# Modification of Douglas-fir mechanical and kraft pulps by enzyme treatment

SHAWN D. MANSFIELD, KEN K.Y. WONG, ED DE JONG, AND JOHN N. SADDLER


## ABSTRACT

*A cellulase enzyme preparation was assessed for its potential to enhance the fiber characteristics of mechanical and kraft pulps derived from Douglas-fir. The effect of enzyme treatment on pulp properties varied with enzyme dosage. A charge of 1 mg protein per gram of ovendry pulp improved handsheet density and smoothness, increased pulp freeness, and reduced fiber coarseness while only slightly diminishing sheet strength properties. In general, fiber-length fractions showed the same response to treatment as the unfractionated whole pulp. However, tensile strength for the kraft fiber fractions increased with enzyme treatments, while the whole pulp suffered a slight decline. This suggests the possibility of improving pulp properties by selective treatment of individual fiber fractions.*

***Application:***

*This study examines the potential of using cellulase enzymes to selectively modify pulp fiber characteristics.*


THE CANADIAN PULP AND PAPER industry is searching for ways to extend its current and future fiber supply. One of the proposed strategies is to supplement and upgrade existing feedstocks with secondary fibers, nonwood fibers, and fiber sources that are now classified as poor quality or undesirable *(1)*. Another approach has been to determine if the wood species that are currently available are being used to produce pulps of highest value, based on the original or modified properties of the pulp fibers.

In coastal British Columbia, Douglas-fir is a valuable wood species that is used primarily in lumber products because of its excellent structural properties. Traditionally, wood residues from Douglas-fir have been used as a furnish for kraft pulp production because their high fiber coarseness *(2)* and high flavonoid content have restricted their use as a feedstock for mechanical pulping processes *(3)*. These coarse fibers are stiff, inflexible, and bulky, and they yield paper products that are relatively rough and weak, since coarse fibers provide poor interfiber bonding *(4)*.

Recent research has focused on the use of enzymes to enhance bleaching *(5)*, dewatering *(6)*, and deinking of various types of secondary fiber *(7, 8)*, and to modify pulp strength properties *(9)*. An extensive investigation by Stork *et al. (10)* assessed the use of cellulases to modify recycled fibers. They attributed the enhanced drainage of recycled pulps to the hydrolysis of amorphous cellulose on the fiber surfaces rather than to the selective hydrolysis of pulp fines. Previous research has shown that limited treatments with low charges of cellulases produce little change in the quality of the recycled fibers, presumably because of a mechanistic peeling of the individual fibrils *(10, 11)*.

Our current work examines the potential of using hydrolytic enzymes to enhance the fiber characteristics of chemical and mechanical pulps derived from Douglas-fir, particularly the coarse fractions of these pulps. The reduction of undesirable pulp characteristics, specifically fiber coarseness and inflexibility, should enhance the papermaking properties of these fibers and increase the potential for their use in markets other than traditional kraft pulp applications.

## RESULTS AND DISCUSSION

### *Enzyme treatment of kraft and mechanical pulps*

Kraft and mechanical pulps derived from Douglas-fir were fractionated in a fiber-length classifier. The fiber fractions for both pulps are given in Table I.

*Kraft pulp.* It was expected that higher enzyme dosages would significantly degrade the cellulose fibers, so our first step was to establish the enzyme concentrations that would minimize liberation of reducing sugars while maximizing desirable pulp characteristics. The results in Fig. 1A show that the kraft pulp was more readily hydrolyzed than the mechanical pulp. Therefore, to minimize losses in yield and strength, kraft pulp was limited to loadings of no more than 10 mg protein/g ovendry (o.d.) pulp. As enzyme loading increased, the freeness of the kraft pulp increased slightly, as seen in Fig. 1B. Coarseness decreased slightly with enzyme charge, as seen in Fig. 1C. Since the initial fines component of the kraft pulp was very low (Table I), the increase in freeness was probably due to defibrillation of the fibers, which reduced their coarseness.

Sheet strength properties such as tensile index, burst index, and tear resistance decreased with increasing

| | FIBER FRACTION (BAUER–MCNETT)* | | | | | | |
|---|---|---|---|---|---|---|---|
| **Pulp type** | **R14** | **R28** | **R50** | **R100** | **R200** | **Total** | **Fines content** |
| Mechanical | 0.9 | 13.7 | 20.6 | 16.6 | 12.6 | 64.4 | 35.6 |
| Kraft | 55.2 | 21.3 | 10.8 | 4.4 | 1.9 | 93.6 | 6.4 |

*Fiber fractions obtained by retention (R) on screens of various mesh in a Bauer–McNett fiber-length classifier

***I. Pulp content in different fiber-length fractions, wt.%***

enzyme loadings for the kraft pulp, as seen in Figs. 2A–2C. This decrease in sheet strength was probably due to the damage inflicted on the individual fibers, since Fig. 2D shows that zero-span breaking length is highly affected by enzyme treatment, even at the low enzyme concentration of 5 mg protein/g o.d. pulp.

Handsheet density for the kraft pulp increased with enzyme loading, as seen in Fig. 3A. The likely explanation for the increased density is that the cellulase enzymes degraded the fibers to the extent that they collapsed under pressure during handsheet formation. The presence of flattened fibers would also explain the observed reduction in handsheet roughness in Fig. 3C. Enzyme treatment also makes the fibers smoother, and this may account for a small portion of the reduced handsheet roughness.

Figure 3B shows porosity data for mechanical pulp, but there are no data for kraft pulp. This is because the kraft handsheets were too porous to obtain accurate readings.

*Mechanical pulp* Pulp freeness for the enzyme-treated mechanical pulp was considerably higher than that of the untreated pulp, as seen in Fig. 1B. The maximum effect was obtained with a relatively small amount of enzyme (1–5 mg protein/g o.d. pulp). Preferential hydrolysis of the fines is the likely explanation for this effect *(12)*. Fiber coarseness decreased progressively with increasing enzyme concentration, as seen in Fig. 1C, with an enzyme loading of 1 mg protein reducing coarseness by 7%.

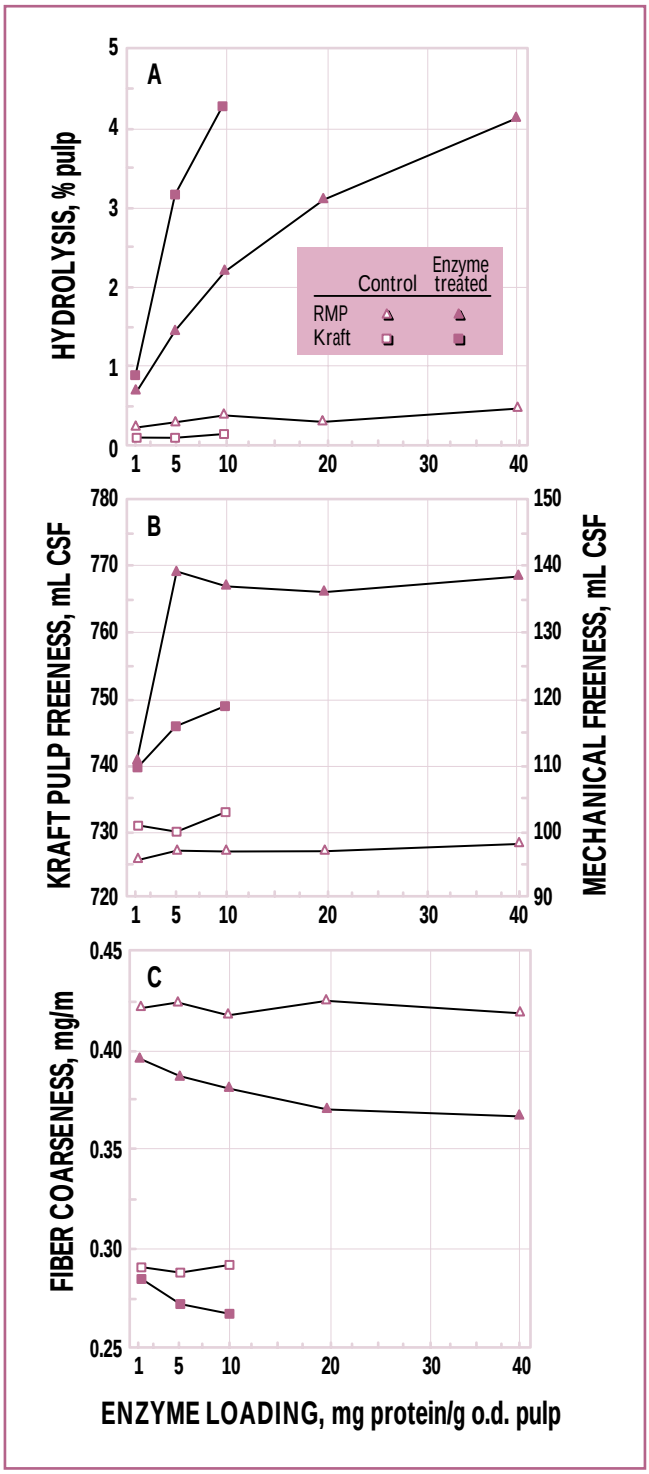
While a reduction in fiber coarseness is desirable, it is important that strength loss be minimized. A progressive loss in tensile, burst, and tear indexes and in zero-span breaking length was apparent with increasing enzyme concentrations, as seen in Figs. 2A–2D, respectively. However, at low enzyme concentrations (1 mg protein/g o.d. pulp), there was no significant effect on the tear index or the zero-span breaking length. At higher enzyme concentrations, the reductions in tensile strength (indicative of interfiber bonding) and zero-span breaking length (indicative of fiber strength) suggested that handsheet strength declined in response to reductions in both the strength of the individual fibers as well as the intrinsic bonding between the fibers.

The density of the mechanical pulp handsheets decreased with increasing enzyme concentration (Fig. 3A), while the porosity increased (Fig. 3B). Although there was a slight decrease in handsheet roughness at low enzyme concentrations (Fig. 3C), increasing the enzyme dose did not produce further decreases in roughness. Because the fines constitute a significant portion of the total mechanical pulp (Table I), a reduction in this component by enzymatic hydrolysis would imply that greater amounts of coarse fibers are required to produce handsheets of an equivalent grammage. The reduction in the fines would also lower the amount of filler present in the handsheets, thus increasing their porosity. Concurrent with the hydrolysis of fines, it is possible that fiber defibrillation occurs. This would also contribute to the observed decrease in handsheet density.

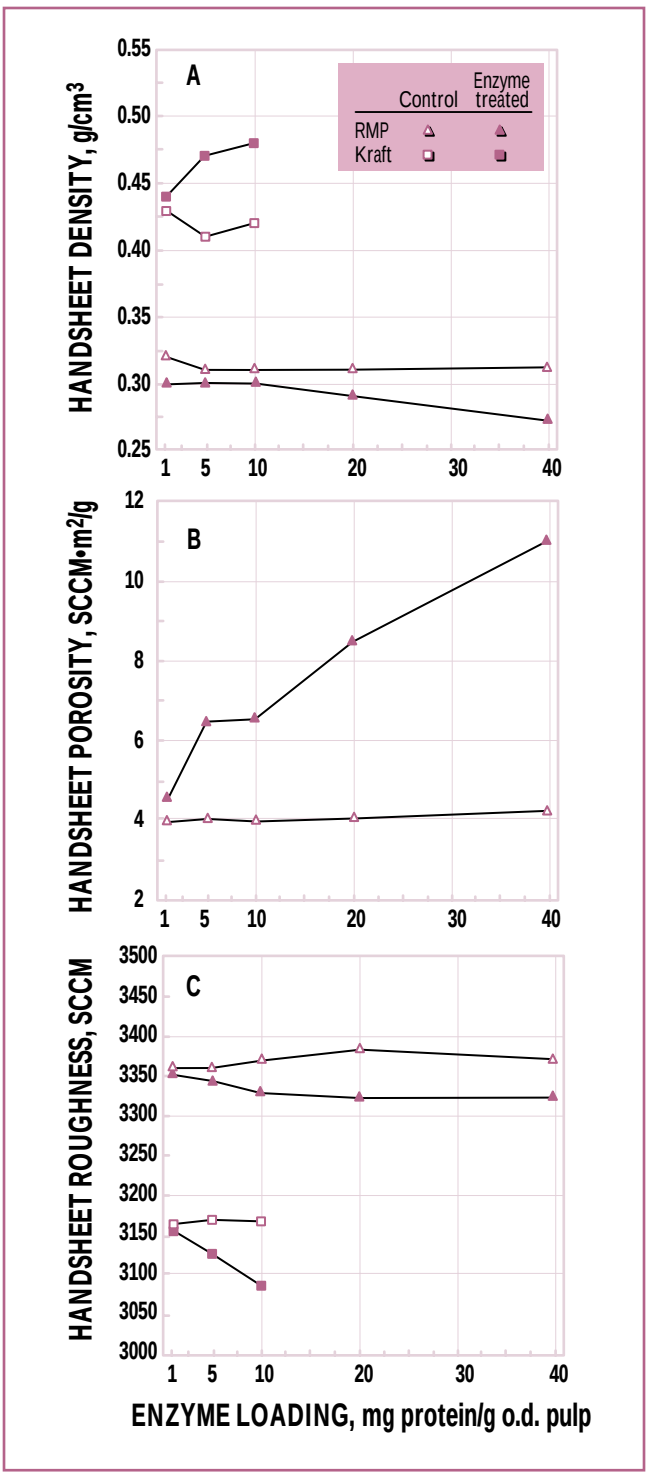
***Enzyme treatment of fractionated pulps***

Previous reports suggested a preferential removal of fines from pulps by enzyme treatments *(12, 13)*. This was explained by the higher surface-area-to-weight ratio of the fines, with the increased surface area providing more sites for enzymatic attack. We wanted to assess the response of the different fiber-length fractions of kraft and mechanical pulps to enzyme treatments. Our objectives were (a) to compare the effects that enzyme treatments might have on individual fiber fractions and (b) to investigate the potential of fractionating the pulp and treating only one fraction.

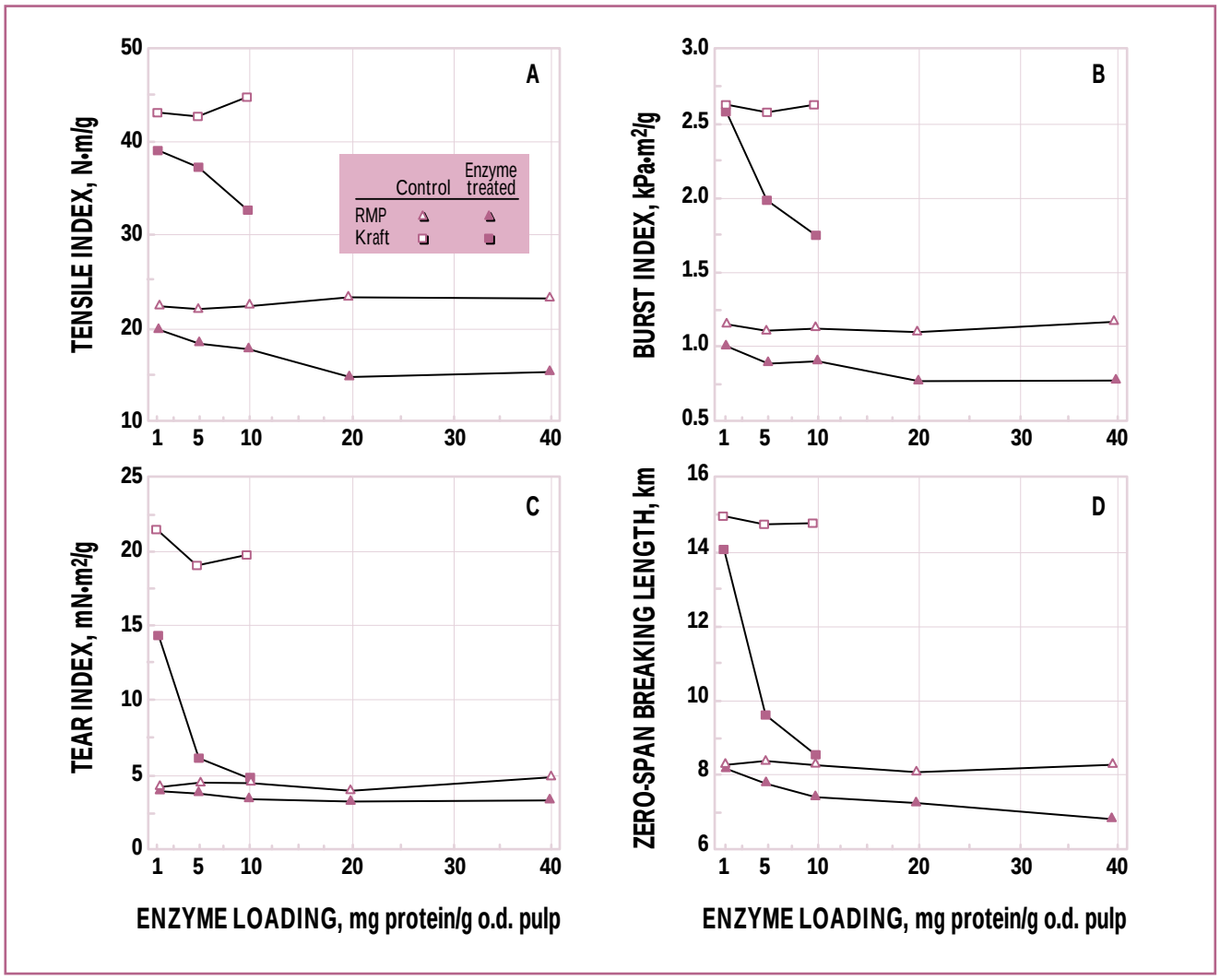
The screening results in Table I showed that the majority of the kraft pulp was composed of long fibers (R14 and R28), with the short fractions (R100 and R200) accounting for only 6.3% of the total pulp (Table I). With the mechanical pulp, there were few long fibers (R14) and a more equal distribution over the other fiber-length fractions. The fines, which we believe constitute the majority of the material that was not collected by the fraction passing through the 200-mesh screen, accounted for a substantially larger proportion of the mechanical pulp (35.6%) compared with the kraft pulp (6.4%).




*1. Effects of enzyme treatment on (A) hydrolysis yield, (B) pulp freeness, and (C) fiber coarseness of kraft and mechanical pulps. Control pulps were treated with heat-inactivated enzyme.*




*3. Effects of enzyme treatment on (A) density, (B) porosity, and (C) roughness of handsheets produced from kraft and mechanical pulps. [Porosity and roughness are measures of air flow in units of SCCM (standard cubic centimeters per minute), i.e., flow as measured at 70°F and 29.92 in. Hg.] Control pulps were treated with heat-inactivated enzyme.*

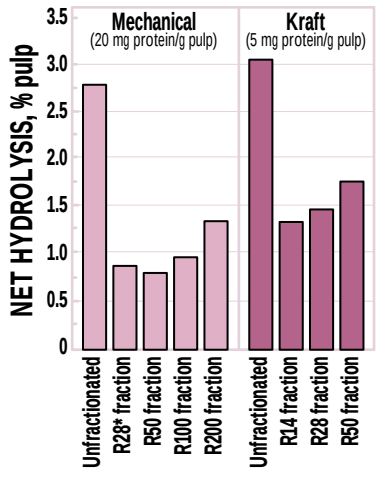


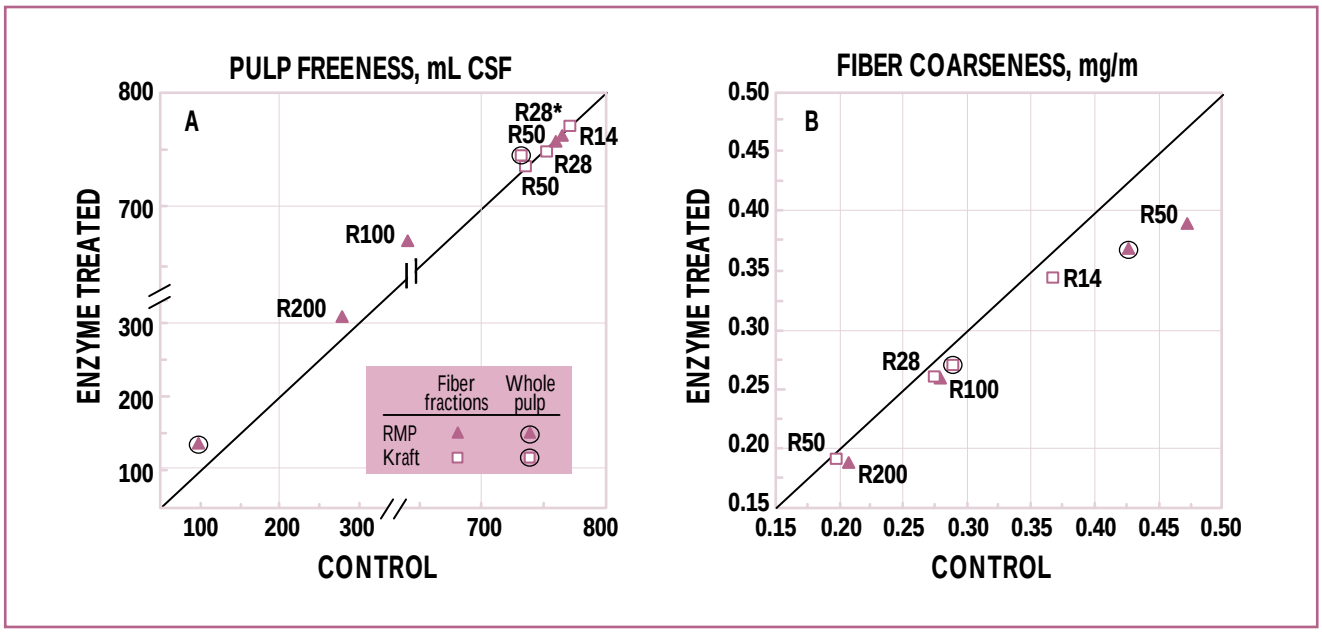

*2. Effects of enzyme treatment on strength properties of handsheets produced from kraft and mechanical pulps. Control pulps were treated with heat-inactivated enzyme.*

Enzyme concentrations for the kraft and mechanical pulps were 5 mg and 20 mg protein/g o.d. pulp, respectively, during the study of fractionated pulps. This was done to ensure that similar low levels of hydrolysis were obtained for both pulps. We also had to combine the R14 and R28 mechanical pulp fractions to obtain enough material to form handsheets for physical testing. This combined fraction is referred to as the R28* fraction.

The amount of reducing sugars released as a result of enzymatic hydrolysis was much greater for the unfractionated pulps than it was for any of the individual fractions, as seen in Fig. 4. This suggested that the fines fraction lost during the fractionation process accounted for the higher hydrolysis in the unfractionated pulp, especially since Fig. 4 shows that the smaller fiber fractions in both pulps released higher quantities of reducing sugars during hydrolysis.

*4. Effects of enzyme treatment on hydrolysis yield for fiber-length fractions of mechanical and kraft pulps*






***5. Effects of enzyme treatment on (A) pulp freeness and (B) fiber coarseness for fiber-length fractions of kraft and mechanical pulps. Circled data points represent unfractionated whole pulps. Enzyme dosages are as listed in Fig. 4. Control pulps were treated with heat-inactivated enzyme.***

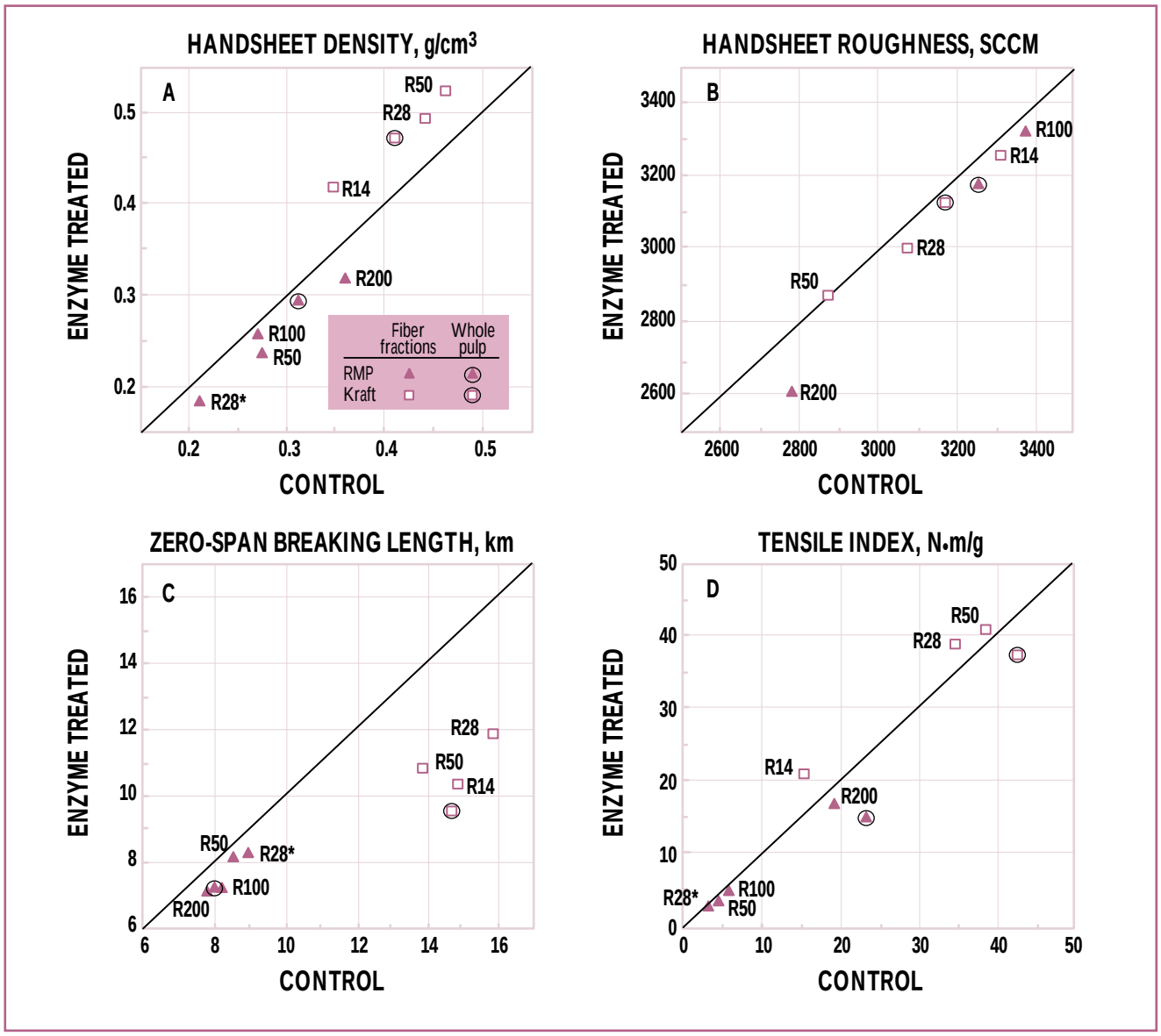
Figures 5 and 6 show the results obtained for the various fiber-length fractions of the kraft and mechanical pulps. Each data point represents two values, one for the enzyme-treated sample (*y*-axis) and the other for the control sample (*x*-axis). The diagonal line represents the points where treated and control values coincide. Points located above the diagonal depict an increase over the corresponding control value, while points below the line represent a decrease.

*Mechanical pulp* As seen in Fig. 5A, the enzyme treatments increased the freeness of the whole mechanical pulp by 39 mL CSF and that of the R100 and R200 mechanical fractions by 30 mL CSF. The longer enzyme-treated fiber fractions (R28* and R50) showed no change in freeness compared with the untreated control. However, Fig. 5B shows a reduction in fiber coarseness for the R50 fiber fraction. Coarseness reduction was lower for the shorter fibers (R100 and R200), even though these fractions were hydrolyzed more readily (Fig. 4). The coarseness of the R28* fraction could not be measured as it caused blockage in the device used to measure fiber coarseness. Since there was a large reduction in the fiber coarseness of the whole pulp, this suggested that the enzymes hydrolyzed the fines and defibrillated or cleaned the outer surfaces of the fibers, as proposed by Oltus *et al. (14)*. This would partly explain why fiber coarseness decreased for all of the fractions and why the release of reducing sugars is greater with the shorter fiber-length fractions.

Physical testing of the mechanical pulp samples showed that the fractionated pulp and the whole pulp responded similarly to enzyme treatment. The reduction in handsheet density (Fig. 6A) and handsheet roughness (Fig. 6B) was likely due to the defibrillation of the fibers. The R28* and R50 values could not be determined as they were outside the standard scale. The fiber-length fractions also showed a reduction in both fiber strength (measured as zero-span breaking length in Fig. 6C) and sheet strength (measured as tensile index in Fig. 6D). The loss of tensile strength in the unfractionated pulp was more substantial than any of the losses observed in the individual fractions.

*Kraft pulp* As seen in Fig. 5A, enzyme treatment increased the freeness of the unfractionated kraft pulp by 16 mL CSF. The only fiber fraction that showed an increase in freeness was the R50 fraction. [Only the R14, R28, and R50 fractions of the kraft pulp were collected in sufficient quantities (Table I) to allow us to carry out further enzyme treatment.] Figure 5B shows that all three of the fiber fractions and the whole pulp experienced a decrease in fiber coarseness after enzyme treatment. However, the reductions were less dramatic than those observed for the mechanical pulp.

Handsheet density increased and handsheet roughness decreased in all the treated fiber fractions, as seen in Figs. 6A and 6B, respectively. In both cases, the changes observed for the fiber fractions were comparable




*6. Effects of enzyme treatment on (A) density, (B) roughness, (C) zero-span breaking length, and (D) tensile index of handsheets produced from fiber-length fractions of kraft and mechanical pulps. Circled data points represent unfractionated whole pulps. Enzyme dosages are as listed in Fig. 4. Control pulps were treated with heat-inactivated enzyme.*

KEYWORDS
*Cellulase, denier, enzymes, enzymolysis, fiber dimensions, fiber fractions, fiber length, fineness, freeness, hydrolysis, kraft pulps, mechanical properties, mechanical pulps,* Pseudotsuga menziesii.

with those observed for the whole pulp.

Figure 6C shows that the three fiber fractions experienced a significant drop in zero-span breaking length after enzyme treatment. The strength reduction for the longer fiber fractions was similar to that observed for the whole pulp. This was expected, since these two fractions (R14 and R28) account for approximately 75% of the unfractionated kraft pulp.

The tensile index for the whole kraft pulp declined after enzyme treatment, as seen in Fig. 6D. In contrast, treatment increased tensile index for all three of the fiber fractions, with the longer fibers showing slightly greater improvement. The observed increase in density (Fig. 6A) suggested that the fibers had col-

lapsed and flattened. Fibers that are flat would be expected to have more surface area available for bonding, and this enhanced fiber-to-fiber contact would increase the tensile index. The results in Fig. 6 show that the shorter fiber fractions produced denser handsheets and had higher tensile indexes, which indicate a tighter fibrous network with closer fiber-to-fiber contact. This proposed mechanism has been reported earlier *(15)*. The tensile index for the unfractionated pulp was slightly greater than that for the R50 fiber fraction and substantially greater than the R14 fiber fraction. However, approximately 55% of the unfractionated pulp was contained in the R14 fraction. These results highlight the importance of the smaller fiber fractions in forming a well-bonded, strong paper product. The probable explanation for why the unfractionated pulp did not exhibit a similar enhancement in tensile index is that the fines, which constitute 6.4% of the unfractionated pulp, were preferentially hydrolyzed by the enzyme (Fig. 4). The positive effect of fiber flattening was thus overshadowed by the removal of the fines.

## CONCLUSIONS

Enzyme treatment reduced the coarseness of fibers in mechanical and kraft pulps derived from Douglas-fir. Coarseness reduction was greater for the longer and coarser fiber-length fractions, suggesting that the reduced coarseness observed for the whole unfractionated pulp was at least partly the result of the reduced coarseness of the longer fibers.

The effects of fiber coarseness on sheet strength have been studied previously *(16, 17)*. Our results indicate that the enzyme treatment affected the strengths of whole pulps (mechanical and kraft) and their fiber-length fractions. The kraft pulp showed a higher degree of susceptibility to strength loss, primarily because of the accessibility and high content of cellulose in kraft fibers. The strength loss for the mechanical pulp seemed to be more a function of fines removal, as proposed by Tuovinen and Liimatainen *(18)*.

It is clear that enzyme treatment could be used to alter the physical characteristics of paper products made from Douglas-fir. In this study, such treatment increased the density and smoothness of kraft handsheets.

Individual fiber fractions generally showed the same response to treatment as the whole unfractionated pulp. The one significant exception was the tensile index for the fiber fractions of kraft pulp. In this case, the enzyme treatments increased the tensile index of the different fiber fractions, while the whole pulp showed a slight decline in tensile index. This highlights the need for further studies to examine the potential benefits of selectively treating specific fiber-length fractions and then recombining the treated and untreated fractions.

## METHODS AND MATERIALS

### *Pulps*

Refiner mechanical pulp (RMP) was made by pulping steam-pretreated Douglas-fir (*Pseudotsuga menziesii*) wood chips using a Sprout–Waldron refiner under atmospheric pressure. Chemical pulp (kraft) derived from Douglas-fir was obtained from a mill (Fletcher Challenge, Crofton, BC). Pulps were fractionated using the Bauer–McNett fiber-length classifier to collect the R14, R28, R50, R100, and R200 fiber-length fractions (TAPPI T 233 cm-82).

### *Enzyme characterization*

Novozyme SP342 (Novo Nordisk, Bagsværd, Denmark), an enzyme preparation derived from *Humicola insolens*, was used for the enzyme treatments. Its activity on carboxymethylcellulose (2% CMC, Sigma, St. Louis), xylan (1% birchwood xylan, Sigma), and filter paper (No.1 Whatman) was measured using methods described previously *(19)*. Proteins in solution were quantified using the bicinchonic acid protein assay *(20)*. The enzyme preparation contained 46.7 mg protein/mL and was shown to possess relatively high xylanase activity (2869 IU/mL) as well as cellulase activities (CMCase, 143.5 IU/mL; filter paper, 9.9 IU/mL).

### *Enzyme treatment of pulp*

The pulp slurries (3% consistency in 50 m*M* phosphate buffer, pH 7.0) were treated for 1 h at 50°C under continuous agitation, with a range of enzyme loadings based on the addition of milligrams of protein per gram of ovendry fiber. The reaction was stopped by placing the pulp in a boiling-water bath for 15 min. Control pulps were similarly treated with equivalent amounts of heat-inactivated enzyme (15 min boiling). The pulps were drained and the filtrates were analyzed for total reducing sugars using the Nelson–Somogyi method *(19)*.

### *Pulp testing*

Fiber coarseness was analyzed using a Kajaani FS-200 instrument (Kajaani, Finland). Pulp freeness was measured at 20°C according to TAPPI T 227 om-94 (CSF tester, R. Mitchell Co.). Handsheets were prepared according to TAPPI T 205 om-88, with the white water being recycled to ensure that the fines were included in the resultant handsheet. For the determination of tensile index (Model 4202 Universal Testing Instruments, Instron), burst index (Mullen Tester, B.F. Perkins & Sons), tear index (Series 400 Monitor/Tear, Testing Machines Inc.), zero-span breaking length (TroubleShooter, Pulmac Instruments Intl.), handsheet roughness (Smoothchek, Sheffield Corp.), density (precision micrometer, Testing Machines Inc.), and porosity (porosimeter, Sheffield

Corp.), tests were conducted according to TAPPI T 494 om-88, T 231 cm-85, T 538 om-88, T 220 om-88, and T 547 pm-88. TJ

*Mansfield is a Ph.D. candidate; Wong is a research scientist; de Jong is a research associate; and Saddler is a professor and chair of forest products biotechnology. All are affiliated with the Department of Wood Science, University of British Columbia, Vancouver, BC, Canada V6T 1Z4.*

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