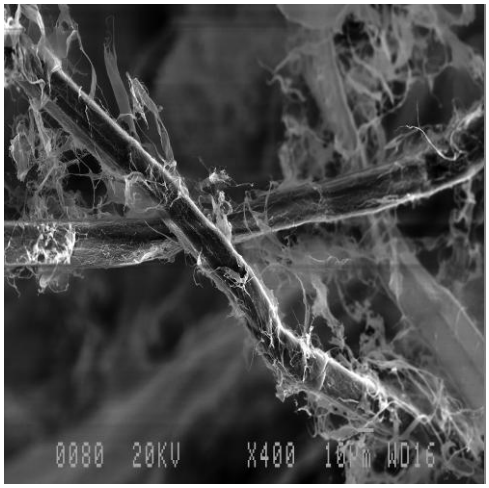

Figure 17. Ultrasonicated, 400x

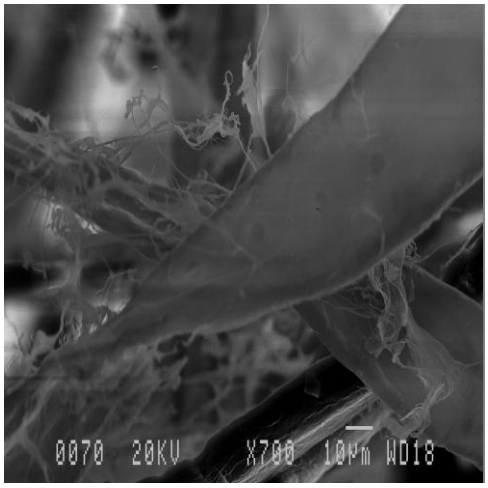

Figure 18. Reference, 700x

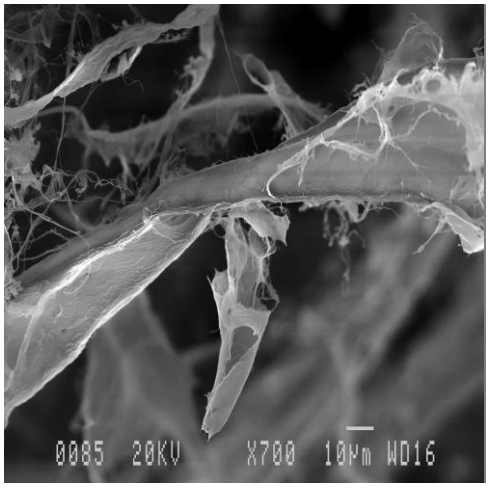

Figure 19. Ultrasonicated, 700x

SW1 dried pulp, 0 kWh/t
In the figures 20 to 29 below are samples of SW1 dried pulp from Experiment 1 visualised. One sample is a reference sample, which has only been defibrated, at 0 kWh/t, meanwhile the other sample was defibrated prior to ultrasonication for 3 min at 1% consistency.

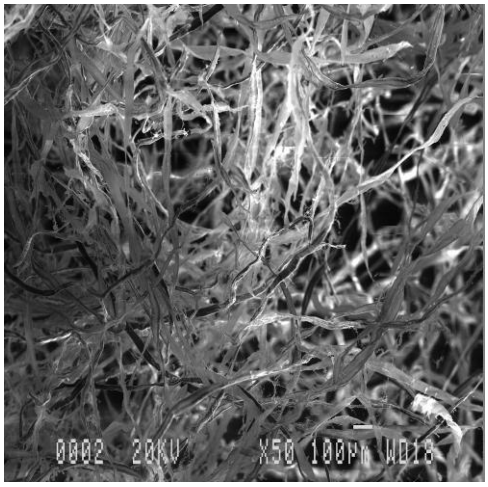

Figure 20. Reference, 50x

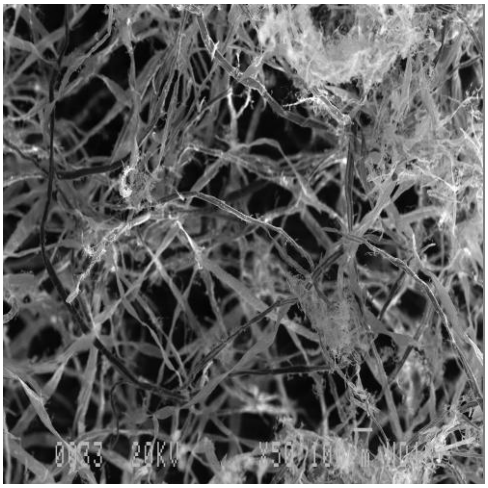

Figure 21. Ultrasonicated, 50x

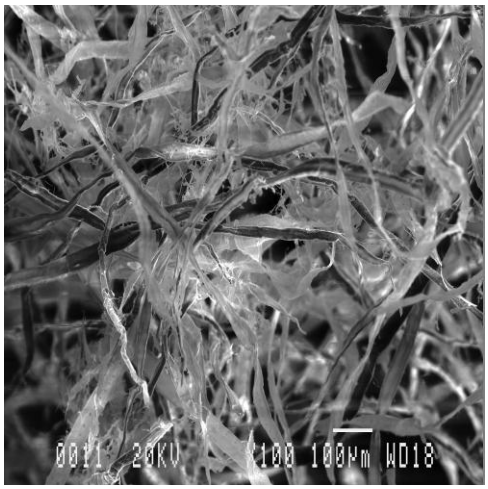

Figure 22. Reference, 100x

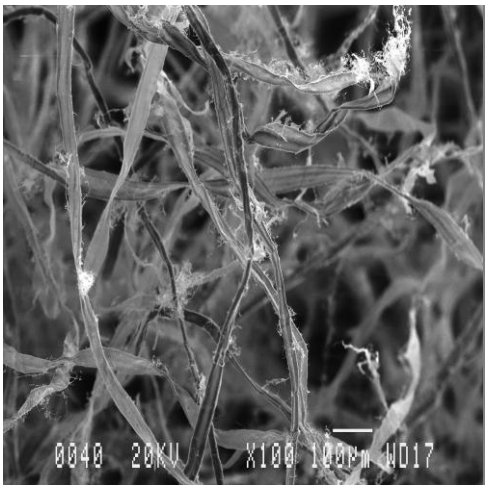

Figure 23. Ultrasonicated, 100x

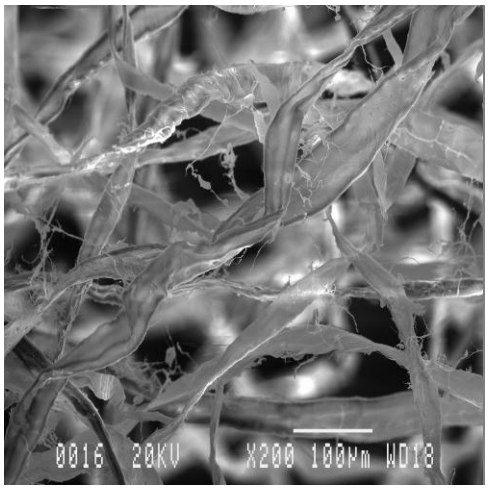

Figure 24. Reference, 200x

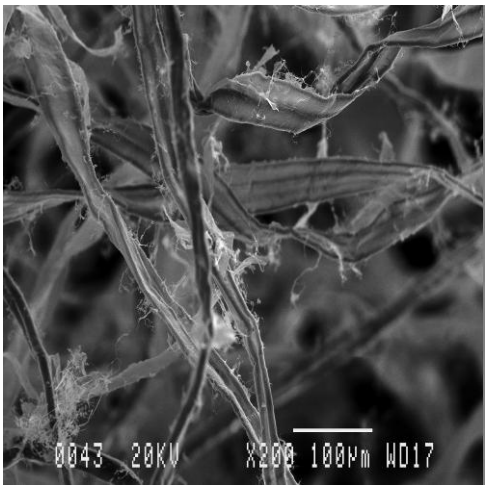

Figure 25. Ultrasonicated. 200x

Figure 26. Reference, 400x

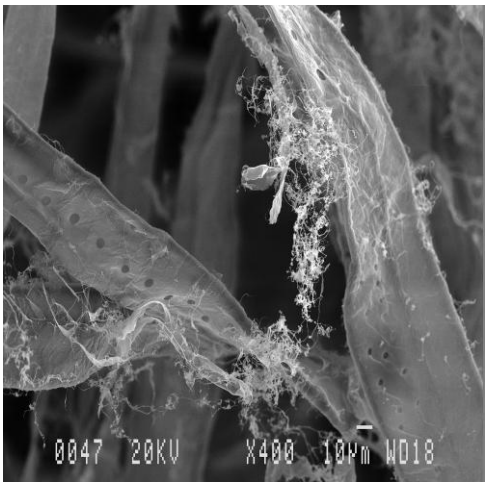

Figure 27. Ultrasonicated, 400x

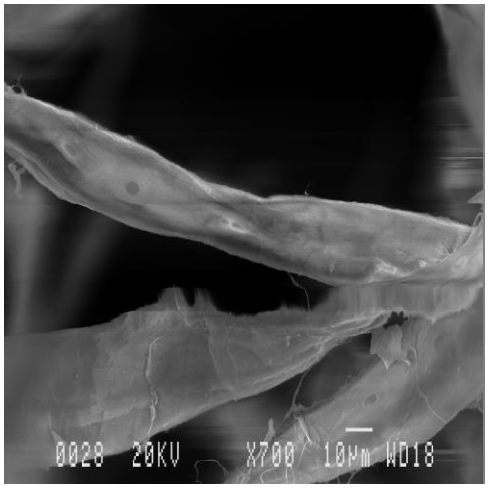

Figure 28. Reference, 700x

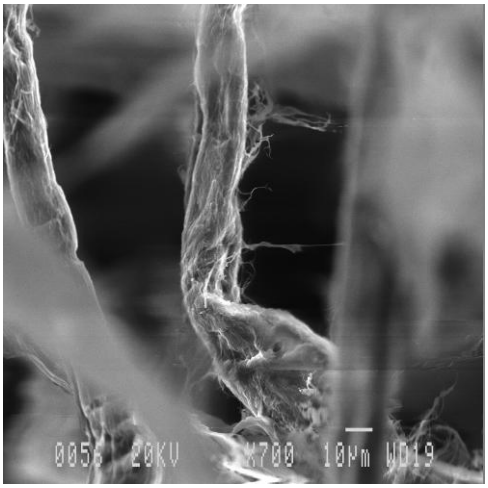

Figure 29. Ultrasonicated, 700x

SW1 dried pulp, 100 kWh/t

In the figures 30 to 33 below are samples of SW1 dried pulp from Experiment 1 visualised. One sample is a reference sample, which has been subjected to mechanical pre-treatment at 100 kWh/t. The other sample received mechanical treatment at 100 kWh/t prior to ultrasonication for 3 min at 1% consistency.

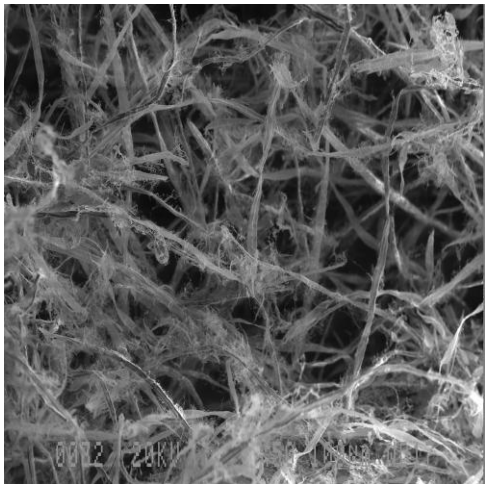

Figure 30. Reference, 50x

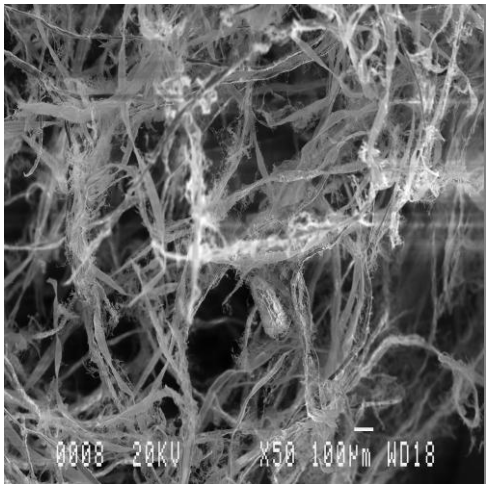

Figure 31. Ultrasonicated, 50x

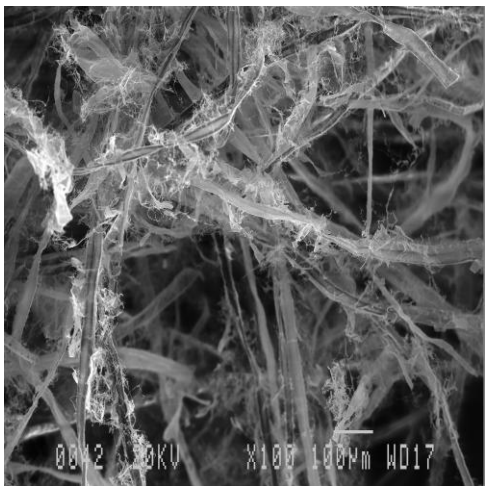

Figure 32. Reference, 100x

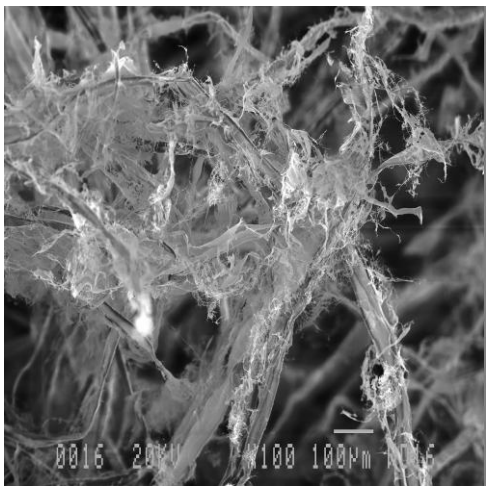

Figure 33. Ultrasonicated, 100x

HW never-dried pulp

In the figures 34 to 45 below are samples of HW never-dried pulp from Experiment 2 visualised. One sample is an untreated reference sample meanwhile the other is ultrasonicated for 15 min at 0.5% consistency without any mechanical pre-treatment.

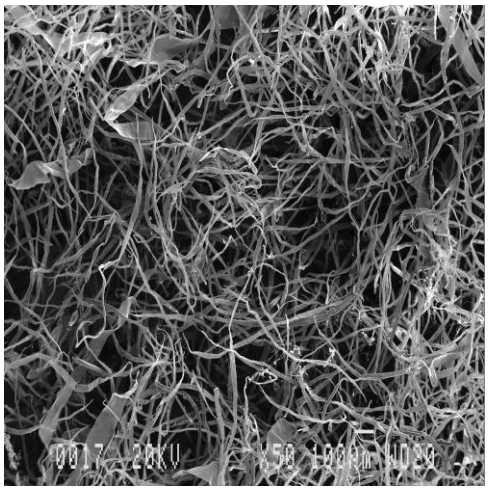

Figure 34. Reference, 50x

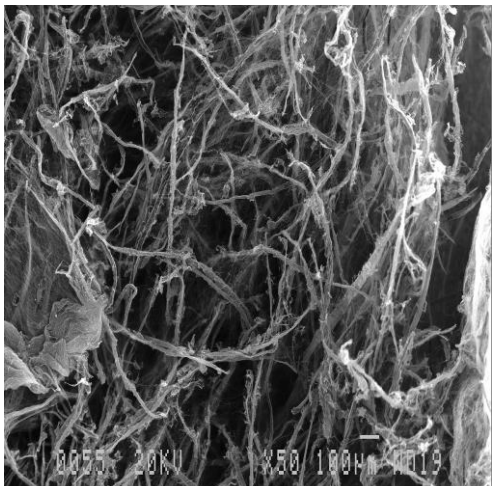

Figure 35. Ultrasonicated, 50x

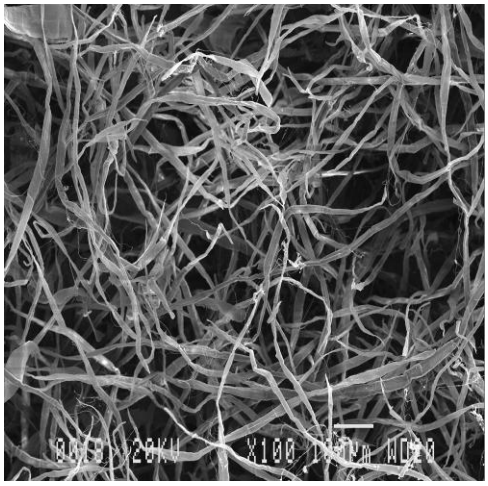

Figure 36. Reference, 100x

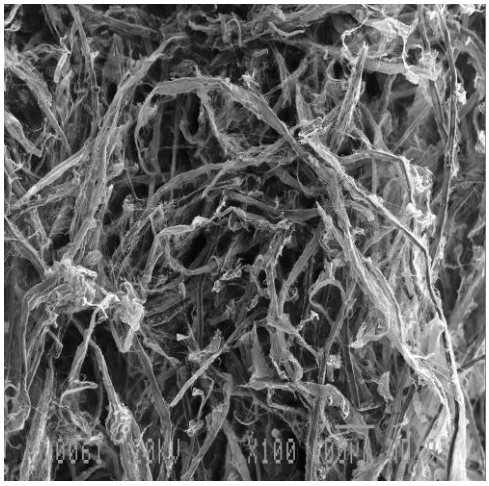

Figure 37. Ultrasonicated, 100x

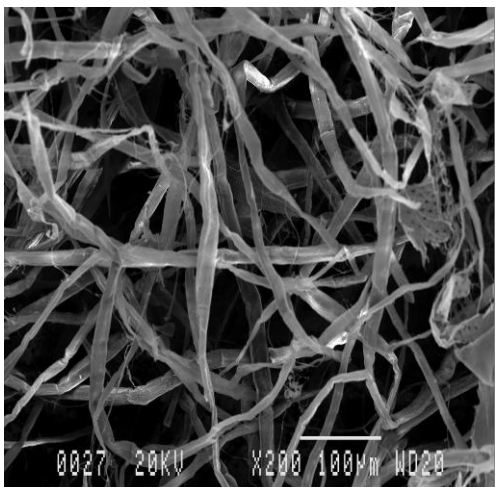

Figure 38. Reference, 200x

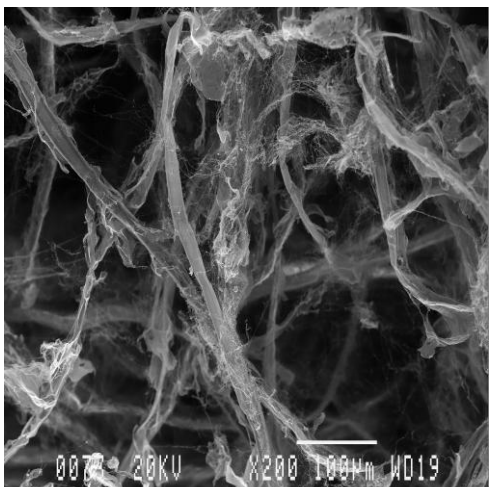

Figure 39. Ultrasonicated, 200x

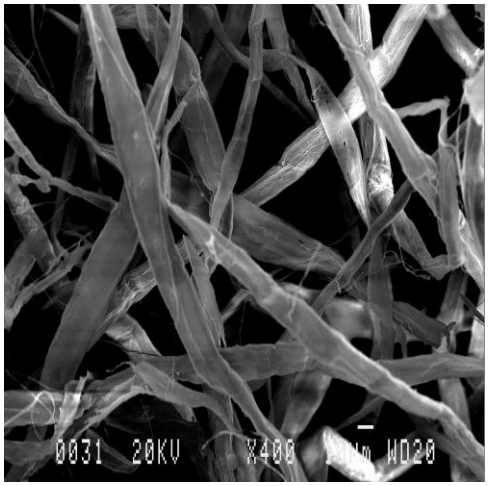

Figure 40. Reference, 400x

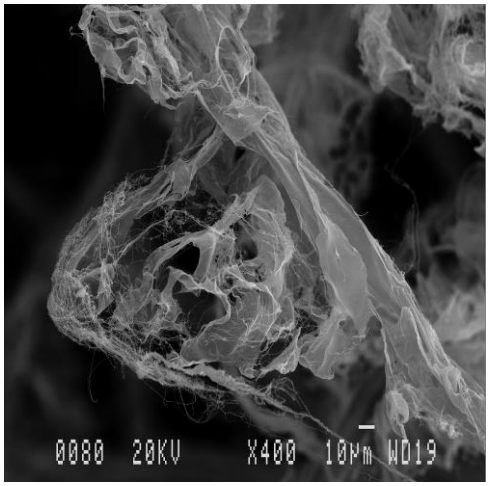

Figure 41. Ultrasonicated, 400x

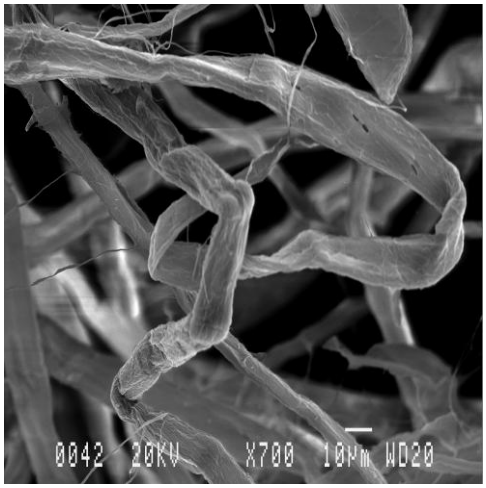

Figure 42. Reference, 700x

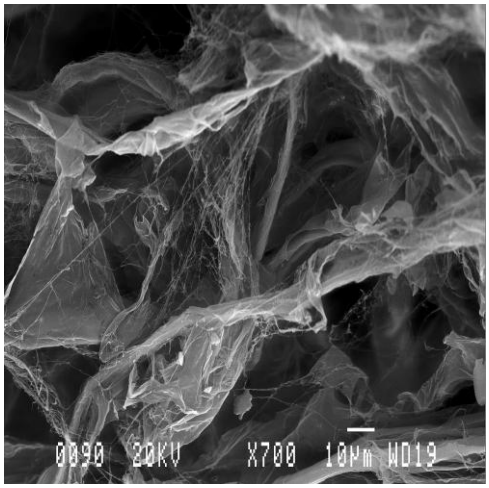

Figure 43. Ultrasonicated, 700x

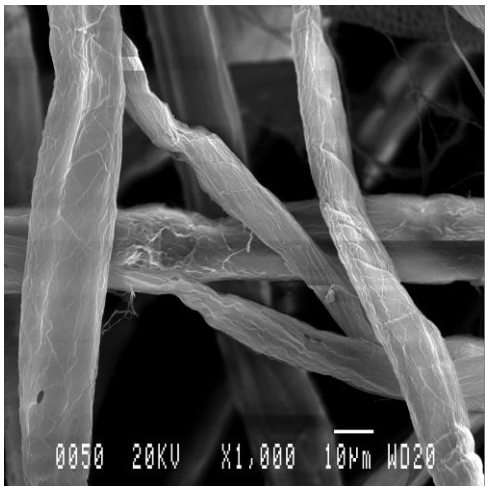

Figure 44. Reference, 1000x

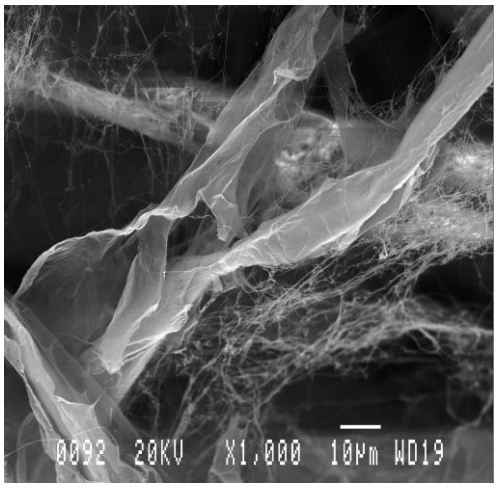

Figure 45. Ultrasonicated, 1000x

According to the microphotographs in figures 10 to 45 it can be concluded that there in some cases is an increase in external fibrillation of fibre surfaces, especially in the never-dried samples this effect is clearly evident. In some other cases it is hard to tell whether or not there really is an increase in fibrillation.

In the case of dried pulps in Experiment 1, which received mechanical pre-treatment in a laboratory refiner before being sonicated, it is hard to tell whether there has been an increase in fibrillation or not. However it is in accordance with the other results on the dried pulp samples in Experiment 1 that there is only a slight (or no) increase in fibrillation as a result of sonication. For example the tensile index was little affected by the sonication. Considering the dried pulp in Experiment 1, which had been defibrated without any mechanical treatment prior to sonication, it seems likely that there is a small effect on fibrillation in the sample even though it is not very clear. In contrast it is very evident that there is an increase in fibrillation in the two never-dried samples, for the SW1 softwood pulp as well as for the HW hardwood pulp the effect is clearly visible.

From the microphotographs it can, besides the increased outer fibrillation, be concluded that there does not seem to be any fibre cutting or visible kink formation. The results are all in accordance with results from the other analyses performed in this project and can as well be supported by other research studies, see e.g. Manning and Thompson [3] and Tatsumi et al. [27].

In the discussion about SEM analysis results it should be added that all pictures taken of the samples are randomly selected and there is a possibility that the fibres look different in other parts of the sample. However large parts of the sample were being scanned in the SEM analysis and a lot of microphotographs were taken to ensure reliable results. The microphotographs presented in this report were considered representative for their respective sample.

4.4. Energy consumption

The energy output of the ultrasonic equipment was calculated for both Experiment 1 and 2 respectively in terms of energy usage in kWh/t, to give a possibility for comparison with conventional refining energy usages. Calculations on conventional refining degrees, to convert these from kWh/t into corresponding sonication times in the ultrasonic equipment, were also performed. The results from the calculations are summarised in tables 5, 6 and 7.

Experiment 1

In Experiment 1 sonication was performed at 1% consistency i.e. 10 g/l and a power of 500 W. Calculations of equivalent energy usages in kWh/t for the specific sonication times are summarised below in table 5. See Appendix A4 for example of calculation.

Table 5. The energy equivalents for the specific sonication duration times applied in Experiment 1.

Sonication time (min)	Energy usage (kWh/t)
1	833
2	1667
3	2500
5	4167

Experiment 2
In Experiment 2 sonication was performed at 0.5% consistency i.e. 5 g/l and a power of 500 W. Calculations of equivalent energy usages in kWh/t for the specific sonication times are summarised below in table 6. See Appendix A4 for example of calculation.

Table 6. The energy equivalents for the specific sonication duration times applied in Experiment 2.

Sonication time (min)	Energy usage (kWh/t)
5	8333
10	16667
15	25000

Conventional refining
The results on calculation of equivalent sonication times for some specific conventional refining degrees are summarised below in table 7. Calculations for Experiment 1 are performed at 1% consistency and for Experiment 2 at 0.5% consistency. See Appendix A4 for example of calculation.

Table 7. Some conventional refining degrees converted into sonication duration times as they would be if applied at the specified conditions of Experiment 1 and 2.

Energy usage (kWh/t)	Sonication time, exp. 1 (s)	Sonication time, exp. 2 (s)
50	3.6	1.8
100	7.2	3.6
200	14.4	7.2

According to the results visualised in table 5, 6 and 7 respectively, it is obvious that ultrasonic refining is much more energy consuming than conventional refining, at least in this type of labscale equipment. To be more energy effective it must be possible to refine at higher consistencies in order to treat more fibres with the same energy input. Another possibility to achieve more energy efficient ultrasonic refining is regarding the design of equipment. Perhaps larger scale ultrasonic equipments would be more energy effective than the labscale piece used in these experiments.

5. Conclusion

In this investigation two types of results were of interest; the effect of ultrasound on the pulp fibres and the energy consumption of the ultrasonic equipment. Regarding pulp properties it was found out that fibre modifications are obtained when exposing pulp samples to ultrasound. In the case of dried pulps, with or without mechanical pre-treatment, the effects of sonication were small if any at all. Probably this is a result of hornification of fibres during the drying operation, which makes the fibres less prone to swelling and fibrillation of the fibre wall when exposed to ultrasound. However it was shown that the never-dried pulps, in the case of softwood as well as hardwood, were refined by the ultrasonic waves.

Analyses of the never-dried pulps showed an increase in inner and outer fibrillation of fibres. These conclusions were drawn from significant increases in WRVs, Schopper-Riegler number and tensile index. The increase in outer fibrillation could also be identified on SEM microphotographs taken of one of the softwood pulps and the hardwood pulp. Another important result on fibre level is the fact that there does not seem to be any fibre cutting or creation of fines material. All the results obtained in the experiments could be more or less supported by each others and the literature study included in the project.

Concerning the energy aspects of sonication in this equipment, the results on energy consumption implies that this technique is not an alternative to conventional refining as it is many times more energy consuming. The values on energy consumption should be considered specific for the particular lab scale equipment used in this project and does not automatically imply that ultrasonic refining always is a waste of energy. Other equipments of a different design may be more efficient and there is also a possibility that ultrasonic refining can be less energy consuming when implemented in larger scale. Perhaps future innovations can make ultrasonic refining beneficial in terms of energy consumption.

6. Suggestions for future work

For further investigation of the method of ultrasonic refining it is above all of interest to evaluate if there are ways to achieve more energy efficient refining than what was the case in this study. It could therefore be of interest to investigate other types of equipment in order to evaluate the energy efficiency of these. Other types of ultrasonic systems and other types of pumps could perhaps be more efficient and suitable for ultrasonic refining of pulp fibres.

As the mono pump used in this project was not very suitable for pulp fibres and had a tendency to plug when coarser softwood fibres were circulated in the system, this could have had a negative impact on the flow properties of the pulp suspension. In this way it may also have resulted in a less efficient ultrasonication process in the flow cell. It is not known whether the larger ultrasonic effect on hardwood fibres, in comparison to the softwood pulps, to some extent had to do with the flow properties of these shorter fibres. It would therefore be of interest to investigate if other equipments with more suitable pump design could result in better flow properties and larger effect on softwood fibres.

Besides it is also of interest to investigate if there are possibilities to pump fibres at higher consistencies. This could be a way to achieve a more energy efficient ultrasonication process. Finally, regarding the physical properties of pulp fibres it could be of interest to investigate if the developed physical fibre properties, which resulted from the ultrasonic treatment, would remain after drying of the pulp.

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Appendices

Appendix A1 Experimental values

Appendix A2 Investigation of pump refining action on pulp

Appendix A3 Complementary SEM microphotographs

Appendix A4 Energy calculations

A1. Experimental values

All the experimental values from determination of WRV, tensile index and Schopper-Riegler number in Experiment 1 and 2 respectively are summarised below in tables A1.1 and A1.2.

Table A1.1. Experimental values in Experiment 1.

Pulp	Sonication time (min)	WRV (g H_2O/g fibres)	Tensile index (kNm/kg)
Never-dried	0	1.46	29
0 kWh/t	1	1.59	40
	2	1.63	50
	3	1.86	58
Dried pulp	0	1.00	24
0 kWh/t	1	1.23	32
	2	1.26	34
	3	1.26	36
	5	1.25	34
Dried pulp	0	1.49	58
50 kWh/t	1	1.43	-
	2	1.50	62
	3	1.53	66
	5	1.56	61
Dried pulp	0	1.64	73
100kWh/t	1	1.69	76
	2	1.71	77
	3	1.76	77
	5	1.72	71

Table A1.2. Experimental values in Experiment 2.

Pulp	Sonication time (min)	WRV (g H_2O/g fibres)	Tensile index (kNm/kg)	°SR
SW1	0	1.46	28	17
	5	1.60	40	18
	10	1.72	48	22
	15	1.85	58	30
SW2	0	1.45	29	16
	5	1.58	43	17
	10	1.72	50	22
	15	1.80	53	33
SW3	0	1.40	23	15
	5	1.52	38	16
	10	1.63	48	20
HW	0	1.61	39	21
	5	1.81	36	25
	10	2.25	42	37
	15	2.54	59	49

A2. Investigation of pump refining action on pulp

To determine whether there was any refining action of the pump on the fibres or if the refining action mainly resulted from ultrasonic waves, WRV was analysed for samples of never-dried SW1 pulp being recirculated in the pump/ultrasonication system. The pulp was only defibrated before being used in the experiment, no mechanical pre-treatment was applied.

In the investigation a reference sample was circulated in the system without any ultrasound applied, only being subjected to pump action. For comparison another sample was exposed to ultrasound during recirculation in the system for the same duration time as the reference sample. The study was performed at different consistencies with constant duration times in one case and at differing circulation/sonication times at constant consistencies in another case. The results are visualised below in figures A2.1 and A2.2 respectively.

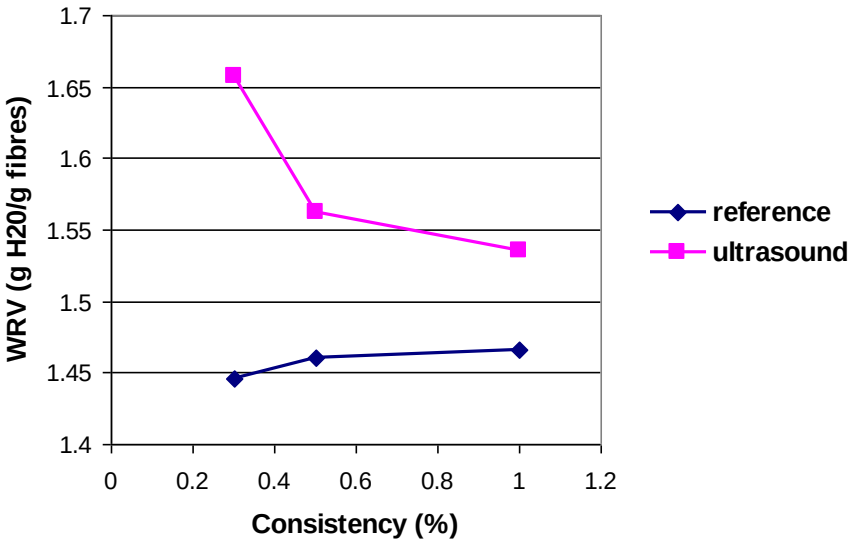

Figure A2.1. The effect on WRV of SW1 never-dried pulp when being circulated in the sonication system for 5 min at different consistencies. One sample being pumped without ultrasonic action (denoted “reference”) and one sample being sonicated while pumped (denoted “ultrasound”).

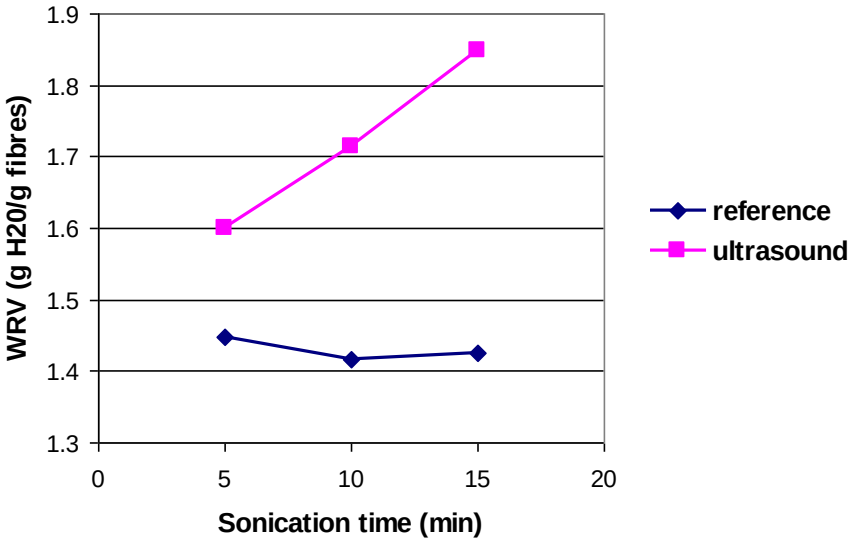

Figure A2.2. The effect on WRV of SW1 never-dried pulp when being circulated in the sonication system at a consistency of 0.5% for different duration times. One sample being pumped without ultrasonic action (denoted "reference") and one sample being sonicated while pumped (denoted "ultrasound").

According to figures A2.1 and A2.2 it can be concluded that the pump has little or no refining action on the pulp fibres. However it should be kept in mind that the pump was cleaned when these investigations were performed. There was a build up of fibres in the pump constantly during experiments and even though the pump was rinsed as far as possible between experiments by letting large amounts of water run through the system it is hard to avoid fibre assembly. As it was a too complicated and time consuming task to open the pump after each trial, the pump was cleaned only a few times. Therefore there is still a risk of fibre refining action from the pump in the sense of build up of fibres which stay in the pump for some time and then go out in circulation. If there are fibres staying in the pump there is also a risk that fibres passing through are refined as a result of a very tight environment in the screw when fibres are built up there.

A3. Complementary SEM microphotographs

In the figures below are samples of SW1 dried pulp from Experiment 1 shown. One sample is a reference sample, mechanically refined at 50 kWh/t, meanwhile the other is ultrasonicated for 3 min at 1% consistency after mechanical pre-treatment at 50 kWh/t. The magnification of pictures are ranging from 50 times (denoted 50x) to 1000 times.

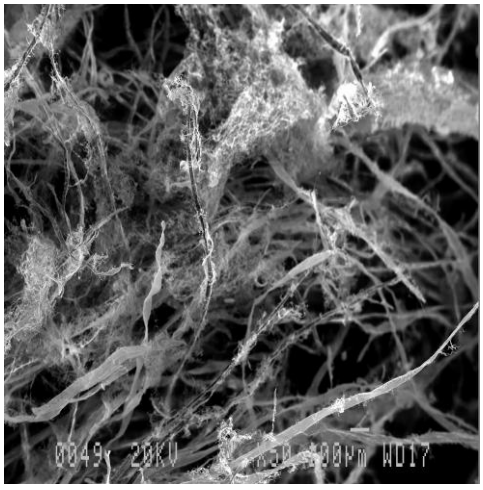

Figure A3.1. Reference, 50x

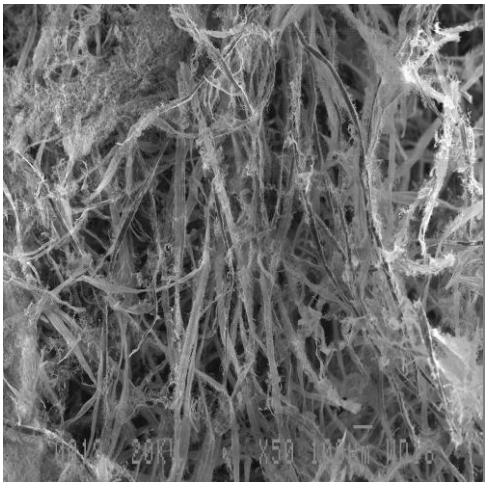

Figure A3.2. Ultrasonicated, 50x

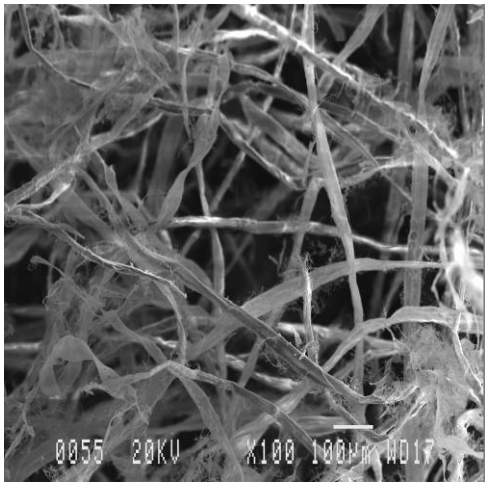

Figure A3.3. Reference, 100x

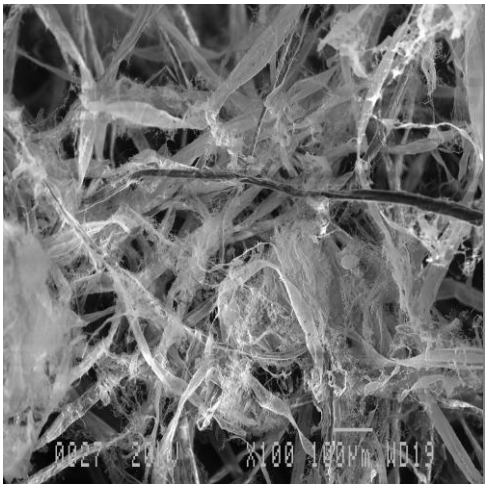

Figure A3.4. Ultrasonicated, 100x

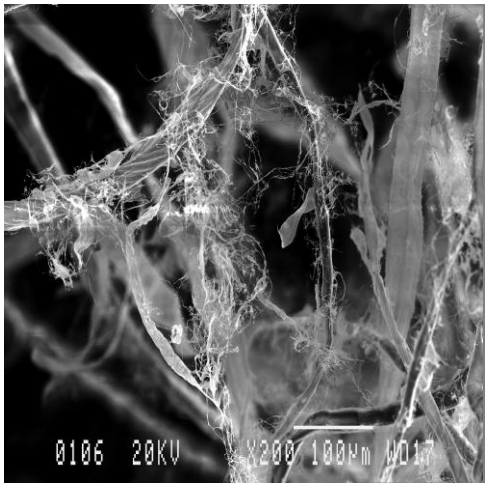

Figure A3.5. Reference, 200x

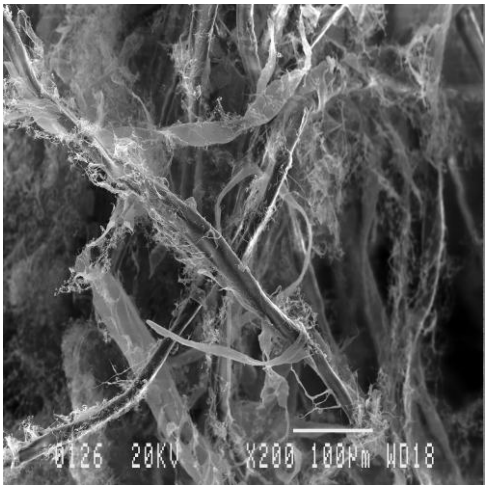

Figure A3.6. Ultrasonicated, 200x

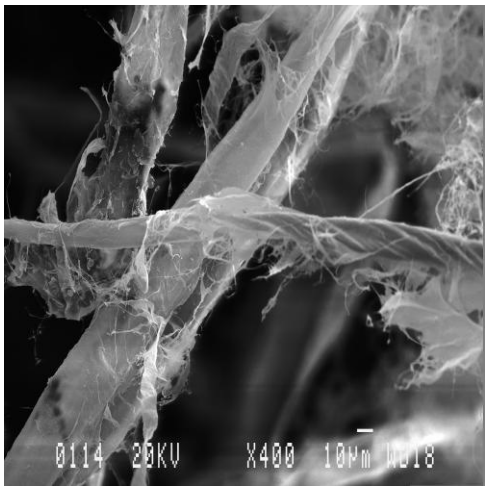

Figure A3.7. Reference, 400x

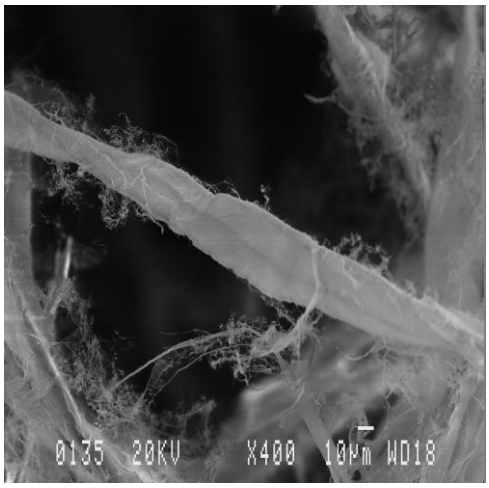

Figure A3.8. Ultrasonicated, 400x

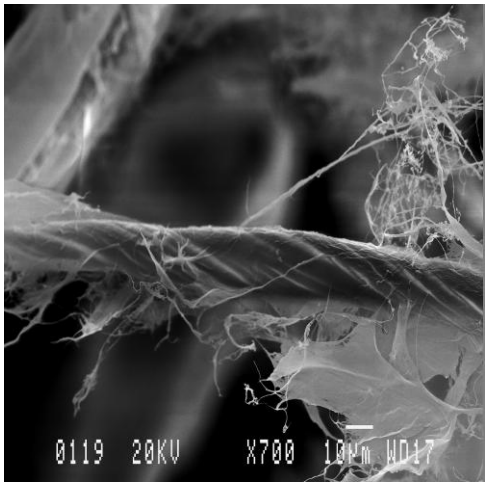

Figure A3.9. Reference, 700x

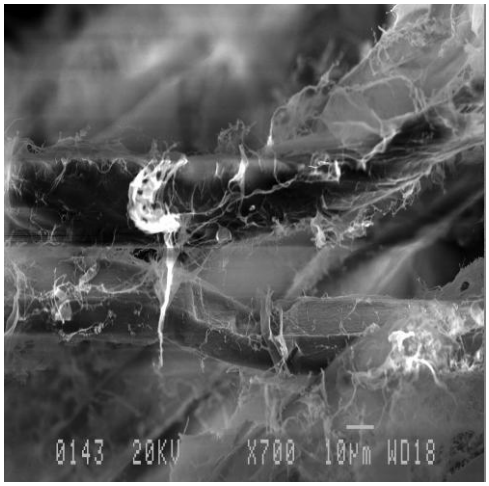

Figure A3.10. Ultrasonicated, 700x

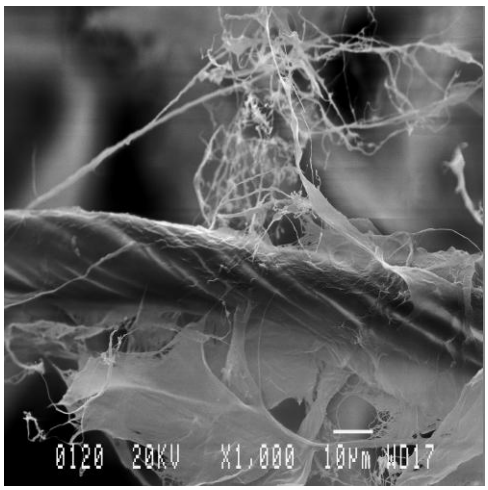

Figure A3.11. Reference, 1000x

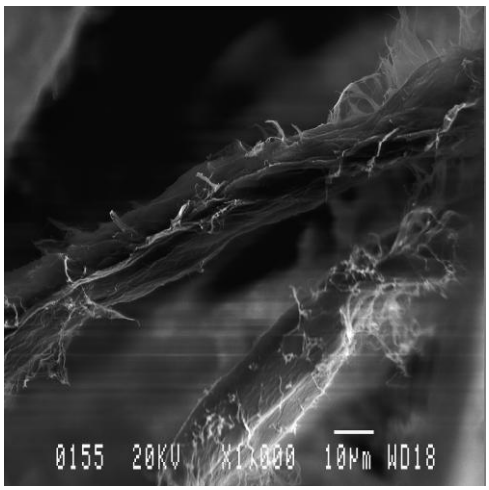

Figure A3.12. Ultrasonicated, 1000x

A4. Energy calculations

Calculation of equivalent energy usages in kWh/t
An example of a calculation of equivalent energy usages in kWh/t for one of the sonication duration times specified in section 4.4 is visualised below.

Ultrasonic power = 500 W
Mass of sonicated pulp = 10 g (1% consistency)
Sonication time = 60 s

$$\frac{500W * 60s}{10g} = 3000Ws / g$$

$$\frac{3000Ws / g * 10^6 g / t}{3600s / h} = 833.33kWh / t$$

Calculation of equivalent energy usages in seconds
An example of a calculation of equivalent energy usages in seconds for one of the specified conventional refining degrees in section 4.4 is visualised below.

Ultrasonic power = 500 W
Mass of sonicated pulp = 10 g (1% consistency)
Refining degree = 50 kWh/t

$$50kWh / t * 3600s / h = 180000kWs / t$$

$$\frac{180000kWs / t}{10^6 g / t} = 180Ws / g$$

$$\frac{180Ws / g * 10g}{500W} = 3.6s$$