ABSTRACT

CHEN, HAO. The Effects of Fines and Enzymatic Treatments on the Drainage Rates of Fiber Mats. (Under the direction of Dr. Martin A. Hubbe and Dr John A. Heitmann, Jr.)

The presence of cellulosic fines in a papermaking furnish can have a dominant effect on the rate of dewatering, sometimes limiting the overall production rate on a paper machine. The more effective removal of water during forming and pressing has the potential to reduce the energy required for drying the paper. Higher levels of fines can result from increased use of mechanical pulp, from increased refining, and from the recycling of paper without deinking. Pulp suspensions drain rapidly if the fines have been removed. Thus, it is economically important to try to find ways to increase drainage rate without impacting paper properties.

In this study, two types of model fines were created using a standard procedure. Bleached hardwood kraft pulp was used as a source of primary fines (collected before refining) and secondary fines (collected after refining of fines-free fiber suspensions). Fines created by refining (secondary fines) slowed drainage to a much greater extent than those originally present in bleached hardwood kraft pulp (primary fines). Results were explainable by a mechanism in which unattached fines are able to move relative to adjacent fibers during the dewatering and consolidation of a mat of fibers. Due to such movement, fines end up in locations where they plug drainage channels in the mat. The contribution of the fines to dewatering increased in inverse proportion to particle size and with increasing surface area, as calculated from the light scattering analysis. The water swollen nature of cellulosic fines

was tested, in comparison to the fibers. Modified water retention value tests based on centrifugal removal of water between the fibers, have been used to estimate the amount of water held within the cell walls of kraft fibers.

In further studies, enzymes were used to remove the fines and polish the fibrillated fiber surface. Research was designed to test a hypothesis that the pulp suspension would drain more rapidly if the fibrils on the fiber surface were removed or reduced by enzymatic treatment. Highly refined hardwood kraft pulp, which is a by-product from making secondary fines was used, and treated with cellulase from *Trichoderma ressei*. Dewatering tests showed that the drainage rate increased substantially after a brief exposure to cellulase, but decreased if the reaction was continued for a long period. The mechanism could be explained based on the enzyme’s ability to clean the surface of the highly refined fiber surface, which initially resulted in an increased drainage rate; however, as the treatment time was increased, the cellulase cleaved fibrils from the fiber surface, generating fines which could migrate freely in the pulp, plug drainage channels, and lead to increase dewatering time. After yet longer treatment times, the generated fines were eliminated by the enzyme and drainage rate again increased. Micrographs and results of particle size distribution analysis also confirm this conclusion.

The Effects of Fines and Enzymatic Treatments on the Drainage Rates of Fiber Mats

by
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1. INTRODUCTION & LITERATURE REVIEW

The ease of removal of water from cellulosic fibers and other materials has a large economic impact on the production of paper. McGregor and Knight (1996) found that the cost of remove one unit of moisture in the forming, pressing and drying sections of a paper machine was related by the ratio of 1:5:220. In principle, there are two ways in which papermakers can benefit if they can remove water quickly from the wet web of paper. First, it is sometimes possible to increase the speed of the paper machine, which means they can produce more tons of paper without increasing the fixed cost. A second possible benefit is energy reduction—the more effective removal of water during forming and pressing also has the potential to reduce the energy required for drying the paper.

Starting back in the 1960s, there was quite a lot of work to try to understand the resistance to the flow of water through a wet web of paper. This work was mostly based on earlier theories by Kozeny and Carman. Kozeny (1927) showed that the resistance to flow through packed beds of granular materials could be explained in terms of the size and number of pores. His ideas were extended by Carman, who verified the equation and introduced such concepts as hydrodynamic radius, specific surface area and the effect of tortuosity. A commonly cited form of the Kozeny-Carman equation is given below.

$$k = (\gamma / \mu)\,(2/C_{\text{K-C}})\,(1/S_o^2)\,[\,e^3/(1 + e)] \tag{1}$$

where k is the permeability (length/time), γ is the unit mass of the fluid, μ is the fluid's dynamic viscosity, CK-C is the Kozeny-Carman coefficient (usually taken to be about 5), So is the specific surface area per unit displacement volume of particulate material, and e is the fractional void volume. The permeability coefficient is defined in reference to d'Arcy's law,

$$\mathrm{d}V / \mathrm{d}t = k\, A\, \Delta P_{\mathrm{f}} / (\mu L) \tag{2}$$

where V is the filtrate volume at time t, A is the cross-sectional area available for flow (disregarding the presence of a solid phase), ΔP_{f} is the pressure drop across the permeable material, μ is the viscosity, and L is the linear length of the column through which the fluid passed through the permeable material.

According to d'Arcy's law the rate of flow through a porous medium is related to the cross-sectional area of flow, the applied pressure, the viscosity of the liquid, and the length of the material through which the liquid is being pushed. Binotto and Nicholls (1976) showed that fiber morphology which is related to growth within a tree significantly influences the filtration resistance of an unbeaten, bleached loblolly pine pulp suspension. Their study showed that most of the influence on filtration resistance is through change in hydrodynamic and geometric specific surface arising from change in fiber diameter, fiber length and the number of fibers per gram. The results implied, with stated assumptions, that including more juvenile wood which has a smaller diameter, would tend to increase the specific surface area and decrease drainage rate.

Another application of Kozeny-Carman equation has been to account for effects of suspended fine materials having a relatively high surface area per unit mass, or "specific surface area". Consistent with this theory, it has been found that fine mater having the smallest size and highest specific surface area tends to have the greatest adverse effect on dewatering. In the literature, fines have been defined differently by different authors. Hinton and Quinn (1964) took all material passing through a 60 mesh screen as fine. Britt and co-workers (1976) defined fines as the fraction passing the 200 mesh screen, while Giertz(1977) suggested that the 100/200 mesh fraction containing fibrils and lamellas should be considered as fines. Jaycock(1978) included all insoluble or colloidal materials in the furnish as fines.

In my research I defined two contrasting types of fines based on the following situations. "Primary fines" are essentially the detached portion of cellulosic materials consisting of lignin, ray cells, tracheids, parenchyma cells, and cellulosic debris. These fines, though somewhat diverse and species-dependent, can generally be described as "short," and their length-to-thickness ratio is usually less than 5. By contrast, "secondary fines" from kraft pulps are produced by refining action, which causes some of the primary wall or secondary wall layers to delaminate and become detached from the fibers, especially at high levels of refining. Such secondary fines tend to be very slender and flexible.

When cellulosic fines are present in significant amounts, they can have a dominant influence on dewatering. Pulp suspensions drain rapidly if the fines have been removed. Higher levels of fines can result from increased use of mechanical pulp, from increased refining, and from the recycling of paper without deinking. Ingmanson and Andrews (1959) found that filtration resistance increased exponentially with beating time and that the level of filtration resistance of a whole pulp depended primarily on the amount of fines and fiber debris produced in the refining action. Liu (2001) showed that a small amount of ultra-fines can play a decisive role in drainage. It was found that the drainage was impaired more by the presence of ultra-fines than by the dissolved pulp components in the white water. Pruden (2005) suggested that fine particles greater in any dimension than 20 μm would be trapped by filtration in the rapidly forming pad of fibers as fast drainage was initiated.

A lot of dynamic drainage studies have tested the extent to which the retention of fine materials depends on their attachment to pulp fibers. Britt (1981) showed that if the agitation was well controlled, the majority of fiber fines in the suspension would remain unattached to fibers. Van de Ven (1984) verified this theory; he concluded that it was very difficult for a small particle to become deposited onto a fiber surface during the dewatering process, due to hydrodynamic effects. Another view is that electrostatic attraction forces may be able to overcome hydrodynamic forces and bind the fines to fiber surfaces. However, fine particles can be flocculated by the addition of a cationic polyelectrolyte. Hunter (1980) has thoroughly discussed fine particle floc formation by the “bridging” mechanism when a high molecular weight polyelectrolyte was employed. Flocculation by bridging can occur for a wide variety of colloidal particles including the smaller size fraction of pulp fines. This results in a large loosely structured floc of the fine particles, held together weakly by the adsorbed long-chain bridging molecules. Sratton (1975) showed that floc size might range from perhaps 10 μm to 500 μm or more in a low shear system. These flocs form very rapidly, can partially degrade by turbulent shear forces and may form again when turbulence ceases. Another mechanism is known as charge patches. High charge density polyelectrolyte was employed this time to create charge patches on the fiber surface. Bhardwaj (2005) showed that maximum dewatering rate and retention could be obtained when aqueous conditions had been adjusted in such a way that the net electrical potential associated with the surface was near to zero.

An alternative way to demonstrate the effect of the specific surface area on dewatering resistance of cellulosic material is to use enzymes. Although the mechanisms are not completely understood, several studies have been carried out to explain the effect of enzymatic treatment on the increased drainage rate. Mooney et al. (1999) reported evidence indicating that increased drainage results from selective digestion of the higher specific surface area cellulose microfibrils from the fiber surface. Pommier et al. (1989) reported that cellulase likely attacked the surface of the fibers, producing a peeling effect, which could clear fibrillation from the fiber surface. If this peeling effect is limited and well controlled, the enzyme will only remove some small colloidal components that have an affinity for water. This reduction of the pulp–water interactions will allow better drainage of the pulp without affecting the final mechanical properties of the paper. It has been reported that the drainability of mechanical pulp can also be enhanced by the addition of hemicellulases. Many different cellulases and hemicellulases have been found to improve freeness. Karsila et al. (1990) claimed that xylanase improved the freeness of deinked recycled pulp while having no detrimental effect on fiber tensile strength properties. Fuentus and Robert (1998) showed that a mixture of xylanase and cellulase enzymes at low concentrations markedly increases the freeness of recycled fibers without substantially reducing yield. Pommier (1990) carried mill trials with an application of a commercial *T. reesei* enzyme mixture called Pergalase A40. It was found that the mixed xylanases and cellulases in the product peeled the surface of the fibers. If treatment was limited, the enzymes remove only elements that have a great affinity for water but which contribute little to inter-fiber bonding potential. By selectively removing these surface components, pulp-water interactions are reduced and drainage increase without noticeable changes in the final mechanical strength properties of the pulp. If the treatment is extended, however, fibrillation becomes pronounced and drainage decreases. If large quantities of crude enzymes are used, the average fiber length is reduced, fines disappear, and the strength properties of the fibers are lost. Therefore, an optimum level of enzyme treatment is required.

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2. OBJECTIVES

As described in the literature review section of this thesis, the removal of water from cellulosic fibers and other materials in the wet web constitutes the most energy-demanding part of the paper manufacturing process. In spite of the large economic importance of removing water quickly from papermaking stock, during the production of paper, there has not been enough research carried out to determine the mechanisms.

The general goal of my study was to better understand what is responsible for the resistance to water release from fiber suspensions during the making of paper. The second goal of our experiment is to test if the water could be released faster from enzymatic modified fiber suspension. Highly refined hardwood kraft pulp was used as our resource, and it was treated with cellulase from *Trichoderma ressei*.

Through the different experiments, it was our hope to be able to evaluate the following hypotheses:

1. It was proposed that unattached fines tend to follow flow of water through the wet web. The fines tend to get stuck in locations where they obstruct flow.

2. It was proposed that a pulp suspension would drain more rapidly if the fibrils on the fiber surface were removed or reduced by enzymatic treatment.

3. PAPERS

3.1 Papers – Part 1

Importance of Cellulosic Fines Relative to the Dewatering Rates of Fiber Suspensions

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Abstract

When cellulosic fines are present in significant amounts they can have a dominant influence on dewatering. Pulp suspensions drain rapidly if the fines have been removed. In this study, the dependency of gravity dewatering rates on the level and properties of cellulosic fine matter was quantified. Bleached hardwood kraft pulp was used as a source of primary fines (collected before refining) and secondary fines (collected after refining of fines-free fiber suspensions). Fractions of fine matter also were obtained from chemithermomechanical (CTMP) pulp. Size distributions of these fines were characterized using a laser diffraction method. Results were explainable by a mechanism in which

unattached fines are able to move relative to adjacent fibers during the dewatering and consolidation of a mat of fibers. Due to such movement, fines end up in locations where they plug drainage channels in the mat. The contribution of the fines to dewatering increased in inverse proportion to particle size and with increasing surface area, as calculated from the light scattering analysis.

1. Introduction

Fine cellulosic particles, i.e. "fines," can play a pivotal role in the manufacture of paper. On the one hand, fines can help to fill in the spaces between fibers in a sheet of paper. This effect typically results in a denser, stronger, and more uniform product.[1-3] On the other hand, high levels of fines can make it more difficult to remove water from the wet sheet of paper, as it is being formed .[4-12] The latter effect can slow down the manufacturing process or increase the amount of energy that is required in order to dry the paper.

Past studies have revealed dramatic differences in the sizes and shapes of cellulosic fine material derived from different sources and resulting from different levels of mechanical treatment.[4, 7, 13-14] The pioneering work of Brecht and Klemm[4] focused on quality aspects of the fines component in groundwood pulps. These authors described some of the fines as granular ("Mehlstoff"), whereas other fines in groundwood are mucilaginous, consisting of slender fibrils ("Schleimstoff"). More recent research has found similar contrasts between the fine components obtained by screening of thermomechanical pulp (TMP) samples.[13-14] Studies of various kraft pulps have likewise revealed two contrasting types of cellulosic fines.[2-3] So-called “primary fines” consist of ray parenchyma cells and other non-fibrous materials that are liberated from the wood by chemical pulping. These fines, though somewhat diverse and species-dependent, can generally be described as “short,” and their length-to-thickness ratio is usually less than 5. By contrast, “secondary fines” from kraft pulps are produced by refining action, which causes some of the primary wall or secondary wall layers to delaminate and become detached from the fibers, especially at high levels of refining. Such secondary fines tend to be slender and flexible.

Previous studies in our research group showed significant differences in the ability of primary vs. secondary fines from bleached hardwood kraft pulp to reduce the rate of water release from fiber suspensions.[9,12] These results left some mechanistic questions unresolved, since primary and secondary fines differ from each other both with respect to size and shape. One objective of the present work was to find further evidence related to these two variables. Accordingly, this study employs a wider range of cellulosic fines, together with more detailed analysis of particle size distributions and microscopic imaging. In addition to primary and secondary fines from bleached kraft pulp, a sample of chemithermomechanical pulp (CTMP) was fractionated to obtain various size ranges of fines. All of the fines were evaluated in the presence of fibers taken from a master batch of fines-free repulped copy paper. The overall aim of the work has been to show how attributes of fiber fines, as well as their proportion in the furnish, affect the rate of release of water from fiber suspensions during a gravity dewatering test. An additional factor that was considered was the water-swollen nature of cellulosic fines, in comparison to the fibers. Water retention value tests,[15-17] based on centrifugal removal of water between the fibers, have been used to estimate the amount of water held within the cell walls of kraft fibers. More recently, Kang and Paulapuro pioneered the use of an alternative method to obtain similar information about fiber fines.[18] Their method was an adaptation of a water retention method that had been developed for evaluation of water retention in coating color formulations.[19] In the present study we have made a further modification to the method in order to be able to express the results as “grams water per gram of dry fiber,” as is the standard form for reporting the corresponding results for water retention values of pulp samples.[15-16]

2. Materials and Methods

2.1. Preparation of default fibers. Except where noted otherwise, the (fines-free) fibers used throughout the study were prepared by dispersing torn pieces of 20lb., 84 brightness, 35% recycled content xerographic copy paper and then collecting the fiber fraction using a Bauer-McNett classifier with a 100-mesh screen (see TAPPI Method T233). The classifier was run for 15 minutes during each batch treatment, and the filtrate passing through the screen was discarded.

2.2. Preparation of hardwood bleached kraft pulp fines. The kraft pulp fines were prepared from dry-lap hardwood bleached kraft pulp from a local paper mill. The wood species distribution was not evaluated. The fibers were bleached by a conventional approach, including chlorine dioxide. The pulp sheets were first torn into *ca.* 5 cm square pieces, soaked for a few minutes in tap water, and then disintegrated in tap water according to TAPPI Method T205. Two different kinds of fines were collected. First, a set of "primary fines" was collected by use of a 100-mesh screen in the final chamber of a Bauer-McNett classifier (see TAPPI method T233). The water passing through the 100-mesh screen was collected in a 50-gallon drum, which was allowed to stand overnight without stirring. The supernatant solution was then siphoned off. The settling and siphoning operation was repeated with a smaller volume for another overnight period in order to achieve the needed solids content of 1% or more.

Secondary fines were prepared by taking the material retained by the 100-mesh screen (*i.e.* fines-free bleached hardwood kraft pulp) and refining it extensively with a laboratory Hollander beater (TAPPI Method T200) to a Canadian Standard Freeness (TAPPI Method T227) of 100 ml. The mixture was then placed in the final chamber of the Bauer-McNett classifer, only this time a 200-mesh screen was used. The finer screen was used based on preliminary observations that the high level of refining rendered the fibers so flexible that they were able to pass through a 100-mesh screen. The filtrate was collected in a 50-gallon drum and allowed to settle for two days before the supernatant solution was carefully siphoned off. As in the previous case, the settling and siphoning process was repeated with smaller volumes, as needed, until a suitable solids content had been obtained.

2.3. Preparation of chemithermomechanical pulp fines. The CTMP fibers were type Q120.60 from Quesnel River Pulp Co. These fibers were provided with a Canadian

Standard freeness of 120 ml and a brightness of about 60%. The fibers were disintegrated in tap water according to TAPPI Method T205. The Bauer-McNett apparatus was used to prepare the following fractions: R100 (passing a 48-mesh screen, but retained on the 100-mesh screen), R150 (passing the 100-mesh screen but retained on the 150-mesh screen), R200 (passing the 150-mesh screen but retained on the 200-mesh screen), and P200 (passing through the 200 mesh screen and collected by over-night sedimentation in a barrel).

2.4. Microscopy. Optical microscopy was carried out with an Olympus BH2 microscope, using either a 10X or 20X objective. Images were recorded with a TV camera. Dimensions were calibrated with a standard length. Samples were placed onto glass slides at various dilutions, with the goal of being able to simultaneously view 10-100 particles in one field, while at the same time avoiding excessive contact or overlap among the particles.

2.5. Particle size analysis. The apparent particle size distributions of cellulosic fine matter were determined with a Horiba LA-300 laser diffraction device. This apparatus measures the intensity of laser light that is scattered at various fixed angles relative to the transmitted light through a dilute suspension. Concentrations of fines samples in water were adjusted so that the percent transmittance of light was within the specified range. Default conditions for ultrasonication (before the measurement) and recirculation of the suspension were used. Particle size distributions were weighted by the software on an effective surface area basis.

2.6. Water release vs. time. Gravity drainage tests were conducted with a portable modified Schopper-Riegler test device assembled and donated by Buckman Laboratories International, Inc. The essential parts of this apparatus match those in the standard Schopper-Riegler test specification (ISO 5267/1, BS 6035/1 and SCAN C19), except that a single, large opening is provided at the base of the collection cone for the filtrate. Also, a 100-mesh stainless steel screen was used. Suspensions were prepared with sufficient Na_2SO_4 so that the solution conductivity was 1000 μS/cm, and dewatering tests were done at room temperature (*ca.* 24 ^oC). Cellulosic suspensions were prepared at a solids content of 0.5%; in other words, the total amount of cellulosic material was kept constant, even if the fines level was varied. The suspensions were stirred with an impeller at a fixed, moderate speed for 30 seconds (or another fixed period in certain sets of tests) before adding the suspension to the top part of the test device. The amount of filtrate was determined with an electronic balance as a function of time after releasing the suspension and allowing it to impinge onto the screen.

2.7. Filtrate turbidity. Turbidity tests were carried out to obtain information related to the retention of cellulosic fines in the fiber mat. During previous work in our lab [9] a good correlation had been obtained between turbidity and the concentration of fines suspended in aqueous solution. The turbidity values were obtained with a DRT-15CE turbidimeter from HF Scientific (Ft. Meyers, Florida, USA). Sample cuvettes were individually inverted about 1-2 seconds before each reading to ensure an even suspension of the fines.

2.8. Water retention. The relative abilities of the fiber and the fines fractions of the bleached hardwood kraft pulp to retain water were evaluated by a modification of the method used by Kang and Paulapuro.[18] The tests were carried out with a Gravimetric Water Retention Meter (design by DT Paper Science Oy, Finland; model AA-GWR), which is usually used to measure the water retention in coating color.[19] The added samples were at 0.5% solids and 5 mL sample volume, for a filter area of 8 cm^2. Polycarbonate 5 μM membrane filters were used, backed by four layers of blotter paper to absorb the expelled water. The applied air pressure was set at 68.9 kPa (10 psi), and the pressure was applied for periods of 5, 20, 30, or 60 minutes. At the end of the selected time, the air pressure was discontinued, and the mass of the damp cellulosic material was determined (damp mass). The cellulosic material was dried at 105 °C for 60 minutes, and then weighed again (to determine dry mass). The water retention was defined according to the following formula,

$$\text{WR} = [\text{wet mass} - \text{dry mass}] / (\text{dry mass}) \qquad (1)$$

3. Results and Discussion

3.1. Cellulosic fines from bleached hardwood kraft pulp. The primary and secondary cellulosic fines, obtained from hardwood bleached kraft pulp, were characterized by light microscopy and laser diffraction particle size analysis. As shown in Fig. 1, the primary fines (the “pass” fraction through a 100-mesh screen, from a suspension of unrefined pulp) consisted mainly of relatively short objects, as would be expected due to the presence of parenchyma cells, parts of vessels, and other small features in delignified hardwood kraft pulp. Though some of the observed objects had length-to-thickness ratios as high as about ten, most of the particles could be described as “blocky” or “rectangular,” rather than “fibrillar.”

Figure 2 shows a representative image of secondary fines, which were obtained by refining the “retained” fraction just described, *i.e.* the bleached hardwood kraft fibers. After refining the pulp to a Canadian Standard freeness of 100 ml, the suspension was classified with a 200 mesh screen. The finer screen was employed because preliminary tests had shown that the 100 mesh screen did not effectively exclude refined fibers from the filtrate, presumably because the extensive refining had greatly increased fiber flexibility. Although some of the objects appearing in Fig. 2 may have the same origin as those in Fig. 1, *i.e.* “primary fines,” the image also shows a lot of highly fibrillated, slender, and almost transparent material. It would be expected that the refining of kraft fibers will cause some delamination of the primary and S1 layers of the fiber, and maybe the outer portion of the S2 sublayer. Indeed, images of fibers (*e.g.* Fig. 3) revealed extensive fibrillation at the fiber surfaces.

Particle size distribution of the kraft pulp fines, based on the laser light diffraction, are given in Fig. 4. As shown, the primary fines had a bimodal distribution. By contrast, the secondary fines were unimodal, and the distribution did not reach values as high as in the case of the primary fines. The difference in effective maximum sizes is consistent with the use of different size screens for the respective fractionation steps. In addition, because the laser diffraction results are affected by both the length and the thickness of the observed objects,[20] very thin, fibrillar material in the secondary fines would be expected to show up as smaller objects, compared to primary fines of equal length.

Results of water retention tests, based on the pressurized air method (see section 2.8) are shown in Fig. 5. As shown, the water retention decreased during the first 30 minutes of pressure application, but essentially the same results were obtained for pressure application times of 30 and 60 minutes. Based on these results it would appear that 30 minutes was a sufficiently long application of air so that dewatering had reached a steady state, and one would not expect the results to be affected by differences in resistance to flow of water around the cellulosic fibers or fines. As shown, the water retention per unit mass of cellulosic material was approximately 2 grams water per gram of solids, for the fibers and the fines from the same refined kraft pulp. Based on the appearance of Fig. 5, slightly higher water retention might be expected in the case of fines due to their higher external surface area and the likelihood that a film of water remains on those surfaces.

3.2 Dewatering rate affected by kraft pulp fines. As shown in Fig. 6, the secondary fines from refined bleached hardwood kraft pulp had a much larger effect on dewatering rates, compared to the same level of primary fines (from unrefined pulp). The same “default” fibers (from recycled paper) were used in all three of the tests represented in the figure. These results are consistent with those obtained in some previous studies[9,12]. The greater effect of the secondary fines is attributed to their slender shape. It is reasonable to expect that slender, fibrillar fines should be more flexible, have a higher external surface area per unit mass, and have a greater tendency to block channels in the wet paper, when compared to the more blocky shape of primary fines.

Figure 7 shows that the rate of water release slowed dramatically with increasing proportions of secondary fines. In addition, it is apparent that the rate of water release tended to slow down considerably after the first 5 to 10 seconds. The slow-down can be explained, first of all, by the absence of a fiber mat at the very beginning of the dewatering process. The process of forming a mat capable of significantly slowing the dewatering rate can be understood as having two parts. In the first part of the process, fibers long enough to be filtered by the forming screen form an initial mat. Secondly, it is reasonable to expect that fines become sieved by the mat of fibers, yielding a strong reduction in permeability, which depends on the level of fines in the mixture. As proposed earlier,[8, 9, 12] one way to explain the increased resistance to dewatering with the passage of time is by the ability of cellulosic fines to plug channels within the freshly-formed mat of fibers.

Results not shown, but corresponding to Fig. 6, were also obtained with different levels of primary fines. However, even at the 40% level of primary fines, the effect on dewatering was no greater than that with just 20% of the secondary fines. Thus, the additional test results supported those in Fig. 6 and showed that the differences between the effects of primary and secondary fines were not limited to a specific proportion of fines in the mixture.

The test results reported in Fig. 8 help to show the effect of fiber flexibility. Though, in terms of the fines content, the tests were identical to those reported in Fig. 6, the fiber fraction had been extensively refined. The freeness level of 100 ml CSF at the end of the refining process can be taken as a rough indication of the extent of refining; however, it should be kept in mind that primary fines previously had been removed from the pulp. In addition, most of the secondary fines were removed at the end of the refining process, after the freeness measurement. When comparing results in Figs. 8 and 7 it is important to note the different scales on the vertical axes; the more flexible refined fibers resulted in much slower dewatering, even when no additional secondary fines were added. The slower dewatering in the absence of fines, compared to Fig. 7, can be understood in terms of the ability of the more conformable refined fibers to form a dense mat, leaving narrower passages for the flow of water. It is notable, however, that when the fines content was raised to the 40% level, the dewatering results were about the same for the two sets of tests in Figs. 7 and 8, again indicating a potentially dominating influence of the fines fraction on dewatering rates.

3.3 Retention of kraft fines in the fiber mat. Further insight regarding the mechanism of fines effect on dewatering can be gained by considering the efficiency with which fines are collected in the fiber mat during the dewatering process. As shown in Fig. 9, there was a nonlinear trend in filtrate turbidity *vs*. fines content in the suspension. The non-linearity implies that the fiber fines had a self-retaining tendency. This can be attributed to a denser pad structure and smaller channels within fiber mats that had a relatively high proportion of fiber fines. Such a mechanism would not be expected to be as important at relatively low levels of fines, since one would expect there to be a multiplicity of alternate channels for the water to take as it passes through a fiber mat with a low level of fines. From the appearance of Fig. 9 it would appear that above a level of 30% fines content the fiber mat structure was sufficiently saturated with fines so that the filtration efficiency of the mat became notably higher.

3.4 Cellulosic fines from chemithermomechanical pulp (CTMP). In an effort to test the generality of the conclusions mentioned above, related experiments were carried out with a contrasting class of cellulosic fines obtained from CTMP. Figures 10-12 show micrographs of three different size classes of these fines. While the figures do show a considerable amount of fibrillar material, much of the fines can be described as "parts of damaged fibers." As one progresses from the R100 (retained on a 100-mesh screen) to a R200, then to the P200 fraction (in the sequence of figures), there is a trend towards smaller particles, but in all cases one sees a wide diversity of shapes.

Figure 13, which is based on laser diffraction analysis, shows relatively wide distributions of particle size. The greatest contrast was between the other samples and P200, which had a modal particle size of about 50 μm, compared to 100-350 μm for the other three fractions that were compared. Modal particle size was taken to be the highest point in the graph of each distribution. The wide distribution of size, as well as the diversity of shape can readily be understood as being a consequence of mechanical fragmentation, as the fibers are torn away from the wood chip and from each other during the refining process. Though thermomechanical pulping has been noted for achieving less reduction in fiber length, compared to stone groundwood pulping, it is clear that many fibers were shortened.

3.5 Dewatering rates affected by CTMP fines. As shown in Fig. 14, resistance to dewatering increased with decreasing modal size of the fines, which were 30% of the dry mass of solids in all cases considered. One of the best-known explanations for this kind of observation has been related to the increasing surface area per unit mass with decreasing size of particles in a filter bed.[6-8]

In order to quantify such a relationship, the smooth lines in Fig. 14 were used to estimate the amount by which different classes of CTMP fines, all at the 30% level, increased the time required to collect 700 ml of filtrate. These results were compared with the modal particle sizes obtained from Fig. 13. As shown in Fig. 15, the results fell approximately on a straight line passing through the origin. Thus, to a first approximation, resistance to dewatering increased in inverse proportion with the particle size, as estimated from the modal diameters determined by laser diffraction tests. These results can be explained in terms of a mechanism in which small, unattached fines are able to migrate through the fiber mat and get stuck in positions where they have relatively large effects on mat permeability. Smaller particles would be expected to have a larger impact, according to such a mechanism, due to their higher surface area per unit mass and due to their greater ability to change their locations relative to the adjacent fibers in the mat.

4. Conclusions

Cellulosic fines collected from unrefined bleached hardwood kraft, from refining the fiber component of the same kraft pulp, and also from chemithermomechanical pulp differed considerably, based on optical microscopy and also based on laser diffraction particle size analysis. Resistance to gravity dewatering generally increased with decreasing size of the fines. For a given mass, the highly fibrillar secondary fines from refined bleached hardwood kraft fibers caused a much greater reduction in dewatering rates than the more compact primary fines obtained from the corresponding unrefined hardwood. Results generally support a hypothesis in which fines become entrapped in the mat of fibers that is collected during a dewatering experiment. Once trapped in the fiber mat, the fines contribute to drainage resistance in inverse proportion to their size, as determined by the laser diffraction method.

Acknowledgments

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Figures

Figure 1 Micrograph of primary fines (collected before refining) from bleached hardwood kraft pulp.

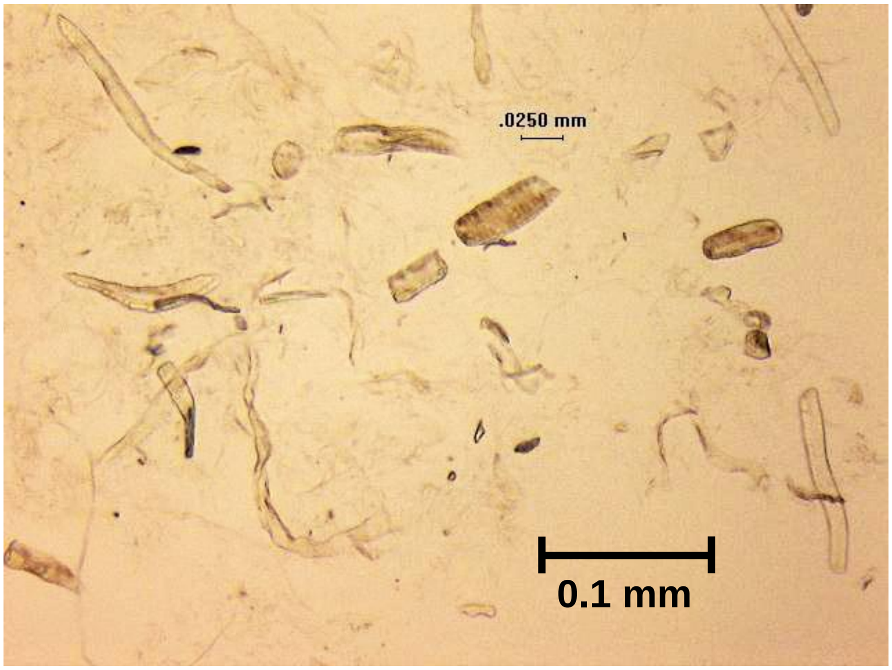

Figure 2 Micrograph of secondary fines (collected after refining fines-free pulp) from bleached hardwood kraft pulp refined to 100 ml Canadian Standard Freeness.

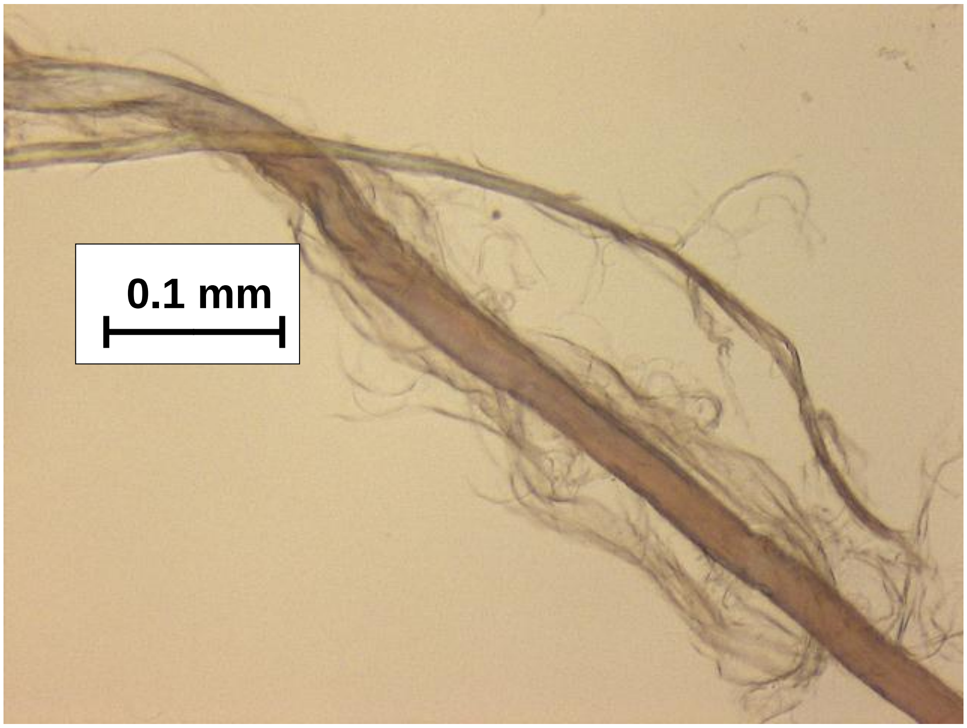

Figure 3 Micrograph of highly refined kraft fibers from the batch that was used in preparation of the secondary fines. Note the fibrillation at the fiber surfaces.

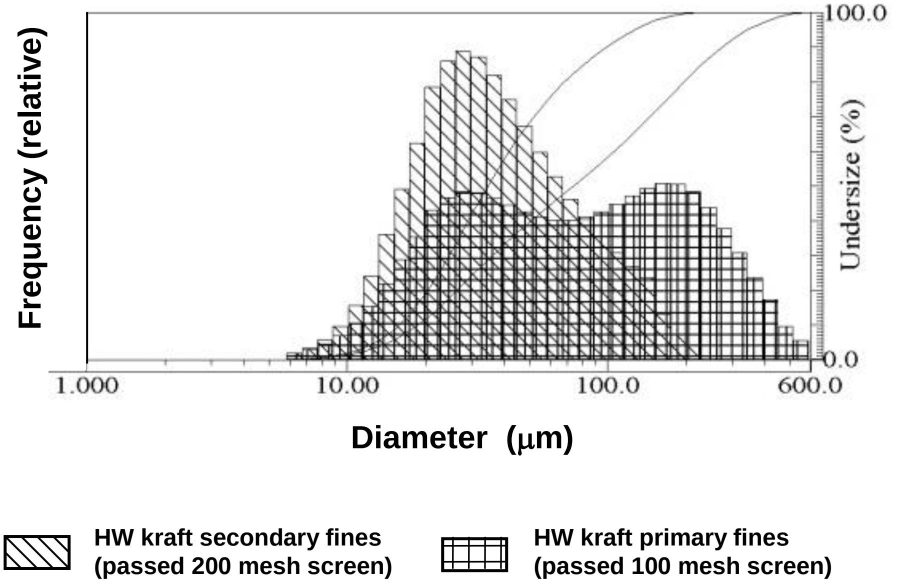

Figure 4 Apparent particle size distributions of primary and secondary fines from bleached hardwood kraft pulp, based on laser diffraction analysis.

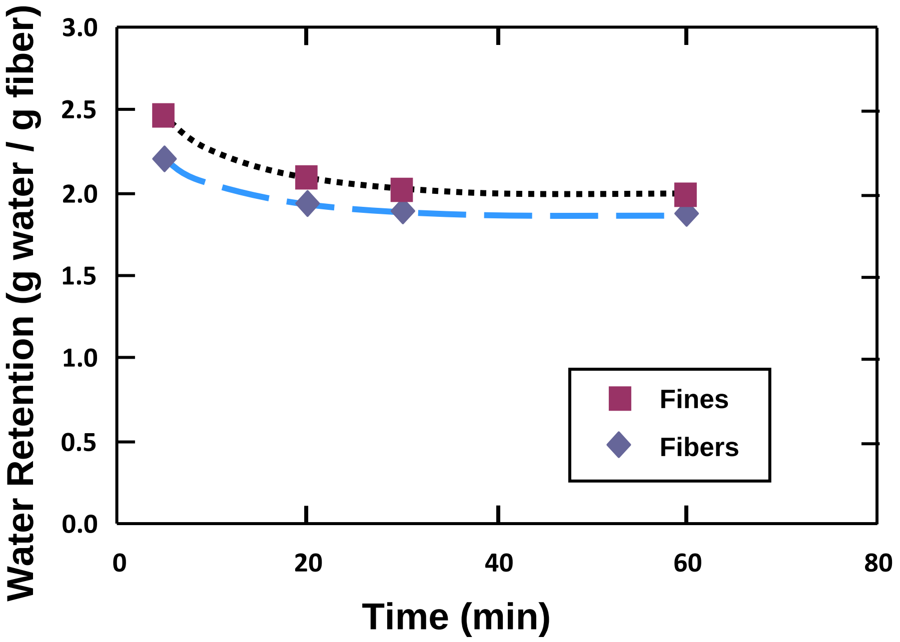

Figure 5 Results of modified water retention tests, using 68.9 kPa air pressure to remove water from between fibers or fines in a pad, followed by weighing, oven-drying, and reweighing.

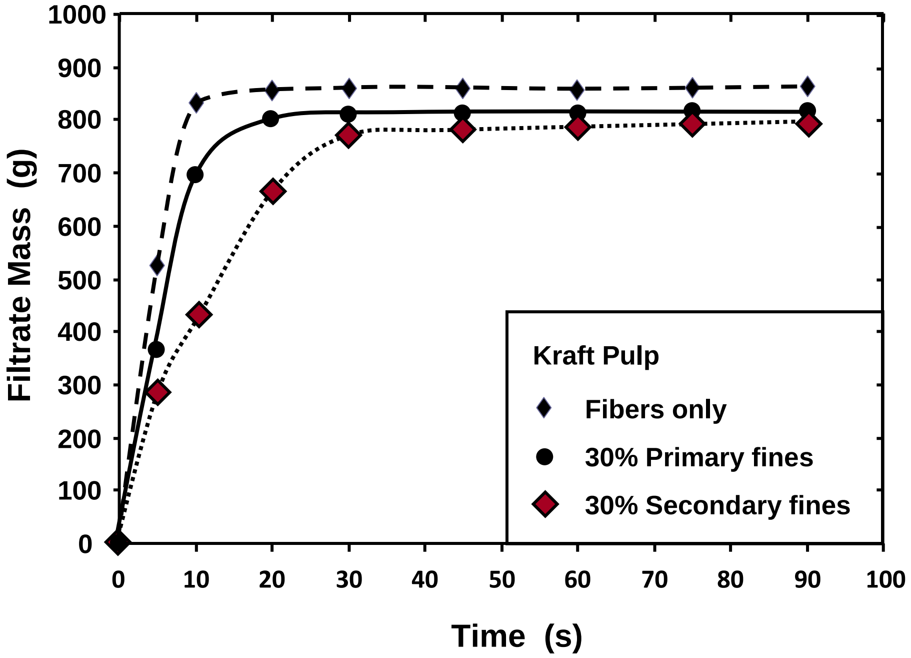

Figure 6 Gravity filtrate volume vs. time for 0.5% solids suspensions (1000 ml each) composed of 30% fines (passing a screen either before or after refining) with 70% by mass of a default sample of recycled kraft fibers.

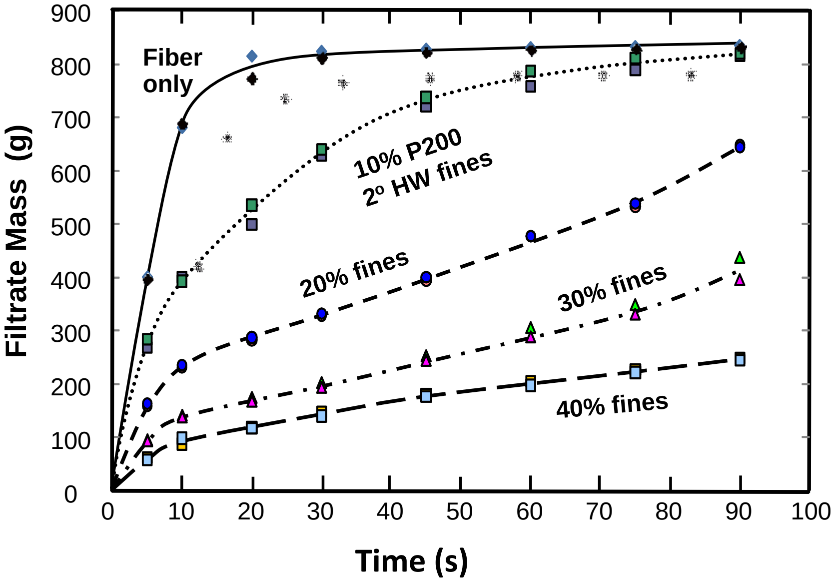

Figure 7 Gravity filtrate volume vs. time for 0.5% solids suspensions (1000 ml each) composed of different proportions of secondary fines with a default sample of recycled kraft fibers.

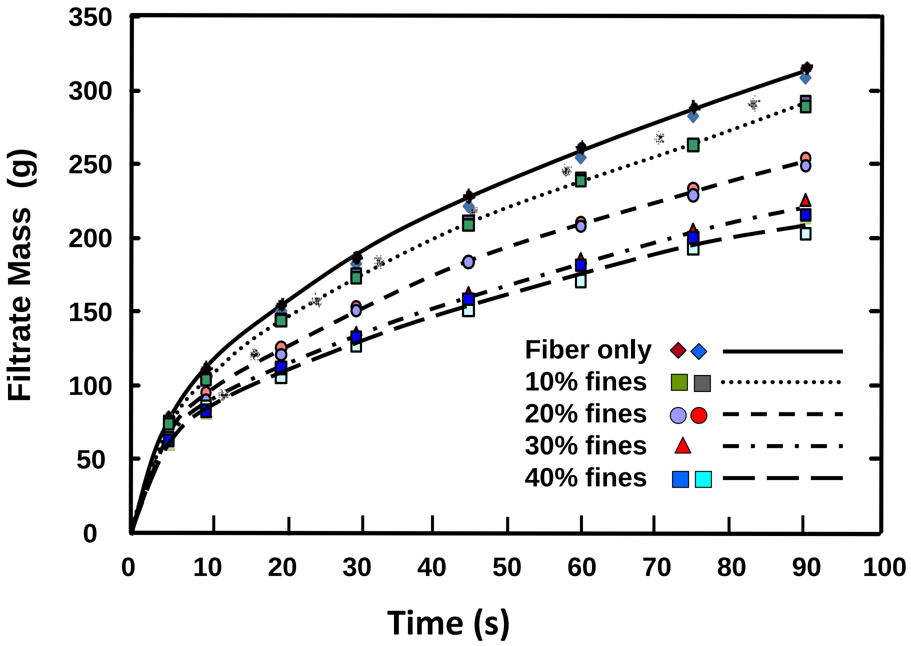

Figure 8 Gravity filtrate volume vs. time for 0.5% solids suspensions (1000 ml each) composed of different proportions of secondary fines with highly refined kraft fibers.

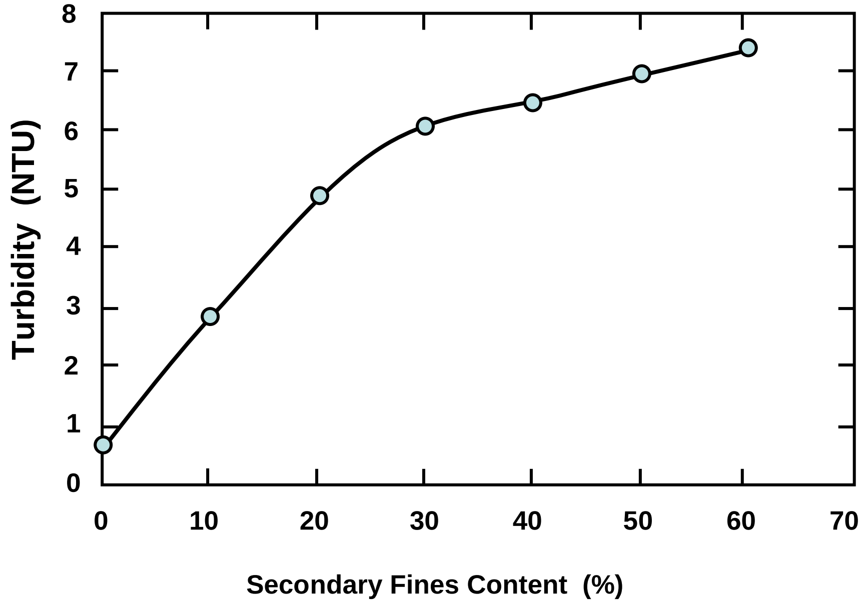

Figure 9 Effect of bleached kraft secondary fines content in the fiber slurry on the turbidity of filtrate collected after freeness tests.

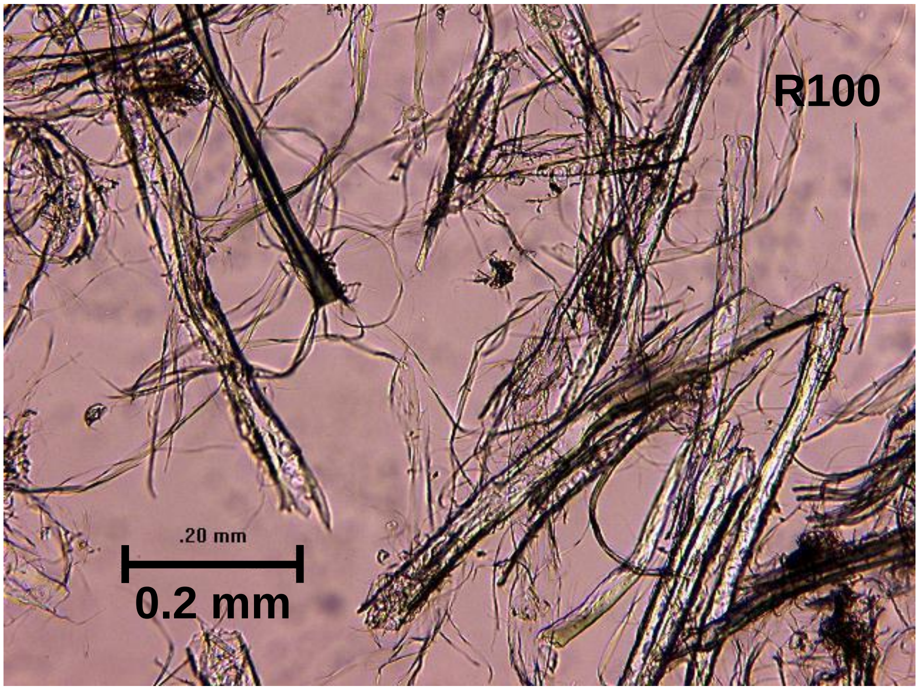

Figure 10 Micrograph of a coarse fraction (retained on a 100 mesh screen) from Bauer-McNett classification of chemithermomechanical pulp (CTMP).

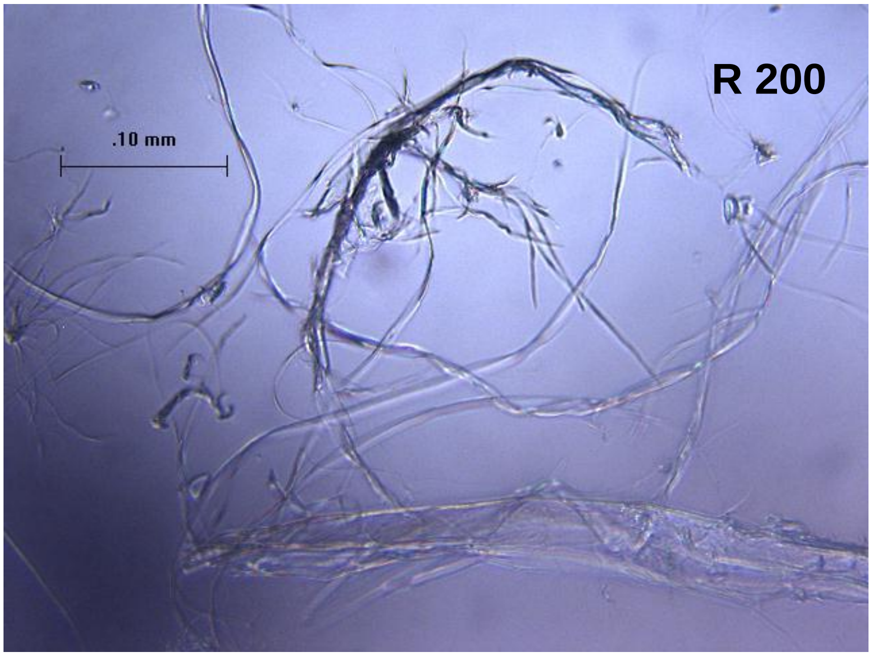

Figure 11 Micrograph of an intermediate fraction (retained on a 200 mesh screen) from Bauer-McNett classification of chemithermomechanical pulp (CTMP).

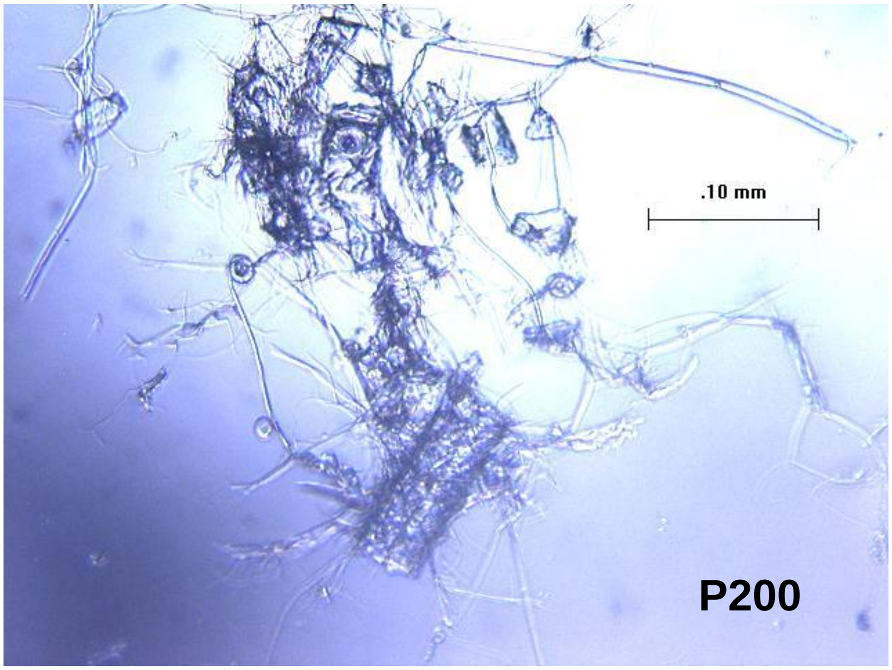

Figure 12 Micrograph of a fine fraction (passing a 200 mesh screen) from Bauer-McNett classification of chemithermomechanical pulp (CTMP).

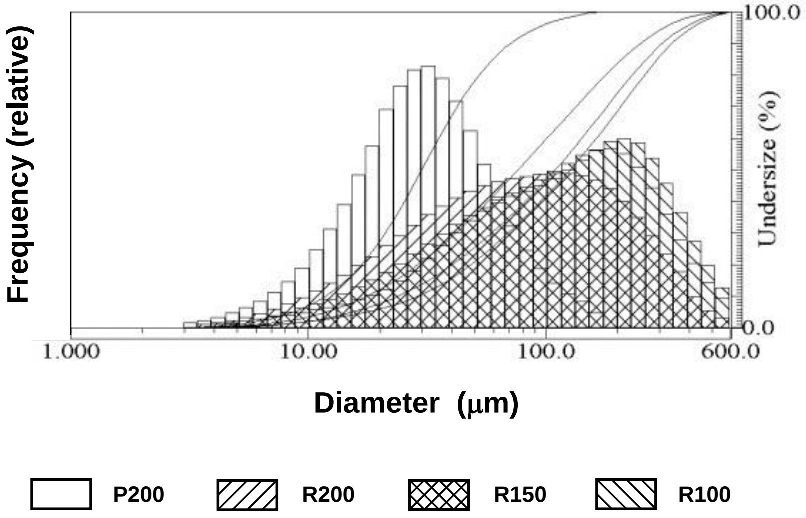

Figure 13 Apparent particle size distributions of chemithermomechanical pulp (CTMP) fractions, based on laser diffraction analysis.

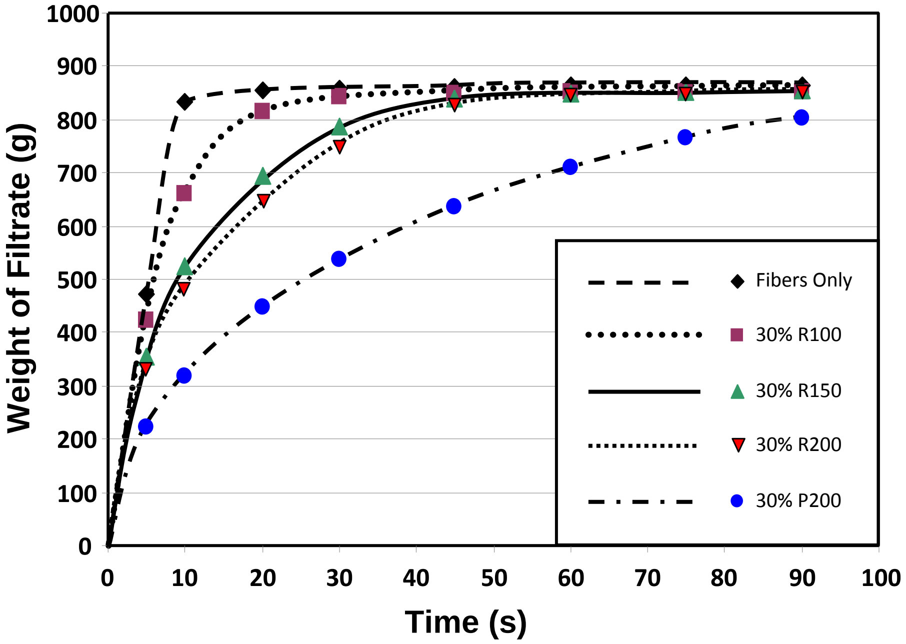

Figure 14 Gravity filtrate volume vs. time for 0.5% solids suspensions (1000 ml each) composed of different size classes of fines from chemithermomechanical pulp (CTMP).

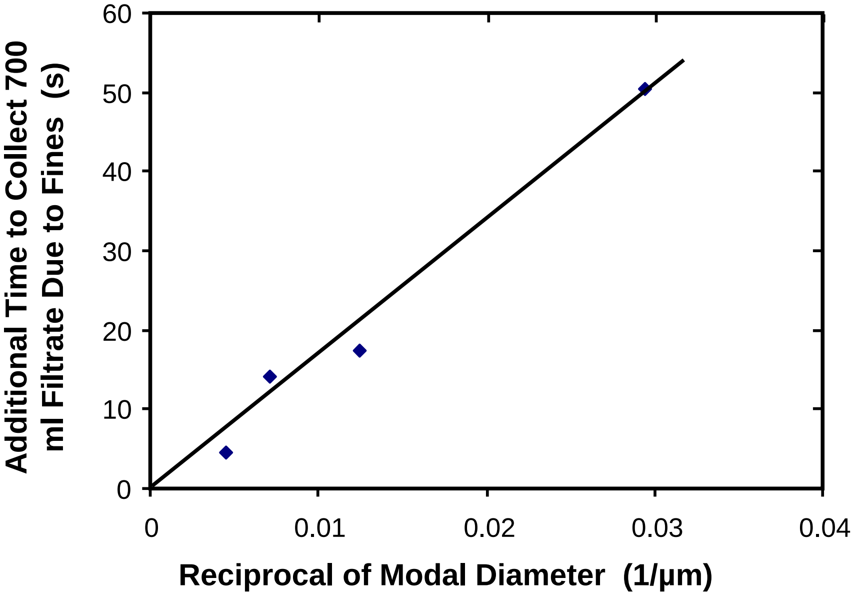

Figure 15 Plot of the effect of fines on the dewatering time to collect 700 ml of filtrate, compared with the reciprocal of modal particle size, based on laser diffraction tests. Note that the times were estimated from Fig. 7 by subtracting "7.5 seconds," the value corresponding to fibers alone.

3.2 Papers – Part 2

The effect of the extent of cellulase treatment on the drainage rate of highly refined hardwood kraft fiber suspension

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Abstract:

The mechanical refining of kraft or sulfite fibers is of critical importance in order to achieve the levels of strength required in various paper products. However, refining tends to slow down the rate of dewatering, an effect that often is attributed to the presence of fines, as well as fibrillation. The present research was designed to test a hypothesis that the pulp suspension would drain more rapidly if the fibrils on the fiber surface were removed or reduced by enzymatic treatment. We used highly refined hardwood kraft pulp as our resource, and treated it with cellulase from *Trichoderma ressei*. Dewatering tests showed that the drainage rate increased substantially after a brief exposure to cellulase, but decreased if the reaction was continued for a long period. The mechanism could be explained based on the

enzyme’s ability to clean the surface of the highly refined fiber surface, which initially resulted in a rapid drainage rate; however, as the treatment time was increased, the cellulase cleaved fibrils from the fiber surface, generating fine materials which could migrate freely in the pulp, plug drainage channels, and lead to increased dewatering time. After yet longer treatment times, the generated fines were eliminated by the enzyme and drainage rate increased again. Micrographs and results of particle size distribution analysis also confirm this conclusion.

1. Introduction:

Recently, interest in the application of enzymes in the pulp and paper industry has increased considerably. Utilization of cellulase and hemicellulase to improve the drainage rate (1, 2, 3) is one of the most promising applications of enzymes. With higher drainage rates, paper machines are able to operate faster and also may require less energy for evaporation in the dryer section. Besides increasing drainage rate by modifying the fiber surface, enzymes also have been used to improve deinking, bleaching (4, 5), and pitch removal from sulfite pulp (6).

Although the mechanisms are not completely understood, several studies have been carried out to explain the effect of enzymatic treatment on the increased drainage rate. Mooney et al. (7) reported evidence indicating that increased drainage results from selective digestion of the higher specific surface cellulose microfibrils from the fiber surface. Pommier et al. (1,2) reported that cellulase likely attacks the surface of the fibers, producing a peeling effect, which could clear fibrillation from the fiber surface. If this peeling effect is limited and well controlled, the enzyme will only remove some small colloidal components that have an affinity for water. This reduction of the pulp–water interactions will allow better drainage of the pulp without affecting the final mechanical properties of the paper. It has been reported that the drainability of mechanical pulp can also be enhanced by the addition of hemicellulases. Many different cellulases and hemicellulases have been found to improve freeness. Karsila et al. (8), claim that xylanase improves the freeness of deinked recycled pulp while having no detrimental effect on fiber tensile strength properties. Fuentus and Robert (9), show that a mixture of xylanase and cellulase enzymes at low concentrations markedly increases the freeness of recycled fibers without substantially reducing yield.

Mill trials have been carried out successfully using a commercial *T. reesei* enzyme mixture called Pergalase A40 (2). It was found that the mixed xylanases and cellulases in the product peel the surface of the fibers. If treatment is limited, the enzymes remove only elements those have a great affinity for water but which contribute little to inter-fiber bonding potential. By selectively removing these surface components, pulp-water interactions are reduced and drainage increases without noticeable changes in the final mechanical strength properties of the pulp. If the treatment is extended, however, fibrillation becomes pronounced and drainage decreases. If large quantities of crude enzymes are used, the average fiber length is reduced, fines disappear, and the strength properties of the fibers are lost. Therefore, an optimum level of enzyme treatment is required.

2. Materials and Methods

2.1 Preparation of default fibers. Except where noted otherwise, the (fines-free) fibers used throughout the study were prepared by dispersing torn pieces of 20lb, 84 brightness, 35% recycled content xerographic copy paper and then collecting the fiber fraction using a Bauer-McNett classifier with a 100-mesh screen (see TAPPI Method T233). The classifier was run for 15 minutes during each batch treatment, and the filtrate passing through the screen was discarded.

2.2 Preparation of highly refined hardwood bleached kraft pulp. The highly refined fiber was prepared from dry-lap hardwood bleached kraft pulp from a local paper mill. The pulp sheets were first torn into *ca.* 5 cm square pieces, soaked for a few minutes in tap water, and then disintegrated in tap water according to TAPPI Method T205. After that we eliminated the "primary fines" by use of a 100-mesh screen in the final chamber of a Bauer-McNett classifier (see TAPPI method T233), the highly refined fibers were prepared by taking the material retained by the 100-mesh screen (*i.e.* fines-free bleached hardwood kraft pulp) and refining it extensively with a laboratory Hollander beater (TAPPI Method T200) to a Canadian Standard Freeness (TAPPI Method T227) of 100 ML. The mixture was then placed in the final chamber of the Bauer-McNett classifer, only this time a 200-mesh screen was used. The finer screen was used based on preliminary observations that the high level of refining rendered the fibers so flexible that they were able to pass through a 100-mesh screen.

2.3 Enzymatic treatments. Commercial cellulase from Trichoderma ressei was applied to highly refined pulp at 0.1% based on OD pulp, and the cellulase was diluted (10% of the total reaction weight) before being added to the pulp, so that better dispersion was achieved. The pulp was diluted to 5% consistency and the pH was adjusted to 5.5. Enzymatic reactions with the pulp were allowed to occur at 50 C for 3, 6, 9, 12, and 24, hours respectively. To finish up the trials, the enzyme was deactivated by increasing the pH to 10. Enzyme dosage and reaction time should be carefully controlled. High dosages of enzyme and long reaction times will destroy the fiber length.

2.4. Microscopy. Optical microscopy was carried out with an Olympus BH2 microscope, using a 20X objective. Images were recorded with a TV camera. Dimensions were calibrated with a standard millimeter scale. Samples were placed onto glass slides at various dilutions, with the goal of being able to simultaneously view 10-100 particles in one field, while at the same time avoiding excessive contact or overlap among the particles.

2.5. Particle size analysis. The apparent particle size distributions of cellulosic fine matter were determined with a Horiba LA-300 laser diffraction device. This apparatus measures the intensity of laser light that is scattered at various fixed angles relative to the transmitted light through a dilute suspension. Concentrations of fines samples in water were adjusted so that the percent transmittance of light was within the specified range. The sample was recirculated with ultrasonification for one minute before the measurement. Particle size distributions were calculated on an effective surface area basis.

2.6. Water release vs. time. Gravity drainage tests were conducted with a portable modified Schopper-Riegler test device donated by Buckman Laboratories International, Inc. The essential parts of this apparatus match those in the standard Schopper-Riegler test specification (ISO 5267/1, BS 6035/1 and SCAN C19), except that a single, large opening is provided at the base of the collection cone for the filtrate. Also, a 100-mesh stainless steel screen was used. Suspensions were prepared with sufficient Na_2SO_4 so that the solution conductivity was 1000 μS/cm, and dewatering tests were done at room temperature (*ca.* 24 ^{o}C). Cellulosic suspensions were prepared at a solids content of 0.5%; in other words, the total amount of cellulosic material was kept constant, even when the fines levels were varied. The suspensions were stirred with an impeller at a fixed, moderate speed for 30 seconds (or another fixed period in certain sets of tests) before adding the suspension to the top part of the test device. The amount of filtrate was determined with an electronic balance as a function of time after releasing the suspension and allowing it to impinge onto the screen.

3. Results and discussion:

3.1 Dewatering test: As shown in Fig 1, the drainage rate increased significantly when the highly refined fiber was treated by the cellulase. However, when the enzymatic treatment was carried out for an extended time, which was 9 hours in our experiment, a decrease in drainage rate was observed. Treatments for yet longer times again increased the drainage rate, reversing the effect observed at 9 hours. One of the best explanations for these observation is that the highly refined fiber has a large surface area per unit mass of solids, which can substantially reduce the drainage rate. It is proposed that cellulase, when it was first added, was especially effective at digesting the most finely divided fibers, which might be described as a polysaccharide gel layer; this digestion cleaned the fiber surface and reduced the surface area, thus increasing the drainage rate. At larger treatment times it is proposed that the cellulase cleaved fibrils from the fiber surface. This action was most effective at points of damage, such as kink points, where the crystalline structure of the cellulose was most disturbed. However, even the un-kinked sections of the generated fines (as well as still-intact fibrils) were solubilized following a sufficiently long exposure to enzymatic treatment.

3.2 Morphology of fiber after different treatment. The default fibers before and after cellulase treatment were characterized by light microscopy and laser diffraction particle size analysis. As shown in Fig. 2, the default fiber obtained from hardwood bleached kraft pulp had a clean surface with a uniform width. The smaller specific surface area would be expected to result in a higher drainage rate compared to the fibrillated fibers. Fig. 3 shows a representative image of highly refined fibers, which were obtained by refining the “retained” fraction that did not pass through the 100 mesh screen as just described, *i.e.* the bleached hardwood kraft fibers. After refining the pulp to a Canadian Standard Freeness of 100 ML, the suspension was classified with a 200 mesh screen. The images of fibers revealed extensive fibrillation at the fiber surfaces. Fig. 4 shows an image of a fiber after 3 hours of cellulase treatment. It is apparent that the density of fibrils became lower and some areas resembled the surface of unrefined fibers. One can still observe some fibrils remaining on the fiber surface; however, the fibrils were thinner and shorter and resulted in a cleaner surface compared to the surface of highly refined fiber.

Microscopic analysis provided evidence that cleaning of the fiber surface occurred. Fig. 5 shows an image of fiber after 9 hours of cellulase treatment. The surface became uneven again and one can observe fines in the fiber suspension as well. As shown in Fig. 6, some fine materials with a diameter of 20 nm were observed. Because the fiber was retained by a 200 mesh screen, the smaller particles must be generated during the enzymatic treatment. Fig. 7 shows the image of fiber after 24 hours of cellulase treatment; not only have fines generated early in the suspension been eliminated, but hairy fibers with slender fibrils have been produced. This kind of evidence indicates that cellulase could continue to work effectively and create fibrils on the surface, but the extent of the peeling action is not as extensive as the mechanical refining. If one puts the microscopic pictures in time sequence, as shown on Fig. 8, one can clearly observe the changes on fiber surface as we have already described earlier.

3.3 Particle size distribution analysis. After the dewatering test, the filtrate was collected and particles size distribution analysis based on laser diffraction was carried out. As shown in Fig 9, the particle size was reduced from 27 µm to 12 µm in the first 9 hours; this means that fines were being generated but at the same time the fines were being attacked by the cellulase. The enzymes are suspected to be absorbed at a higher amount per unit mass on those materials that have a higher specific surface area. This means that the fines are attacked preferentially, followed by degradation of the microfibrils, and the long fibers become substantially degraded after a yet longer time of treatment. As the cellulase treatment continues, the size of fines becomes smaller, which corresponds to the result of the dewatering tests and microscope pictures.

4. Conclusion:

Cellulase treatment of the fiber surface significantly affects the drainage rate of highly refined cellulosic fiber suspensions. The mass of filtrate shows a rapid initial increase, with a relatively small amount of enzyme dosage, but the treatment time should be well controlled, since extending the reaction time with large concentrations of enzyme is detrimental. Microscopic pictures suggest that at the beginning, fibrils are eliminated gradually and the fiber surface becomes clear. More fines or debris are continuously generated by degradation of the fiber because of the enzymatic effect. In particular, the level of fines increases when the time of enzymatic treatment is just sufficient to cleave fibrils from highly fibrillated fibers surfaces. However, as the reaction continues, the fines are consumed by cellulase.

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9. Fuentus, J. L.; Robert, M. European Patent 262040, 1998

Figures

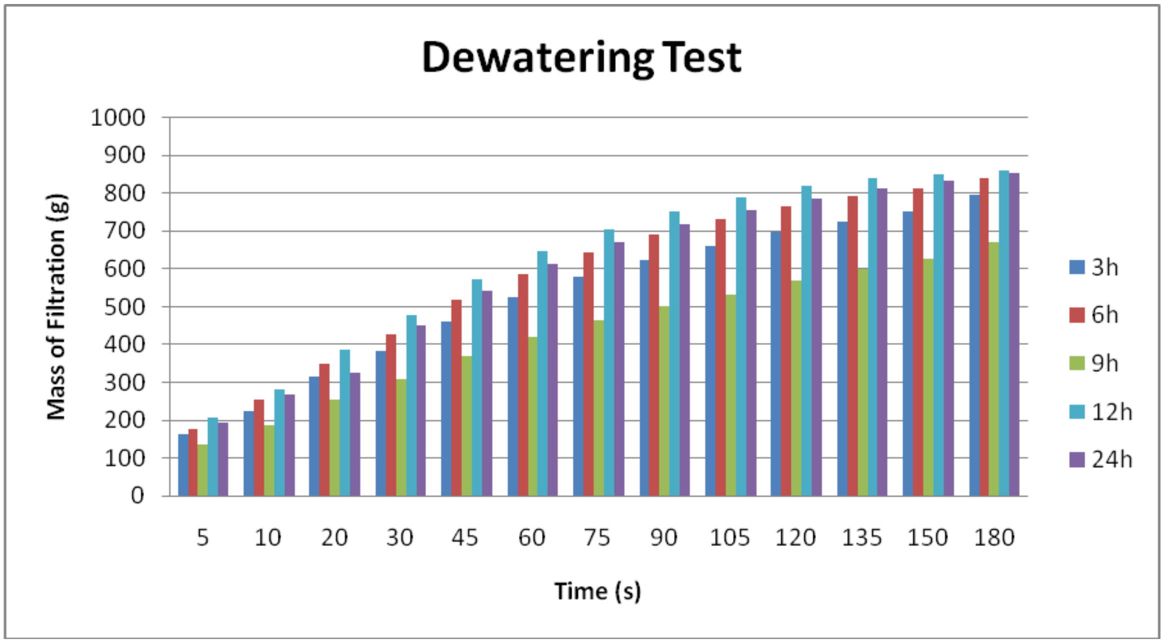

Figure 1 Gravity filtrate mass vs. time for 0.5% solids suspensions (1000 ML each) obtained after different enzymatic treatment time.

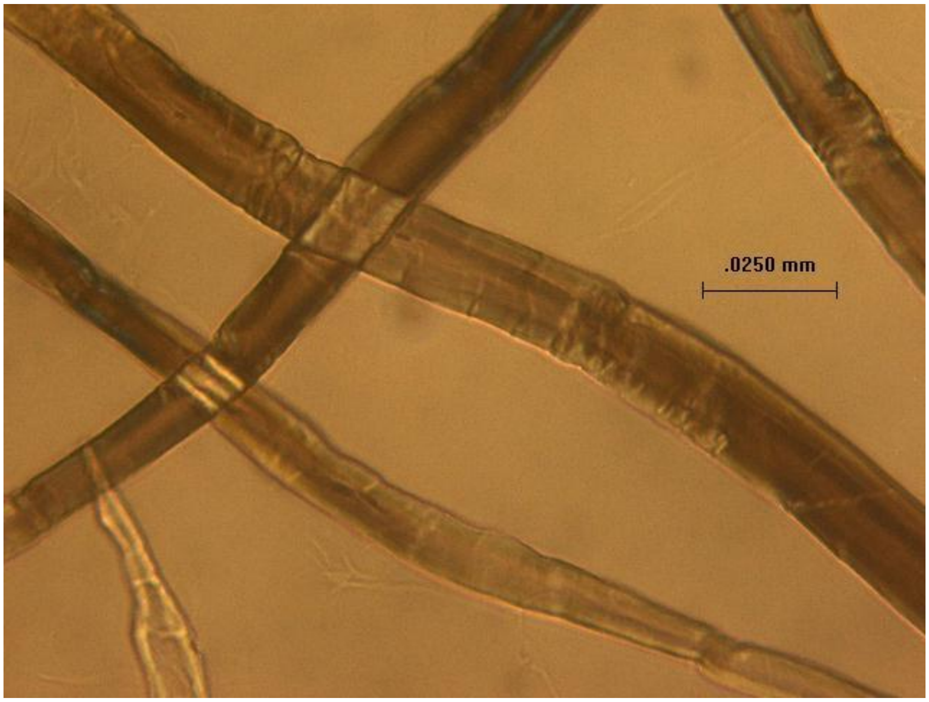

Figure 2 Micrograph of default fiber (collected before refining) from bleached hardwood kraft pulp.

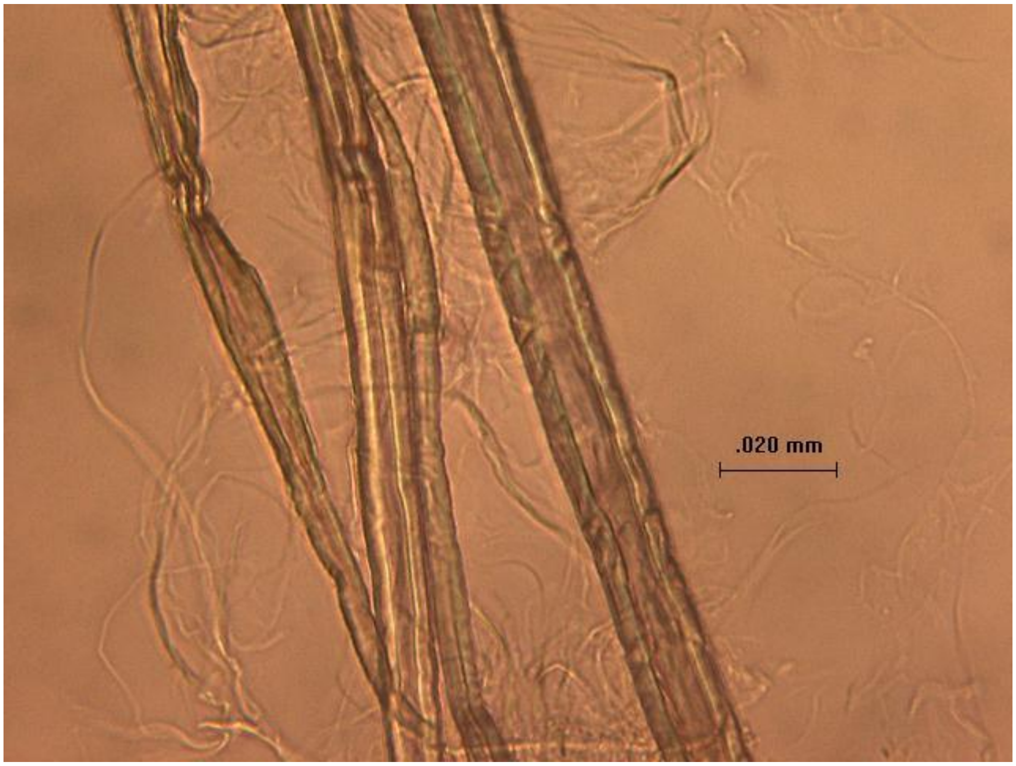

Figure 3 Micrograph of highly refined kraft fibers from the batch that was used in preparation of the secondary fines. Note the fibrillation on the fiber surfaces.

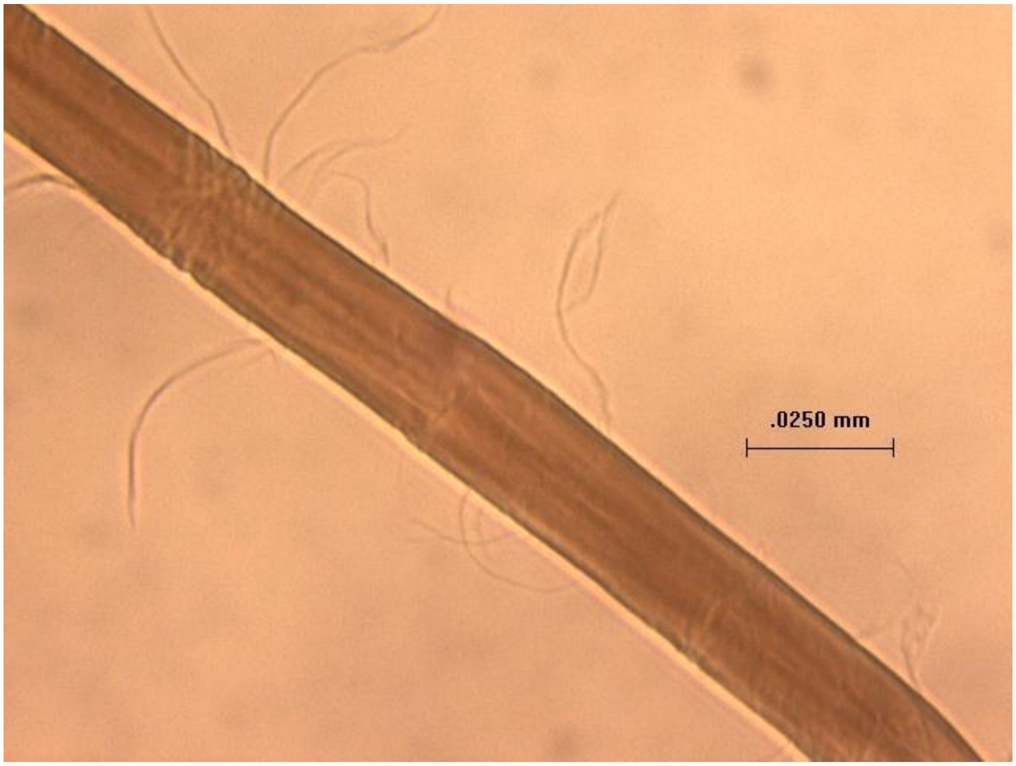

Figure 4 Micrograph of highly refined kraft fibers after 3 hours enzymatic treatment.

Figure 5 Micrograph of highly refined kraft fibers after 9 hours enzymatic treatment.

Figure 6 Micrograph of fine particles generated in highly refined kraft fibers after 9 hours enzymatic treatment.

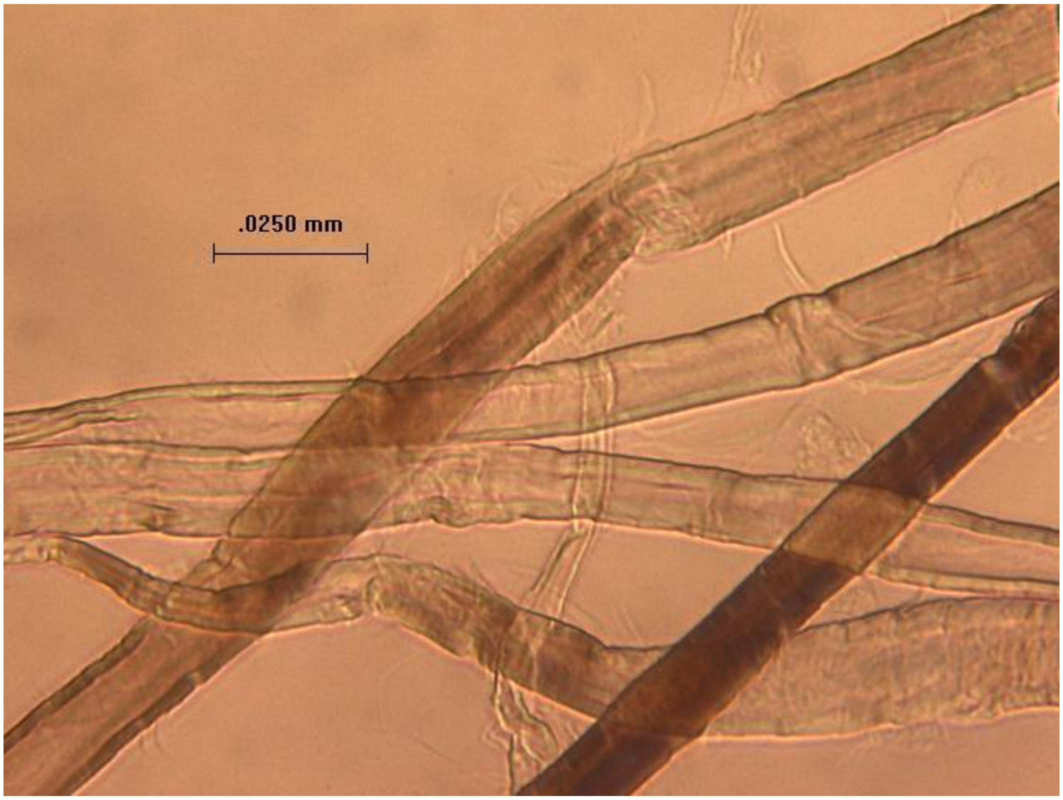

Figure 7 Micrograph of highly refined kraft fibers after 24 hours enzymatic treatment.

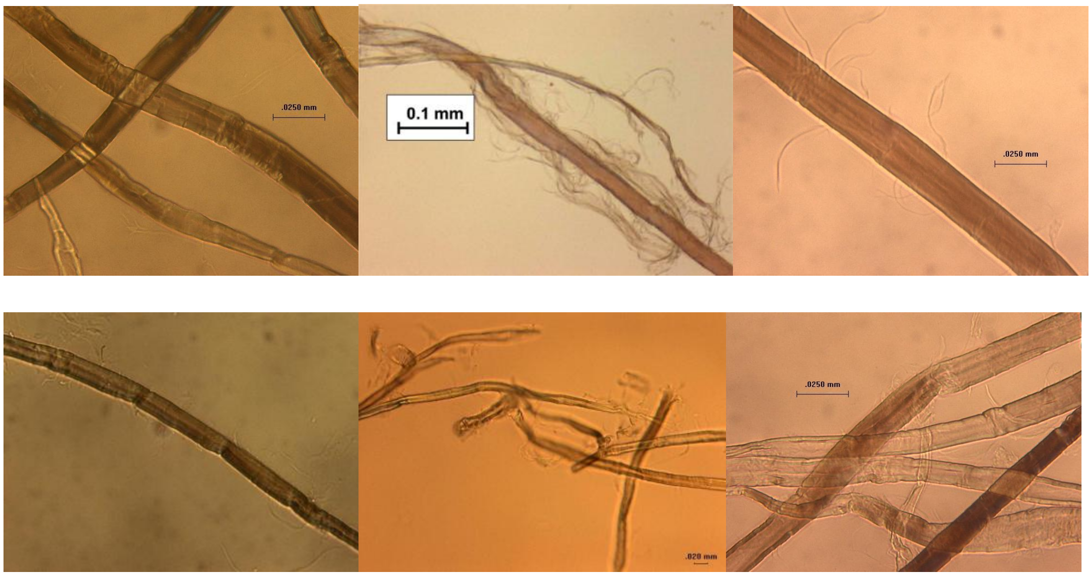

Figure 8 Micrograph of highly refined kraft fibers after a certain time of enzymatic treatment. The time sequence shown is as follows (starting with the upper left): Default fiber, highly refined fiber (no enzyme treatment), 3 hours enzymatic treatment, 6 hours treatment, 9 hours treatment, and 24 hours treatment.

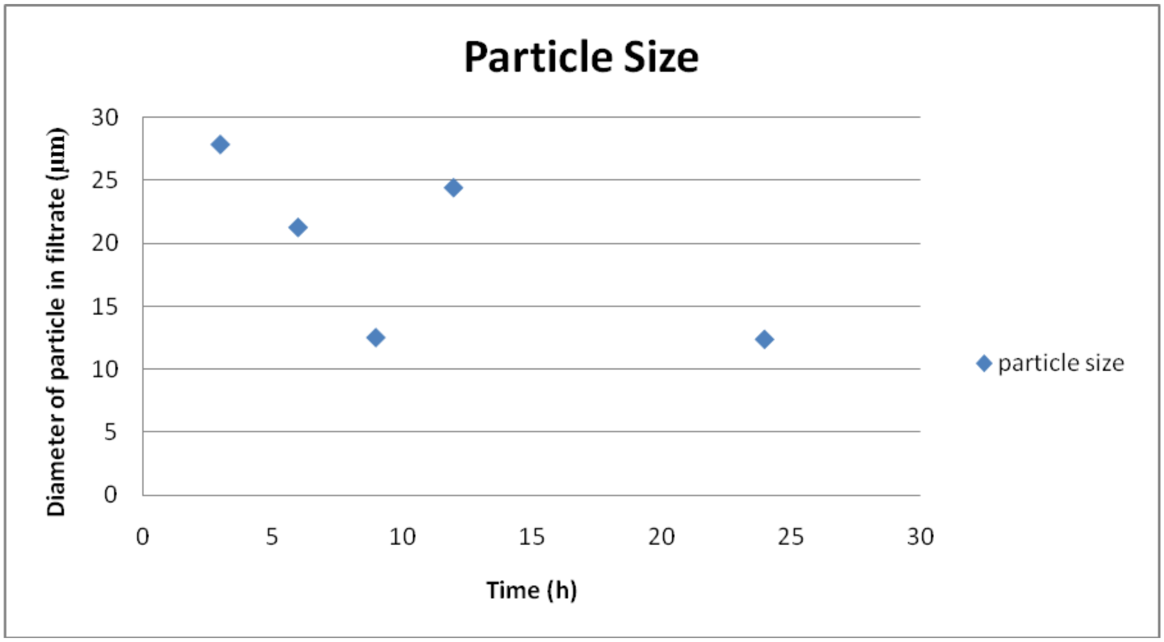

Figure 9 Particle size distribution of fines in filtrate after different cellulase treatment time.

4. CONCLUSIONS

In addition to the more specific conclusions provided in the preceding two main sections, corresponding to submitted research articles, it is possible to summarize some of the main conclusions as follows:

1. Cellulosic fines collected from unrefined bleached hardwood kraft and from refining the fiber component of the same kraft pulp differed considerably in shape and effect on drainage rate. Resistance to gravity dewatering generally increased with decreasing size of the fines. Secondary fines, which were obtained by refining of bleached hardwood kraft fibers, had much greater effects on dewatering in comparison with primary fines, which were obtained from unrefined bleached hardwood kraft pulp.

2. Results were explainable by a mechanism in which unattached fines are able to move relative to adjacent fibers during the dewatering and consolidation of a mat of fibers. Due to such movement, fines end up in locations where they plug drainage channels in the mat.
3. Cellulase treatment on the fiber surface significantly affects the drainage rate of highly refined cellulosic fiber suspensions. Freeness shows a rapid initial increase, with a relatively small amount of enzyme dosage. Microscope pictures suggest that, at the beginning, fibrils are eliminated gradually and the fiber surfaces become clear, which initially results in an increased drainage rate.

4. As the treatment time was increased, the cellulase cleaved fibrils from the fiber surfaces, generating fine materials which could migrate freely in the pulp, plug drainage channels, and lead to increased dewatering time. After yet longer treatment times, the generated fines were eliminated by the enzyme and drainage rate increased again. Micrographs and results of particle size distribution analyses also confirmed this conclusion.

5. Enzymatic modification is a promising method to increase drainage rate, but the treatment time should be well controlled, since extending the reaction time with large concentrations of enzyme can be detrimental.

5. SUGGESTIONS FOR FUTURE RESEARCH

The results obtained in this study have raised several questions that related to the fines behavior in the suspension and effects on physical properties of paper made from enzymatically modified fibers.

The following list suggests a few topics for future research that may help in further understanding the characteristics of fines and the pattern of action of enzymes on papermaking fibers.

1. I have already demonstrated that the secondary fines have a large impact on drainage rate compared to primary fines. However in reality the pulp consisted of all kinds of fine materials which have a broad size distribution. It is important to make model fines of different size and combine them together at different ratios to determine more precisely their effect on drainage rate.
2. My work showed evidence to support a model in which fines follow the flow of water and get stuck at locations where they cannot pass through the fiber mat. I concluded that the smaller the fines, the larger decrease in the drainage rate. It would be interesting to investigate the other extreme. What would happen if the size of fines was so big that it could not be carried freely within a channel and it was caught at the initial stage of the dewatering process? And what if the fines had such a large size and density so that they deviated significantly from the streamline trajectory and therefore collided with fiber surfaces? Furthermore, work is needed to explore the

possibility that a class of fines might be so small that they can pass through the smallest openings in a fiber mass and not become trapped to a significant extent.

3. My microscopic pictures clearly showed that fibrils were eliminated in the beginning of enzymatic treatment which resulted in more rapid drainage, however an extended treatment can reduce drainage rate since continuous enzymatic hydrolysis would cause fiber degradation and release of new fines. Could we find other methods to support our finding and further prove this hypothesis? One possible approach might be to use an HPLC method to detect the extent of hydrolysis by measuring reduced sugar.
4. My research showed that we can make the water release from fiber suspension easier by well controlled enzymatic modification. Such situations are favorable to reducing required energy. Another issue we should not ignore is the physical properties of papers. A study should be designed to connect these two parts.