Hydrothermal Treatment of Sugar Maple (*Acer saccharum*) Followed by Bleaching

K. Dölle, C. Schomann, and J. J. Amaya

This laboratory study examines the basic suitability of hydrothermal treatment prior to sulfate pulping followed by bleaching using sugar maple (*Acer saccharum*) as a pulp fiber source. Sugar maple is an abundant hardwood source in the State of New York for paper products that require high whiteness. One portion of the sugar maple chips were pre-treated prior to sulfate cooking with a hydrothermal treatment that removes hemicellulose. After sulfate cooking, the pulp fractions undergo a four-stage bleaching sequence followed by beating in a Valley beater before forming of the handsheets. Paper properties of each pulp fraction were measured and compared to bleached sulfate pulp as well as commercial eucalyptus sulfate pulp. The hydrothermal treatment was found to increase the freeness slightly and the specific volume and porosity significantly. Whiteness was increased slightly and opacity considerably. The strength properties of the hydrothermal treated pulp were sharply decreased.

Keywords: Bleaching; Sulfate pulp; Hydrothermal; Refining; Beating; Hydrolyses; Pre-preparation; Paper properties

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INTRODUCTION

Environmental and economic considerations make regenerative energy sources increasingly important in comparison to fossil fuels. Fossil fuels, the primary source of energy on earth, are finite and have adverse effects on greenhouse gas emissions and the environment (Ivanhoe *et al.* 1995). Declining petroleum reserves and concerns about future energy security require finding new alternative energy systems that utilize technologies to minimize the impacts of fossil fuel utilization (Hall *et al.* 2007; Maggio and Cacciola 2009; Rehrl and Friedrich 2006; Schade and Pimentel 2010).

One of these renewable energy sources is wood. Wood can be used as raw material for the production of paper and wood products as well as for the production of solid and liquid biofuels. However, biofuel produced from wood is in competition with the pulp and paper industry for biomass resources (Liu 2012; Van Heiningen 2006). To which extent the pulp and paper industry with their existing infrastructure is able to participate and benefit from this development is still unsure, and therefore very dependent on how future processes can be implemented at existing and new pulp and paper mill sites in an economic an sustainable way.

The extraction of hemicellulose from wood by means of hydrothermal treatment, also known as hot-water extraction, might be one solution to produce value-added

chemicals and biofuels as well as valuable cellulosic raw material for pulp and paper production (Goyal *et al.* 2007).

The hydrothermal treatment of wood is in general a hydrolysis process without the use of NaOH (Amidon and Liu 2009). By treating wood chips with steam, the degree of polymerization of the hemicelluloses is reduced by about 30% and chemical bonds to lignin are reduced. Acetic acid can be produced by the removal of acetyl groups from the hemicelluloses, whereby the pH is reduced to a value of about 4. In softwoods, organic material is dissolved at a level of 10 to 15% and for hardwoods at a level of 15 to 20% (Duarte *et al.* 2007).

Assessing the suitability of a hydrothermal treated pulp product for paper production is the focus of this laboratory study. Sugar maple is an abundant hardwood source for paper production in the State of New York. Sugar maple sulfate pulp with and without hydrothermal pretreatment is processed through a four stage bleaching system. The bleached pulp then is screened and beaten, followed by handsheet forming and evaluated for the use in paper applications.

METHOLOGY

The methodology section describes the equipment, procedures and materials used for this study. As part of this study several test methods were applied. These are described in detail in the following subsections. All tests were performed and reported according to TAPPI standards or as noted otherwise. Repeatability of the results stayed in between the allowable margins of the TAPPI testing standards, whereas paper testing variance ranged from 0.05 to 0.27 relative to the mean values.

Materials

For the study eucalyptus bleached kraft (EBK) pulp obtained from a kraft mill in Columbia and sugar maple *(acer saccharum) (SM)* was used. The SM was chosen due to its abundance in New York State. The SM was harvested at the State University of New York, College of Environmental Science and Forestry (SUNY-ESF) Heiberg Forest in Tully, NY.

Material Preparation

The SM logs with a diameter between 150 mm and 200 mm (6 in and 8 in) and 1.2 m (4 feet) in length were manually debarked and processed with a commercial Carthage wood chipper that allows the processing of a maximum log diameter of 200 mm. After chipping, the chips were presorted with a vibrating shaker screen with a square mesh opening of 31.75 mm (1.25 in) for the top screen and a 3.2 mm (0.125 in) for the bottom screen. The SM wood chips remaining on the top screen and the SM material falling through the bottom screen were rejected. The remaining SM fraction on top of the bottom screen was further processed in a large shaker screen using sieves with a hole diameter of 28.58 mm (9/8 in), 22.23 mm (7/8 in), 15.88 mm (5/8 in), and 9.53 mm (3/8 in). The chips remaining on the two central perforated screens, 22.23 mm (7/8 in), 15.88 mm (5/8 in) were used for the bleaching investigation.

TAPPI methods used

Pulp refining was done according to T 200 sp-06, "Laboratory beating of pulp (Valley beater method)". Handsheets for physical testing were prepared accordance with T 205 sp-06, "Forming handsheets for physical tests of pulp". Physical testing of handsheets was performed in accordance to T 220 sp-06, "Physical testing of pulp handsheets". The freeness of pulp was measured as Canadian Standard Freeness (CSF) according to T 227 om-09 "Freeness of pulp (Canadian standard method)". Viscosity of pulp was measured according to T 230 om-08, "Viscosity of pulp (capillary viscometer method)". Kappa number of the recycled pulp was measured in accordance with T 236 om-06, "Kappa number of pulp". Screening of pulp was performed in accordance to T 274 sp-08, "Laboratory screening of pulp (Master Screen-type instrument)"; the instrument used was a Valley type Screen with a 350 µm screen plate and a Voith Valley screen with 150 µm screen plate. Conditioning of the paper samples was done according to T 402 sp-08, "Standard conditioning and testing atmospheres for paper, board, pulp handsheets, and related products". The grammage was determined by T 410 om-08 "Grammage of Paper and Paperboard (weight per unit area)". The thickness was measured by T 411 om-10 "Thickness (caliper) of paper, paperboard, and combined board". Moisture content of pulp was determined by T412 om-06 "Moisture in pulp, paper and paperboard". The tear strength was done by following the T 414 om-12, "Internal tearing resistance of paper (Elmendorf-type method)". Opacity of paper handsheets was performed according to T 425 om-06, "Opacity of paper (15/d geometry, illuminant A/2°, 89% reflectance backing and paper backing)". Brightness of pulp was measured according to T 452 om-08, "Brightness of pulp, paper and paperboard (directional reflectance at 457 nm)". Porosity of the paper samples was tested according to T 460 om-06, "Air resistance of paper (Gurly method)". Tensile strength was performed following T494 om-06, "Tensile properties of paper and paperboard (using constant rate of elongation apparatus)".

EXPERIMENTAL REGIME

In this study, the process sequence illustrated in Fig. 1 was carried out. The chosen process sequence allowed subsequent studies of the fibers not only for the comparison to the bleached eucalyptus kraft pulp, but also allowed an evaluation of the impact of hydrothermal pretreatment before the sulfate pulping process. An MK digester was used for the hydrothermal and sulfate pulping process. After the sulfate pulp cooking the hydrothermal treated sulfate and the SM sulfate pulp undergo a screening process using a Valley type screen with a slot width of 350 microns. To improve the optical properties of the processed pulp, a four-stage bleaching process ($O_2D_0E_PD_1$) was performed, containing a sequence of oxygen bleaching (O_2) for the first stage. The second bleaching stage was chlorine dioxide bleaching (D_0). The third stage contained peroxide bleaching (E_P) process, followed by the fourth stage a second chlorine dioxide bleaching step (D_1). For the O_2-stage a Quantum Reactor was used. The following stages were done using a bag bleaching method in a hot water bath. After pulping and each bleaching sequence, samples were taken to measure Kappa number, whiteness, pH, and viscosity according to TAPPI standards. After bleaching, the bleached pulp was refined

with a Valley beater, followed by a second screening step with a Valley type screen using a screen plate with a slot width of 350 microns. After this process step, handsheets were made for paper testing according to TAPPI standards.

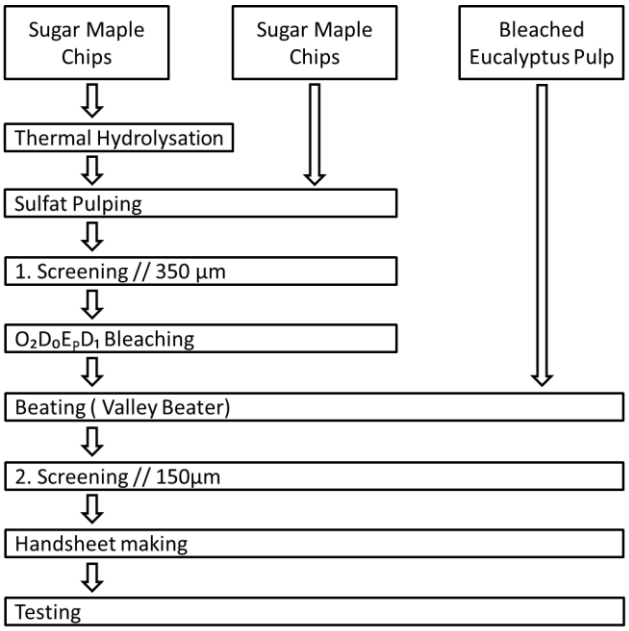

Fig. 1. The study sequence

Thermal Hydrolyzation

In the process of TH, hemicellulose of SM wood chips is solubilized through water steam without the use of chemicals in a MK digester (Fig. 2 a). For the TH process 500 g of oven dry (OD) wood chips are loaded in a holding vessel (Fig. 2 b,c).

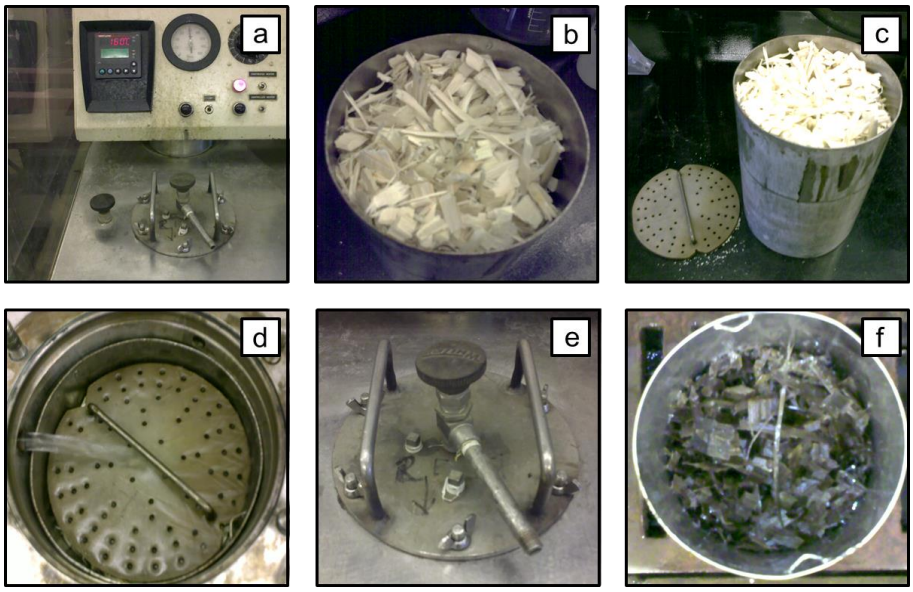

Fig. 2. Thermal hydrolyzation process study sequence

The vessel is placed in the MK digester and covered with a perforated cover that allows the circulation of water in the MK digester (Fig. 2 d). Process water is filled into the MK digester at a ratio of water to OD wood of 4:1. Then, the MK digester is closed and quickly preheated to 160 °C, followed by a 2 hour cooking phase at 160 °C (Fig. 2 e). After the cooking process, the temperature is lowered to 80 °C and the hydrolysate is discharged. Two 15 minute washing cycles with water at 80 °C follow with the objective to remove the remaining hydrolyzed hemicellulose from the 77 % remaining OD thermal hydrolyzed chips in the MK digester (Fig. 2 f). The remaining thermal hydrolyzed wet chip mass in the MK digester has a moisture level of approximately 60%. Based on the thermal hydrolyzed wet chip mass moisture level, the wash water ratio is kept at 4:1. After washing, the thermal hydrolyzed chips are ready for sulfate cooking.

Sulfate Cooking

For the sulfate cooking, the TH wood chips and SM woodchips are loaded in a holding vessel of the MK digester. The vessel is placed in the MK digester and covered with a perforated cover that allows the circulation of the process chemicals solution in the MK digester. The chemical addition is based on a liquor activity of 86% based on 16% active alkali and 25% sulfidity with a 4:1 ratio of water to OD wood.

After the MK digester is filled and closed, the cooking process is started. The chips' chemical solution is heated during a 1 hour preheating phase to the cooking temperature of 155 °C, followed by a 25 min cooking phase. After the cooking phase the MK digester is depressurized and the black liquor is discharged. The wood chips in the MK digester holding vessel are washed for 2 minutes with deionized water followed by a second washing process with deionized water after the holding vessel is extracted from the MK digester.

The cooked HTSM wood chips and SM wood chips are dispersed in a laboratory disperser, followed by the addition of water to increase the volume two-fold. The produced pulp is then dewatered using a 15 cm Büchner funnel. The Büchner funnel is attached to a 20 liter filter flask which is connected to a vacuum system. A paper machine former fabric is added to the Büchner funnel instead of a filter paper, maximizing dewatering and to prevent clogging of the funnel pores. The HTSM pulp fractions are then screened with a Valley type screen having a screen plate width of 350 microns to remove larger impurities such as splinters that did not get pulped during the sulfate cooking process. After screening, the pulp fractions are dewatered a second time using the above Büchner funnel method. The dewatered fraction is discharged.

Bleaching

The chemical addition for the four-stage bleaching sequence for the HT and SM pulp is shown below. All process parameters are based on OD fiber material of the HT and SM pulp material. The water content is based on the needed process consistency including the addition of liquid chemicals.

Oxygen bleaching (O_2)

In the O_2 bleaching stage a Quantum Mark IV reactor is used. The bleaching is performed at a consistency of 12% using 200 g of OD pulp. Before initiating bleaching,

the reactor is filled with deionized water and preheated to 90 °C during a 40 minute period. After the preheating phase, the reactor is drained and dried with paper towels. The pulp and bleaching chemicals consisting of: 0.5 % of magnesium sulfate heptahydrate ($MgSO_4*7H_2O$), also called Epson salt, dissolved in water, 2.25% caustic soda (NaOH), and distilled water is added to the pulp to achieve a final consistency of 12% for the bleaching process. This reactor with pulp and process chemicals needs to be loaded very quickly to reduce the cooling of the reactor. Therefore advance preparation of the process components is essential. The reactor is closed and the bleaching process started by heating the reactor to 90 °C process temperature. After the process temperature is reached, O_2 is added to the process at a pressure of 6.2 bar (90 psi) and then the 60 min bleaching process is started. After the bleaching process is started, the O_2 supply to the reactor is shut off. After 60 min of bleaching, the pressure in the reactor is relieved and a liquor sample for pH measurement is taken. The bleached pulp is removed from the reactor and dewatered using a 15 cm Büchner funnel, as mentioned earlier. Then 25 mL sodium hydrogen sulfite ($NaHSO_3$) is added to eliminate possible oxidation and a loss of brightness.

Chlorine dioxide bleaching (D_0)

The ClO_2 bleaching stage is performed as bag bleaching using a water bath with a temperature of 70 °C. The D_0 bleaching sequence is performed under a consistency of 10% for 120 minutes. Prior to bleaching, the required amount of pulp, chemicals, and water is filled in a plastic bag. The plastic bag is sealed with a bag laminator. The content of the bag is then kneaded by hand to homogenize it for one minute. The bag is then heated for one minute in a microwave at a power setting of 300 watts, followed by another minute of hand kneading and further heating in the microwave for one minute. The plastic bag is then placed in the water bath and covered with a weight to ensure complete submersion. Every 30 minutes the bag is removed and kneaded by hand for one minute. After the specified bleaching time, the plastic bag is removed from the water, opened with scissors, and the contents are emptied into a Büchner funnel attached to a filter flask connected to a vacuum system. Part of the filtrate is sampled for pH measurement. The remaining filtrate is emptied back into the Büchner funnel to recover fines. The dewatered pulp is weighed and the dryness is tested.

Approximately 25 g OD of the bleached pulp is sampled and placed in a beaker with deionized water for testing of kappa number, brightness, and viscosity. After bleaching, 25 mL of sodium hydrogen sulfite ($NaHSO_3$) solution is added to eliminate further oxidation and an associated loss of brightness. The remaining bleached pulp is disintegrated and dewatered with a Büchner funnel. The resulting fibrous filter pad is placed on a drying paper and dried for 24 hours under a hood, after which the solids content is evaluated.

Peroxide bleaching (EP)

In the third bleaching stage, hydrogen peroxide (H_2O_2) is used as a bleaching agent. The bleaching process takes place in a highly alkaline environment allowing the H_2O_2 to react with certain functional groups of lignin such as the carbonyl groups. The E_P bleaching process and sample regime is the same as for the D_0 bleaching stage except for

the bleaching consistency, temperature and bleaching chemical addition. The E_P process has a bleaching consistency of 12 % at a bleaching temperature of 80 °C. The chemical addition is 0.25 % H_2O_2, 0.1 % $MgSO_4*7H_2O$, 2 % NaOH, and distilled water to achieve final bleaching consistency.

Chlorine dioxide bleaching (D_1)

The end of the bleaching sequence consists of a second chlorine dioxide bleaching stage D_1. Less bleaching chemical is used, because the lignin content has been greatly reduced and the strong oxidative reaction would attack the cellulose fibers excessively. The bleaching process and sample regime is the same as for the D_0 and E_P bleaching stage except for the bleaching consistency, temperature, and bleaching chemical addition. The D_1process uses a bleaching consistency of 10% at a bleaching temperature of 70 °C. The chemical addition is 0.5 % ClO_2 based on lignin content, 0.15% NaOH, and distilled water to archive final bleaching consistency.

Beating of Pulp

For beating of the three pulp fractions (hydrothermal treated sulfate SM pulp, SM sulfate pulp, and industrial eucalyptus sulfate pulp), a Valley beater in accordance with TAPPI T 200 was used. Prior to beating, the eucalyptus pulp is soaked for 12 hours in deionized water. The HT sulfate SM pulp and the SM sulfate pulp did not undergo a soaking process because the HT process required liquid processing with deionized water. After the pulp with a consistency of 1.57±0.04% and a temperature of 23±2 °C was loaded into the Valley beater, which initially was operated with no load for 3 min. After that the initial sample was taken and the beating was initiated applying a weight of 5500g to the grinding plate lever.

Screening of Pulp

After beating, each sample of the TH sulfate SM pulp, SM sulfate pulp, and the eucalyptus sulfate pulp was screened. The screening process followed the TAPPI T 274 testing method, using a Voith Valley screen with a 150 µm screen plate. Before screening, the pulp was diluted with deionized water and disintegrated to achieve good screening performance. The screened fibers are used to prepare the TAPPI handsheets for paper testing.

Handsheet Preparation

After screening of the individual pulp samples, handsheets with a basis weight of 60g/m² were prepared for paper testing according to TAPPI T205 testing method.

RESULTS AND DISCUSSION

In this study, the focus was to investigate hydrothermal treatment of sugar maple before kraft pulping for the use in paper applications that require a high whiteness. In this section the results of the individual studies are presented and interpreted. Standard deviations in the charts are not shown; however all tests are performed to TAPPI test methods within the allowable testing deviations.

pH Values

After each bleaching stage the pH values were measured. Figure 3 shows the highly alkaline environment in the first and third bleaching stage as well as the acidic environment of the second and third bleaching stage.

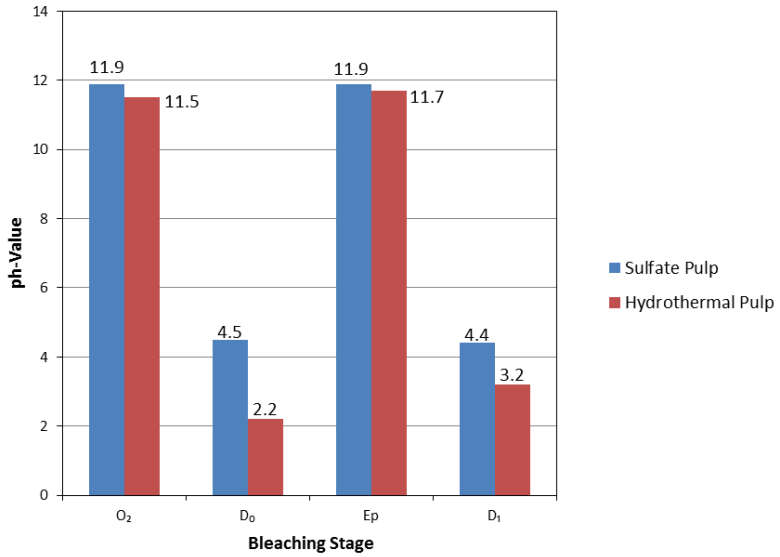

Fig. 3. pH value for $O_2D_0E_PD_1$ bleaching sequence

The pH of the hydrothermal treated pulp after each bleaching stage was lower than that of the sulfite pulp. For the chlorine bleaching stage the pH value was half that of the sulfate pulp. This indicates that the hydrothermal treated pulp will require a smaller amount of bleaching process chemicals in the acidic range of pulping.

Kappa Number

The Kappa number values of the $O_2D_0E_P$ bleaching sequence for hydrothermal treated SM and sulfite SM pulp are shown in Fig. 4. The hydrothermal treated pulp had an initial Kappa number 9.8 points higher than the sulfate pulp. This can be explained as follows: For the determination of the Kappa number using T 23 om-06 for both pulp materials, the same amount of oven-dry pulp material was used. By partially removing hemicellulose through hydrothermal treatment, a higher percentage of lignin is therefore contained in the hydrothermally treated pulp.

After the O_2 bleaching stage, the Kappa number of hydrothermal treated pulp dropped 19 points compared to 6.1 points of the SM pulp. This indicates that the hydrothermal pulp was more receptive to the O_2 bleaching than the SM pulp and might require less process chemicals.

For the remaining D_0 and E_P bleaching stages, the Kappa number of the hydrothermal treated pulp was below the SM pulp at a 1.0 and 2.6 point lower Kappa number, respectively. This indicates that the sulfate SM pulp responded better to the D_0 bleaching stage after oxygen bleaching. The Kappa number for the hydrothermal treated pulp could be not determined due to the low residual content of lignin after the D_1 bleaching stage.

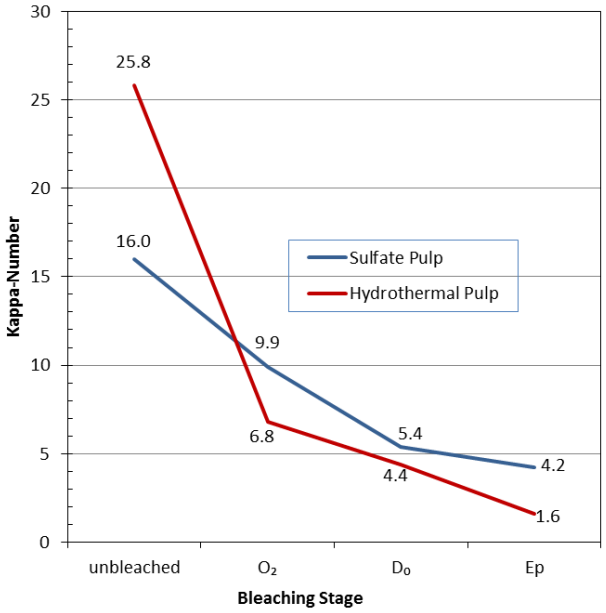

Fig. 4. Kappa number for $O_2D_0E_P$ bleaching sequence

Whiteness

The degree of whiteness values of the $O_2D_0E_PD_1$ bleaching sequence for hydrothermal treated SM and sulfite SM pulp are shown in Fig. 5. The hydrothermal treated SM pulp whiteness was 8 points below the level of the sulfate SM pulp at the beginning, which can be explained by the higher lignin content.

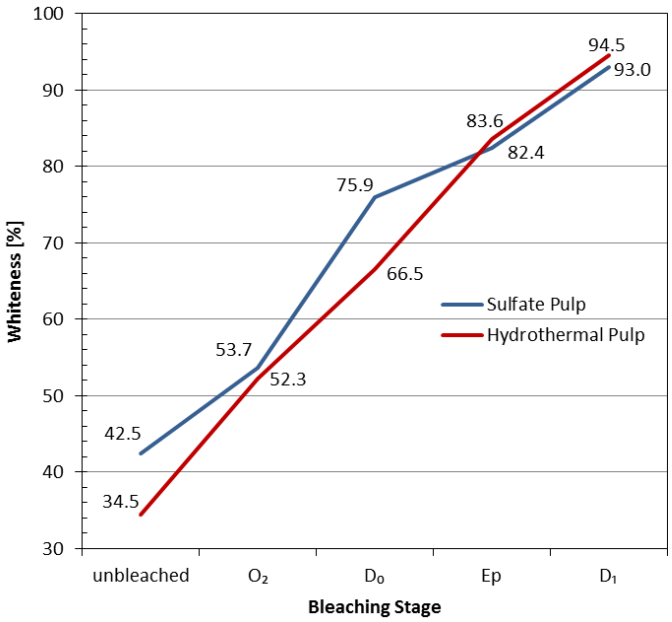

Fig. 5. Whiteness value for $O_2D_0E_PD_1$ bleaching sequence

The whiteness gap was reduced to 1.4 points after the O_2 bleaching stage and increased to 9.4 points after the D_0 bleaching stage. This indicates that the SM sulfate pulp responded better to D_0 bleaching stage after oxygen bleaching. After the E_P and D_1 bleaching stage, the whiteness value of the hydrothermal treated SM pulp was 83.6 and 94.5, respectively, which was 1.2 and 1.5 whiteness points higher than that of the SM sulfate bleached pulp.

Viscosity

The viscosity values shown in Fig. 6 fell as expected, while the pulp materials passed through the $O_2D_0E_PD_1$ bleaching sequence. Before initiating the bleaching sequence, the hydrothermally treated SM pulp showed an 8 cP higher viscosity than the SM sulfate pulp. After the O_2 bleaching stage, the hydrothermal treated pulp had a 7 cP lower viscosity than the sulfate SM pulp. After the D_0 bleaching stage, the hydrothermal treated SM pulp had a 1.3 cP drop in viscosity, whereas the SM sulfate pulp had a 4.7 cP drop in viscosity. After the E_P and D_1 bleaching stages, the two pulps were at a near equal level. This indicates that the hydrothermal treated pulp will require a smaller amount of process chemicals in the acidic range of pulping as well as requiring less energy for pumping and conveying.

This also indicates that hydrothermal treated SM pulp was more receptive to an O_2 bleaching and less receptive to the D_0 bleaching stage, and that a hydrothermally treated SM pulp will require a smaller amount of process chemicals in the acidic range of pulping.

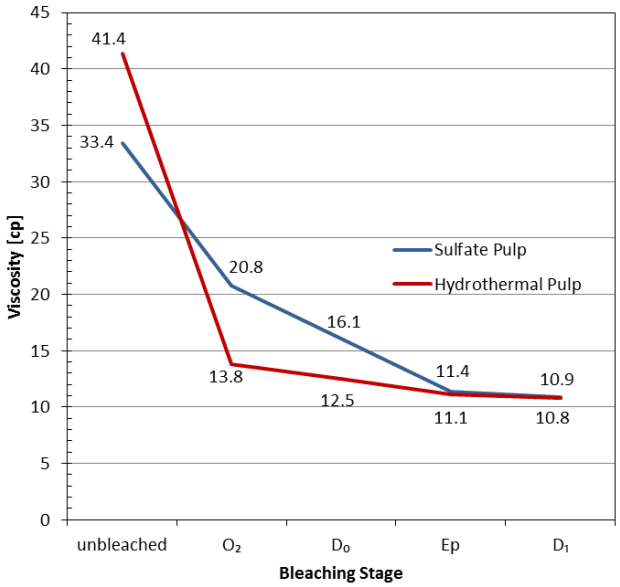

Fig. 6. Viscosity value for $O_2D_0E_PD_1$ bleaching sequence

Beating

The beating curve for bleached and unbleached SM hydrothermal treated sulfate pulp is shown in Fig. 7. Commercial eucalyptus bleached pulp is also shown as a reference. The dewatering behavior of all pulp fibers is shown in mL Canadian Standard

Freeness (CSF). As expected, with increased beating time, the dewatering behavior decreased steadily, except in the case of the SM sulfate bleached pulp, which reversed the CSF value after 40 minutes beating time to 244 mL and 50 minutes beating time to 280 mL. The hydrothermal treated SM unbleached and bleached pulp had the highest initial freeness at 597 mL and 492 mL CSF. The SM sulfate unbleached and bleached pulp had an initial freeness of 481 mL and 417 mL. The hydrothermal bleached, SM sulfate unbleached, and commercial eucalyptus pulp had almost identical initial CSF values of 492 mL, 481 mL, and 497 mL, whereas the SM sulfate bleached pulp had the lowest initial CSF value of 417 mL.

The CSF curve showed that hydrothermal treatment of SM pulp significantly increased the CSF value of the SM pulp with and without post bleaching, indicating a lower proportion of fines in the hydrothermal treated SM pulp.

The CSF values of 455 mL and 412 mL for the hydrothermal bleached and unbleached SM pulp and CSF of 355 mL and 305 mL of SM sulfate bleached and unbleached pulp did not show a significant difference in the first 20 minutes of beating compared to the commercial bleached eucalyptus pulp at 384 mL. After 20 minutes of beating, the hydrothermal treated SM bleached pulp showed less impact by beating, resulting in a higher CSF of 335 mL compared to 310 mL CSF for the hydrothermal treated unbleached SM pulp after 50 minutes of beating time. This indicates that the hydrothermal treated pulp will generate less fines and therefore not decrease its dewatering properties. This might have an impact on future paper machine operations in regards to speed and dryness at the former and press operation if the pulp refining is optimized for the specific pulp used for papermaking (Danforth 1986).

Beating of hydrothermal treated unbleached and unbleached sulfite SM pulp showed the same response to beating, keeping the initial CSF gap of 116 mL at the initial stage to 114 mL at the 50 minutes beating mark with 310 mL CSF for the hydrothermal treated unbleached and 196 mL for the sulfate unbleached pulp.

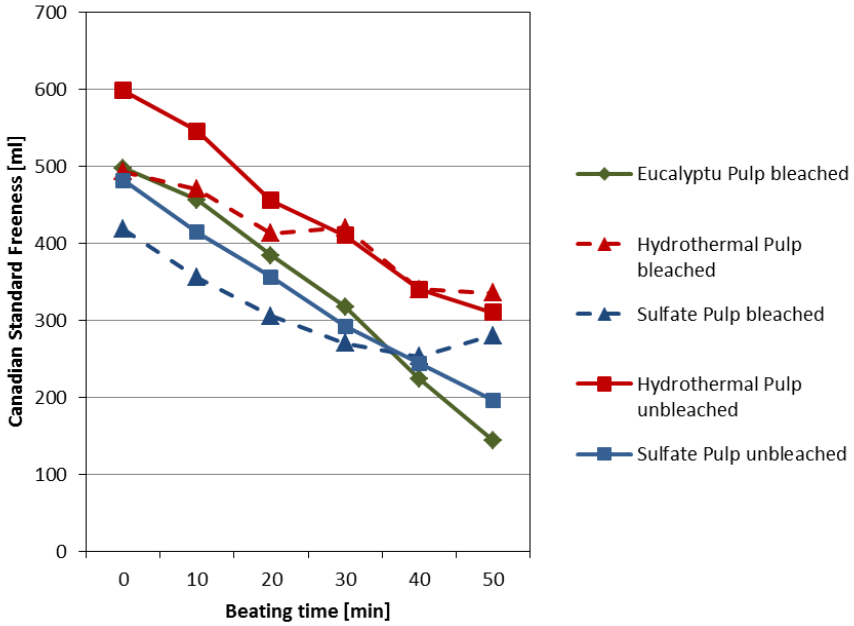

Fig. 7. CSF value for bleached pulp

Basis Weight and Bulk

Figure 8 shows the variation of the specific volume of the studied pulps based on beating time. The bulk was selected to compensate for the variations in the thickness and basis weight between individual samples of the same material. With increased beating time, the specific volume decreased, which means that the density of the fiber material increased. This can be explained with the higher proportion of fines produced during the beating process. With a constant basis weight the caliper decreases due to fines placement in the voids of the paper sheet, thus a more dense fiber network is formed.

The hydrothermal treated SM bleached and unbleached pulp formed a handsheet with a higher specific volume due to its lower fines content compared to the SM bleached and unbleached sulfite pulp.

Usually, the specific volume of a paper decreases with bleaching processes due to a higher fines production. This effect can be seen here for the bleached and unbleached SM sulfate pulp. For the hydrothermal SM bleached and unbleached pulp, this effect was reversed. The hydrothermal treated bleached pulp had a significantly higher specific volume than the other pulps with a range from 0.28 cm³/g to 0.17 cm³/g for the bleached eucalyptus pulp and 3.66 cm³/g to 0.41 cm³/g for the SM sulfate bleached pulp. This might indicate that hydrothermal treated SM bleached pulp might have an application as partial pulp fiber supplement for low basis weight printing paper to maintain required caliper and at the same time increasing paper filler content, decreasing expensive pulp fibers, and maintaining bulk properties (Doelle and Amaja 2012; Cheng *et al.* 2013).

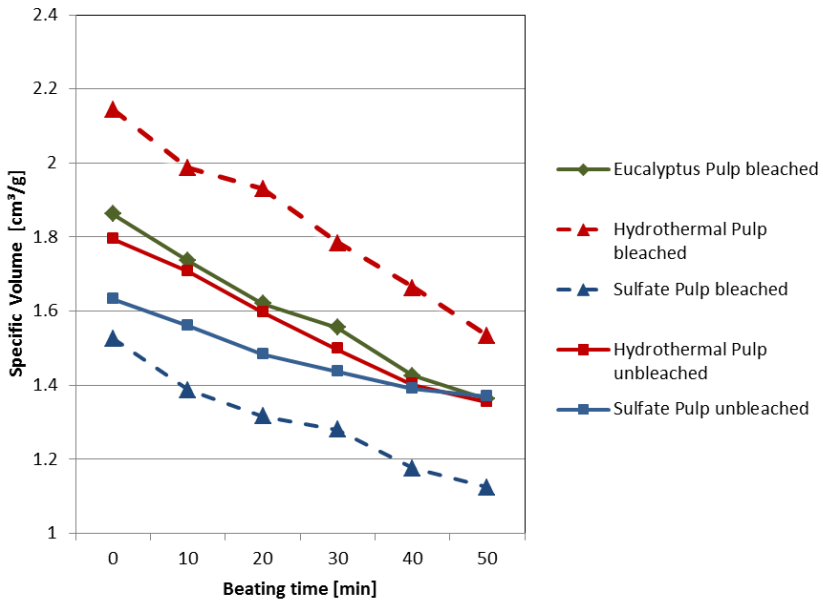

Fig. 8. Specific volume for bleached pulp

Porosity

The development of resistance to air permeation through the sheet with increased beating time is shown in Fig. 9. The Gurley Densometer value is defined as the time in seconds that a volume of air with a constant pressure of 100 cm³ needs to flow through the paper sample. An increasing amount of time means a decreasing porosity. The

porosity curve shows in general the same trend. All investigated pulps had a decreased porosity with increased beating time. The initial porosity for the hydrothermal treated pulp was 2.1 s and 2.6 s for the sulfate unbleached pulp. An increase in beating time from 10 min. to 50 min. shows that the porosity of the hydrothermal treated unbleached pulp had a 40% to 61% increased porosity compared to the sulfate unbleached pulp.

For the hydrothermal treated bleached pulp, a significant decrease in porosity values could be observed. The initial porosity was 0.8 s and 4.2 s and 6.4 s for the 40 min. and 50 min. beating time, whereas the sulfate bleached pulp showed 3.5 s for the initial porosity and 278.2 s. for the 40 min. beating time. The 50 min. porosity value could not be measured due to sample restrictions.

The significant decrease in porosity values could be linked to the decreased fines content of the hydrothermal treated pulp and might have advantages for the manufacture of sack kraft paper products and other paper products that require a low porosity value that allows high filling speeds by allowing air to pass through the paper product while the product is filled into the paper bag (Paulapuro 2000; Billerud 2012). The porosity values for the commercial eucalyptus pulp are plotted for reference purpose only.

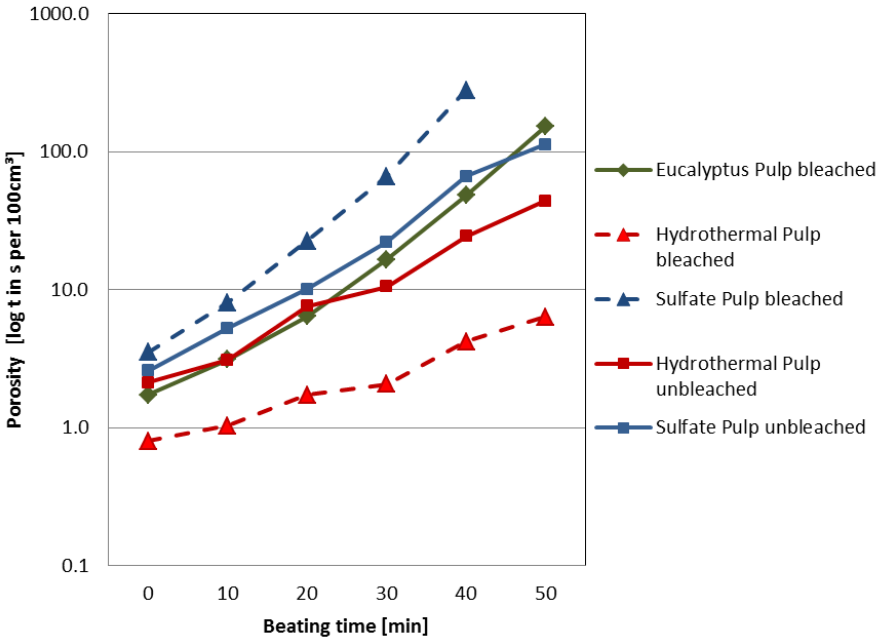

Fig. 9. Porosity value for bleached pulp

Tensile Index

Figure 10 shows the tensile index in Nm/g as part of the investigation of the mechanical paper properties. The tensile index was selected to compensate the variations in the thickness and basis weight between individual handsheets of the same material. The tensile index increased with beating time. This was attributed to fibrillation of the fibers, which can form more hydrogen bonds during handsheet formation.

All bleached pulps showed a positive effect on the tensile index development with increased beating time. The initial tensile index of the hydrothermal bleached SM pulp was 27.6 Nm/g, whereas the hydrothermal bleached SM pulp had 55.4% lower tensile

index, 12.3 Nm/g. The initial tensile index for the SM unbleached sulfate was 48% higher at 53.1 Nm/g and 73.8% higher for the bleached SM sulfate pulp at 47.0 Nm/g. After 40 min. of beating the tensile index development decreased for the unbleached hydrothermal treated SM pulp and the unbleached and bleached SM sulfite pulp at a value of 54.4, 86.3, and 80.8 Nm/g, respectively. The tensile index after 50 min. of beating for the hydrothermal treated SM bleached pulp was 33.5 and for the unbleached SM pulp 56.1. In comparison to the unbleached sulfate pulp with 89.5 and bleached SM sulfate pulp at 82.8, the difference in tensile index for the hydrothermal treated pulp was 59.4% lower for the bleached and 37.3% lower for the unbleached hydrothermal treated pulp. The tensile index values for the commercial eucalyptus pulp are plotted for reference purpose only.

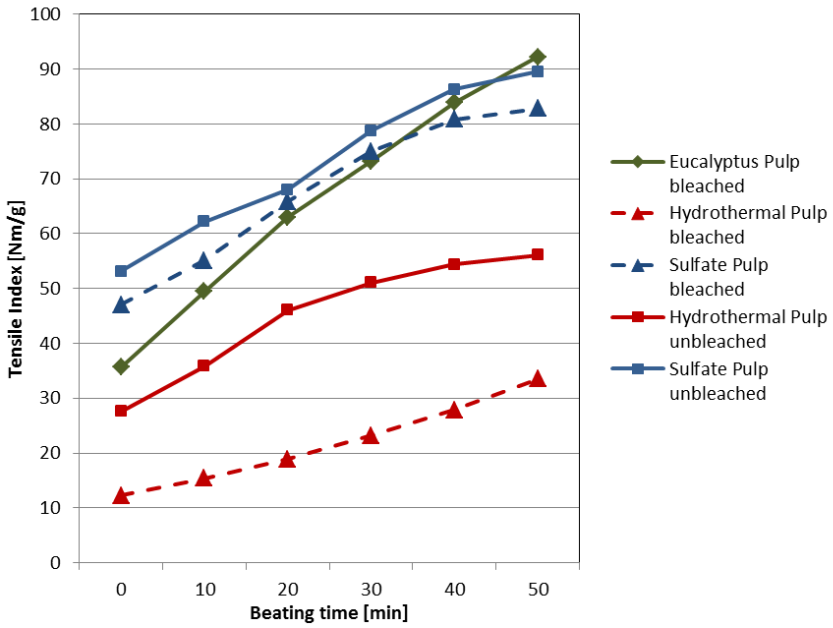

Fig. 10. Tensile index for bleached pulp

Tear Index

The tear index in gf is shown in Fig. 11 as part of the investigation of the mechanical paper properties. The tear index was selected to compensate the variations in the thickness and basis weight between individual handsheets of the same material. The tear index for the hydrothermal treated bleached SM pulp at a value of 12.0 was 50% lower than the tear index of the unbleached pulp at a value of 23.9, and 69.4% and 66.0% lower compared to the bleached and unbleached SM sulfate pulp at a value of 39.3 and 35.3 respectively. The tear index increased with beating time for the hydrothermal treated SM bleached and unbleached pulp fractions and dropped after 40 minutes of beating time, whereas the SM sulfate pulp increased and then dropped after 20 minutes beating time for both the bleach and unbleached. The resulting tear index after 50 min. of beating for the hydrothermal treated SM bleached pulp was at 31.2 and for the unbleached SM pulp at 33.9. In comparison to the unbleached sulfate pulp with 39.8 and bleached SM sulfate pulp at 32.6, the difference in tensile index for the hydrothermal treated pulp was

4.3% lower for the bleached and 15.2% lower for the unbleached hydrothermal treated pulp. The tear values for the commercial eucalyptus pulp are plotted for reference purpose only.

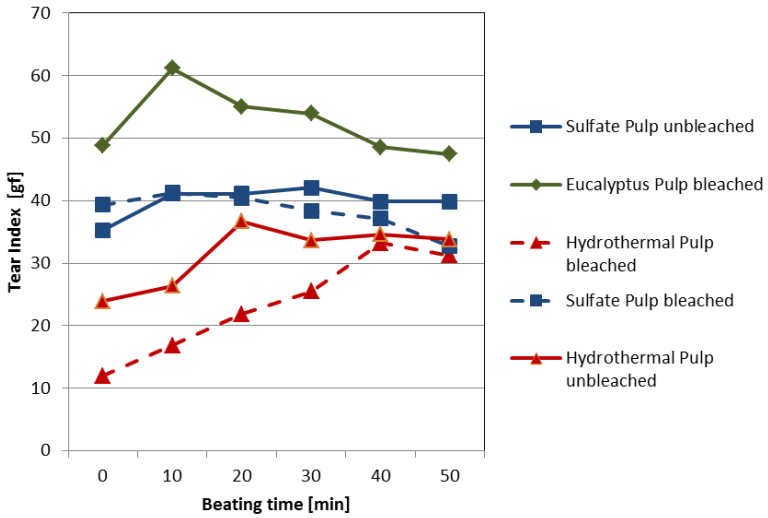

Fig. 11. Tear index for bleached pulp

Optical Properties

Brightness

The course of the degree of brightness over the beating time is shown in Fig. 12. The brightness measurement was performed with an Elrepho Devise with a standard illuminant light D65 and glass filter R_{457}. The curve shows the typical decrease in brightness based on beating time. The unbleached hydrothermal treated pulp has an initial brightness of 32.6, lower than the unbleached sulfate pulp with a value of 39.5. This can be explained by the higher lignin content of the hydrothermal treated pulp.

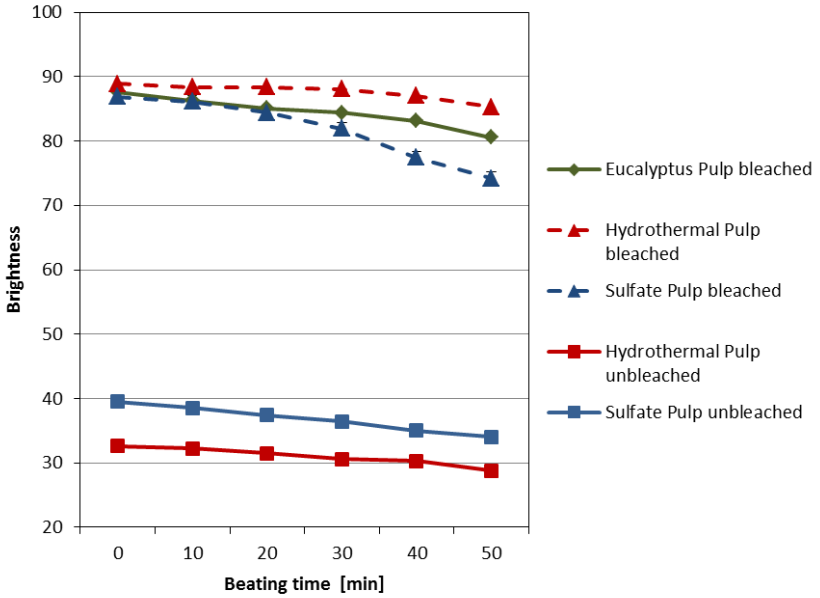

Fig. 12. Brightness value for bleached pulp.

The bleached hydrothermal treated SM pulp had a brightness value of 88.9 and the bleached SM sulfite pulp of 86.9. The commercial eucalyptus pulp brightness was 87.5. The decrease in brightness value after 50 min beating time was 28.8 for the unbleached hydrothermal treated SM pulp and 34.0 for the unbleached SM sulfite pulp. The bleached hydrothermal treated SM pulp had a final brightness number of 85.3, whereas the bleached sulfite SM pulp and eucalyptus pulp had a final brightness number of 74.2 and 80.6. The resulting brightness number after 50 min. of beating shows that the hydrothermal treated SM unbleached and bleached pulp had the lowest reduction in brightness of 11.6% and 4% to values of 28.8 and 85.3at 31.2. The brightness reduction for the unbleached and bleached SM sulfite pulp was 13.7% and 14.6% with brightness values at 28.8, 74.2 and 33.9. In comparison the commercial eucalyptus pulp showed a reduction in brightness of 8% to a brightness value of 80.5.

Opacity

Opacity refers to how much light can penetrate through the paper and was measured with an Elrephro meter. The opacity is calculated as the ratio of the reflection factor of a single sheet of paper over a black body as a reflection factor. Figure 13 shows the change in opacity of the pulps tested based on a beating time of 50 minutes. The opacity-reducing effect of bleaching can be seen in the bleached sulfate and commercial eucalyptus pulp. The unbleached hydrothermal treated SM pulp increased its opacity by 3.6% from the initial value of 96.0 to 99.6 whereas the unbleached sulfite SM pulp decreased its value by 2.3% from 97.6 to 95.33.

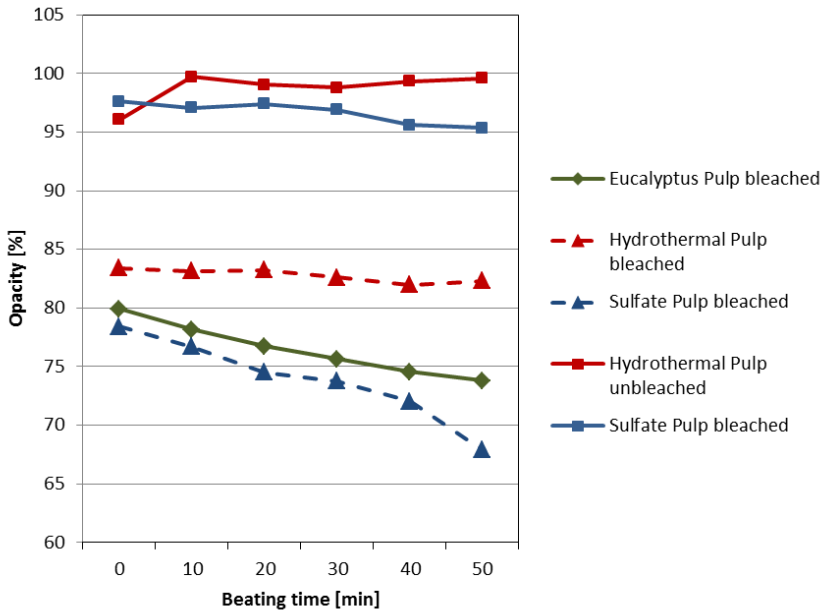

Fig. 13. Opacity for bleached pulp

The decrease in opacity for the bleached hydrothermal treated SM pulp was 1.3% from its initial value of 83.4 to 82.3. The bleached sulfate SM pulp and the commercial l eucalyptus pulp showed a significant decrease in opacity of 13.4% and 7.6% from their initial brightness value of 74.2 and 79.9 to 67.9 and 73.81, respectively.

CONCLUSIONS

The main results of this study indicate that the hydrothermal treatment of SM had an influence on the pulp preparation and physical, optical, and strength properties of paper handsheets.

1. The hydrothermal treated SM pulp was more receptive to an O_2 bleaching than the SM sulfite pulp due to its lower pH value that is half that of the sulfite pulp.
2. Hydrothermal treated pulp was more receptive to O_2 bleaching.
3. Initial Kappa numbers were higher for the hydrothermal treated SM pulp.
4. Whiteness levels achieved for the hydrothermal treated SM pulp were higher than for the SM sulfite pulp after the $O_2D_0E_PD_1$ bleaching sequence.
5. Viscosity numbers were lower for the hydrothermal treated SM pulp, indicating that the pulp was more receptive to an O_2 bleaching and less receptive to the D_0 bleaching stage. E_P and D_1 bleaching stages showed no difference.
6. Hydrothermal treated bleached and unbleached SM pulps had higher CSF values than the sulfite SM pulp.
7. The hydrothermal treated SM bleached and unbleached pulp formed handsheets with a higher bulk compared to the SM bleached and unbleached sulfite pulp and bleached commercial eucalyptus pulp.
8. The hydrothermal treated pulp had a significantly higher air resistance than the compared sulfite SM and commercial eucalyptus pulps.
9. Tensile index and tear index showed significantly lower values for the hydrothermal treated SM pulp.
10. Brightness and opacity values for the hydrothermal treated SM pulp showed significantly higher values after beating compared to the SM sulfite pulp.

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