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Brightness measurement of cellulosic materials

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ABSTRACT

The objective of this bachelor's thesis was to study which factors influence the brightness measurement of brightness cakes made from microcrystalline cellulose (MCC). The aim was to determine the factors that have the least favorable effect on brightness and find a method that helps to achieve the most easily repeatable and reliable brightness measurement of sheet brightness.

As a material, MCC is quite difficult because it is sensitive to changes in the surrounding conditions. Its temperature resistance is limited, and as a result, MCC is prone to yellowing when exposed to excessively high temperatures. The MCC particle size is relatively small and because of its crystalline structure their bonding strength is weaker than cellulose fibers. This is the possibly reason for the cracking of the cakes. Another problem is that the brightness cakes curl up while they are drying.

In order to avoid the aforementioned problems, the study started with making brightness cakes with a set of variables. The variables were pH, filtration, rolling, compressing, compression pressure and time, and different drying methods including an air-conditioning room, grill and vacuum dryer. The brightness cakes were made from three different MCC raw materials, and three cakes from each type of material were made. Thus, each series included nine brightness cakes.

Of the different drying methods, the best brightness results and the smoothest cakes were achieved with a vacuum dryer. In the air-conditioning room, the brightness cakes darkened and curled. The grill was found to considerably darken the cakes made from one of the raw materials, which is why it was rejected at an early stage. Rolling was found to be a better method than compression and it provided better brightness regardless of whether the drying method was an air-conditioning room or a vacuum dryer.

The best brightness measurement was achieved when the pH was adjusted to slightly acidic conditions and the cakes were rolled and dried in a vacuum dryer. In this study, different pH was not found to have a significant effect on the brightness of the cakes, but a higher pH slowed filtration through the büchner funnel. With rolling and vacuum drying, the cakes differed the least in appearance, making the method most easily repeatable and reliable.

Keywords: brightness measurement, brightness, sheet brightness, yellowing

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TIIVISTELMÄ

Tämän opinnäytetyön tarkoituksena oli tutkia, mitkä tekijät vaikuttavat MCC vaaleuskakkujen vaaleusmittaukseen. Tavoitteena oli haarukoida vaaleuteen eniten vaikuttavat tekijät ja löytää menetelmä, jolla saavutetaan luotettavin sekä toistettavin vaaleusmittaus arkkivaaleudesta.

MCC on materiaalina hankala, sillä se on herkkä erilaisille ympäristön muutoksille. Sen lämmönkestävyys on rajoittunut, mikä johtaa siihen, että MCC on myös altis jälkikellertymään liian korkean lämpötilan vaikutuksesta. MCC:n partikkelikoko on suhteellisen pieni, ja kiteisen rakenteensa vuoksi sen sitoutumislujuus on heikompi kuin selluloosakuitujen. Tämä saattaa aiheuttaa kakkujen halkeilua. Toinen ongelma on, että vaaleuskakut käpristyvät kuivumisen aikana.

Tutkimusongelmien välttämiseksi tutkimuksessa tehtiin vaaleuskakkuja erilaisilla muuttujilla. Muuttujina olivat pH, suodattuminen, kaulinta, puristus, puristuspaine ja -aika sekä eri kuivausmenetelmät, joihin kuuluivat ilmastointihuone, grilli ja vakuumikuivain. Vaaleuskakkuja tehtiin kolmella eri MCC-raaka-aineella, joista jokaisesta tehtiin kolme rinnakkaista kakkua. Jokaiseen sarjaan syntyi yhdeksän vaaleuskakkua.

Eri kuivausmenetelmistä vakuumikuivaimella saavutettiin parhaimmat vaaleustulokset ja sileimmät kakut. Ilmastointihuoneessa vaaleuskakut tummuivat ja käpristyivät. Grillin huomattiin tummentavan yhdestä raaka-aineesta tehtyjä kakkuja huomattavasti, jonka takia grilli hylättiin jo alkuvaiheessa. Kaulinnan huomattiin toimivan paremmin kuin puristuksen, ja sillä saavutettiin parempi vaaleus riippumatta siitä, oliko kuivaustapa ilmastointihuone tai vakuumikuivain.

Paras vaaleusmittaus saavutettiin, kun pH säädettiin hieman happamiin olosuhteisiin, kakut kaulittiin ja kuivattiin vakuumikuivaimella. Tutkimuksessa eri pH:lla ei huomattu olevan suurta vaikutusta kakkujen vaaleuteen, mutta korkeampi pH hidasti suodattumista büchner-suppilon läpi. Kakkujen kaulinnalla ja vakuumikuivaimen käytöllä kakut erosivat vähiten ulkonäöltään toisistaan, minkä perusteella kaulintaa ja vakuumikuivaimen käyttöä voidaan pitää toistettavimpana ja luotettavimpana menetelmänä.

Asiasanat: vaaleusmittaus, vaaleus, arkkivaaleus, jälkikellertyminen

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1 INTRODUCTION

Microcrystalline cellulose (MCC) is a potential material for many future applications, for example in food industry, pharmaceuticals and composites. However, it is very susceptible to various changes in the surrounding conditions, such as heat and humidity, which affects the physical properties of MCC. These include the cracking of the surface made from the material and colour changes. The purpose of this bachelor's thesis is to study which factors affect the brightness cakes made from MCC. The primary objective is to find a method that would give the most reliable and repeatable result on sheet brightness and to gain a better overall understanding of which factors have an effect on brightness and in which way.

As a background for the study, factors influencing brightness of pulp and paper had been sought from literature and expert studies and described in the theoretical part of the study. Radiation has been proved to be the greatest factor that affects the brightness of pulp and paper (Parkås & Paulsson 2012, 12). Other factors include the raw material itself and the chemical compounds it contains as well as heat, moisture, oxygen, and process-related factors such as bleaching, washing and the effect of pH. (Stenius 2000.) The theoretical part of this study also includes an examination of brightness and colour theory.

In the experimental part of the thesis, cakes were made from three different MCC's. Several variables affecting the brightness, such as pH, compression pressure and time, rolling and different drying methods were varied in the making of the cakes. The drying methods that were used were an air-conditioning room, grill, and a vacuum dryer. The brightness measurement was performed by using an L&W Elrepho spectrophotometer.

2 THEORY OF BRIGHTNESS AND COLOUR

There are a few factors that affect how we perceive the brightness and colors of the objects around us. One important factor is the light that illuminates the object. In addition, the perception of brightness and colour is affected by the reflectance and absorption qualities as well as how easily the eye recognizes light at different wavelengths. (Levlin & Söderhjelm 1999, 165.) The brightness

and colour of a paper sample can be measured with different instruments, and there are a variety of different light sources that are suitable for these measurements.

2.1 Brightness measurement

Brightness measurement was originally developed to observe pulp bleaching process. The brightness measurement is focused on short wavelength region because the reflectivity changes the most in that region. The wavelength of 475 nm is the effective brightness function that is also called ISO brightness. (Pauler 2012, 54.) The brightness can be calculated (Equation 1) by multiplying the brightness function with the spectral reflectance value (Niskanen 2008, 149).

$$R = \sum R(\lambda)F(\lambda) \quad (1)$$

When

R (λ)	Spectral reflectance	[-]
F (λ)	Brightness function	[-]

Paper is considered to be bright if it can reflect back most of the light that has fallen onto it (Häggblom-Ahnger & Komulainen 2003, 101). When measuring brightness, we actually measure the ability of a sample to reflect blue light (Maijanen 2013, 16). The fibers and the lignin in them are naturally yellowish, and even after bleaching, a yellow tint is noticeable. The colour yellow reflects green and red and, therefore, they should not be used in brightness measurements. (Häggblom-Ahnger & Komulainen 2003, 101.) However, yellow absorbs blue light which makes the measurement more accurate because the changes in the intrinsic reflectance factor R_∞ that have occurred in bleaching appear the most in the blue light region of the spectrum (440-480 nm). (Know-pulp 2001).

2.1.1 ISO brightness

There are many ways to measure paper brightness that use different optical instruments and light sources. Today, spectrophotometers are most com-

monly used to measure diffuse reflectance. The L&W Elrepho spectrophotometer is widely used in Scandinavia and Western Europe to measure the ISO brightness of paper (Arjas 1983, 248).

The two primary brightness measurement systems that use different light sources are ISO brightness and D65 brightness. A paper sample can be illuminated with a CIE illuminant C light source which is a daylight illuminant containing a certain amount of UV and used for ISO brightness measurement. Another measurement system is called D65 brightness (ISO 2470-2). The light source for this measurement is CIE illuminant D65 that contains more UV energy than CIE illuminant C light source. (Sappi 2017, 4-5.)

Light and measurement geometry are defined in the standards ISO 2469 and ISO 2470. According to these, the light source used in the measurements is a standard illuminant C. (Häggblom-Ahnger & Komulainen 2003, 101.) ISO 2470 is titled as Paper, board and pulps – Measurement of diffuse reflectance factor – Part 1: Indoor daylight conditions (ISO brightness) and it contains ISO brightness and D65 brightness measurements. (ISO 2009.) According to ISO 2469 standard, the optical geometry used in ISO brightness measurement is defined as d/0° geometry. In order to achieve the desired geometry, the spectrophotometer contains a sphere of 150 mm in diameter which is coated with white barium sulfate pigment on the inside. The illuminant is diffusively reflected onto a paper sample that is placed under the sphere. The light reflected from the paper sample is measured perpendicularly above the sample at an angle of zero. (Pauler 2012, 27.)

2.2 Colour

Colour perception is created when light reflects from a colored object to the retina of the eye (Häggblom-Ahnger & Komulainen 2003, 48). It is affected by the way the energy in the light is divided into different wavelengths (Pauler 2002, 45). A human can distinguish over a hundred different shades of colour, several hundred brightness options and twenty degrees of purity. In order to be able to see the colors of the objects, three factors are needed: light, a colored object reflecting light and an observer. (Häggblom-Ahnger & Komulainen 2003, 48.)

The act of colour measurement is called colorimetry. It defines numerical values for parameters such as hue, colour brightness and colour strength. In 1931, CIE (Commission Internationale de l'Eclairage) introduced a system for colorimetry which is built around Young & Helmholtz's three-colour theory. The CIE system makes it possible to standardize certain illuminant functions and colour matching functions in different wavelengths based on the sensitivity of a human eye. (Pauler 2012, 36.) Colour matching functions determine the tristimulus values X (red), Y (green), Z (blue) which determine the colour (Pauler 2012, 39).

All colour measurements are based on the tristimulus values, but it is difficult to perceive the actual colour of a sample by only paying attention to these X, Y and Z values. For this reason, a CIE colour triangle has been invented where tristimulus values are converted into corresponding values of hue, saturation, and lightness. (Pauler 2002, 52.)

2.2.1 CIE colour triangle

The CIE triangle or so-called chromaticity diagram indicates how different colors of light are distributed and mixed with each other. The curve in the diagram displays monochromatic colours, and the wavelength corresponding to the colour is indicated along the curve as seen in Figure 1. The chromaticity co-ordinates x_1 and y_1 are calculated from the tristimulus values, and the intersection point is recorded in the CIE triangle.

The dominant wavelength of paper which is represented by hue can be found when a straight line from a neutral point through the point x_1y_1 intersects with the spectral locus. By calculating the distance from the neutral point to the point x_1y_1 as a percentage of the distance from the neutral point to the spectral locus, the saturation or excitation purity is obtained. (Pauler 2012, 43.) There is no wavelength in the purple line, between 360 nm and 780 nm, because purple does not appear in the spectrum.

Y value is the third dimension of the chromaticity diagram where the co-ordinates x and y form two dimensions. The chromaticity diagram acts as a projection in the x- and y-plane, and a colour solid is obtained. Optimum colours which are the colours with the highest possible saturation for a given luminance and dominant wavelength are defined by the surface of this colour solid. (Pauler 2012, 45.)

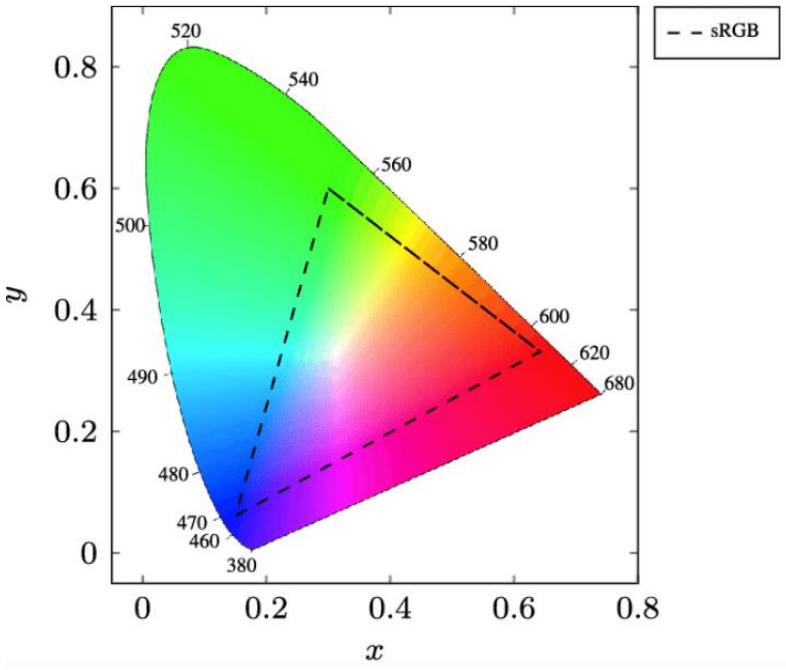

Figure 1. CIE colour triangle. (Amara, Couderc, Gérenton, Lemiti, & Mandorlo 2017, 2)

2.2.2 CIELAB system

The CIE colour triangle has a disadvantage of not illustrating the subjective impression of colour difference well enough. It has also been noticed that in the different regions of the CIE colour triangle, the same perceived colour difference corresponds to different distances. (Pauler 2012, 45.) These problems have been corrected in the CIE L*a*b* system which is the most well-known colour system today.

The CIELAB system is based on four basic colours that are yellow, blue, green and red. It is a three-dimensional colour system which consists of a grey scale axis ***L**** representing lightness, a red-green axis ***a**** and a yellow-blue axis ***b****. (Pauler 2012, 46.) The basic colour tone of a paper can be found by reading scales a and b where *a* positive is red tone and *a* negative is green tone. Similarly, *b* positive is yellow tone and *b* negative is blue tone. Paper is

white when the absolute value of a or b is close to zero and contains pure hues when the absolute value is between 60-90. (Häggblom-Ahnger & Komulainen 2003, 51.)

3 FACTORS AFFECTING BRIGHTNESS

Discoloration or yellowing is a severe problem for many pulp and paper products. It has been predominantly studied in products containing lignin, but it also appears in lignin-free materials such as MCC. Many factors cause yellowing either individually or when they interact with each other. The main sources to singly cause discoloration are light and heat in which case terms such as photoyellowing and thermal yellowing are used. However, humidity and oxygen contribute to some extent to these yellowing processes. In addition, wood contains compounds such as chromophores and carbohydrates that are known to cause discoloration. Some process-related factors that have effects on brightness are bleaching, washing and pH.

3.1 Raw material

The optical properties of pulp and paper are significantly affected by the used raw material. Different wood species contain different amounts of lignin which causes the dark colour of the pulp. Hardwood pulps contain less lignin than softwood pulps, which makes them more photostable, and that is why they are preferred when striving for high quality. In addition to lignin, hemicelluloses have a significant effect on brightness. Hemicellulose contains sugars that begin to burn and decompose under the influence of heat. This leads to a browning reaction called caramelization.

The colour of a wood material varies much based on from which part of the tree the material is taken. Colour is not evenly distributed along the tree trunk, which can be seen during seasonal changes. Thus, the colour of wood taken from the upper parts of a tree differs from that of the lower parts. Brightness can differ in mechanical pulps over five brightness units if the raw material is taken from different heights of the tree. (Stenius 2000, 296.)

3.2 Lignin

Lignin is an amorphous polymer whose primary function is to act as a binder for wood cells (Alén 2011, 43). Softwood contains approximately 26-32% and hardwood approximately 20-25% of lignin (Sjöström 1993, 72). At least 70% of lignin is located in the secondary wall although the lignin concentration is higher in the middle lamella. This is because the secondary wall of wood cell is thick. (Sjöström 1993, 87.)

Lignin is defined as a polyphenolic material formed by dehydrogenative polymerization of three precursors of phenylpropanoids: coniferyl alcohol, sinapyl alcohol and paracoumaryl alcohol. Polymerization involves a variety of oxidative coupling reactions of phenoxy radicals that result in the formation of an irregularly cross-linked macromolecule. (Alén 2011, 43.) The precursors in lignin consist of methoxyl groups, phenolic hydroxyl groups and some terminal aldehyde groups in the side chain. Only a few phenolic hydroxyl groups are free because they form bonds to the phenylpropane units next to them. The precursors are attached to each other by ether bonds or bonds between carbon atoms to form a network-like structure. (Alén 2011, 44-45.)

3.2.1 Chromophores

The colour of a material and low brightness stability is usually caused by chromophoric groups. Chromophores are located mainly in the lignin compound of the wood but in some wood species they are also high in extractives. (Stenius 2000, 296.) The most common chromophores in lignin are coniferylaldehyde and α-carbonyl groups as well as different quinone structures. Wood also contains compounds such as phenolic groups that are not originally colored but can change to colored structures as the temperature rises. (Lönnberg 2009, 364)

A chromophore is a molecule or part of the molecule that is capable of absorbing wavelength-selective light. A viewer recognizes material to be colored if absorption takes place in the UV/visible region. Absorption can sometimes cause for a compound such an increase in energy that a chemical reaction occurs which either generates new chromophoric compounds or destroys inherent chromophores in the material. Therefore, chromophoric structure elements

can function as photosensitizers for the yellowing process. (Stenius 2000, 279-280.)

3.3 Carbohydrates

Along with cellulose, hemicellulose is an important carbohydrate-based polymer produced in nature. Hemicelluloses are not crystalline, and the degree of polymerization is moderately low (100-200) compared to cellulose. This is also believed to affect the lower chemical and thermal stability of hemicelluloses. Hemicelluloses are heteropolysaccharides while cellulose is a homopolysaccharide. (Stenius 2000, 34-36.) Heteropolysaccharides are formed by two or more kinds of monosaccharide units, and homopolysaccharides contain one kind of monosaccharides (Sjöström 1993, 51).

The main purpose of most hemicelluloses and celluloses is to be a supporting element in the cell walls. The hemicellulose content of a dry weight of wood is generally 20-30%. Hemicelluloses can be hydrolyzed with acid to their monomeric components that consist of D-glucose, D-mannose, D-galactose, D-xylose, L-arabinose and small portions of other components. (Sjöström 1993, 63.)

3.3.1 Caramelization

Hydrolysis is a degradation reaction that needs a certain temperature to begin. MCC can be produced by hydrolysis in which the solid residue MCC begins to darken as the hydrolysis continues. The darkening of a cellulose caused by high temperature and low pH can also be called caramelization where carbohydrates go through dehydration and condensation reactions. (Dahl & Vanhatalo 2014.)

In the caramelization process, sugars begin to decompose under the influence of heat. This is a nonenzymatic browning reaction. The formation of brown caramel comes from heating reducing as well as non-reducing sugars that do not contain nitrogen compounds. Reducing sugars are comprised of glucose and non-reducing sugars are comprised of sucrose. Both high heat and low pH release the reactions occurring in caramelization. (Cui 2005, 47-48.)

In the caramelization of sucrose, a caramelan ($C_{24}H_{36}O_{18}$) is first created where heating causes the sucrose to lose four molecules of water. When some more time has passed, the formation of a caramelen ($C_{36}H_{50}O_{25}$) begins where approximately every three sucrose molecules lose eight water molecules. The heating of sugar further leads to the formation of yet larger molecule called caramelin ($C_{125}H_{188}O_{80}$) which dissolves poorly.

Another non-enzymatic browning reaction is the Maillard reaction that causes colours as well as flavours. In the Maillard reaction, reducing sugars are in contact with amino acids. (Field 2012, 175-174.) In the first stage of the reaction, glucose, fructose and mannose are converted into 1,2-enediols. When heating continues, they go through dehydration reactions which result in the formation of 5-hydroxymethylfurfurals. If the sugar being degraded under heat is pentose, the final product after dehydration is 2-furaldehyde (furfural). It is commonly perceived that the colored pigment is formed when these furfural derivatives polymerize. (Cui 2005, 47-48.)

3.4 Radiation

Radiation is considered to be the main cause of discoloration. The discoloration of a material is affected by the wavelength of radiation which is better absorbed by many materials at shorter wavelengths (Parkås & Paulsson 2012, 5). Radiation in the wavelength between 360-740 nm appears to the eye as visible light. It comes mainly from the sun, and the intensity decreases as it passes through the atmosphere. Approximately 80% of solar radiation is visible light as its wavelength is located in the visible region. Invisible light is under a wavelength of 400 nm and is called ultraviolet radiation (UV). Ultraviolet radiation causes yellowness by photo-oxidation of lignin and, therefore, affects the brightness stability of pulp. (Pauler 2012, 12.)

The wavelength has an important effect on the outcome of the photoyellowing reaction since it determines the energy of the radiating photons. The main wavelength of light to cause light-induced yellowing is between 300-400 nm. (Parkås & Paulsson 2012, 8-9.) This has been noted by Andtbacka and Nolan who noticed that the yellowing reaction probably depends on the wavelength.

The reaction proceeds faster under irradiation when exposed to short-wavelength UV-light. (Andrady, Song & Parthasarathy 1991.)

The photochemistry can be divided into two processes: primary and secondary. In the primary process, the photon is absorbed into the molecule and excites the molecule which causes it to lose energy in many ways. In the secondary process, post-irradiation reactions take place in which the energy transfer initiates a chain of events. For example, an excited molecule forms a singlet oxygen that oxidizes the chemical component. The amount of oxygen, humidity and temperature are important factors in the outcome of radiation in the secondary process but not essential in the primary process. (Parkås & Paulsson 2012, 4.)

Yellowing occurs because chromophoric compounds in lignin cause photoreactions when they absorb ultraviolet radiation in sunlight. Approximately 50% of the colour changes occur at a depth of circa 20 µm (Parkås & Paulsson 2012, 5). There are a variety of different chromophoric groups such as alpha-carbonyl compounds and orulo- and para-quinonoid structures that are formed when lignin absorbs light (Andrady, Song & Parthasarathy 1991). The mechanism of photoyellowing in materials containing lignin can be divided into three phases:

i. Chromophoric groups in lignin absorb energy.
ii. Intermediate structures, such as phenoxyl radicals are formed.
iii. Chromophores are formed by absorbing light from intermediates. (Parkås & Paulsson 2012, 7.)

Yellowing induced by radiation could be prevented by identifying the wavelength range that causes it and regulating the absorption of radiation in these regions (Andrady, Song & Parthasarathy 1991).

3.5 Heat

The brightness of pulp and paper is also affected by temperature. When pulp or paper is in contact with hot surfaces or high temperatures, it speeds up the

thermal processes. Mechanical pulps are more sensitive to heat-induced yellowing because they contain more lignin and phenolic structures than chemical pulps. (Castellan & Grelier 2016, 531–552.)

Thermal degradation occurs when the temperature is above 100°C. Different components of wood degrade in different temperatures. Hemicelluloses start to degrade at a temperature of 200-260°C, cellulose at 240-350°C and lignin at 280-500°C. When temperature rises to approximately 270°C, thermal degradation no longer requires heat from the outside since the process has turned into exothermic. (Sjöström 1993, 234.)

The thermal yellowing process was observed by Beyer who noticed that polysaccharide chains begin to decompose and produce short-chain products or sugar monomers when pulp is heated. Polysaccharides are mainly derived from hemicellulose which are able to partially oxidize and degrade. Hemicelluloses contain the most of oxidizing groups in the pulp, such as carboxyl groups which produce low molecular weight precursors. These result in the formation of dehydration products which lead to the formation of coloured condensation products. (Castellan & Grelier 2016, 531–552.)

3.6 Humidity

The combined effect of humidity and temperature has been found to cause thermo-oxidative degradation. The colour reversion is usually more intense when the humidity is high but the temperature remains constant. (Stenius 2000, 295.) This is because when the temperature remains constant, the water content of the cellulose depends on the ambient humidity. (Kolar & Strlic 2005, 109.) Thus, increased water content can result in increased degradation of cellulose.

Peroxides are known to be involved in the oxidation of cellulose. Kleinert and Marracini have studied the role of relative humidity in oxidation at temperatures below 100°C. The results show that high relative humidity also leads to high peroxide content. (Kolar & Strlic 2005, 107.) However, the oxidative degradation is a complicated process which can be seen from the fact that the

degradation rate is the lowest when the relative humidity is 20% or 95% but increases when the RH is somewhere in between those values. (Kolar & Strlic 2005, 117.)

3.7 Oxygen

Oxygen has been found to have an effect on photoyellowing but its effects on thermal yellowing have not been studied extensively. However, many studies have shown that oxygen is involved in the decomposition of lignin and in the formation of chromophoric groups. Oxygen also participates in photo-oxidative degradation and thermo-oxidative degradation.

The degradation rate of lignin increases when pulp contains singlet oxygen. Important intermediates that are oxidized by singlet oxygen for light-induced yellowing are phenoxy-free radicals. They are oxidized to chromophoric structures of carbonyl compounds as well as ortho- and para-quinonoids. The quinones in lignin absorb efficiently ultraviolet radiation and undergo photochemical reactions that lead to the formation of colour substances through excited compounds and free radicals. Free radicals are involved in the oxidation and degradation of lignin leading to the formation of coloured unsaturated carbonyl compounds and discoloration in the pulp. (Chen, Fan, Gao, Liu, Stark & Tshabalala 2012.)

It has been discovered that the combined effect of oxygen, humidity and elevated temperature is a significant factor in the darkening of pulp during heat treatment. The formation of chromophores during heat treatment is mainly influenced by oxidative and hydrolytic reactions. Hydrolytic reactions are usually most predominant under humidity conditions because the reaction requires water. When water is present and high temperature and oxygen are combined, a hydrolysis reaction is initiated by heat. This can lead to the formation of flavonoids which are by their molecular weight low and yellow phenolic substances. (Chen, Fan, Gao & Stark 2012.)

3.8 Bleaching

The purpose of bleaching is to remove residual lignin but also to alter chemical reactions that reduce the formation of colour-causing chromophoric groups

(Lönnberg 2009, 362). The bleaching of chemical pulps is referred to as lignin-removing bleaching and the bleaching of mechanical pulps is called as lignin-retaining bleaching since due to its high content it would not be practical to remove the lignin in mechanical pulps. This would require the use of too many chemicals which would affect yield. (Lönnberg 2009, 366.)

In bleaching, the light absorption decreases which is necessary in order to reach high brightness. Unbleached pulp has a high light absorption at the shorter wavelengths which is in the blue part of the spectrum. When mechanical pulp is bleached, the objective is not to remove lignin but to transform chromophoric groups into low light absorbent molecules. This is accomplished by hydrogen peroxide bleaching or sodium hydrosulfide bleaching.

3.8.1 Lignin-removing bleaching

Brightness in the chemical pulp is higher than in the mechanical pulp since the chemicals used in lignin-retaining bleaching do not remove all colored structures. However, not all chromophoric groups can be eliminated in lignin-removing bleaching which is why even highly bleached chemical pulps have a yellow tint. Highly bleached chemical pulp has a lower reflectivity at shorter wavelengths, and light absorption clearly increases as the wavelength decreases resulting in a yellow tint. At the visible wavelength, the light scattering coefficient of the chemically bleached pulp remains fairly constant. (Pauler 2012, 81.)

Lignin removing (delignifying) bleaching achieves high and relatively permanent brightness. It takes place in a multi-step bleaching sequence using bleaching chemicals and sodium hydroxide as alkali. The most commonly used bleaching chemicals have been chlorine, chlorine dioxide and oxygen, but chlorine is partially replaced by chlorine-free chemicals such as oxygen, hydrogen peroxide and ozone for environmental reasons. (Sjöström 1993, 165.)

Oxygen delignification continues the lignin removal that was started in the cooking phase. Pulp cannot be cooked to an extremely low kappa number without loss of yield which is why a gentler oxygen delignification method is

used. In the delignification process, lignin is decomposed and oxidized to an alkali-soluble form, and the coloured compounds of the lignin as well as the impurities in the pulp are removed. (Knowpulp 2001.) Residual lignin can be removed more efficiently with bleaching chemicals than with cooking, but the use of chemicals is more expensive. For this reason, the delignification in the cooking stage should be prolonged as much as possible. However, the oxygen delignification cannot be extended to a low lignin content, and only 50% of the residual lignin can be removed during the oxygen delignification process. The remaining residual lignin must be removed using other bleaching agents. (Sjöström 1993, 177-178.)

3.8.2 Lignin-retaining bleaching

Lignin-retaining bleaching is used for mechanical pulps containing large amount of lignin and chromophoric groups. Due to the high concentrations of colour-causing compounds, the purpose is not to remove chromophoric compounds since this would require an excessive use of chemicals. Thus, the aim is to change the chromophoric structures. Bleaching chemicals used in the lignin-retaining bleaching are mainly hydrogen peroxide and sodium dithionate. In order to achieve high brightness, the bleaching stages are performed sequentially with the same chemical. (Hintz & Lawal 2018.)

The chromophoric structures are changed by reducing bleaching or by oxidative bleaching. Reducing bleaching is based on the use of reducing agents that are affected by the redox potential of the pulp to be bleached. Residual lignin contains quinone structures with redox potentials of approximately 0.7-0.9 V. They are reduced with sodium dithionite to the corresponding hydroquinones. Nonetheless, the hydroquinones can be oxidized back to quinones by oxygen and light which is why reducing bleaching does not achieve permanent brightness. Theoretically, sodium dithionite achieves the best brightness at a temperature of 20-60°C and at pH of 8-9. The actual pH is 5-6 which prevents the decomposition of dithionite and alkali-induced darkening of lignin since oxygen cannot be completely isolated from the system.

In oxidative bleaching, hydrogen peroxide is mainly used as the bleaching chemical. Hydrogen peroxide is a weak acid but its active compounds adhere

to carbonyl structures and convert them to less chromophoric structures without lignin decomposing or dissolving. Peroxide decomposes in the presence of heavy metal ions. In order to avoid this, stabilizers are used, for example magnesium silicates and binders. Under optimized conditions, it is possible to achieve 25% increase in ISO brightness, but the result is also influenced by the pulp being used. (Sjöström 1993, 199-201.)

3.9 Washing

The purpose of washing is to remove dissolved substances from the pulp. The quality of water used in the industrial processes can vary significantly, but a common problem is the presence of humic acids and metal ions in the water. Humic acids can colour the raw water into a brownish colour. They contain phenolic groups, such as lignin, and together with metal ions (Fe^{3+}) they cause discoloration. (Stenius 2000, 296-297.)

Efficient washing reduces the use of bleaching chemicals and increases the brightness of the pulp. Distilled water has been found to affect brightness more than tap water but washing efficiency is a more important factor affecting brightness than water quality. (Sillanpää 2005, 26.) In the washing phase, the most important matter is to remove all transition metals and sugars. Reducing sugars can accelerate the catalytic decomposition of hydrogen peroxide and may react with hydrogen peroxide which reduces brightness and increases the consumption of bleaching chemicals (Sillanpää 2005, 34).

3.9.1 Metal ions

Metal ions can be divided into two groups based on how strongly they affect colour stability. Al^{3+}, Mn^{2+}, Zn^{2+}, Pb^{2+}, Ni^{2+} and Ba^{2+} are considered to be harmless metal ions. However, for example manganese reacts in peroxide bleaching. Fe^{2+}, Fe^{3+} and Cu^{2+} are considered to be more harmful metal ions. Fe^{2+} ions are more significant in light-induced yellowing than Fe^{3+} ions because pulp can absorb them better. (Stenius 2000, 297.)

The most common transition metals that are harmful in the bleaching process are iron and manganese ions. In the degradation of peroxide, some reactions occur that allow iron and manganese ions to form colourful structures in the

pulp. Even as little as 5 mg of active manganese per ton of pulp can be harmful for the peroxide bleaching process since Mn^{2+} and Mn^{3+} are particularly efficient catalysts for peroxide. High temperature and pH can increase the occurrence of unwanted properties of transition metals in peroxide bleaching. (Lönnberg 2009, 369.)

The darkening of pulp is due to the formation of coloured compounds between lignin functional groups and metal ions. Metal ions affect the brightness of the bleached mechanical pulp more than unbleached pulp as new phenolic hydroxyl and carbonyl groups are formed during peroxide bleaching. Iron ions darken the fibers even further by increasing light absorption. Therefore, it is important to keep the amount of metal ions low as even a small amount would affect the final brightness. Metal ions are removed either by adjusting the pH level (2-3) or by using a chelating agent. (Konn, Lillandt, Paltakari & Varhimo 2013.)

3.10 pH

The importance of pH in heat-induced yellowing is significant but its contribution to light-induced yellowing is unclear. Some of the early studies have shown that the best brightness value would be achieved at a pH of 3-4.5, while other studies favour a pH approximately of 6. The optimum pH value would seem to be between 5-7, which corresponds to the same pH range (5-6) where the mechanical pulp remains the most stable against thermal discoloration. Neutral pH is preferred to avoid discoloration when the combined effect of light and heat takes place.

Low pH values can lead to acid-catalyzed hydrolysis of carbohydrates, and in the caramelization of sugars this would result to the darkening of pulp. High pH values are also harmful because they can cause alkaline hydrolysis, bond breakage and depolymerization. Furthermore, under alkaline conditions the colour of phenolic compounds in lignin are more intense than under acidic conditions. (Stenius, 2000, 298-299.)

4 MICROCRYSTALLINE CELLULOSE (MCC)

MCC is a partially depolymerized and purified form of cellulose that does not contain fibrous structures. It consists of porous particles and resembles a white crystalline powder that is odourless and tasteless. (Abd El-Wahab, Adel, Al-Shemy & Ibrahim 2010.) MCC is produced by treating alpha-cellulose with mineral acids. Generally, the degree of polymerization (DP) is less than 400, and at maximum 10% of the particles are less than 5 µm by size. The average particle size of commercial MCC products is between 20-250 µm. (Vanhatalo 2017, 15.)

MCC can be prepared into a powder by drying it into a fine particle form. Another mechanism is to process it with a water-soluble polymer that will turn it to a colloidal form. One of the most important properties of MCC is its high degree of crystallinity which is between 55-80%. (Garba, Lawan, Wang, Yuan, Zhang & Zhou 2019, 3.) However, MCC also has some poor qualities such as high moisture absorption properties, poor wettability, limited temperature resistance and incompatibility with most polymer matrices. (Chuin, Fazita, Haafiz, Hassan, Hussin, Sabar, Taiwo & Trache 2016, 790.)

5 CURRENT BRIGHTNESS MEASUREMENT METHOD

The current method for making brightness cakes in XAMK Fiber laboratory is making them with 5 g of abs dry pulp and by adjusting the pH to 5. After this, the pulp is filtrated through a büchner funnel. Cakes are dried either in an air-conditioning room where they are inside of blotting papers and under a weight more than a day, or in a vacuum dryer for 25 minutes. Before drying the cakes in the air-conditioning room, they are first compressed for five minutes at 0.5 MPa. It was observed that the cakes that were dried in the vacuum dryer cracked more than the ones dried in the air-conditioning room, but the latter darkened more. The vacuum-dried cakes had also less brightness deviation when they were measured.

The purpose of the experimental part of the thesis was to find a better method for making the brightness cakes since there were disadvantages in both of the aforementioned methods. Therefore, in this study the focus on defining which factors have the greatest effect on brightness and the brightness deviation of the cakes made from MCC.

6 MATERIALS AND METHODS

For the purposes of this study, cakes with a diameter of 110 mm were made from three different MCC's. While making the cakes, attention was paid to the darkening, cracking and curling qualities of the cakes with the aim of determining how much the chosen methods would cause these phenomena. Various parameters that were tested in the experiment are tabulated in Chapter 6.3 Table 1.

6.1 Materials used in the study

The raw materials for the experimental part of this thesis study were made in advance, thus the preparation of raw materials was not part of the thesis. Three different MCC's were used in the making of the cakes and they are referred to as MCC1, MCC2 and MCC3. MCC1 had been made in the summer of 2020 when the results below including pH, particle size and brightness were also measured. MCC2 was made in the spring of 2020 as well as related pH, particle size and brightness measurements. MCC3 was made very shortly before the tests that were conducted in March 2021.

The raw material for MCC1 was bleached softwood. MCC1 had been cooked longer than the other MCC's and the cooking process was more intensive. It was more prone to turn yellow since the carbohydrates it contained start to degrade and caramelize already in the hydrolysis. MCC1 was made with hydrolysis preceded by acidification which was conducted with 93% of sulfuric acid. The pulp was then hydrolyzed and after that washed with a blanket washer. After blanket washing, the pH was 4.4. The degree of polymerization (DP) was 321, and the Malvern 2000 particle size d (0.5) was 23 µm. (Pakkasmaa 2020, 3) The ISO brightness of MCC1 was 54, and the dry solids content of MCC1 was 36% before starting the tests.

MCC2 was made from bleached mixed hardwood (eucalyptus and oak), and the cooking phase was milder than with MCC1. The pulp was acidified with 93% of sulfuric acid and hydrolyzed. After that, it was washed with a blanket washer, and the resulting pH was 4.70±0.25. The degree of polymerization (DP) was 305±19 and the ISO brightness of the cakes after vacuum drying was 70.8±1.6. The Malvern particle size d (0.5) was 22.103 µm. (Pakkasmaa

2020, 1-4.) Before starting the tests, the dry solid content of MCC2 was measured to be 57.7%

MCC3 pulp was prepared by bleaching MCC1 pulp with hydrogen peroxide in a mixer. The ISO brightness of MCC3 was an average of 82 with the traditional method of making brightness cakes that was described in Chapter 5 and the dry solid content was 31.7% before starting the tests.

6.2 Preparation of the sheets

The cakes were primarily made by the same method, but some of the parameters were varied. Three cakes were made from each raw material for reference measurements which means that one series consisted of nine cakes. Altogether, twenty-eight different series were performed in the experiments.

The making of the cakes began by weighing the right amount of MCC to which the dilute water (250 ml) was added. Then, the mixture was decomposed with a mixer for 60 seconds. After that, an additional 150 ml of tap water was added, and the mixture was adjusted to the desired pH. The initial pH was between 7-8 and it was further adjusted with sulfuric acid or sodium hydroxide. During the pH adjustment, the pulp was allowed to stand in a magnetic stirrer. Having been shaped from the pulp, the cakes were filtered over a büchner funnel, where they were stacked between two plates and blotting papers. The blotting papers were stacked as follows: old-old-new-new-sample-new-new-old-old where old refers to a used blotting paper, new refers to a not used blotting paper and sample refers to the cake. Finally, the different parameters were tested and observed.

6.3 Testing parameters

The cakes were made differently by varying testing methods. Each series in this experiment were different and done by changing some of the variables (Appendix 1). Air suction was compared with having no suction at all and different compression pressures and times were compared to each other. The methods of compression and rolling as well as different drying methods, namely, an air-conditioning room, grill and a vacuum dryer were compared to

each other. In addition, different pH's were under comparison. The different parameters are described below in Table 1.

Table 1. Testing parameters.

Pulp amount	The cakes were made with 3.8 g of abs dry pulp and 5 g of abs dry pulp.
Filtration through büchner funnel	In the first testing method, only water was filtered through a büchner funnel. In the second method, air was sucked for 60 seconds after water filtration.
pH	The pH was tested by adjusting it to the values of 3, 5, 7 and 9.
Compression (MPa)	The compression pressure parameters were 0.1, 0.3 and 0.5 MPa.
Compression time (s)	Compression time was set at 60 s and 240 s.
Rolling	The cakes were stacked between blotting papers and rolled over 6 times, turned over and rolled 6 times again with a 10.9 kg roller.
Air-conditioning room	The cakes were dried in an air-conditioning room. Each sample was placed between two blotting papers which were set on a drying plate.
Grill	The cakes were dried in a grill for a total of nine minutes. Each sample was placed between new and old blotting papers as follows: old-new-new-sample-new-new-old. The two outermost blotting papers were removed after 5 minutes, 2 minutes and again after 2 minutes.
Vacuum dryer	The cakes were dried in a vacuum dryer (95°C) for 25 minutes. Before this, the blotting papers were replaced with new ones on both sides of the sample.

6.4 L&W Elrepho

The testing equipment used for measuring the brightness of the cakes was a L&W Elrepho spectrophotometer (Figure 2) which is based on ISO 2469 standard. (Maijanen 2013, 2-3.) In this spectrophotometer, the sample is placed on top of a sample lifter, and the measuring sensor measures the brightness perpendicularly above the sample. The measuring range is 30 mm in diameter. (Maijanen 2013, 5.) When measuring with L&W Elrepho spectrophotometer, it is possible to use several different UV lights, but the most commonly used are D65 and C light sources. The measuring device has automatic UV calibration for the D65 and C UV levels. (Maijanen 2013, 21.)

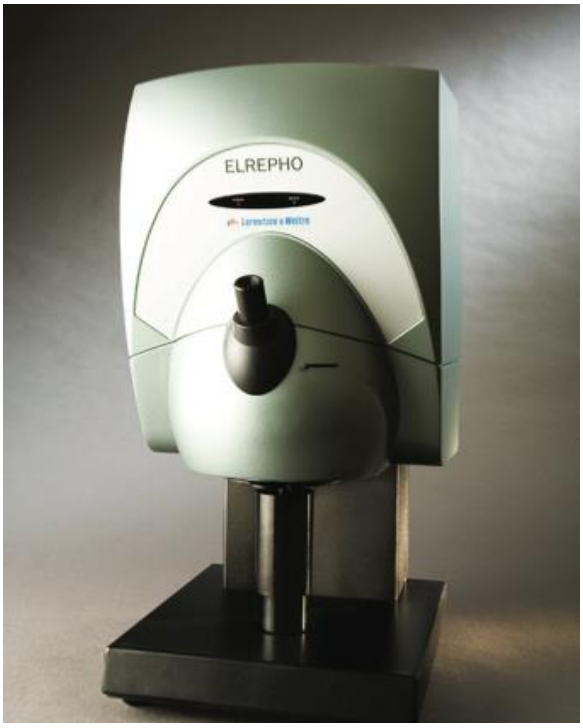

Figure 2. L&W Elrepho spectrophotometer. (ABB 2016)

The spectrophotometer measures two different values at the same time. A reference channel measures the spectrum of light entering the sample, and a measurement channel measures the spectrum of light reflected from the sample (Figure 3). When these measurements are added together, a reflection spectrum is obtained. After that, the computer program connected to spectrophotometer can calculate the actual properties according to the standard with the help of using tristimulus values. (Maijanen 2013, 13.)

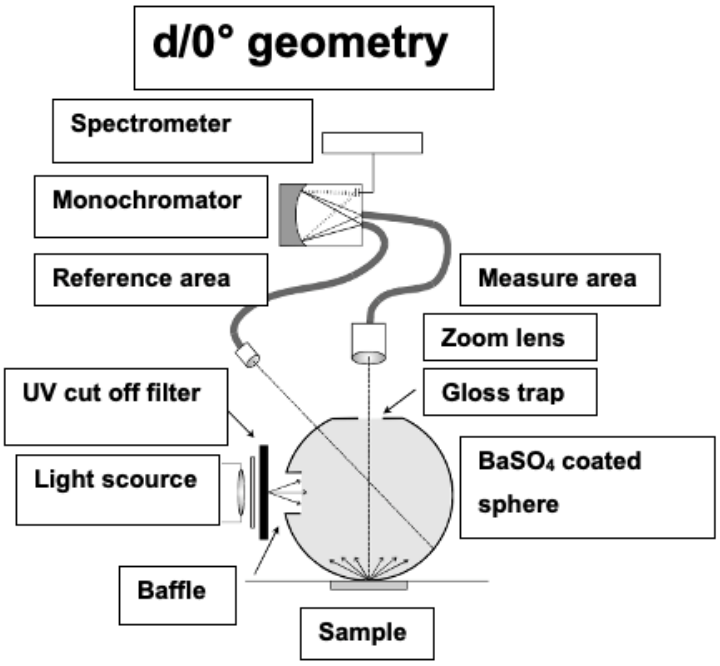

Figure 3. Measuring geometry for L&W Elrepho spectrophotometer. (Maijanen 2013, 11)

7 RESULTS

The results of the tests are presented and discussed in the following paragraphs. The main factors influencing brightness are drying, compression and pH. The brightness of the cakes made in the studies were measured with a L&W Elrepho spectrophotometer. The L&W Elrepho spectrophotometer was used to measure three values taken from different places of the cake. The software connected to the measuring device generated a report from the results, which showed the mean value of brightness, presenting also the min value and max value, as well as the standard deviation from the average of these measurements. Figures 4-6 and 8 indicate the mean value of brightness and percentual standard deviation as well as error bars which demonstrates the uncertainty of the measurements. The standard deviation percentage is not presented in Figure 7.

The effect of different compression pressures and times were tested in the experiments, and the results can be seen from Figure 4 and Figure 5. Figure 4 indicates the effects of different compression pressures on brightness when the compression time is 60 seconds. The brightness increases when the pressure is lower. The differences are minor for MCC2 and MCC3, but the effect

can be clearly seen with MCC1. Similar results were also obtained when compression time was 240 seconds, which is shown in Figure 5. Standard deviation percentage is larger when the pressure is higher and is the largest with MCC1. Standard deviation percentage is the lowest and almost non-existent for MCC2 as shown in Figure 4.

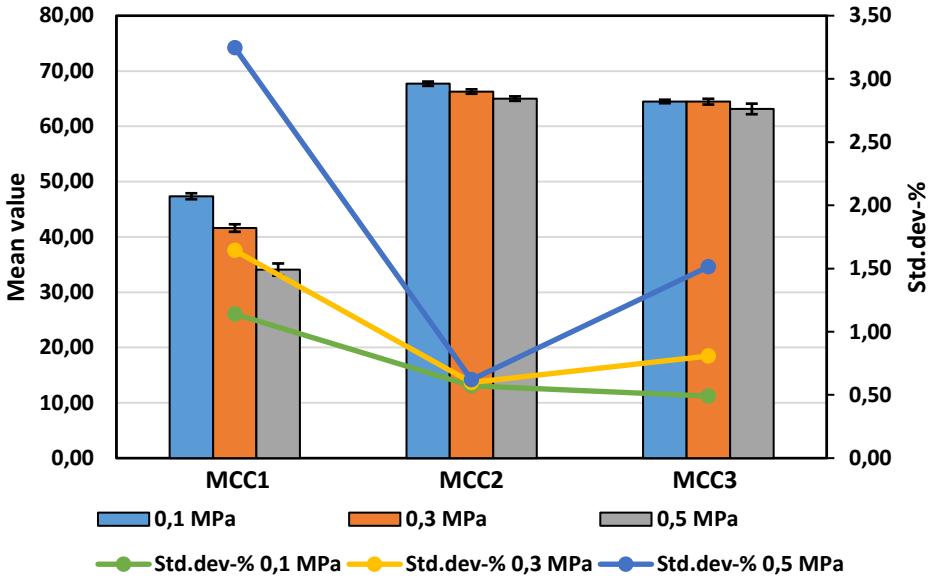

Figure 4. The effect of compression pressures on brightness with a compression time of 60 s.

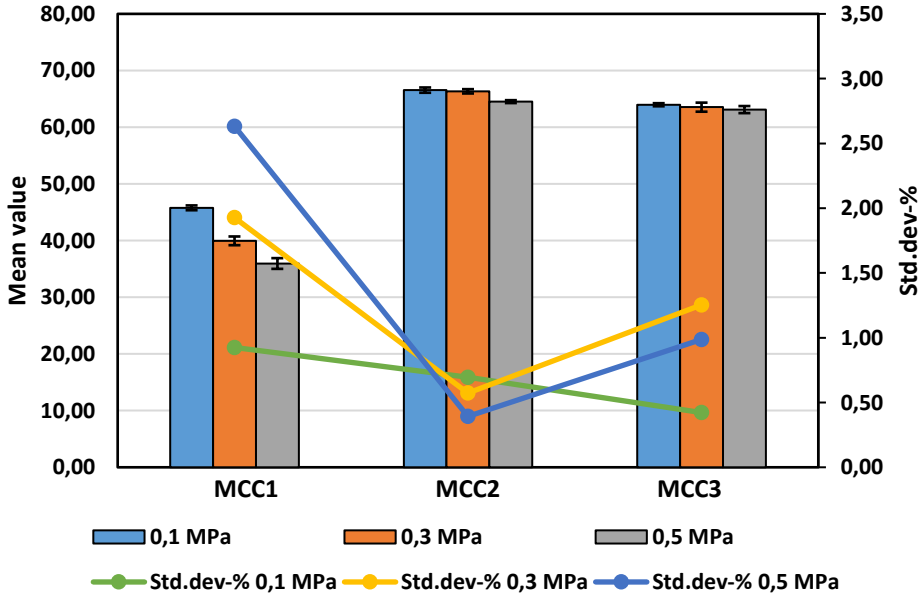

Figure 5. The effect of compression pressures on brightness with a compression time of 240 s.

Although a lower compression pressure increased the brightness of a cake, it did not have a major effect, especially on cakes made with MCC2 or MCC3.

Therefore, the main factor of compression was chosen to be 0.5 MPa pressure and 60 s compression time which were principally used in the tests. Rolling was also included as the main factor in the compression.

The pulp was filtered mainly through a büchner funnel so that only water was separated. Three series of cakes were tested with air suction through the funnel for 60 seconds after filtrating the water. The brightness was better with no suction of air in MCC1 and MCC2 as seen in Figure 6. The standard deviation-% was larger with no suction although the cakes made with air suction cracked more. Therefore, the originally intended method with no air suction was followed.

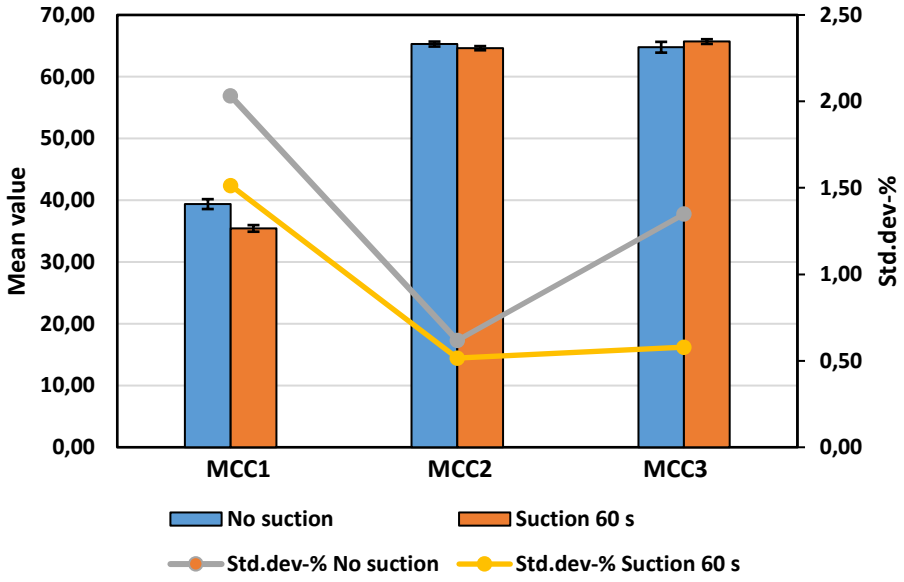

Figure 6. The effect of suction vs no suction on brightness.

In addition, pH was not found to have a major effect on the brightness, especially on cakes made from MCC2 or MCC3, apart from the fact that a lower pH increased the brightness slightly which can be seen from Figure 7. Therefore, pH 3 and 5 were defined as the main pH factors. The best brightness was obtained with MCC1 and MCC2 pulp when the pH was 5 which is the standardized pH for MCC. The best brightness for the cakes made from MCC3 was obtained when the pH was 3 which is close to the conditions during and after hydrolysis.

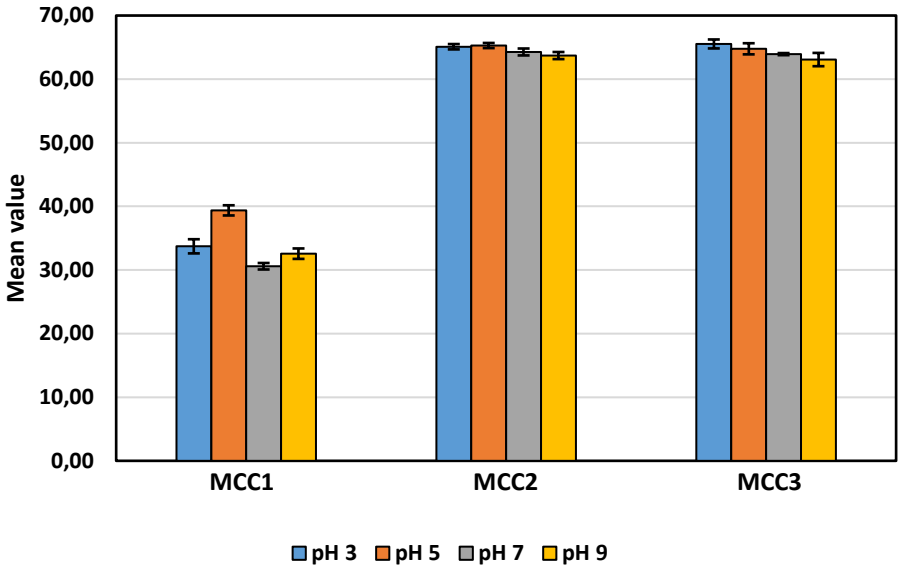

Figure 7. The effect of different pH's on brightness.

The main factors in the drying methods were the use of an air-conditioning room and a vacuum dryer. The grill was used in three different series, but it was rejected as it was found visually to darken MCC3 cakes significantly. It also caused much more cracking on MCC1 and MCC2 cakes compared to the air-conditioning room or the vacuum dryer. The different drying methods are shown in Figure 8. The brightness value is the highest when the cakes are dried in a vacuum dryer. The standard deviation percentage is the lowest with a vacuum dryer, except for MCC2, which indicates that the use of a vacuum dryer is a repeatable drying method. In general, the cakes darkened the most in the air-conditioning room, except for the MCC3 cake that was dried in a grill. When the cake made from MCC3 pulp was dried in a grill, it darkened significantly. The standard deviation percentage was the largest when the cakes were dried in an air-conditioning room, which may be due to the fact that the cakes curled up considerably and darkened especially around the edges. Cakes made with different drying methods are shown in Chapter 8 in Figure 12.

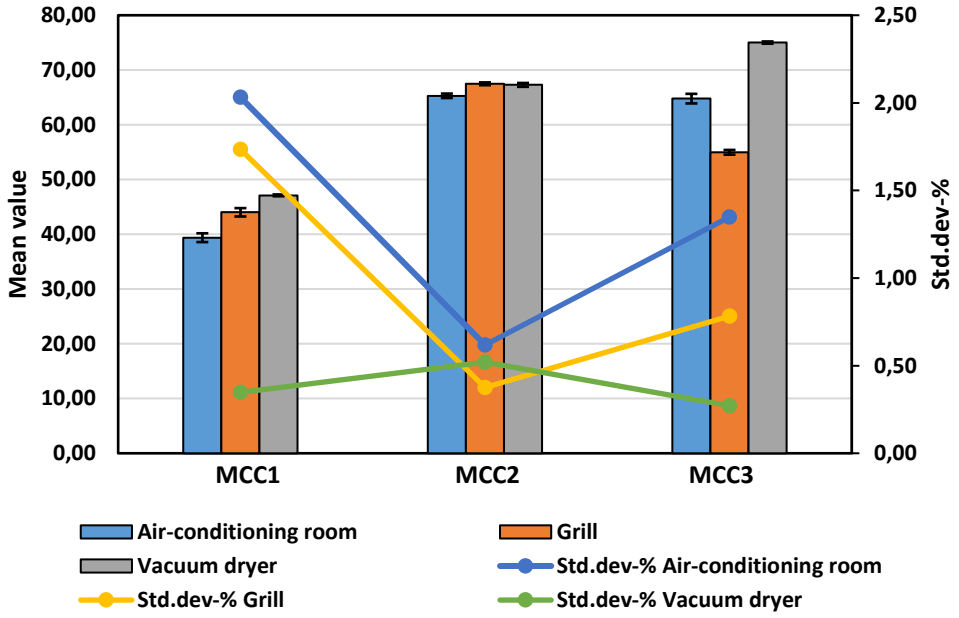

Figure 8. The effect of different drying methods on brightness.

7.1 Factor effects

Because some factors were not significant for the level of brightness, they were not taken in to consideration. These factors included, for example pH of 7 and 9, compression of 0.1 MPa and 0.3 MPa and a grill. The main factors, such as pH, compression and drying method give a better understanding of how different conditions affect brightness. These factors and their main effects as well as combined factor effects are presented in the following paragraphs. The figures indicate when brightness increases or decreases due to some factors and how the effects differ with different pulps. The results are presented by calculating the main effects and combined factor effects with a 2^3 factorial design (Appendix 2) (Montgomery 2013, 245-246). The main factors and their two levels in the experiment are presented in Table 2. A lower level (-) and a higher level (+) are defined for each factor.

Table 2. Main factors and their two levels.

pH	Compression	Drying
3 (-)	0.5 MPa (-)	Air-conditioning room (-)
5 (+)	Rolling (+)	Vacuum dryer (+)

Figures 9-11 show the main factor effects and combined factor effects of pH, compression and drying affecting the brightness of the cakes made from different MCC. All the MCC's are similar in the way that pH 3 or 5 have almost no effect on brightness, but the choice of drying method can be particularly important. A compression of 0.5 MPa has a lowering effect on all MCC's brightness compared to rolling which is particularly detectable with MCC1. Drying has the highest effect on MCC3 with the brightness increasing significantly when the air-conditioning room is changed into a vacuum dryer. The effect of drying might be so prominent because MCC3 has been bleached, but the same improvement occurs with MCC1 and MCC2 as well.

The combined factors are parallel in MCC1 and MCC2. With both pulps, brightness increases when the combined factors of pH and compression, pH and drying as well as compression and drying are effective. When all three factors occur at the same time the effect is negative (Figure 9 and Figure 10). However, the combined factor effects are the opposite with MCC3 where brightness decreases when combined factors of pH and compression, pH and drying as well as compression and drying effect. When all three factors occur at the same time, the effect is positive (Figure 11). This phenomenon is difficult to explain, as not everything is yet known about the properties of the raw material.

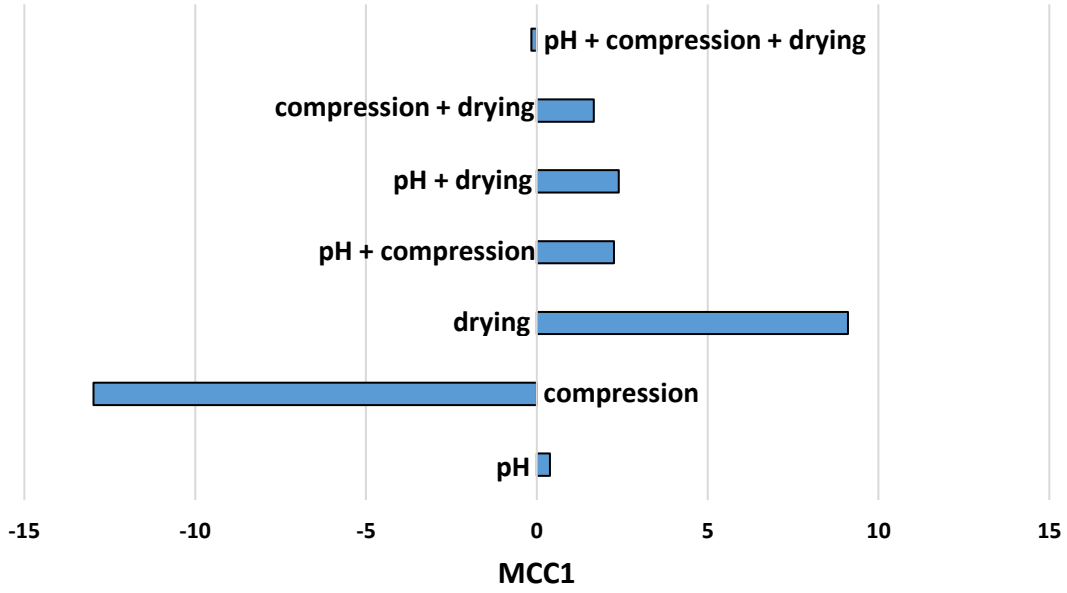

Figure 9. Main factors and combined factor effects of MCC1.

The combined effect of pH, compression and drying is very minor on MCC1 as seen in Figure 9. Different factors seem to cancel each other out. The pH does not seem to have a great effect on its own either, but the compression and drying singly have a great effect. The compression of 0.5 MPa decreases brightness approximately 13 units compared to rolling. Drying with a vacuum dryer increases brightness approximately 9 units compared to an air-conditioning room. The greatest combined factor effects are formed by the combined effect of pH and drying as well as pH and compression. Brightness increases when pH rises from 3 to 5, and when compression is replaced by rolling or an air-conditioning room is replaced by a vacuum dryer.

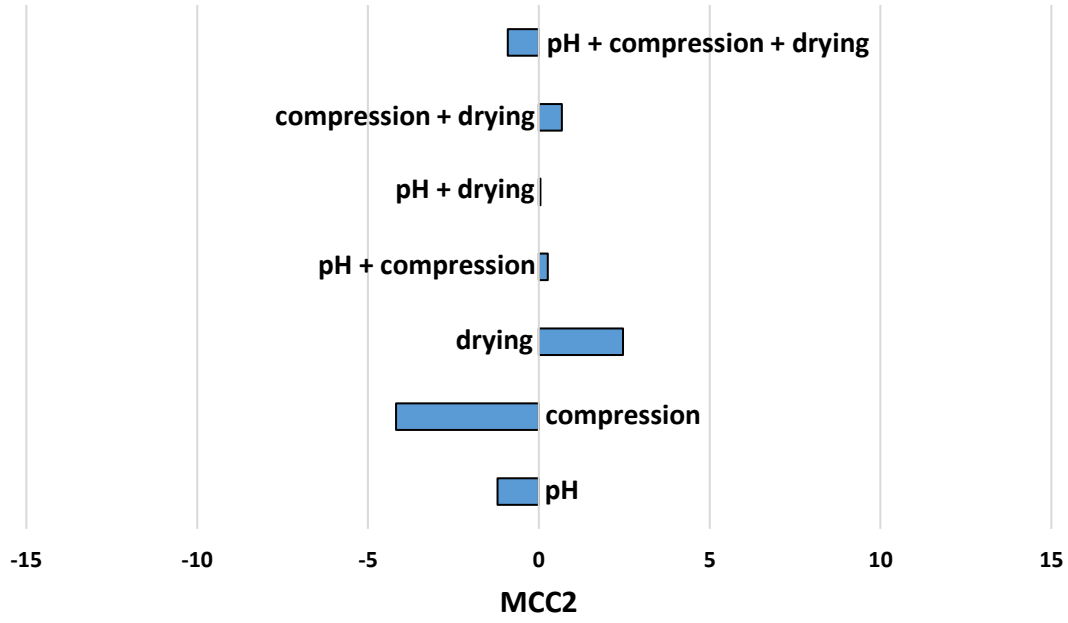

Figure 10. Main factors and combined factor effects of MCC2.

Figure 10 indicates that all factor effects are minor with MCC2. Once again, compression and drying are the most effective main factors, but the effects are not as remarkable as with MCC1. The greatest combined factor effect comes from the combination of all three factors, pH, compression and drying, which is in stark contrast to MCC1. However, even that effect is not significant for the results of MCC2. It is also interesting that pH and compression alone have a negative effect on brightness but together the effect is positive, although very minor. The small effects of different factors may be influenced by the fact that MCC2 behaved in the least changeable way between parallel

cakes compared to MCC1 or MCC3 when different factors were varied. MCC2 was also the driest in terms of dry matter content.

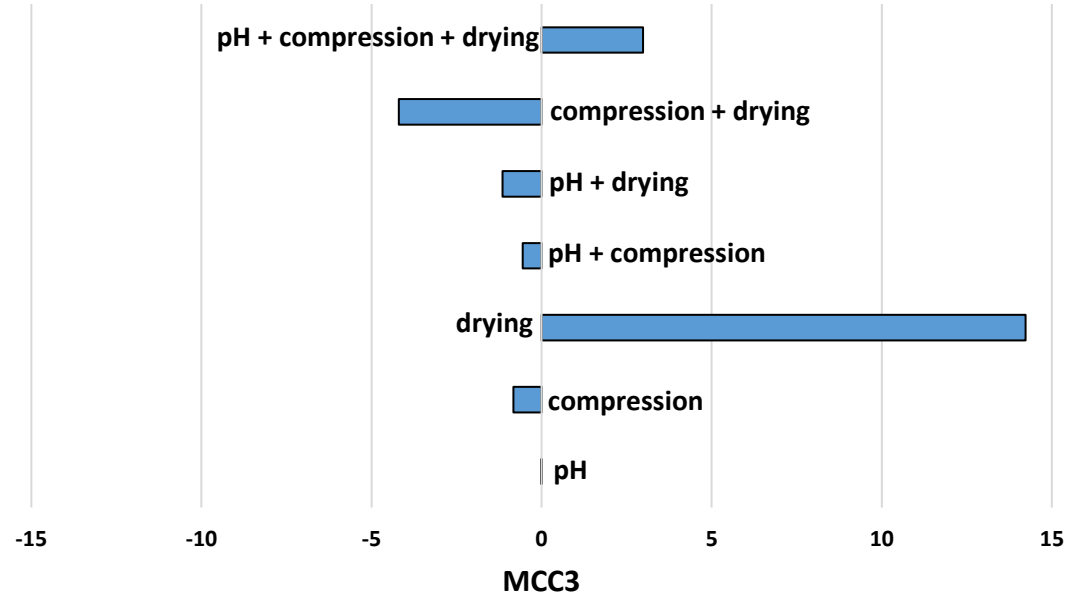

Figure 11. Main factors and combined factor effects of MCC3.

When Figure 11 is examined, the effect of drying stands out to the eye. It indicates that when an air-conditioning room is changed to vacuum dryer, the brightness improves approximately 14 units. It can be concluded that the drying has the greatest effect on bleached MCC. As for the combined factors, the combination of compression and drying has the largest effect. It shows that brightness decreases when compression is changed from rolling to a compression of 0.5 MPa and when drying is performed in an air-conditioning room instead of a vacuum dryer. The effect of all the factors combined is the largest with MCC3 with brightness increasing when pH decreases from 5 to 3, compressing is changed to rolling and the air-conditioning room is replaced by the vacuum dryer.

8 EVALUATION OF TEST METHODS

The cakes were primarily made with 5 g of abs dry pulp, but the first three series were tested by using a smaller amount of pulp, more specifically 3.6 g of abs dry pulp. From the table of all brightness measurement results (Appendix 3), some of the results of the first two series are missing. This is because when a lower amount of pulp was used, some of the cakes adhered to the

blotting paper making it impossible to remove the paper from the cake. For this reason, the cakes could not be measured. From the other cakes in these series, it could be seen that the cakes also cracked more when less pulp was used.

The brightness was found to be better when a vacuum dryer was used as a drying method instead of an air-conditioning room when the cakes were compressed or rolled. The grill was rejected at an early stage of the tests as it was found to darken MCC3 cakes significantly and cause more cracking in MCC1 and MCC2 cakes. When an air-conditioning room was used as a drying method, the cakes curled up and visually darkened. The curling made it more difficult to measure the cakes, which might be the reason why the standard deviation percentage was the largest when the cakes were dried in an air-conditioning room. The smoothest cakes were obtained with a vacuum dryer. The different drying methods and their effects on cakes are shown in Figure 12.

Figure 12. Cakes dried with different drying methods. An air-conditioned cake on the left, a grilled one in the middle and vacuum dried cake on the right. Bottom row MCC1, middle row MCC2 and top row MCC3.

The difference between compression and rolling was found to have a surprisingly large effect on the cakes. Better brightness was achieved by rolling rather than compressing. After compression and vacuum drying, the cakes cracked more than after rolling and a vacuum dryer as seen in Figure 13.

However, the largest cracks in all series occurred after rolling and using an air-conditioning room as seen in Figure 14. The standard deviation percentage was also larger on the cakes that had large cracks on the surface. Apparently, compression increases the strength of a cake more than rolling since the pressure is higher and the pressure time is longer. During the experiments, it was also found that after compressing MCC3 cakes and some of the cakes made from MCC1 stick to the blotting papers a phenomenon, which did not occur after rolling. Adhesion was exacerbated by a higher pH.

Figure 13. On the left side are rolled cakes and on the right side are compressed cakes. Both were dried in a vacuum dryer. Bottom row MCC1, middle row MCC2 and top row MCC3.

Figure 14. On the left side are rolled cakes and on the right side are compressed cakes. Both were dried in an air-conditioning room. Bottom row MCC1, middle row MCC2 and top row MCC3.

Different compression pressures did not significantly affect the brightness of the cakes except for MCC1 where it could be seen that the brightness was better when the pressure was lower. The lower pressure did not cause more cracking on the cakes, from which it can be concluded that the compression pressure of 0.1 MPa is also valid. However, the pressure time had an effect in the making of the cakes. With a longer pressure time of 240 s, it was more difficult to detach the cakes from the blotting papers after compression.

The pH adjustment had a minor effect on the brightness of the cakes, except for MCC1 where pH 5 delivered the best brightness. However, pH affected the rate of water filtrating through the büchner funnel when MCC3 was used. When pH was adjusted to 9, MCC3 cakes took approximately 25 minutes to filter. The time was circa 10 minutes when pH was adjusted to 3. Under normal conditions, which is at pH 5, filtration takes approximately 20 minutes. This may be due to the swelling of the fibers under alkaline conditions, which slows down filtration.

There were also some differences during the filtration of pulp through the büchner funnel. When the water was only filtered through the funnel, the cakes cracked less during drying. On the other hand, when the air suction of

60 seconds was tested the cakes were easier to detach from the blotting papers. Although the cakes cracked less when no suction was used, the standard deviation percentage was larger. However, both cracking and the adhesion of a blotting paper affected the brightness measurement. When the cracks were large, the measuring device registered the brightness from the background filter paper. It was also impossible to take a brightness measurement from a smooth point if the cracks were large or there was a great number of them since the measuring range was 30 mm and the cake was 110 mm in diameter. The brightness value also seemed to be better when the whiter blotting paper was a little attached on the surface of the cake.

9 CONCLUSIONS

In this thesis, the factors influencing brightness were studied. The objective was to determine a method that allows to achieve the most reliable and repeatable brightness measurement. The brightness of a paper or pulp decreases by the influence of radiation, heat, moisture, oxygen, and various compounds contained in the wood, such as lignin. Lignin contains coloured compounds that are called chromophoric groups that can be formed by the action of radiation or heat. Hemicelluloses contained in wood participate in thermal yellowing which is induced by heat. Polysaccharide chains derived from hemicelluloses start to decompose under the influence of heat and begin to produce sugar monomers. When sugars start to decompose under an elevated temperature, it causes caramelization process. As a result of caramelization, the pulp darkens.

There are also some process-related factors that cause discoloration or yellowing. These are bleaching, washing and pH. If pulp contains lignin, bleaching is an important factor in removing it and improving the brightness result. Better brightness is obtained with lignin-removing bleaching, but lignin-retaining bleaching can be used for mechanical pulps that contain large amounts of colored compounds, wherefore an excessive amount of bleaching chemicals cannot be used. In the washing phase, the most important matter is to remove transition metals and sugars. Reduced sugars can fasten the degradation of hydrogen peroxide and allow metal ions, such as iron or manganese to form coloured structures in the pulp. A lower pH can cause sugars to caramelize,

but under alkaline conditions phenolic compounds of lignin are more intense by colour.

The material used in the studies was MCC which is a challenging material since it is sensitive to surrounding conditions. High temperature causes it to darken since the temperature range of MCC is limited. It also absorbs moisture to itself. Because MCC particle size is relatively small and due to its crystalline structure, the bonding strength is weaker than in cellulose fibers. This is a possibly reason for the cracking of the cakes. Other problems included the fact that the MCC cakes adhered to the blotting paper and they curled up while drying. These disadvantages made the brightness measurement difficult to take, and the reliability of the results was to some extent compromised.

This thesis aimed to provide a better understanding of what factors affect the brightness of the cakes. Brightness cakes with a diameter of 110 mm were made from three different MCC pulps. The main factors under examination in this experiment were pH, compression and drying. The potential of hydrogen (pH) was tested with four different variables. When the method of compression was used, different compression pressures and time were also tested. Drying was tested with three different drying methods comprised of an air-conditioning room, grill and a vacuum dryer. The amount of pulp in each cake was primarily 5 g of abs dry pulp but 3.8 g of abs dry pulp was also used for comparison. However, there were no results from the cakes where a lower amount of pulp was used because the cakes adhered to the blotting papers after drying.

From the results, it can be concluded that the best method of making brightness cakes is by adjusting the pH to more acidic conditions, rolling the cakes and drying them in a vacuum dryer. The combined effect of rolling and a vacuum dryer may be beneficial due to the fact that rolling is not as a severe method as compression since the vacuum dryer also presses the cake during the drying. The combination of compression and vacuum drying seemed to create more cracks. However, the largest cracks were formed by the combination of rolling and air-conditioning which indicates that the compression created by these two methods is not sufficient to strengthen the structure of the cake. The vacuum dryer was not expected to be the best drying method, but it

allowed the cakes to obtain the best brightness values and the smoothest surfaces. In addition, the cakes differed the least in appearance from each other which makes the method most reliable.

The reliability of the results is considered somewhat reduced by the fact that three parallel cakes may be too few to make conclusions. If two cakes are successfully made but one fails, it will affect the mean value of the brightness considerably. Another problem is that the L&W Elrepho spectrophotometer does not take well into account the changes in brightness or standard deviation caused by cracking. In order to achieve a better accuracy and understanding of the effect of cracks on brightness, an optical formation measurement could be used which would identify the tonal differences in the cakes, in other words the cracks. Also, this study could be extended to examining all the factors by means of factor design calculation since this thesis was limited to three main factors measured at two levels. A wider factor design calculation might provide a better understanding of which factors are likely to have an improving or deteriorating effect on brightness in the future.

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Figure 10. Main factors and combined factor effects of MCC2.

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Figure 12. Cakes dried with different drying methods. An air-conditioned cake on the left, a grilled one in the middle and vacuum dried cake on the right. Bottom row MCC1, middle row MCC2 and top row MCC3.

Figure 13. On the left side are rolled cakes and on the right side are compressed cakes. Both were dried in a vacuum dryer. Bottom row MCC1, middle row MCC2 and top row MCC3.

Figure 14. On the left side are rolled cakes and on the right side are compressed cakes. Both were dried in an air-conditioning room. Bottom row MCC1, middle row MCC2 and top row MCC3.

Appendix 1

VARIABLES OF DIFFERENT SERIES

Table. Variables of different series.

Series	Pulp amount g abs dry	pH adjustment	Büchner (air suction)	Compression (MPa)	Compression time (s)	Rolling	Drying Air-conditioning room	Drying Grill	Drying Vacuum dryer
1	3,8	5	Only water	0,5	60		x		
2	3,8	5	Only water	0,5	60			x	
3	3,8	5	Only water	0,5	60				x
4	5	5	Only water	0,5	60		x		
5	5	5	Only water	0,5	60			x	
6	5	5	Only water	0,5	60				x
7	5	5	60s	0,5	60		x		
8	5	5	60s	0,5	60			x	
9	5	5	60s	0,5	60				x
10	5	5	Only water	0,1	60		x		
11	5	5	Only water	0,3	60		x		
12	5	5	Only water	0,1	240		x		
13	5	5	Only water	0,3	240		x		
14	5	5	Only water	0,5	240		x		
15	5	5	Only water			x	x		
16	5	5	Only water			x			x
17	5	3	Only water	0,5	60		x		
18	5	7	Only water	0,5	60		x		
19	5	9	Only water	0,5	60		x		
20	5	3	Only water	0,5	60				x
21	5	7	Only water	0,5	60				x
22	5	9	Only water	0,5	60				x
23	5	3	Only water			x	x		
24	5	7	Only water			x	x		
25	5	9	Only water			x	x		
26	5	3	Only water			x			x
27	5	7	Only water			x			x
28	5	9	Only water			x			x

Appendix 2

FACTOR EFFECTS

Equation for 2^3 design

$$A = \frac{1}{4n}(a - (1) + ab - b + ac - c + abc - bc) \quad (1)$$

$$B = \frac{1}{4n}(b + ab + bc + abc - (1) - a - c - ac) \quad (2)$$

$$C = \frac{1}{4n}(c + ac + bc + abc - (1) - a - b - ab) \quad (3)$$

When			
	A	pH	[-]
	B	Compression	[-]
	C	Drying	[-]
	n	Replicates	[-]

Combined factor effects

Equation for 2^3 design

$$AB = \frac{1}{4n}(ab - a - b + (1) + abc - bc - ac + c) \quad (4)$$

$$AC = \frac{1}{4n}\big((1) - a + b - ab - c + ac - bc + abc\big) \quad (5)$$

$$BC = \frac{1}{4n}((1) + a - b - ab - c - ac + bc + abc) \quad (6)$$

$$ABC = \frac{1}{4n}(abc - bc - ac + c - ab + b + a - (1)) \quad (7)$$

When

A	pH	[-]
B	Compression	[-]
C	Drying	[-]
n	Replicates	[-]

Appendix 3/1

BRIGHTNESS MEASUREMENT RESULTS

Table. Brightness measurement results.

Series	1	2	3	4	5	6	7	8	9	10	11	12	13	14
ka														
MCC1	47,09	48,71	48,98	39,37	44,01	47,11	35,44	44,43	45,67	47,35	41,60	45,78	39,95	35,95
MCC2	68,08	68,79	69,25	65,29	67,48	67,28	64,62	67,93	67,35	67,70	66,29	66,55	66,34	64,52
MCC3	-	60,25	78,41	64,77	54,97	75,01	65,69	54,17	73,82	64,49	64,46	63,97	63,54	63,11
Std.dev														
MCC1	0,20	0,60	0,33	0,80	0,76	0,16	0,54	0,71	0,43	0,54	0,68	0,42	0,77	0,95
MCC2	0,31	0,45	0,12	0,40	0,25	0,35	0,33	0,41	0,33	0,39	0,40	0,46	0,38	0,25
MCC3	-	1,74	1,59	0,87	0,43	0,20	0,38	0,26	0,35	0,32	0,52	0,27	0,80	0,62
Std.dev-%														
MCC1	0,42	1,22	0,67	2,03	1,73	0,35	1,51	1,61	0,95	1,14	1,64	0,92	1,93	2,63
MCC2	0,45	0,65	0,17	0,62	0,38	0,52	0,52	0,60	0,49	0,57	0,60	0,70	0,57	0,39
MCC3	-	2,88	2,02	1,35	0,78	0,27	0,58	0,47	0,47	0,49	0,81	0,42	1,25	0,99
All cakes	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
	ka	ka	ka	ka	ka	ka	ka	ka	ka	ka	ka	ka	ka	ka
MCC1	48,08	46,93	49,86	39,16	46,21	47,02	35,35	45,28	46,38	48,28	41,55	45,69	40,17	34,44
	46,64	51,16	50,12	40,03	42,03	46,93	35,93	44,79	45,06	46,97	41,25	46,24	41	38,82
	46,56	48,04	46,97	38,93	43,79	47,37	35,03	43,21	45,57	46,81	42,01	45,4	38,69	34,6
MCC2	67,89	68,86	69,04	66,28	66,56	67,23	65,48	67,79	66,68	68,26	66,07	66,8	65,83	64,18
	68,41	68,77	69,14	64,47	67,86	67,57	64,29	68,41	68,14	68,15	66,97	66,93	66,22	65,03
	67,95	68,73	69,56	65,11	68,02	67,04	64,09	67,58	67,22	66,69	65,82	65,91	66,96	64,34
MCC3	-	66,94	78,16	63,53	55,76	75,33	65,2	52,55	73,13	64,35	64,13	63,2	63,65	64,21
	-	53,55	79,43	64,46	53,37	75,08	66,13	54,26	74,46	64,7	65,27	64,88	63,5	63,62
	-	-	77,63	66,33	55,78	74,62	65,74	55,7	73,87	64,43	63,97	63,82	63,47	61,5
Series	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
	Std.dev	Std.dev	Std.dev	Std.dev	Std.dev	Std.dev	Std.dev	Std.dev	Std.dev	Std.dev	Std.dev	Std.dev	Std.dev	Std.dev
MCC1	0,17	1,16	0,21	1,51	0,81	0,08	0,56	0,63	0,19	0,41	0,97	0,49	1,21	1,73
	0,2	0,54	0,22	0,4	0,93	0,2	0,25	0,27	0,68	1,05	0,12	0,1	0,81	0,45
	0,22	0,09	0,56	0,49	0,55	0,21	0,8	1,24	0,43	0,16	0,96	0,68	0,29	0,66
	0,58	0,31	0,11	0,58	0,56	0,41	0,33	0,82	0,38	0,56	0,32	0,28	0,62	0,25
MCC2	0,07	0,61	0,11	0,51	0,06	0,39	0,59	0,03	0,01	0,14	0,24	0,38	0,35	0,03
	0,27	0,43	0,13	0,12	0,14	0,25	0,08	0,38	0,59	0,46	0,63	0,73	0,17	0,48
	-	3,25	1,06	0,15	0,69	0,19	0,53	0,15	0,47	0,32	0,15	0,29	0,62	0,88
MCC3	-	0,22	3,14	1,02	0,18	0,09	0,28	0,12	0,17	0,26	0,53	0,34	1,05	0,19
	-	-	0,56	1,45	0,42	0,33	0,33	0,5	0,4	0,37	0,88	0,18	0,72	0,8

Appendix 3/2

BRIGHTNESS MEASUREMENT RESULTS

Table. Brightness measurement results.

Series	15	16	17	18	19	20	21	22	23	24	25	26	27	28
ka														
MCC1	46,32	56,31	33,72	30,59	32,57	42,22	42,76	41,26	50,75	50,46	48,49	55,64	52,00	51,72
MCC2	68,69	71,44	65,10	64,27	63,71	69,09	65,81	67,73	71,11	68,81	68,87	71,94	70,70	70,84
MCC3	63,31	77,61	65,53	63,94	63,08	73,73	69,33	66,46	58,63	59,91	60,10	81,18	76,70	75,86
Std.dev														
MCC1	1,99	0,19	1,11	0,51	0,82	0,55	0,85	0,72	1,17	0,74	0,76	0,12	0,38	0,48
MCC2	0,88	0,03	0,42	0,54	0,56	0,23	0,33	0,49	0,51	0,61	0,48	0,06	0,12	0,24
MCC3	0,56	1,18	0,70	0,16	1,04	0,71	0,45	0,61	1,04	1,06	0,60	1,18	1,45	1,79
Std.dev-%														
MCC1	4,29	0,33	3,30	1,67	2,52	1,31	1,98	1,74	2,31	1,47	1,57	0,21	0,72	0,93
MCC2	1,28	0,04	0,65	0,85	0,87	0,34	0,50	0,72	0,72	0,88	0,69	0,08	0,17	0,34
MCC3	0,88	1,52	1,07	0,26	1,65	0,96	0,64	0,92	1,77	1,77	1,00	1,45	1,89	2,36
All cakes	15	16	17	18	19	20	21	22	23	24	25	26	27	28
	ka	ka	ka	ka	ka	ka	ka	ka	ka	ka	ka	ka	ka	ka
MCC1	46,21	56,56	34,38	30,03	34,06	44,78	43,66	40,77	49,92	51,57	48	55,81	51,88	51,9
	45,47	56,17	34,49	30,41	31,68	41,32	43	41,55	51,65	50,92	49,72	55,93	52,06	51,45
	47,28	56,21	32,3	31,33	31,96	40,56	41,62	41,47	50,68	48,9	47,74	55,17	52,07	51,81
MCC2	68,61	71,49	66,11	63,51	61,95	69,65	62,27	67,64	70,81	69,14	69,22	71,99	70,83	70,8
	69,01	71,43	65,22	64,7	64,33	68,97	68,16	67,69	71,39	69,17	69,01	72	70,78	70,74
	68,44	71,39	63,96	64,61	64,85	68,64	66,99	67,86	71,13	68,13	68,37	71,83	70,49	70,97
MCC3	62,45	77,96	65,41	63,25	63,04	74,9	69,87	67,46	61,92	59,03	61,08	81,7	78,58	75,26
	63,16	74,91	65,64	64,48	63,63	74,67	69,52	65,45	57,98	61,16	61,05	79,1	73,81	77,91
	64,32	79,96	65,55	64,08	62,57	71,63	68,6	66,48	55,99	59,54	58,16	82,75	77,72	74,42
Series	15	16	17	18	19	20	21	22	23	24	25	26	27	28
	Std.dev	Std.dev	Std.dev	Std.dev	Std.dev	Std.dev	Std.dev	Std.dev	Std.dev	Std.dev	Std.dev	Std.dev	Std.dev	Std.dev
MCC1	1,32	0,28	0,81	0,06	0,56	0,56	0,83	0,25	1,46	0,49	0,14	0,08	0,28	0,6
	1,72	0,08	1,19	0,2	1,32	0,44	0,64	0,48	0,64	0,52	0,75	0,12	0,15	0,13
	2,92	0,2	1,34	1,27	0,58	0,66	1,07	1,42	1,42	1,21	1,39	0,15	0,7	0,71
MCC2	1,02	0,03	0,11	0,53	0,46	0,24	0,65	0,37	1,06	0,23	0,68	0,04	0,04	0,14
	0,52	0,03	0,42	0,93	0,08	0,04	0,12	0,22	0,15	0,97	0,39	0,09	0,03	0,43
	1,1	0,02	0,73	0,17	1,13	0,42	0,22	0,87	0,32	0,62	0,36	0,04	0,28	0,16
MCC3	1,09	1,81	0,7	0,15	0,5	0,19	0,51	0,34	0,91	1,44	0,9	0,6	1,44	2,81
	0,4	0,91	0,59	0,23	1,02	0,2	0,57	0,87	0,18	0,7	0,35	2,69	0,8	0,9
	0,18	0,82	0,82	0,11	1,61	1,73	0,26	0,62	2,02	1,04	0,56	0,24	2,1	1,65