Effect of enzyme pretreatments on conventional kraft pulping

CHAVONDA J. JACOBS, RICHARD A. VENDITTI, AND THOMAS W. JOYCE

ABSTRACT

Sycamore chips were pretreated using a cellulase/hemicellulase mixture prior to conventional kraft pulping. Treatment conditions were 24 hours at 50°C, pH 5, and a cellulase/hemicellulase solution at 5 filter paper units (mmols of reducing sugar per milliliter) per gram ovendry wood. After enzyme pretreatment followed by kraft pulping, the kappa number of the control was as much as 10% higher than that of the treated chips. In addition, enzyme-treated pulps required less ClO_2 per ton pulp (≈ 20 lb ClO_2) than the control. Pulp strength properties for the pretreated chips were comparable to kraft pulps receiving no enzyme pretreatments. Pulp viscosity was lower in pulps treated with cellulase/hemicellulase alone.

Application:

Enzyme pretreatments can increase the delignification in kraft pulping by up to 10%.

INCREASING ENVIRONMENTAL PRESSURES have made it necessary to investigate methods for reducing the amount of energy-, sulfur-, and chlorine-containing compounds used during pulping and bleaching. These pressures have also lead to the design of many technologies aimed at lowering the lignin content of the pulp entering the bleach plant. Lowering the kappa number of the pulp by increasing the efficiency of the pulping process has lead to a reduction in chemicals necessary for pulp bleaching and a concomitant reduction in pollutants discharged from the bleach plant.

We previously investigated the effects of enzyme pretreatments on the diffusion of sodium hydroxide in wood *(1)*. That research showed that a hemicellulase/cellulase solution can increase the diffusion of sodium hydroxide in both hardwoods and softwoods. It was observed that the enzyme-pretreated samples had significantly higher mean diffusion rates when compared to the untreated samples. Diffusion was as much as 110% higher in pretreated hardwood samples. The increase in mean diffusion rate was dependent on both species and direction of flow. In the case of softwoods, the magnitude of the diffusion difference was 60% in the tangential direction and 93% in the longitudinal direction.

This increase in diffusion could be attributed to various factors, including the dissolution of pit membranes and the removal of carbohydrates from the lignin–carbohydrate matrix. Numerous studies on the treatment of wood with biological agents have revealed the attack of these substances on pit membranes *(2–4)*. In hardwoods, the primary pathways for liquid transport are vessels that are not occluded by tyloses, while fiber tracheids are responsible for conducting fluid in softwoods. In both hardwoods and softwoods, fluid is communicated from one cell to the next through interconnecting pits. The membranes of these pits, which offer resistance to flow, are primarily composed of lignin, pectin, and hemicellulose. These findings have significant implications for pulp mill design. For conventional kraft pulping systems, it is imperative that research be conducted that can assist mills in meeting environmental regulations.

The residual lignin removal phase during kraft pulping, which occurs at about 90% delignification, is characterized by slow delignification coupled with rapid carbohydrate degradation reactions. The low rate of delignification is believed to be caused by the presence of alkali-stable lignin carbohydrate bonds *(5, 6)*. In kraft pulping, initial delignification occurs preferentially in the secondary wall. At about 50% delignification, the lignin in the middle lamella and cell corner areas dissolve rapidly, leaving the residual lignin in the secondary wall. This topochemical effect is the result of physical and chemical factors *(7, 8)*.

Experimental evidence suggests that the topochemical variations in delignification can be partially attributed to the difference in the structure of lignin from the secondary wall and middle lamella regions *(9, 10)*. In addition, important physical factors, such as the differential penetration of reagents into various morphological regions, the accessibility of lignin, and the diffusibility of degraded lignin, may lead to topochemical effects. The dissolution of secondary wall lignin has been related to the pore size of the cell wall and thus the removal of hemicellulose *(11, 12)*. The location of residual lignin has a significant bearing on the bleachability and papermaking properties of pulp fibers.

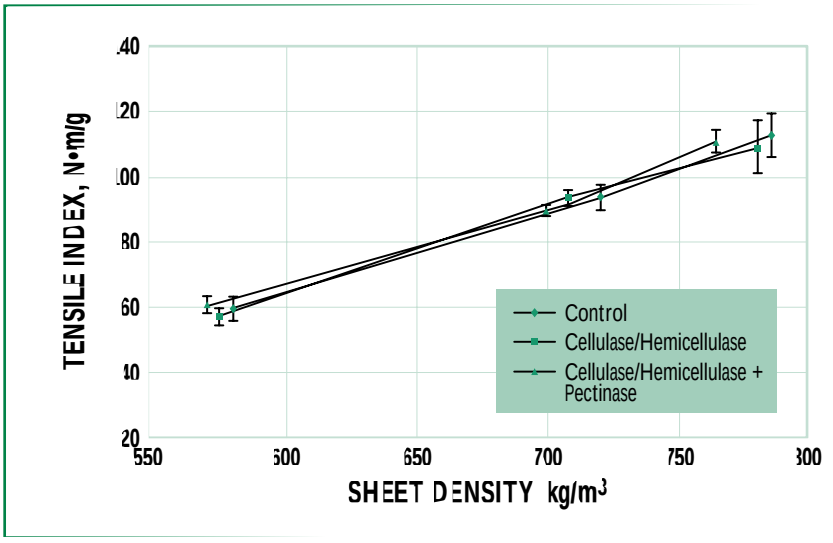
This study is an interim step that investigates the potential of enzymatic pretreatment for enhancing conventional kraft pulping. The objective was to determine the effect of enzyme pretreatment on final pulp viscosity, kappa number, strength properties, and yield. Further studies may lead to the development of a more effective, less time-consuming pretreatment.

Parameter	Control (Cook 1, Cook 2)	C/H (Cook 1, Cook 2)	C/H+P (Cook 1, Cook 2)
Pergalase dosage,	- filter paper units/g	5	5
Pectinase solution dosage,	- % on o.d. basis	-	1
Kappa no.	17.6,17.5	16.3, 16.0	15.6, 15.9
Average viscosity, mPa·s	50.6, 51.4	46.5, 46.9	50.2, 50.0
Unscreened yield, %	49.1, 49.8	48.6, 49.9	46.2, 48.2
Screened yield, %	43.1, 44.9	43.4, 45.3	43.7, 44.9

I. Pulping data for enzyme-pretreated and conventional kraft cooks. Cellulase/hemicellulase = C/H. Cellulase/hemicellulase + pectinase = C/H+P.

	COMPOSITION OF CARBOHYDRATES			
	Glucose,	Xylose,	Arabinose,	Mannose,
Pulp	%	%	%	%
Control	88.6	11.1	<0.1	0.2
C/H	85.6	14.1	<0.1	0.2
C/H +P	85.6	14.2	<0.1	0.2

II. Sugar analysis of enzyme-pretreated and conventional kraft pulps. Cellulase/hemicellulase = C/H. Cellulase/hemicellulase + pectinase = C/H+P.



1. Sheet density–tensile index analysis of sycamore chips receiving enzyme treatment. The chips were pulped using 1000 H factor, 15% AA, and 30% sulfidity. 5 U/g wood Pergalase (C/H), 5 U/g wood Pergalase + 1% pectinase solution on o.d. pulp (C/H+P).

MATERIALS AND METHODS

Enzyme pretreatment

Prior to pulping, 650 ovendry (o.d.) grams of chips were treated with Pergalase A40 (CIBA, Greensboro, NC), which had a filter paper activity of approximately 70 filter paper units (mmols of reducing sugar per milliliter). Pergalase activity was determined using a filter paper assay described by Mandels *(13)*. The filter paper activity was determined from liberated reducing sugar as measured by the dinitrosalisylic acid method using glucose as a standard *(14)*. The protein concentration of Pergalase was determined to be 175 mg/mL using Lowry's precipitation method *(15)*. The Pergalase enzyme preparation contains exoglucanase, endoglucanase, and xylanase activities. The predominant activity is endoglucanase. Mixtures of Pergalase and pectinase were also used.

The pectinase preparation was obtained from Novo Nordisk Biochem North America, Inc. The dosage of Pergalase was applied at 5 filter paper units (FPU) per o.d. gram of pulp, while the pectinase preparation was charged at 1% on o.d. chip weight. The chips were placed in stainless steel bombs along with the enzyme preparation, citrate buffer (pH=5), and water. Enzyme impregnation was aided by applying 20 in. of vacuum to reach bomb. The chips were reacted in a constant-temperature device for 24 hours at 50°C. The control chips were treated as previously described, but without enzyme addition.

Pulping conditions

Sycamore sapwood chips were pulped in a 7-L M&K digester vessel using the following conditions: 15% active alkali (AA), 30% sulfidity, 4:1 liquor-to-wood (L/W) ratio, and 1000 H factor. The chips were screened and sorted to remove bark and knots. A quantity of 650 o.d. grams of chips was used for all cooks. At the completion of the cook, the spent black liquor was blown into a holding vessel. The chips were not blown under pressure but were removed manually, washed, disintegrated, and screened. The screened pulp was centrifuged to approximately 30% consistency and fluffed.

Pulp testing

Control and enzyme-treated pulps were beaten in a PFI mill at a 10% consistency with an applied load of 1.8 kg/cm. Samples were collected at predetermined intervals between 0 and 6000 revolutions. Pulp fiber length, coarseness, kink, and curl were determined using a Fiber Quality Analyzer (Optest Inc.). Handsheet properties, pulp viscosity, fines analysis, and kappa number were determined for each sample using TAPPI Test methods.

Pulp sugar analysis

Pulp sugars were measured by anion exchange liquid chromatography of their borate complexes, followed by a post-column reaction to produce a blue copper complex. The absorbance of the copper complex is measured by a detector set at 560 nm. Quantification was done by comparing sample peak heights to those produced by a standard *(16)*.

RESULTS AND DISCUSSION

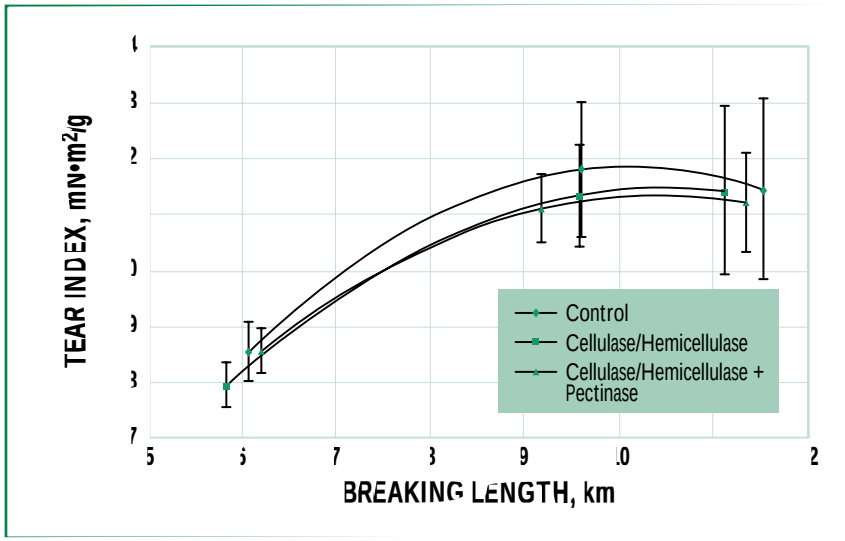
Effect of enzyme pretreatment on lignin removal

The effects of 24-hour enzyme pretreatments on pulp delignification, viscosity, and yield are listed in **Table I.** When compared to the control kraft pulp, both enzyme treatments resulted in higher levels of delignification. The cellulase/hemicellulase (CH) mixture resulted in approximately a 1.5-point kappa difference while maintaining similar unscreened yield values. The level of delignification was further increased by adding pectinase to the enzyme mixture. Screened yield values were comparable for all cooks.

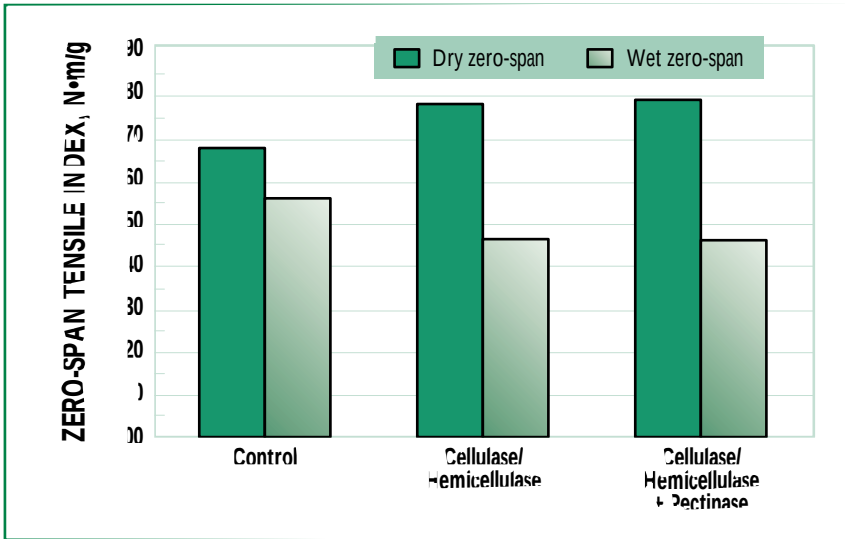
Effect of enzyme pretreatment on viscosity and pulp strength properties

Cellulase/hemicellulase/pectinase (CHP) was capable of lowering the kappa number of the pulp while maintaining similar viscosity values. Pretreatment with CH alone resulted in lower final pulp viscosities than the control and chips that were treated with CHP. The main differences in the carbohydrate compositions of the pulps were in the xylose and glucose compositions (**Table II**). Arabinose and mannose contents were low in each pulp. Somewhat surprisingly, more xylose was detected in the enzyme-pretreated pulps than in the pulp receiving no pretreatment.

The reprecipitation of xylan during kraft pulping occurs when almost all of the xylan side chains have been cleaved off *(17)*. This may indicate that the additional hydrolysis of xylan side chains during pretreatment could have resulted in increased xylan reprecipitation during pulping. Filtrate obtained directly after enzyme pretreatment was analyzed using a method outlined by Mandels *(13)*. Effluent following enzyme pretreatment had significantly higher



2. Tear/tensile analysis of sycamore chips receiving enzyme treatment. The chips were pulped using 1000 H factor, 15% AA, and 30% sulfidity. 5 U/g wood Pergalase (C/H), 5 U/g wood Pergalase + 1% pectinase solution on o.d. pulp (C/H+P).



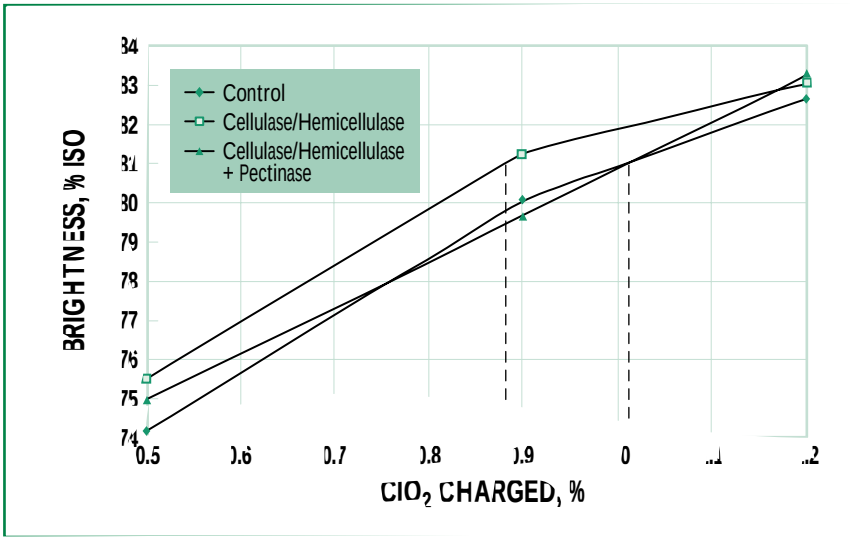
3. Zero-span tensile strength of sycamore chips receiving enzyme treatment. The chips were pulped using 1000 H factor, 15% AA, and 30% sulfidity. 5 U/g wood Pergalase (C/H), 5 U/g wood Pergalase + 1% pectinase solution on o.d. pulp (C/H+P).

Pulp	Avg. fiber length, mm	Fines, %
Control (15% AA)	0.52±0.01	13.4±0.80
Control (16% AA)	0.62±0.01	9.6±0.19
C/H	0.67±0.01	8.2±0.21
C/H+P	0.73±0.0	5.8±0.35

III. Fiber analysis for enzyme-pretreated and conventional kraft pulps. Cellulase/hemicellulase = C/H. Cellulase/hemicellulase + pectinase = C/H+P.

Pulp	Brownstock kappa no.	DE kappa no.	DE brightness	FINAL BRIGHTNESS 0.5% ClO_2	0.9% ClO_2	1.2% ClO_2
Control	17.6	4.68	51.0	74.2	80.1	82.7
C/H	16.2	4.77	52.6	75.5	81.3	83.1
C/H+P	15.8	4.75	52.3	75.0	79.7	83.3

IV. Bleaching results. DED bleaching sequence for enzyme-pretreated and conventional kraft pulps. Cellulase/hemicellulase = C/H. Cellulase/hemicellulase + pectinase = C/H+P.



4. Bleaching of pulps using a DED sequence. Pergalase (C/H), Pergalase + 1% pectinase on o.d. pulp (C/H+P).

levels of reducing sugars than the control. Using the high-performance liquid chromatography (HPLC) method, traces of galactose, arabinose, and glucose were identified in filtrate following pretreatment. Material also eluted in the trisaccharide and disaccharide regions near cellobiose for each sample, but the peaks were too small to quantify.

The physical properties of each pulp were tested before and after refining. In **Fig. 1,** it can be seen that, although the tensile index is not significantly different for the three pulps at the 95% confidence level, the pulp receiving pectinase treatment had a higher tensile index at each level of sheet density. At any given breaking length, the control pulp was higher in average tear strength than the enzyme-pretreated pulps but was not significantly different at the 95% confidence level (**Fig. 2**).

Enzyme-pretreated pulps had higher dry zero-span tensile strength than the untreated pulps (**Fig. 3**). The breaking length of a sheet is influenced by both the fiber length and variations in the level of bonding. Zero-span tensile is decreased by reductions in fiber length and increased by higher levels of bonding in the sheet *(18)*. Higher dry zero-span tensile strength would indicate that the individual fibers resulting from enzyme pretreatment and kraft pulping were stronger than those from kraft pulping alone. After further evaluation of pulp average fiber lengths and fines content using the Fiber Quality Analyzer and TAPPI T 261 pm-80, it was determined that the untreated pulp had lower average fiber lengths and higher fines contents than the enzyme-pretreated pulps (**Table III**). Both of these factors would lead to lower levels of bonding in the untreated pulps and therefore to lower dry zero-span tensile readings.

The wet zero-span test has been suggested as a method for removing the influence of fiber bonding on zero-span tensile strength *(19)*. This is based on the assumption that in wet sheets, all interfiber bonds are effectively broken. The wet zero-span tensile strength is lower for a wide range of pulps due to the weakening of the individual fibers that make up the sheet. This loss in strength depends on the extent of chemical and mechanical damage to the interfibrillar matrix of fibers during processing. The weaker the supporting lignin–hemicellulose matrix holding the cellulose microfibrils together, the larger the reduction in zero-span strength upon wetting *(20)*. Enzyme pretreatments with cellulase and hemicellulase are capable of degrading the interfibrillar matrix. This could be shown in the manner in which the enzyme pulps behave upon wetting. The enzyme-pretreated pulps exhibited approximately an 18% reduction in zero-span strength upon wetting, while the control pulp experienced only a 6% reduction.

The active alkali charge of the conventional kraft process was increased to produce a control pulp with a kappa number that was comparative to the enzyme-pretreated samples (kappa no. 15.2). The pulp was cooked using 16% AA, 1000 H factor, and 30% sulfidity. The wet zero-span tensile was

KEYWORDS
Alkalis, bleachability, cellulase, chemical consumption, diffusion, enzymes, hardwoods, hemicellulase, kappa number, kraft pulping, mechanical properties, pectinase, platanus, pretreatment, pulp properties, sodium hydroxide, viscosity.

13% lower than the dry zero-span tensile. This pulp exhibited a larger reduction in zero-span strength (6%) upon wetting than the control pulp, which was cooked at 15% AA. This may be attributed to the higher loss of hemicelluloses with the increase in active alkali.

The pulps were similar in levels of kink (0.90 kinks/mm), coarseness (16.5 mg/100 m), and curl index (0.06).

Effect of enzyme pretreatment on bleachability

Pulps were bleached using a DED bleaching sequence to determine the effect of the enzyme pretreatment on final bleaching properties. Each pulp was bleached using a kappa factor of 0.18 in the first D stage. The results are listed in **Table IV.** Results indicate that pulps treated with cellulase/hemicellulase (CH) alone had slightly higher final brightness at each level of chlorine dioxide charged than the control. **Figure 4** shows that at 0.5% and 0.9% ClO_2 charge on o.d. pulp in the final D stage, there was an increase in brightness of up to 1.3% ISO when using pulps treated with CH alone.

To reach a final brightness of 81% ISO, the CH-treated pulp required a ClO_2 charge of 0.88%, while the control required a ClO_2 charge of 1.01%. These differences in ClO_2 charge translate into chemical savings of 18.44 lb ClO_2/ton pulp bleached. In addition, the lower incoming kappa number of the enzyme-pretreated samples allowed reductions of up to 1.8 lb ClO_2/ton pulp in the first D stage. This indicates that the bleaching of pulps receiving cellulase/hemicellulase treatment was more efficient, resulting in higher-brightness pulps.

CONCLUSIONS

This study demonstrates that enzymes can enhance kraft pulping while maintaining comparable tensile and burst strength properties. Enzyme pretreatments can increase the delignification in kraft pulping by up to 10%. In pulping, a pectinase preparation in addition to a cellulase/hemicellulase solution was found to be more effective than a cellulase/hemicellulase preparation alone. Brownstock viscosity was lower in pulps treated with a cellulase/hemicellulase solution alone. Pulps treated with a cellulase/hemicellulase solution produced higher-brightness pulps than the control and pulps treated with cellulase/hemicellulase in addition to a pectinase solution at identical chemical charges. TJ

Jacobs is an assistant professor of paper science and engineering at the University of Washington, Division of Paper Science and Engineering, Box 352100, Seattle, WA 98195. Venditti is an assistant professor of wood and paper science at North Carolina State University, Box 8005, Raleigh, NC 27695. Joyce is chairman and professor of paper and printing science and engineering at Western Michigan University, Kalamazoo, MI 49008-5060.

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