STUDY OF THE EFFECT OF MECHANICAL TREATMENT AND SUPERCRITICAL CO$_2$ EXTRACTION ON ASPEN BCTMP BY SURFACE CHARGE MEASUREMENTS AND SEM

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Cellulose is the most abundant organic polymer and is utilized in many forms in industry. Sustainable use of materials includes the utilization of renewable resources like cellulose and selecting methods that allow saving energy and avoiding pollution. Because a complete purification of cellulose demands a lot of energy and chemicals, there are many products in which cellulose is used only partly purified. For example, products like bleached chemi-thermo mechanical pulp (BCTMP) have been developed to be used as a component in paper making. In this article an attempt to further refine aspen BCTMP is reported. The aim is to find an energy effective and environmentally friendly way to affect the surfaces of BCTMP fibres, in other words, to peel and fibrillate the pulped aspen wood cells. Agitation in a bag mixer and supercritical carbon dioxide (scCO$_2$) extraction were selected as methods to treat the fibres. The effects of the treatment were analysed by the surface charge measurement and scanning electron microscopy (SEM). The surface charge of pulp fibres is important as it influences interfibre and fibre-additive interactions in the pulping process, as well as in other applications. In this work, the effect of mechanical treatment scCO$_2$ extraction on the surface charge of aspen BCTMP was evaluated. Dried and ground BCTMP was dispersed in water, treated with a BagMixer (BM) with a nylon separator, extracted with scCO$_2$ with and without ethanol-water co-solvent. The influence of 1% sodium hydroxide was also studied. Polyelectrolyte titration was used to measure the surface charge. The processes were carried out at various times and in different order of succession. A relatively high surface charge was gained by a gentle mechanical and chemical treatment. SEM analysis showed the relation of surface fibrillation to the surface charge of the fibres. Washing with sodium hydroxide removed both the fibrils from the surfaces and the surface charge. The results can be used as a guide to further fibrillation of aspen BCTMP for various applications. Fibrillated intermediates are aimed for processing to, for instance, aerogels and other nanostructured materials.

Keywords: SEM, surface charge, cellulose, titration, supercritical CO$_2$, electrolyte, polyelectrolyte, p-DADMAC, aspen, aspen pulp fibres, BCTMP, thermo-mechanical treatment, fibre surface

INTRODUCTION

Sustainable use of materials has been agreed to be imperative in the 21st century. This is the reason why so much attention has been paid to novel bio-based materials. Especially cellulose, the most abundant biopolymer on earth, has been the subject of very active research. Nanomaterials have been developed to provide new functionalities, to improve existing products, to lower the need for resources and to enable sustainability. Nanocellulose, a material composed of nano-sized cellulose fibrils, has unique and potentially useful features. It combines important cellulose properties, such as hydrophilicity, broad chemical modification capacity and the formation of versatile semi-crystalline fibre morphologies with the specific features of nano-sized materials.[1] Nanocellulose has a number of applications, e.g. (nano)paper, barrier in greaseproof paper, reinforcing component in paper coatings, composite reinforcement. Due to its nontoxic, hydrophilic and rheological properties, nanocellulose is also used in food, pharmaceuticals and cosmetics.[1]

Wood fibres (wood cells) are composed of three main chemical components: cellulose, hemicelluloses and lignin, which are all

differently influenced during the pulping process. When talking about fibres, only libriform cells are considered as fibres in hardwood. Typical lengths of wood fibres are 1 to 3 mm and typical widths are 10 to 50 µm;[2] for aspen (*Populus tremula*) dimensions are approximately 0.9 mm and 19 µm, respectively.[3] The fibre wall thickness is roughly between 1 and 5 µm. The fibre wall consists of defined layers, including the primary wall (P) and several secondary wall layers (S1, S2 and S3), between the fibres there is lignin-rich middle lamella. Each cell wall is characterised by a specific arrangement of fibrils. Wood fibre consists of cellulose microfibrils, which have a maximum diameter of 35 nm.[4] Microfibrils are composed of bundles of elementary fibrils, with a diameter of approximately 3.5 nm.[5] Microfibrils are arranged differently in various layers of the fibre wall structure, i.e. in primary and secondary walls.

Nanocellulose can be divided to three main types: microfibrillated cellulose (MFC), nanocrystalline cellulose (NCC) and bacterial nanocellulose (BNC). A further classification of these materials is given in a comprehensive review by Klemm *et al.*[1] MFC (also called nanofibrillated cellulose, nanofibres, nanofibrils, microfibrils)[2] is a material usually made of wood cellulose fibres by detaching individual cellulose microfibrils from each other. The length of fibrils is relatively high (up to 1 µm), fibre diameter is in the range of 5-60 nm.[1] MFC is industrially an interesting material; however, the production via pure cellulose is complex and energy demanding. As the industrial production of nanocelluloses is growing, the price of NCC is predicted to lower to the level of a few Euros per kilo, as for the grades of MFC and MFC, they have prices of up to hundreds of Euros per kilo.[6]

Bleached chemi-thermo mechanical pulp (BCTMP) is a useful material for higher grade paper manufacturing.[7] However, by applying further treatments, it is possible to obtain new potential applications for this industrial pulp. In BCTMP, almost all lignin is still on the surface of wood fibres, hindering the inter-fibre bonding and bonding to additives. During mechanical pulping, outer cell wall layers have not been removed and lignin is still on the surface of wood fibres, mostly in the middle lamella region and primary wall, as they are the most lignin-rich areas in wood fibre.[7,8] These fibres are hydrophobic, because lignin is hydrophobic. If outer cell wall layers are removed (middle-lamella, primary wall and S1

layer), the S2 layer becomes visible with nice cellulose microfibrils oriented more or less parallel to fibre axis. This S2 layer has the highest content of cellulose and is therefore hydrophilic.

As a rule, kraft pulp is used for nanocellulose preparation. The morphology of kraft pulp fibres differs completely from mechanical pulp fibres. On the surface of kraft pulp fibre, the S2 layer is already visible, for mechanical pulp on the contrary S2 layer is hidden under outer cell wall layers.[7] For nanocellulose preparation, it is therefore more convenient to use kraft pulp. The major disadvantage of the usage of kraft pulp is that a heavy chemical treatment has been used and the yield of pulp is much lower compared to the mechanical pulp. Therefore, in order to make a far more environmentally friendly product, BCTMP has been examined.

The purpose of this work is to examine possibilities for further refining aspen BCTMP for various potential applications. $ScCO_2$ extraction and mechanical treatment are tested for peeling off outer cell wall layers.[12] Co-solvents, e.g. ethanol-water mixtures, are tested for delignification. These kinds of treatments are well-known from organosolv pulping.[13] Ethanol treatment facilitates fibre separation in the middle lamella region.[1] The selectivity of delignification might also be improved by the addition of NaOH, by increasing alkali charge from 5% to 35% and by using ethanol up to 40% by volume. The residual lignin content has been reported to decrease from 20% to 3%.[10,11]

The aim of the $scCO_2$ extraction is to treat wood without using any hazardous chemicals. $ScCO_2$ is becoming an important commercial and industrial solvent, due to its role in chemical extraction, in addition to its low toxicity and environmental impact. $ScCO_2$ is also non-flammable, chemically inert and inexpensive.[12] $ScCO_2$ extraction has been used to remove lignin and small molecular weight extractives from wood. Organic solvents (acetic acid, ethanol and methanol) are used as co-solvents. The use of $scCO_2$ extraction before pulping enhances the penetration of pulping chemicals.[13,14,15]

Wood pulp fibres are negatively charged at all pH values due to the presence of acidic groups (carboxyl, sulphonic acid, phenolic or hydroxyl), which either derive from cell wall constituents or are introduced during pulping or bleaching of fibres. The negative surface charge of BCTMP is most probably due to carboxylic groups and sulphonic groups are not expected to be present.

The charged groups are located either on the fibre surface or inside the cell wall; therefore they are referred to as surface and bulk charges. The number of charged groups depends on the origin of the fibre and on the chemical and mechanical treatment during pulping and refining. The surface charge of pulp has been reported to be 0.5-50 µeq/100 g fibre.[16,17]

Surface charges influence fibre-fibre bonding and interactions with high molecular mass additives. Surface charge of cellulosic fibres increases linearly with increasing refining (beating).[18,19,20] It is because the refining process opens up the fibre surface and, as a consequence, there is more area for fibre-fibre contacts and subsequently more bonds between fibres.[18] The fines produced early in the refining have more charged groups than the fines produced later in the refining process.[21] As mechanical pulp contains more fine material than chemical pulp, the surface charge of mechanical pulp tends to be higher.[22]

A well-known method for determining the surface charge of cellulosic fibres is polyelectrolyte titration. The procedure is based on the fact that polyelectrolytes can form complexes with oppositely charged polyelectrolytes or surfaces. It is possible to determine the charges on cellulosic fibres by measuring the amount of the cationic polymers adsorbed on cellulosic fibres. The method can be used to determine the anionic surface charge of fibres if a cationic polyelectrolyte has a sufficiently high molecular weight that it does not penetrate the cell wall.[22]

Direct polyelectrolyte titration was pioneered by Terayama,[23] who determined the concentration of a cationic polyelectrolyte solution by titration with an anionic polyelectrolyte in the presence of a cationic indicator. Polyelectrolyte titration was later applied to cellulosic fibres (indirect titration).[24]

Linear polyelectrolytes of high charge density are used to apply this method.[23,24] In a typical titration, the pulp mixture is first treated with a known excess of highly cationic polymer, such as p-DADMAC. Then it is filtered or centrifuged to remove solids (the content of fines plays a major role in polyelectrolyte titrations, as it increases the amount of polymer required to neutralize the charge).[22] A small amount of indicator dye (usually toluidine blue-O-OTB) is added and then the blue solution is back-titrated with an anionic polyelectrolyte, such as potassium poly-

vinylsulfate (KPVS) to a purple-pink endpoint. Complexation takes place between the dye and the negatively charged polymer, causing the colour-change to pink. We have modified the back titration and used, instead of anionic polymer, potassium hydroxide and, instead of indicator dye, potentiometric indication to determine the amount of the cationic polymer.

The most important factors that affect surface charge values are surface and polyelectrolyte charge density, ionic strength and molecular weight of the polyelectrolyte.[13] It was concluded that at least three criteria must be met for a 1:1 stoichiometry to prevail when measuring the surface charge content: 1) a high charge density of the cationic polyelectrolyte, 2) a high molecular mass of the cationic polyelectrolyte, and 3) sufficiently low electrolyte concentration. There must also be no non-electrostatic interactions between the polyelectrolyte and the fibre.[22]

To fulfil these criteria, high molecular mass polydiallylodimethylammonium chloride (p-DADMAC) was used as cationic polymer and the titrations were carried out at low electrolyte concentrations.

This study is focused on wood fibres; therefore solid particles were removed for further investigation and fine particles containing liquid were not used during titrations.

The aim of this study was to find out how scCO$_2$ extraction, together with mild chemical and mechanical treatment, influences the surface charge and structure of aspen BTCMP fibres. Surface charge results were combined with SEM analysis for assessing the effects on the fibres, considering further fibrillation.

EXPERIMENTAL
Materials

Aspen BCTMP was obtained from Estonian Cell. All pulps were oven dried at 105 °C and ground in a coffee-grinder. Commercially available technical grade CO$_2$ with a purity of 99.7% from AGA was used in the scCO$_2$ extraction process. Technical Acetone with 99.5% purity from APChemicals was used in the solvent exchange process. Polydiallyldimethyl-ammoniumchloride (p-DADMAC) was used as cationic polyelectrolyte and potassium hydroxide (KOH) as titrant. P-DADMAC was supplied by Sigma Aldrich as a 20 wt% concentrate. Mw of p-DADMAC was 100000-200000 g/mol. NaOH was supplied by Sigma Aldrich, with M = 40000 g/mol. KOH and ethanol were of laboratory grade

and used without further purification. Distilled water was readily used from the laboratory distilled water system.

Equipment

Commercially available disperser T 25 digit Ultra Turrax from IKA laboratory equipment was used as part of the mechanical treatment process of the cellulosic fibres. The device is composed of the digital disperser, an extension arm, a support screw and an exchangeable nozzle. The T-25 digital model is designed to work at high circumferential speeds, ranging between 6-24 m/s, which accounts for 3400-24000 rpm.

Commercially available BagMixer 400W from Interscience was used for the homogenisation and mechanical treatment process of the cellulose fibres. The blending occurs during a back and forth movement of two patented paddles. As one of the paddles is in the forward position, the other is in the backward position. The blending speed is set to a constant value of 8 strokes/min by the manufacturer. One cycle of the machine can maximally last for 360 seconds and the machine automatically comes to a stop as the timer has counted the set time. The device allows for processing volumes ranging between 50-400 ml. The processed medium is held in a blending bag, which is mounted inside the stainless steel body.

A supercritical CO_2 extraction system SES-UK 1 was started up to carry out the $SCCO_2$ extraction experiments.

Figure 1 depicts the reactor system composed of the liquid CO_2 source (1), liquid CO_2 pump (2), a valve for injection of a co-solvent that can be used as a valve for closing off the reactor from the pump (3), the reactor (4), which is placed inside a thermostat (9), a triplet (5) that separates the outlet into two valves (6 and 7), of which 6 is used for releasing the solvent from the system and 7 is the back-pressure regulator.

The Supercritical 24 constant flow-constant pressure dual piston pump is used for providing the supercritical processing system with sufficient pressure to operate in the supercritical region of CO_2. The pump is built to operate in two distinct modes: constant pressure and constant flow regimes. Pressure is adjustable from 0 to 10000 Psi with an error of 0.01. In the constant pressure mode, a maximum value for the flow rate is set for the pump, which then is one of the determining factors of the pace at which the set constant pressure threshold is achieved.

Commercially available Carbolite PF30 convection oven is used as thermostat in the supercritical processing system. The maximum temperature of the system is 200 °C. The reactor is placed inside the thermostat.

The two valves at the end of the system serve as the back-pressure regulator and a way to release the solvent from the reactor. The system allows for precise control of pressure and temperature, which are the most important parameters defining the supercritical state. The processing time is also adjustable and variable at need. The system can operate under pressures up to 190 bars and temperatures up to 200 °C.

Commercially available titrator, Mettler Toledo T90 was used; it consists of a titrator with terminal, pH board, integrated burette drive and magnetic stirrer. It is expandable with two sensor boards (pH and/or conductivity) and up to seven additional burette drives (for dosing and titration purposes).

Methods

The experimental part of this study consisted of two main parts: pre-treatment processes of wood pulp and the surface charge measurement. SEM images of the samples were also taken in order to evaluate the correlation between surface charge and visual appearance.

The pre-treatment process consisted of the following steps: dispersing in water, treatment with BagMixer (BM) with a nylon separator, supercritical CO_2 extraction with and without ethanol:water co-solvent, mild chemical treatment with 1 wt% NaOH solution. For pre-treatment procedures, an experimental plan was composed in order to vary the position of different treatments to each other and to find out the optimum conditions for the highest surface charge (best fibrillation).

After each treatment, surface charge was measured and SEM images were taken. For surface charge measurements, pH was measured with Mettler Toledo electrode DG-112 Pro calibrated with Mettler Toledo pH buffer solutions (4.01; 7.00; 9.21) and connected to a Mettler Toledo automatic titrator T90 under N_2 flow.
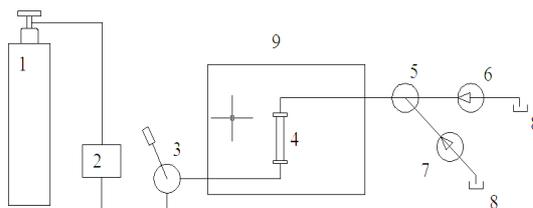
Figure 1: A set-up of the SC extraction system

The dry-grinding of the aspen pulp was carried out in an ordinary grinder under atmospheric conditions. The initial sample was then dispersed in distilled water at concentrations of 0.5 wt% and 1 wt% of pulp in water. The dispersing was carried out at 12000 rpm for 5 minutes.

The pulp was separated by filtration in the Büchner funnel by using a metallic sieve with a mesh size of 50 μm. Then the pulp was weighed and used for titrations and further treatments. The filtrate of the pulp dispersion was not used during the titrations as the interest was to investigate the pulp fibres rather than dispersion.

After dispersing, the sample with water was mechanically treated for six minutes by the BM; the sample was placed inside the bag with the nylon separator in the middle, with a mesh size of 300 μm. For the BM treatment, the pulp was put inside the bag and BM pushed the pulp through the sieve, the blending occurred during a back and forth movement of two patented paddles.

For supercritical CO_2 treatment, dry samples were prepared in stainless steel netting and placed inside the reactor. The samples from the dispersing or bag mixer treatment, i.e. in water solution, were dried at the critical point after the solvent exchange from water to acetone. The samples for the SC treatment process were then again placed in stainless steel netting and into the reactor.

In the case of using water-ethanol 1:1 solution as a co-solvent, it was injected into the system at the point where temperature reached its plateau value. In current experiments, 40 μl were injected.

$ScCO_2$ experimental equipment is imaged in Figure 2. Working parameters were chosen as follows: pressure 160 bars, temperature 120 °C and treatment time of 50 minutes starting from the point where temperature reached 60 °C.

For SEM studies, dry samples were placed with a fine pipette to a metallic stub, using a double-sided adhesive tape. Then the samples were placed into an ion sputtering chamber JFC-1100 for one minute and 40 seconds and coated with gold and platinum under vacuum to enhance electrical conductivity. Coating was restricted to 1.9 kV and 10 mA. The SEM examination was carried out with EVO MA 15 at accelerating voltage from 12 to 15 keV.

To carry out critical point drying of wet pulp samples, solvent exchange to acetone was performed, followed by SEM analyses. Solvent exchange is a method for shifting material from one solvent to another. The samples in water solutions were transformed into acetone via solvent exchange using acetone-water solutions (30, 50, 70, 90, 100, 100 wt% of acetone). During each step, segregation was assured by mixing in an ultrasonic bath for 2-3 minutes. The wood fibre mass was then filtered (50 μm pore size stainless steel filter) and placed in the next solution until no water was left.

A typical critical point drying was conducted in the Balzers apparatus. The wood fibre mass in acetone was placed in the chamber, which was cooled to 5-7 °C, sealed, pressured and flushed with liquid CO_2 3-4 times. Finally, the chamber was heated to 40 °C and gassed out.

Surface charge measurements

The titrations were performed using a high-precision, microprocessor-controlled auto-titrator (Mettler Toledo T90) connected with a pH glass electrode, DGi 112 Pro. The electrode was calibrated using buffer solutions of pH 4.01, 7.00, and 9.21. During the titrations, a propeller stirrer was used to mix the pulp suspension. The rate of titrant addition was controlled at 0.05 ml/s. The data were recorded. Titrations were performed under N_2 flow to prevent the absorption of CO_2 into the test samples during the titrations.

Preliminary experiments were made with and without pulp in fibre dispersions and no remarkable changes in the results were noticed by two different techniques.

Therefore, it was not necessary to remove the pulp from the dispersion.

For titrations, 0.25 g of dry sample was weighed, then 47.5 ml of 1% p-DADMAC solution was added. The mixture was stirred with a propeller stirrer to completely neutralize the anionic charge in the pulp by poly-DADMAC.

The stirring lasted until the pH of the dispersion was stable, approximately for 10-15 minutes.

Then the pulp mixture was titrated with 0.06 M KOH solution until the equivalence (end) point. Fibre charge was calculated according to Bhardwaj *et al.*[19]

Figure 2: Sc experimental devices

When a wet sample was taken, 1.75 g of the sample was weighed and 48.25 g of 1% p-DADMAC was added. Further procedures were the same as described above. The wet sample mass was calculated under the same conditions and it was 7 times heavier than the dry sample.

The surface charge of the samples was calculated using the following equation:

$$q = (V_2-V_1) \times C \times 1000/W \qquad (1)$$

where: q is the specific surface charge (mmol/kg); (V_2-V_1) is the difference between volumes of KOH used for p-DADMAC solution with and without pulp; C is the titration agent concentration; 1000 is the conversion factor; w is the weight of a sample (oven dry basis).

To insure the integrity of the results, all the experiments were duplicated.

RESULTS AND DISCUSSION

Table 1 summarises the surface charge values after different mechanical and thermal treatments of aspen BCTMP.

A sample of titration curve is exemplified in Figure 3. The equivalence point of titration was calculated by a computer program. It is the point where inflection is most abrupt and this indicates the situation where protons in the solution were replaced with KOH ions. Based on the data of the equivalence point, surface charge was calculated.

Experiment 1

In the first experiment, the initial sample (1.1), dried and ground BCTMP (3 g) was dispersed in

water. Then, BM processing was used (1.2) and finally the sample was treated under $scCO_2$ conditions (1.3).

The surface charge of the initial sample (1.1) is quite low, 5.78 mmol/kg. It increased immensely after the BM treatment (q = 65.1 mmol/kg). The increase in surface charge continued after $scCO_2$ treatment (q = 75.12 mmol/kg).

The mechanical treatment in BM in combination with $scCO_2$ treatment had a good effect on the surface charge of pulp fibres; this kind of pulp processing could be a very effective way to generate surface charges. As can be seen from the SEM image, there are many fine fibrils that cause charges (see Figure 4).

Experiment 2

In the second experiment, the initial sample (3 g) was treated under $scCO_2$ conditions (2.1). Next, it was dispersed in water (2.2) and finally treated with BM (2.4).

An upsurge in the surface charge after $scCO_2$ treatment (q = 78.08 mmol/kg) occurred, with a slight decrease after dispersing in water due to loss of fine material (q = 54.95 mmol/kg), but there was again an increase in the surface charge after BM treatment (q = 64.43 mmol/kg).

Experiment 3

In the third experiment, the initial sample (3 g) was processed under $scCO_2$ conditions with 1:1 ethanol water co-solvent (3.1). Then, it was treated with 1% NaOH, and the pulp mixture was

put into the Büchner funnel with a metallic sieve with a mesh size of 50 µm and washed with distilled water. Once the pH neutrality was attained (3.3), the sample was submitted to BM treatment (3.5). An abrupt surface charge increase after scCO$_2$ treatment with 1:1 et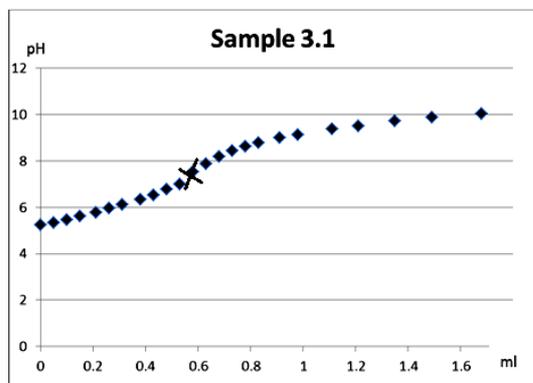hanol water co-solvent (q = 83.77 mmol/kg) occurred. Surface charge plummeted after NaOH treatment and washing with distilled water. There was no detectable equivalence point in the titration curve. However, surface charge showed an upward trend after BM treatment (q = 3.39 mmol/kg).

Figure 3: Illustration of a titration curve (the capital X indicates the equivalence point)
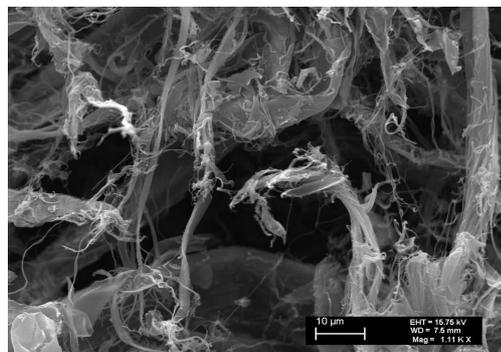
Figure 4: SEM image of sample 1.4 treated in BM and with scCO$_2$

Table 1
Surface charge for differently treated pulp fibres

Treatment	Surface charge, mmol/kg
Dried and ground pulp (1.1)	5.78±0.1
Dried and ground, BagMixer (BM) (1.2)	65.1±0.1
Dried and ground, BM, ScCO$_2$ (1.4)	75.12±0.1
ScCO$_2$ (2.1)	78.08±0.1
ScCO$_2$, dispersed in water (2.2)	54.95±0.1
ScCO$_2$, dispersed in water, BM (2.4)	64.43±0.1
ScCO$_2$, with 1:1 ethanol water co-solvent (3.1)	83.77±0.1
ScCO$_2$, with 1:1 ethanol water co-solvent; 1% NaOH, washed with distilled water (3.3)	-
ScCO$_2$, with 1:1 ethanol water co-solvent; 1% NaOH, washed with distilled water; BM (3.5)	3.39±0.1
ScCO$_2$; dispersed in water; BM; scCO$_2$ (4.2)	63.99±0.1
ScCO$_2$, with 1:1 ethanol water co-solvent; 1% NaOH, washed with distilled water; ScCO$_2$ (5.2)	-
ScCO$_2$, with 1:1 ethanol water co-solvent; 1% NaOH, washed with distilled water; ScCO$_2$, BM (5.4)	18.34±0.1

Experiment 4

In the fourth experiment, the initial sample (3 g) was treated under scCO$_2$ conditions. Then, it was dispersed in water and treated with BM. Finally, the sample was treated with scCO$_2$ (4.2) again.

Experiments 2 and 4 are similar; the only difference was that in Experiment 4 there was a second supercritical CO$_2$ treatment at the end. However, the second scCO$_2$ treatment did not play a role in the surface charge value. The surface charge for sample 2.4 was 64.43 mmol/kg and for sample 4.2 (treated with scCO$_2$ twice) it was 63.99 mmol/kg.

Experiment 5

In the fifth experiment, the initial sample (3 g) was treated under scCO$_2$ conditions with 1:1 ethanol water co-solvent. Then, it was treated with 1% NaOH and washed with distilled water in the Büchner funnel until neutral pH. Following this, the sample was submitted to BM treatment (5.4). The fifth experiment resembled the third experiment; the only difference was the scCO$_2$

treatment process between 1% NaOH treatment and BM treatment.

However, the surface charge values of samples 3 and 5 are quite different (3.39 mmol/kg and 18.34 mmol/kg, respectively). This means that the scCO$_2$ treatment has an influence even between mechanical treatments.
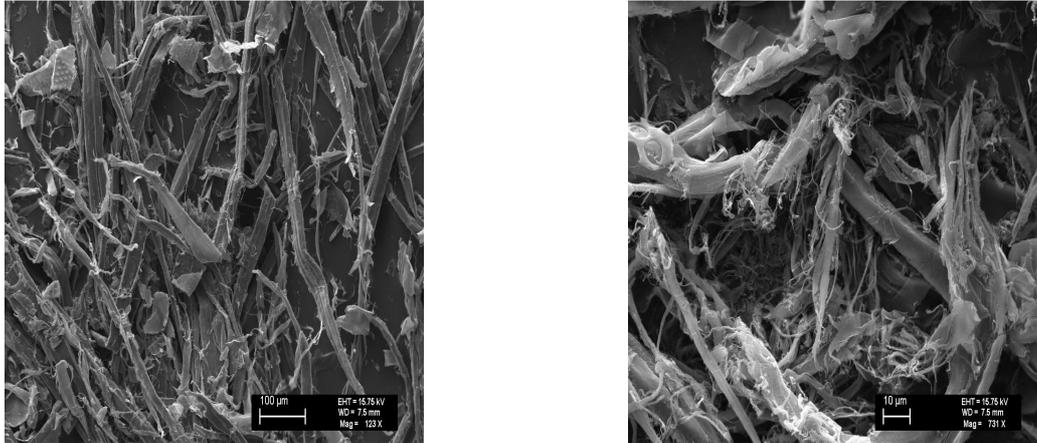

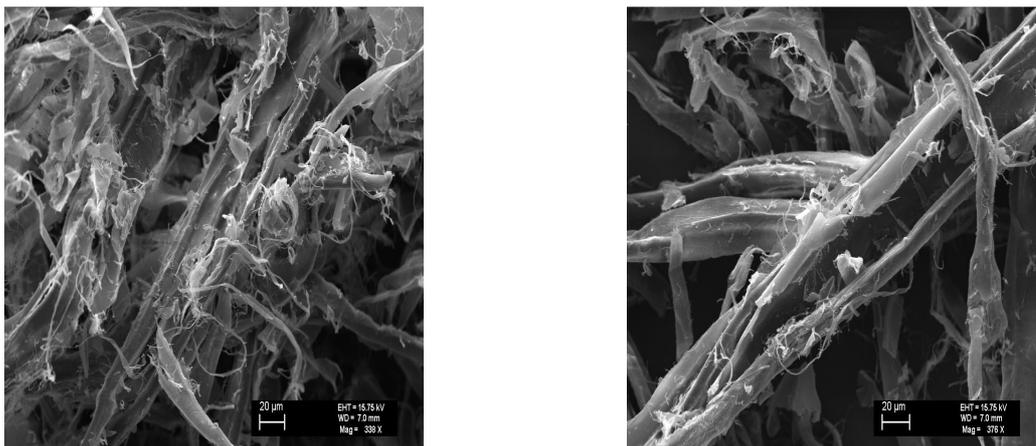Figure 5: Samples 1.1 (left) and 1.2 (right) showing the influence of BM treatment

Figure 6: Samples 2.1 (left) and 3.1 (right) showing similar results after scCO2 treatment regardless of ethanol-water solvent used for sample 3.1

Effect of BagMixer treatment on the surface charge

The result was quite significant before and after BM treatment, in samples 1.1 and 1.2, respectively. Surface charge increased considerably, comparing the surface charge before and after BM treatment. This is in agreement with SEM images, which show that there is an abundance of lamellas, unbroken fibres, but no fibrillous parts, in sample 1.1, while in sample 1.2, on the contrary, the fibres are broken and there are more fibrillous parts. It can be concluded that fibrils were separated from the fibres during mechanical treatment. The influence of BM treatment is depicted in Figure 5.

Effect of scCO$_2$ extraction on surface charge

The surface charge showed the largest values for samples after scCO$_2$ treatment. However, there was no significant difference between samples 2.1 and 3.1, treated under scCO$_2$ conditions and by scCO$_2$ treatment with 1:1 ethanol-water co-solvent, respectively. This means that either ethanol-water did not influence the surface charge, or the amounts of co-solvent were too small.

Figure 6 shows similar results for samples 2.1 and 3.1 despite the 1:1 ethanol-water treatment of sample 3.1. SEM images for the samples also yielded similar results. The results of scCO$_2$ treatment are illustrated in Fig. 6.

Effect of supercritical CO₂ and BagMixer treatment on surface charge

A strong influence of $scCO_2$ in combination with BM treatment was found. The surface charge for sample 1.4 was 75.13 mmol/kg and for sample 4.2 it was 63.99 mmol/kg. Nevertheless, the surface charge value did not rise after the second $scCO_2$ treatment (sample 4.2). The influence of $scCO_2$ in combination with BM treatment is illustrated in Figure 7.
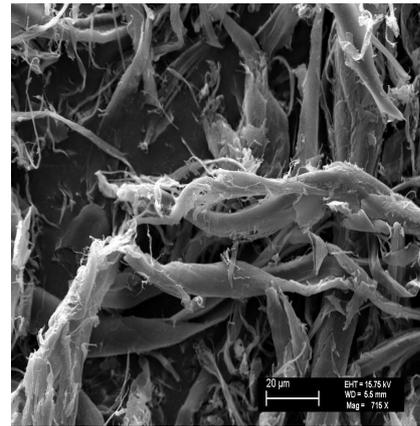
Effect of 1% NaOH on surface charge

Surface charge was the lowest for the samples that were treated with 1% NaOH and then washed until neutral reaction. Samples 3.3 and 5.2 did not show any result and sample 3.5 had the lowest determined values.

These results were in good agreement with the SEM images of samples 3.3 and 3.5, which have no fibrillous structure or fines that could cause significant fibre charge (Figure 8).
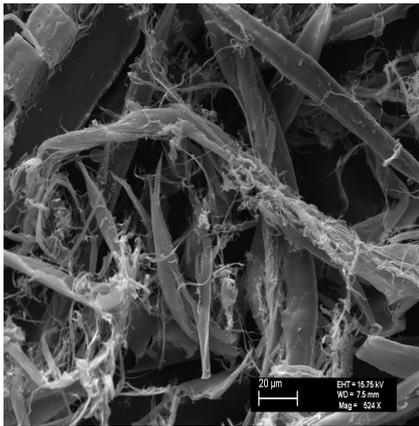

Figure 7: Samples 1.4 (left) and 4.2 (right), displaying the influence of scCO2 in combination with BM
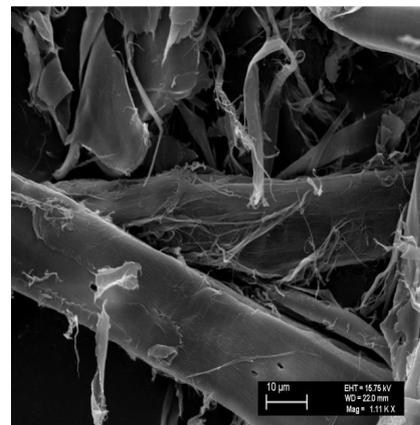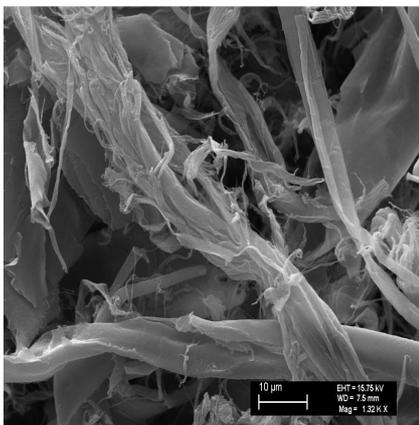

Figure 8: Samples 3.3 (left) and 3.5 (right), showing large lamellas with no fibrillous part after 1% NaOH treatment

That might be also the consequence of washing, as all the fine material that induces higher charge values is swept away from the fibre surface.

CONCLUSION

The main objective of this study was to investigate how different thermo-mechanical treatments and their order influence the surface charge of cellulosic fibres in aspen BCTMP. Various treatments of pulps were conducted and surface charges were measured. SEM images were also taken to investigate the correlation between surface charge value and visual appearance.

A new experimental method was practiced in order to measure the surface charge of cellulosic fibres. It was a combination between the polyelectrolyte titration technique and potentiometric titration. In this method, cationic polyelectrolyte, p-DADMAC was used (polyelectrolytic titration) for pulp dispersions and KOH solution was used as titrant, then pH was measured for end point determination

(potentiometric titration). According to these data, the surface charge of the samples was calculated. This method helped to analyse how different treatments influenced the surface charge of cellulosic fibres.

Dried and ground BCTMP pulp of aspen was dispersed in water, treated with BM with a nylon separator, treated with $scCO_2$ with and without 1:1 ethanol water co-solvent and treated with 1% NaOH. The processes occurred at various times and order of succession. After each treatment the surface charge was measured and SEM images were taken.

There was a good agreement between the titration results and SEM pictures, as much of the fibrillous structure was seen where the surface charge was higher and smooth surfaces of fibres were found where the surface charge of cellulose fibres had a lower value. This suggests that the surface charge of cellulosic fibres could be measured by using this new experimental method.

It is not possible to compare the surface charge results with those of other authors, as the method is completely different from those used by other authors who measured the charge of filtrate and removed the pulp before titrations. It was of interest to measure the surface charge of the pulp and therefore the filtrate was never used for titrations. However, there is a good correlation between the changes in fibre morphology and the electrokinetic character of the fibres.

In future studies, the surface charge of the pulp could be measured by using all suspension material, including the filtrate. By measuring the surface charge of the filtrate, the result should be somehow different; the surface charge should be higher, as the filtrate contains much fine material that gives surface charges.

In the future, it is possible to bind some other material with pulp fibres that has high surface charge. One possibility is to make cellulose hydrogel and bind it with hydroxyapatite.

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