Effect of pH and enzymes on strength of recycled fibers during refining

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ABSTRACT: Recycled fiber-based papermaking in America is experiencing a persistent reduction in the strength of the incoming fiber. To maintain paper strength properties, paper mills respond by increasing basis weight, dry strength, etc. On average, the fiber cost component in recycled paper is approximately 40% of the total manufacturing cost. Increased fiber weight results in higher operating cost and has a negative effect on production rate, especially on dryer-limited paper machines. Increased pH and use of certain enzymes can improve strength during subsequent refining. The ProLab refiner was used to generate laboratory refining curves to evaluate changes in fiber bonding. The effect of pH and enzymes pretreatment on the strength development and change in drainage of recycled fibers with refining was evaluated.

Application: This study can demonstrates potential uses and net positive effects of enzyme treatments of recycled fiber.

Papermaking fibers can either be sourced from the trees and nonwood species or recovered from existing paper products. The recovery of fiber from existing paper products involves collecting used paper materials and processing these materials in a pulp mill. Paper collection involves gathering used paper products from end users into centralized facilities. The paper in the collection centers is separated from extraneous materials, such as metals, plastic, and food. The paper products are then sorted by fiber type and quality and sent to mills in bale form where the recycled paper is mechanically defibrated in a hydropulper. The resulting pulp slurry is sent through coarse screens to remove plastic and other foreign materials. Fine screens and hydrocyclones may be used to remove fiber clumps, flakes, coating pieces, etc. This equipment also may be used to fractionate fibers by length. The strength of the resulting fibers may be augmented by mechanical treatment in refiners and by strength aids such as starch and other dry strength polymers.

Refining involves passing the fibers through a narrow gap between rotating discs that have metal bars and grooves on the surface of each disc. The refining action produces fibrils on the surface of the fibers, which significantly increases the total fiber surface area and, thereby, the inter-fiber bonding. The increase in strength from higher inter-fiber bonding is limited by fiber damage and cutting during refining. Paper strength is reduced each time paper is reused [1]. A potential cause for the strength reduction with reuse of paper has been attributed to fiber hornification [2-5]. When chemical pulp fibers are dried, either in sheet or pulp form, the internal fiber volume shrinks. If the fibers are rewetted in water, the original water-swollen state is not regained. The physical change manifested by this inhibited reswelling is termed "hornification" [6]. The potential mechanisms for hornification tend to fall into two categories; either some of the hydrogen bonds are stabilized and are retained after rewetting [7] or some of the fibrils and fibers are covalently bonded, and the bond cannot be broken when water is added to the dried pulp [5]. Refining may be used to promote fiber swelling; however, refining tends to generate fines, which inhibit drainage. Refining might also result in fiber damage, which reduces the strength potential of the pulp and ultimately that of the resulting paper.

Certain classes of enzymes are used to improve fiber swelling, which can increase OCC strength. Fibril separation may be aided by breaking the inter-fibril bonds with cellulases and hemicellulases [8]. Within cellulases are three broad families of enzymes: 1) endocellulases, 2) exocellulases, and 3) beta-glucosidases. The endocellulases react with cellulose in amorphous regions. The exocellulases react with cellulose chain ends and cleave mono and dimeric groups. The beta-glucosidases are significantly smaller enzymes and can only hydrolyze mono and dimers to glucose [9]. Generally, endocellulases and exocellulases tend to be used in enzymatic strengthening of pulp. Depending on the mechanism of the enzyme reaction, some of the charge end groups also might be destroyed, which results in a net reduction in fiber charge, fines, colloidal material, and dissolved organics, all of which help improve the efficacy of wet end chemicals.

Certain oxidases are used to create aldehyde end groups in lignin, which can then bond with cellulose and other polymers [10].

Recycled pulp contains hydrophobic materials. Sources of hydrophobic content include wood extractives (fatty acids, fatty acid esters) and defoamers present in the pulp slurry or binders and glues added to paper (e.g., PVAc, styrene, acrylate components) [11]. If the pulp has significant hydrophobic

Parameter	Value
Rotor diameter, mm	184
Pulp consistency, %	3.5
Pulp flow, cc/s	1500
Rotational speed, rpm	2200
Filling gap, mm	0.2
Specific refining energy rate, kW.h/ton per min	12.2

I. Technical specifications of the ProLab laboratory refiner

loading, this might interfere with the formation of hydrogen bonds. Certain lipases may be used to break down the hydrophobic materials in pulp [12].

Changes in certain process variables tend to promote fiber fibrillation with minimum fiber damage. These include a reduction in refining intensity by an increase in the number of bars on the refiner plate, an increase in pulp consistency during refining; an increase in temperature and/or pH to increase fiber swelling and flexibility, and the treatment of the fibers with certain enzymes before refining.

EXPERIMENTAL METHODS

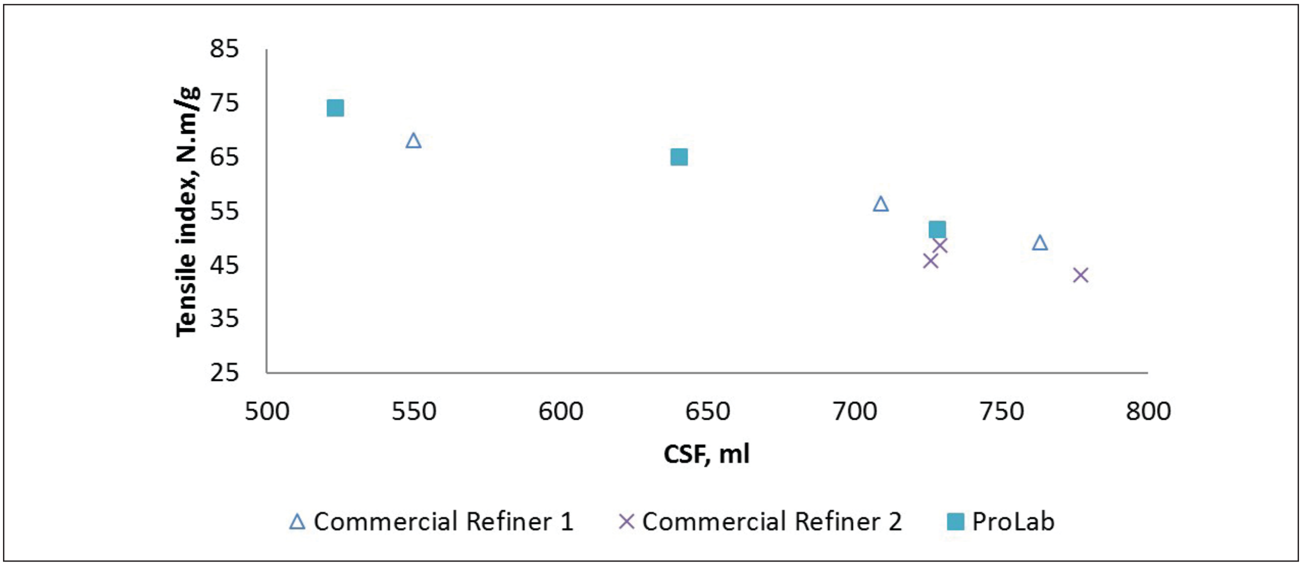
The ProLab refiner (Valmet; Espoo, Finland) [13] used in this study is located at the WestRock R&D Laboratory (Richmond, VA, USA). **Table I** shows some of the technical specifications of the refiner. The disc refiner plates used in this study were supplied by AFT (Sherbrooke, QC, Canada) and were designed to simulate the refiner plates at one of the company's recycle mills. This laboratory refiner is able to closely match the performance of commercial scale refiners (**Figs. 1 and 2**) [14].

The laboratory refiner's rotor is moved axially to adjust the refiner plate gap, and the stator plate axial position is fixed. The axial position of the rotor plate is determined by an inductive position sensor. The axial position for zero gap is determined with the refiner running dry at 1500 rpm; a vibration sensor is used to indicate plate clashing. The gap between the refiner disc fillings is calculated by the relative axial distance of the rotor from the zero position. All the refining runs for this work were done at a fixed plate gap of 0.2 mm.

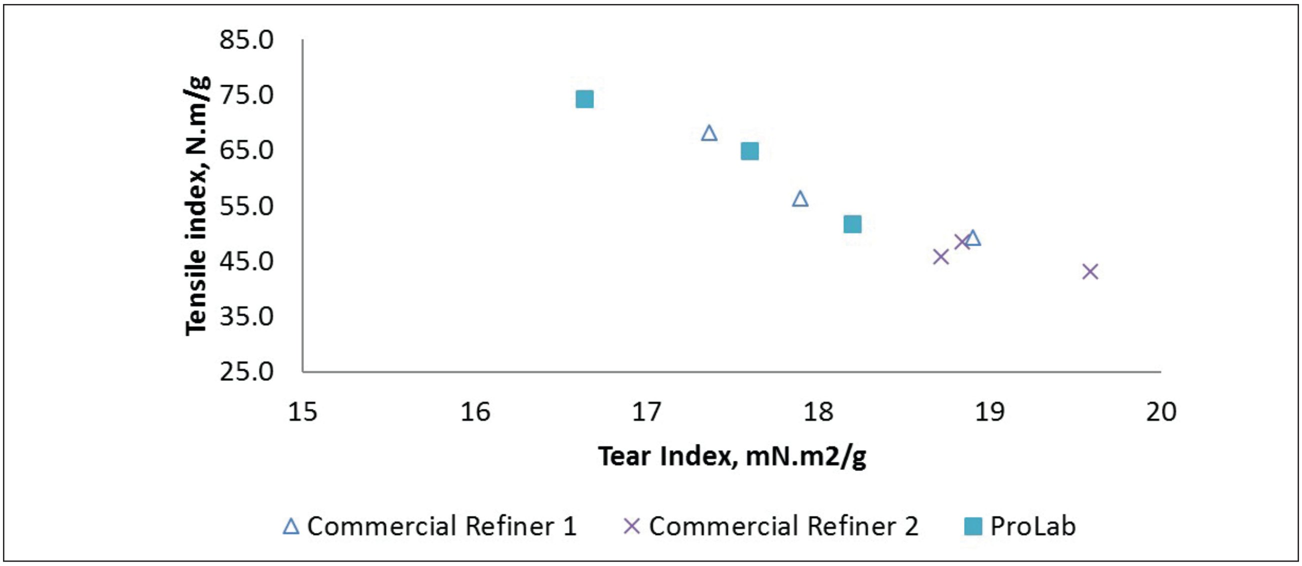
This study used old corrugated container (OCC) pulp obtained from a WestRock pulp mill at about 25% consistency. The pulping process included coarse screening, fine screening, hydrocyclone treatment, and thickening. The pulp was diluted to 3.5% consistency before pretreatments for pH and enzyme application. Treatment for each process was applied at 120°F for 1 h. For this study, the same set of refining conditions (refiner plates, revolutions per minute, and flow) were used to maintain similar refining intensity and specific refining energy. The refiner has a 40 L feed tank. The pulp was recirculated through the refiner back to the feed tank. The specific refining energy was increased about 0.62 horsepower days/ton (hp-d/ton) per minute of refining. The pulp was sampled at different times, which corresponded to a range of 0 to 3 hp-d/ton at 0.5 hp-d/ton increments.

Canadian standard freeness (CSF) and fiber length properties were measured for all samples. The fiber length, fines, and kink measurements were done with an FQA-360 fiber quality analyzer (OpTest Equipment Inc.; Hawkesbury, ON, Canada) [15]. Handsheets of 120 g/m^2 basis weight were made for pulp samples above 300 mL CSF. The handsheets were tested for physical properties, which included density, porosity, tensile, burst, short span compression, and z-direction tensile (ZDT). The testing procedures were done according to the TAPPI Standard Test Methods (**Table II**).

The enzyme treatments for this study were done at pH 7.5 and 120°F for 1 h using a commercial enzyme formulation, referred to as "Enzyme A," obtained from Enzymatic Deinking



1. Comparison of commercial and ProLab refining of softwood: drainage versus tensile.



2. Comparison of commercial and ProLab refining of softwood: tear-tensile.

TAPPI Standard Test Methods
T-205 — Forming handsheets for physical tests of pulp
T-220 — Physical testing of pulp handsheets (basis weight, caliper, density)
T-227 — Freeness of pulp (Canadian standard method)
T-403 — Bursting strength of paper
T-460 — Air resistance of paper (Gurley method)
T-494 — Tensile properties of paper and paperboard (using constant rate of elongation apparatus)
T-541 — Internal bond strength of paperboard (z-direction tensile)
T-826 — Short span compressive strength of containerboard

II. TAPPI Test Methods used in the study

Technologies (EDT) (Norcross, GA, USA). The enzyme selection was based on an unpublished internal study in which several commercial EDT "cellulase-based" enzyme formulations were evaluated on OCC refining.

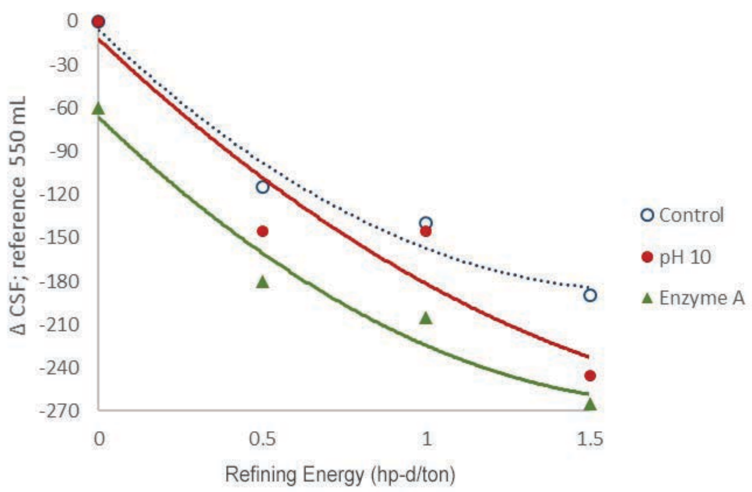
RESULTS AND DISCUSSIONS

OCC pulp has a relatively short storage life before going rancid. Therefore, the pH and enzyme studies were done with fresh OCC samples that were produced at different times at the recycle mill. Although the sample location was the same, the pulp samples had significantly different properties, which highlights the variability inherent with OCC pulps. Because the controls for each of the trials were different, the test results have been graphed as a difference from the respective control values. The handsheet strength data were normalized for basis weight.

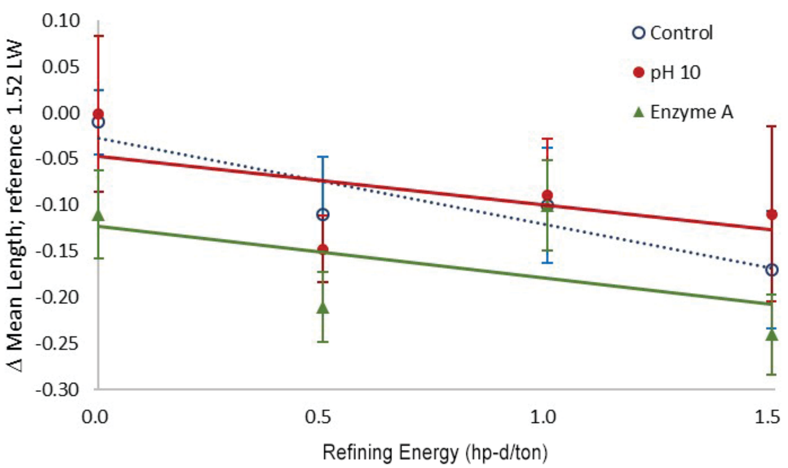
The freeness reduction as a function of specific refining energy was similar when pulp pH was increased from 7.5 to 10 (**Fig. 3**). The energy required to achieve the target desired freeness was significantly lower with Enzyme A than for the control (Fig. 3).

Figures 4-6 show, respectively, the length-weighted average fiber length, percent fines, and kinks resulting during refining. Each time paper is recycled, fiber damage occurs and is expressed as fiber length reduction and increased fines content. Fines have a significantly higher surface area for a given weight than do whole fibers. The fines compete with whole fibers for chemicals added at the wet end. Fines that are retained in the sheet clog the pores in the sheet and reduce dewatering. The fines that are not retained in the sheet end up in the white water and add to the dirt and organic load of the wet end system. The data showed no distinctive difference in any of the three variables (fiber length, percent fines, and kinks), which suggests that none of the pretreatments reduced measurable fiber damage during refining.

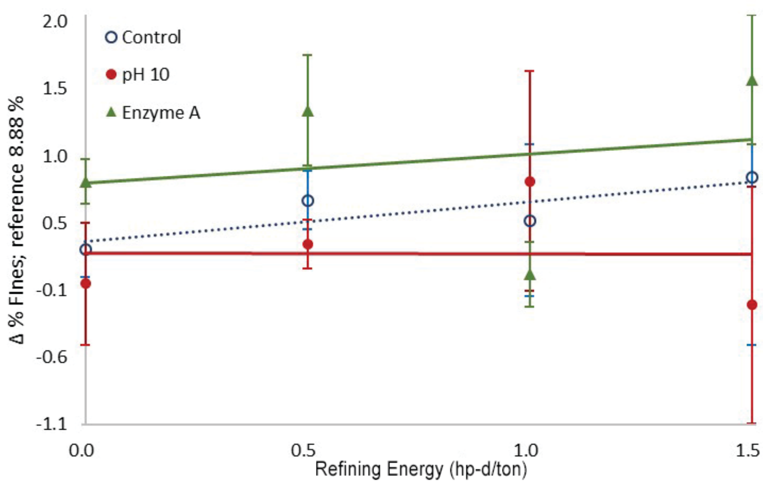
Significant changes in paper properties were apparent with enzyme treatment. An increase in pH from 7.5 to 10 had little effect on STFI strength (i.e., the short span compression



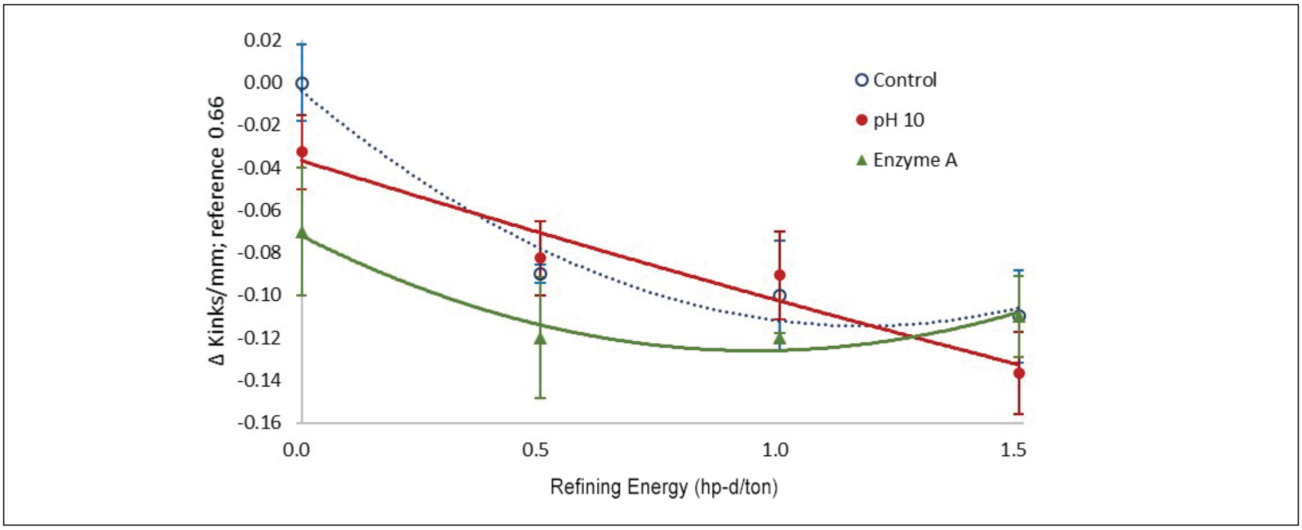
3. Pulp freeness as function of specific refining energy.



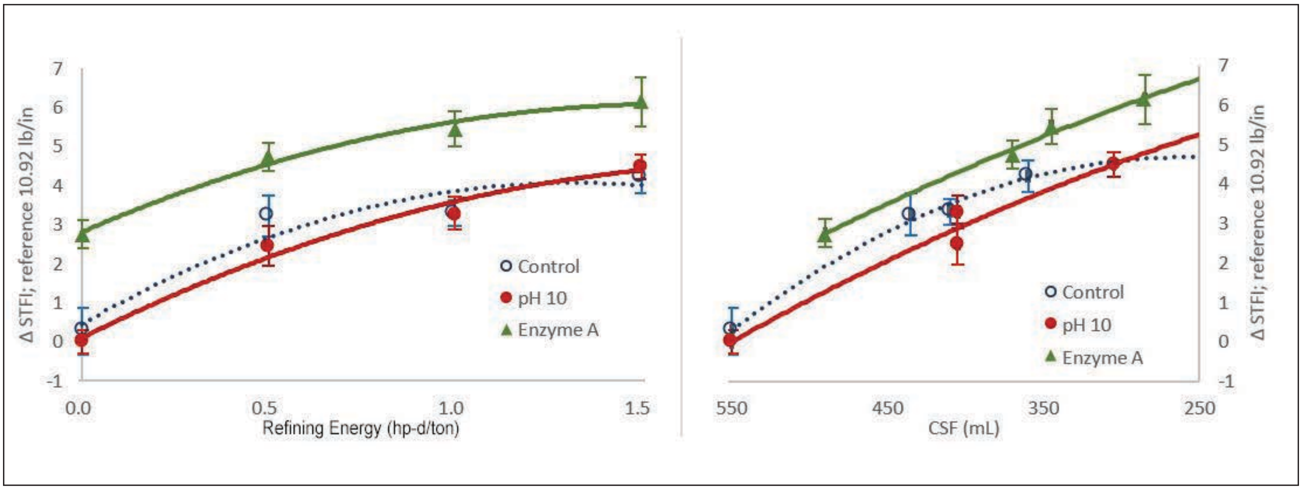
4. Effect of refining on fiber length of old corrugated container (OCC).



5. Effect of refining on fines content of OCC.



6. Effect of refining on fiber damage of OCC.



7. Short span compression (STFI) as function of refining energy and CSF.

test [SCT]) (**Fig. 7**). At similar refining energy, the Enzyme A treatment resulted in 1.5 points higher SCT than did the control. When compared at the same SCT, the freeness was significantly higher for the Enzyme A treated pulp than for the control pulp. For the papermaker, the flexibility of optimizing the process for either increased strength or increased drainage, and maintaining strength properties, is a significant advantage.

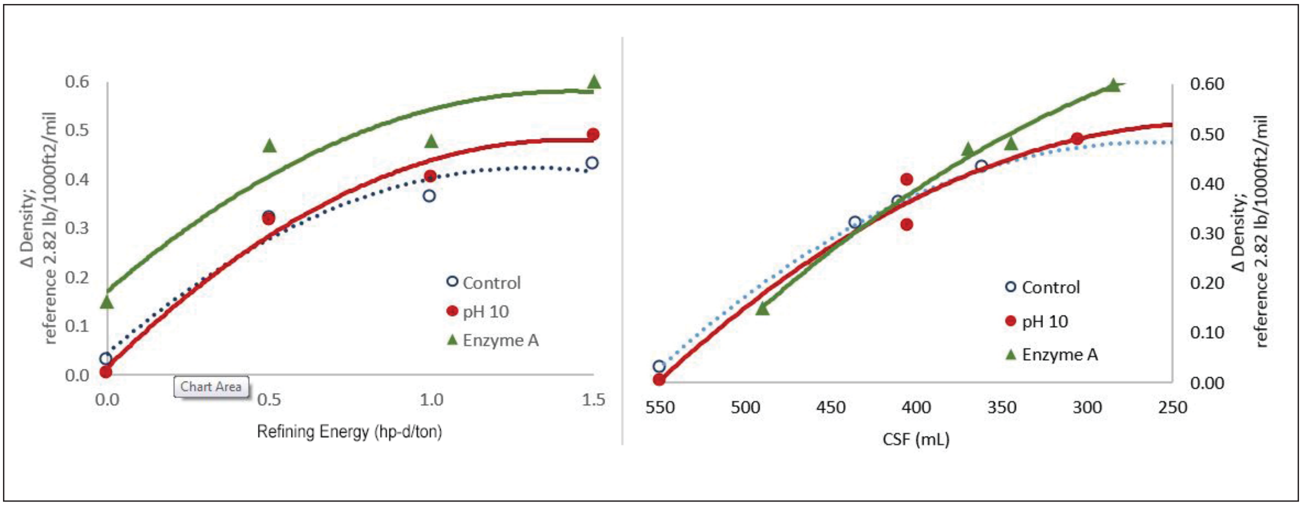
Enzyme-treated pulp exhibited higher density compared with control at similar refining energy, while the density at pH 10 was similar to that of the control (**Fig. 8**). We saw no significant differences in freeness vs. density (Fig. 8). The effect on density (bonding), with no effect on drainage, suggests that the enzymatic treatment might make it easier for the fibrils to separate during the refining process, without increasing the fines content.

Handsheet porosity at pH 10 was generally similar to that of the control, except for the sample at the highest refining energy (1.5 hp-d/ton) (**Fig. 9**). Enzyme A treatment resulted in significantly higher porosity compared with control at any given refining energy (Fig. 9). Less refining energy would be required with enzymatic treatment. Sheet porosity was similar when compared at a given pulp freeness (Fig. 9).

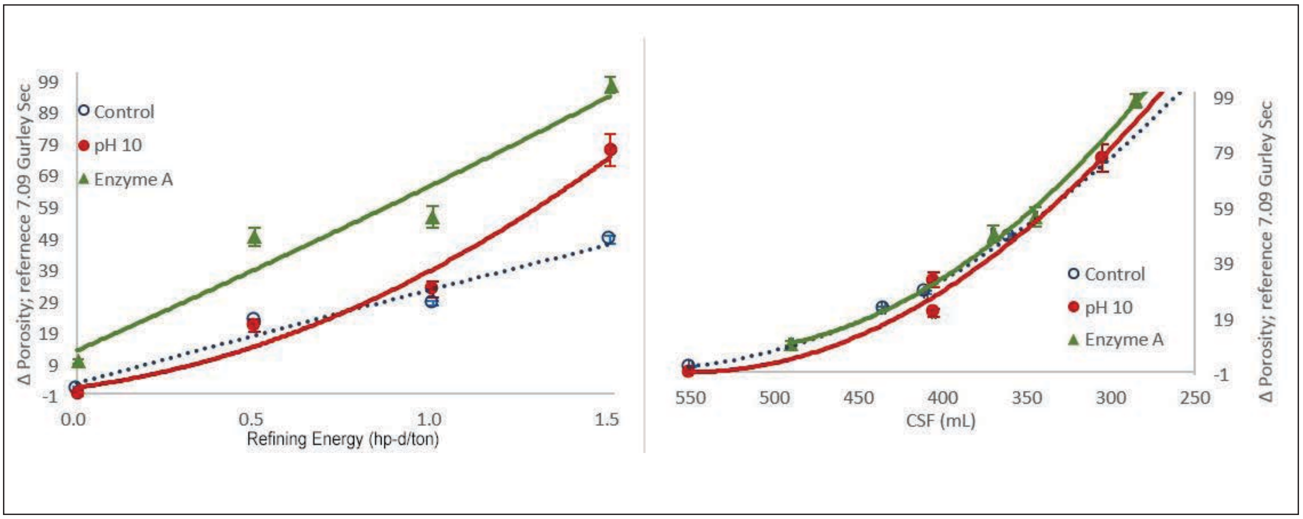
Handsheet ZDT analysis showed no relevant difference in results between pH 10 and control samples (**Fig. 10**). The ZDT values with Enzyme A were significantly higher than with control at the same refiner energy (Fig. 10). Significant energy savings could be achieved using enzyme treatment to influence ZDT.

Burst strength showed negligible difference between the pH 10 and control samples for a given refining energy (**Fig. 11**). The enzyme treatment resulted in significant burst increase (Fig. 11) for a given energy input. At a given freeness, the enzyme treated samples had higher burst strength than the control. Results for the pH 10 samples closely matched those of the control (Fig. 11).

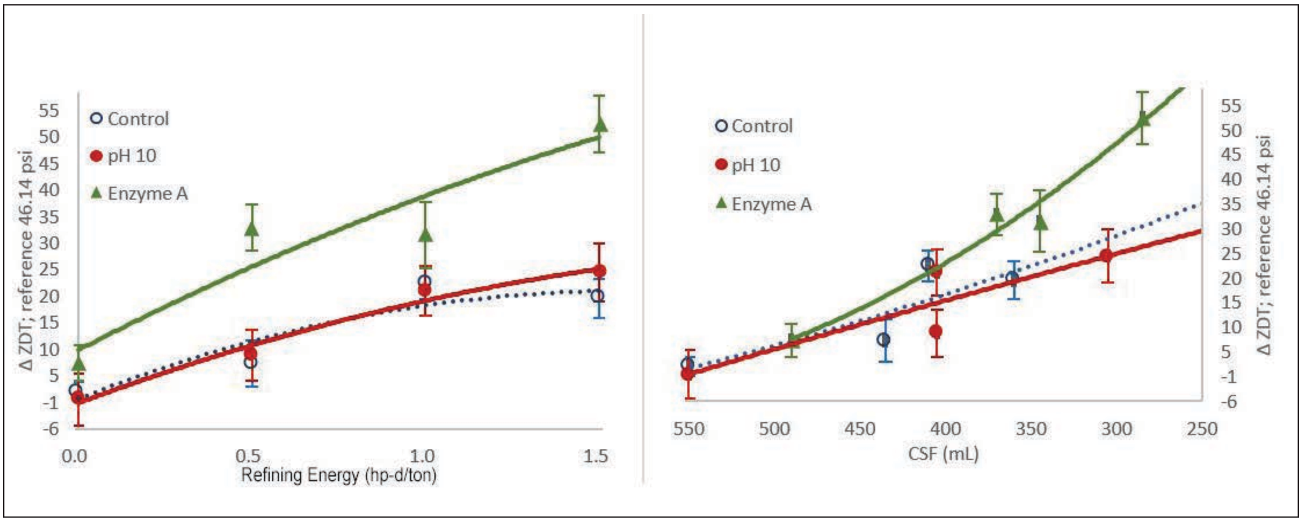
Several researchers have investigated the effect of high pH on strength development during refining of recycled fibers;



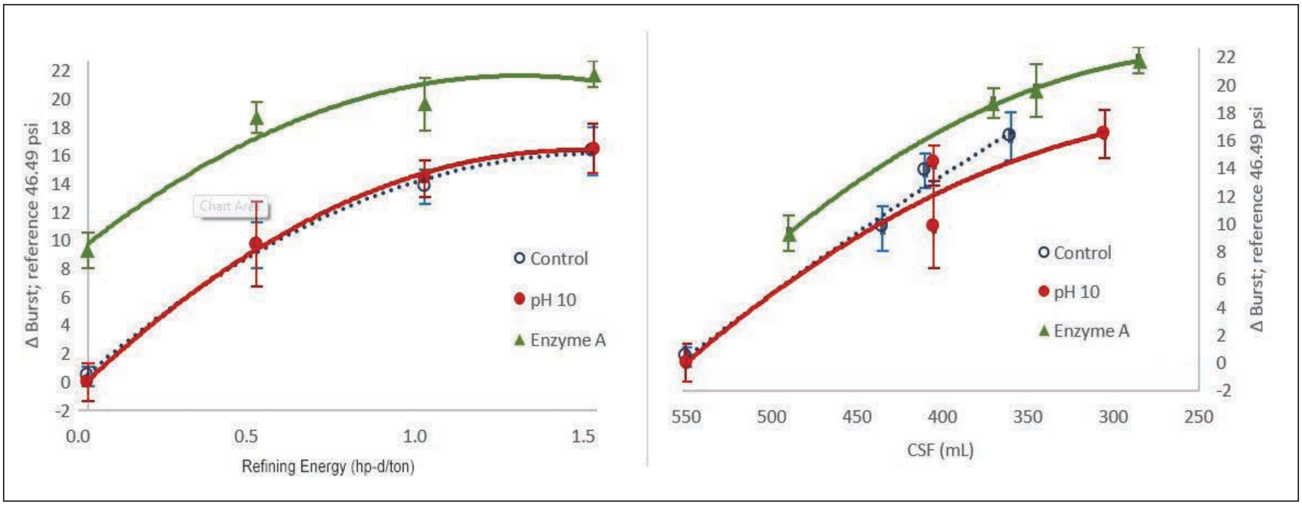
8. Density as function of refining energy and CSF.



9. Porosity as function of refining energy and CSF.



10. Z-direction tensile (ZDT) as function of refining energy and CSF.



11. Burst as function of refining energy and CSF.

some found net positive effects [16-20], others saw no significant effect [21]. Several investigators have used caustic dosages in excess of 2% on pulp [16-19], which is very high and might require additional capital costs to capture and reuse the residual caustic to be efficient. Additionally, there may be extra costs to neutralize the caustic carryover in the pulp. The present work was done at pH 10 using about 0.4% caustic on dry pulp, which are more realistic conditions to evaluate the effect of caustic addition to an existing recycle plant.

Several authors have reported using a PFI mill for refining OCC in the laboratory. This could be an issue because a PFI mill has a very low refining intensity, whereas commercial pulp refiners have significantly higher refining intensity, which results in more fiber damage [16,19].

Some of the earlier studies were done with OCC that contained significant quantities of wet strength resins [16]. Wet strength resins, such as polyamide-epichlorohydrin (PAE), generally require a pH of 12 or higher to degrade [1]. In the absence of high pH and temperature, the repulping of OCC containing wet-strength resin tends to be incomplete, which results in high screen rejects and low repulper yields. Additionally, increasing the repulper time to break apart the fiber bundles caused by the wet strength resin also increases the chances that the fibers will be damaged during defiberation, which lowers overall pulp strength. Hence, recycling paper that contains significant quantities of wet strength resin might confound the results, because increasing the pH can improve defibration of the wet strength paper.

The enzyme-treated pulp samples did not show any significant change in particle charge demand (PCD), streaming zeta potential (SZP), conductivity, and turbidity (**Table III**). These observations suggested that the enzymatic reactions with the dissolved and colloidal materials were unlikely to be a major factor in the increase of pulp strength. PCD is a measure of the anionic trash in the system. The anionic trash might interfere with the fiber-fiber bonding. Because the charge levels did not significantly change, we can assume that there were no significant changes in the anionic trash content. In this study, the laboratory handsheets were made without any dry strength polymers. If chemical strength adjuncts are added to the pulp, the efficacy of the polymers to enhance pulp strength might improve with reduction in dis-

Enzyme Dosage, lb/ton	Turbidity, NTU	SZP, mV	Conductivity, µS/cm	PCD, µeq/L
0	191	-34.4	581	-574
0	190	-35.5	574	-539
0	200	-33.4	588	-583
1.5	202	-33.4	571	-550
1.5	219	-33.4	560	-571
1.5	227	-33.6	575	-602

III. Effect of Enzyme A on particle charge demand (PCD), streaming zeta potential (SZP), and other characteristics of old corrugated container (OCC) slurries with mill white water.

solved/colloidal anionic trash in the pulp slurry going to the paper machine.

The addition of Enzyme A to the OCC aided strength improvement during subsequent refining. The energy required to achieve a targeted freeness value was less with the enzyme application. In addition, the strength achieved at a given freeness was higher for the enzyme-treated pulp. Additionally, enzyme treatment alone caused a reduction in pulp freeness and an increase in pulp strength properties, without subsequent refining. Some earlier studies have reported increased fibrillation during the refining of pulps when treated with enzymes [23,24]. Other studies have reported that enzyme treatment alone did not increase freeness [22]. This discrepancy might be a result of the choice of enzymes in the formulation, as well as the pulp and white water characteristics. Indeed, in some cases, certain cellulases and hemicellulases have caused reductions in strength with improvements in drainage [25].

CONCLUSIONS

Various paper properties made with OCC pulp can be improved with an enzyme treatment, whereas a high pH treatment (pH 10) is relatively ineffective. Enzyme treatment helped to improve fiber reswelling, which resulted in increased fiber strength properties at a given refining energy. The improved pulp drainage could be used to increase paper machine production, which would depend on machine configuration and dryer steam availability. Potential next steps in future investigations will include the evaluation of the effect of certain specific cellulase and lipase strains on the strength of the paper made with recycled fibers. **TJ**

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ABOUT THE AUTHORS

The fiber cost component in recycled paper is approximately 40% of the total manufacturing cost. The overall recycled fiber quality has been deteriorating. To maintain paper strength properties, paper mills respond by increasing basis weight, dry strength, etc.

The methods used in this study (increased pH and enzymes) previously have been evaluated in recycled paper. Several authors have found the effect of pH 10 to be net positive, while others found it to not have any effect. This study evaluated the effect of raising pH on recycled paper furnish that does not contain wet strength paper. We also did a head-to-head comparison between pH and enzymes. In addition, the work was done on a disc refiner, which is known to provide more realistic results than a Valley beater or other laboratory refiners.

OCC pulp has a relatively short storage life before going rancid. Therefore, the pH and enzyme studies were done with OCC samples that were produced at different times at the recycle mill. Although the sample location was the same, the pulp samples had significantly different properties, which highlight the variability inherent with OCC pulps. Because the controls for each of the trials were different, the test results have been graphed as a difference from the respective control values.

The enzyme formulations can be a bit "black-box" when it comes to applying the work to the various production sites. The effect of certain enzymes can provide significant gains; however, the effect varies significantly depending on fiber type.

Some mills are hesitant in using enzymes, either because it's "new," or they had bad experience in the past. The authors hope this work will add to the body of evidence in the net positive effect of enzyme treatments.

Our next step is to evaluate individual enzyme strains to build better understanding of the enzyme action on various substrates.

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