Bleaching of softwood kraft pulps with the EnZone process

Jan L. Yang, Dwight H. Cates, S. Edward Law, and Karl-Erik L. Eriksson

ABSTRACT: Different types of softwood kraft pulps were fully bleached with a totally chlorine-free (TCF) process comprised of enzyme treatment in combination with oxygen, ozone and alkaline peroxide stages. Extensive studies have been carried out to determine the compatibility of an endo-xylanase (X) with bleaching chemicals such as oxygen (O), ozone (Z), alkaline extraction (Ep) and hydrogen peroxide (P). Xylanase treated pine kraft and superbatch pulps delignified with ozone were found to have consistently lower kappa number and higher brightness than control pulps treated with an equivalent ozone charge without enzyme. In order to achieve sufficient delignification and proper brightness of softwood kraft pulps before entering the final peroxide brightening stage, it was necessary to precede the ozone stage with an alkaline extraction enhanced with peroxide, i.e., an EpZ combination. The pulps bleached with enzymes and oxygen-based chemicals were found to have superior brightness stability, easier beatability, similar tensile index, and lower tear index compared to the reference pulps.

KEYWORDS: Alkali extraction, batch process, bleaching, brightness, enzymes, hydrogen peroxide, kraft pulps, multistage process, oxygen, ozone, physical properties, Pinus, xylanase.

The evolution of pulp bleaching processes has come to a transitional period between traditional chlorine-based bleaching processes and newly developed alternatives such as enzyme enhanced, peroxide, and ozone bleaching *(1–2)*. During the last decade, the pulp and paper industry has initiated an unprecedented modernization of pulping and bleaching processes. Installations of extended kraft cooking, oxygen delignification and substantial replacement of elemental chlorine with chlorine dioxide have drastically reduced the formation of dioxins and AOX (adsorbable organic halogen), and their environmental impact has therefore significantly decreased *(3–4)*.

At the same time, an increased public environmental awareness has led to increasingly competitive market conditions for the pulp and paper industry, favoring pulp bleached with elemental-chlorine-free (ECF) or totally chlorine-free (TCF) processes. This now has become the most important driving force for development of environmentally benign bleaching processes. This trend of development is likely to continue and will influence both cooking and bleaching technologies. Processes such as superbatch cooking, isothermal kraft cooking, and ozone bleaching can be foreseen to increase in their importance. TCF bleaching seems to be necessary in the near future to meet the demands of certain markets, although the technical feasibility and environmental impact have not yet been fully demonstrated on a commercial scale. However, ECF bleaching of kraft pulps has already been successfully implemented in many mills *(5–6)*. Hydrogen peroxide bleaching, long considered economically unfeasible, is now a very competitive and much used bleaching stage.

Alternative bleaching techniques, such as the use of xylanase treatment or ozone delignification as individual

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stages in a bleaching sequence, are promising candidates to substitute for chlorine and chlorine derivatives, and are in an active phase of commercialization *(7–8)*. However, many hurdles associated with xylanase treatment and ozone bleaching have yet to be overcome before a widespread implementation becomes realistic. The pulp and paper industry is a capital-intensive industry and any segmental change involves enormous replacement costs. Implementation of any new process must therefore be guided by solid scientific studies and well demonstrated pilot plant trials. In our previous paper, bleaching of eucalyptus kraft pulps with the EnZone process using a non-chlorine bleaching sequence, i.e., oxygen, xylanase treatment, ozone, and hydrogen peroxide was reported *(9)*. In this paper, bleaching of pine kraft and superbatch cooked pulps according to various EnZone sequences is described. Chemical and physical properties of fully bleached pulps with brightness 85–92% are presented and discussed.

I. Characteristics of the mill-produced pine kraft pulps

Pulp	*Kappa no.*	*Viscosity, mPa·s*	*Brightness, % ISO*
		Pine kraft pulp	
Unbleached	41.8	50.5	23.4
Oxygen-bleached	12.0	18.4	33.6
		Pine superbatch pulp	
Unbleached	10.6	8.6	31.4

II. Conditions used to bleach kraft pulps

Symbol	*Chemical charge, %*	*Reaction time, min*	*Treatment temp, °C*	*pH*	*Consistency, %*
		Oxygen-bleached pine kraft pulp			
X	2 U xylanase/g pulp	90	50	5.0	10
Ep	H_2O_2:0.5 NaOH:2.0	180	70	>11	10
Z	O_3:0.1-2.0	3-10	ambient	2-3	35-45
P	H_2O_2:2.0 NaOH:2.0 Na_2SiO_3:3.0	180	70	>11	10
		Superbatch pine kraft pulp			
X	2 U xylanase/g pulp	90	50	5.0	10
Ep	H_2O_2:0.5 NaOH:2.0	180	70	>11	10
Z	O_3:0.1-2.0	3-10	ambient	2-3	35-45
P	H_2O_2:2.0 NaOH:2.0 Na_2SiO_3:3.0	180	70	>11	10
		Reference sequence: (O)DEDED			
D1	as active chlorine: 2.0	120	60	2.5-3.0	10
E1	NaOH:1.0	10	60	>11	10
D2	as active chlorine:2.0	90	70	2.5-3.0	10
E2	NaOH: 1.0	10	70	>11	10
D3	as active chlorine: 0.75-1.0	90	70	2.5-3.5	10
Washing	as SO_2:0.1	15	ambient		10

Materials and methods

Pulp samples

Mill-produced unbleached and oxygen-bleached pine kraft and pine superbatch pulps were obtained from pulp mills. The pulps were further washed in our laboratory. The characteristics of these pulps are presented in **Table I.**

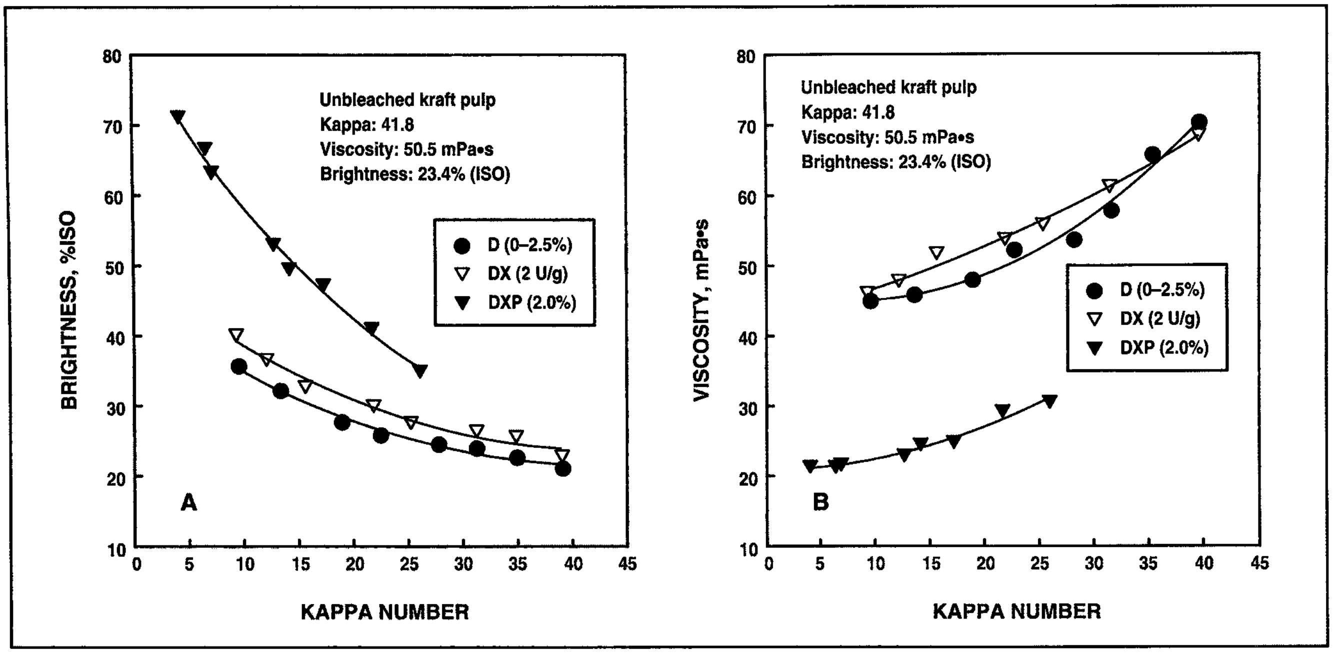
Enzyme production and preparation

The xylanase was produced in batch fermentation by the fungus *Aureobasidium pullulans*. The cultivation and subsequent preparation of the culture filtrate has been described previously *(10)*. By testing against birchwood xylan, mannan, carboxymethylcellulose, and arabinogalactan, the hydrolytic activity of this culture filtrate was found to consist solely of endo-xylanase activity (480 units/mL). One unit of xylanase activity was defined as the amount of enzyme releasing one µmol of xylose equivalent per minute at a preset temperature.

Pulp bleaching procedure

Pulps were disintegrated by 10,000 revolutions in a disintegrator (Noram, PQ, Canada) at room temperature before bleaching. The pulp suspensions were filtered on a Buchner funnel and then placed in double-layer polyester bags. The xylanase treatment (X) was carried out at a pulp consistency of 10% in 50 m*M* sodium acetate buffer pH 5.0 with a xylanase charge of 2 units/g pulp at 50°C for 90 min. After the enzyme treatment, the pulps were washed with water. Treatment of all pulps in the control sequences was carried out under identical conditions but without enzyme.

1. Effect of xylanase treatment on a pine kraft pulp delignified with chlorine dioxide. An alkaline peroxide stage was applied subsequent to xylanase treatment. A: Effect on brightness and kappa number. B: Effect on viscosity and kappa number.



Ozone delignification was carried out batchwise at high consistency conditions. Pulp samples were first acidified with sulfuric acid to a pH range of 2–3 and then centrifuged to a pulp consistency of around 35%. The pulps were subsequently fluffed in a hammermill prior to the ozone treatment. An ozone generator used in this study had production capacity of 80–200 g ozone/h, yielding ozone concentrations of 1–5% (w/w). The reaction of a typical batch ozone treatment, containing 50 g o.d. pulp with ozone charges of between 0.1 to 2.0% (w/w), was carried out for 3–15 min at ambient temperature and pressure. Ozone concentration was determined by iodometric titration.

Following the ozone stage and before entering the peroxide stage, pulps were chelated with 0.2% diethylenetriaminepentaacetic acid (DTPA) and 3.0% $NaHSO_3$ calculated as SO_2 on o.d. pulp at a consistency of 10%, pH 4.5 for 15 min at 80°C (Q).

For the hydrogen peroxide (P) stage, pulp and water were heated to the desired temperature and mixed with the bleaching chemicals to a final consistency of 10%. This procedure was also done when chlorine dioxide (D) and alkaline extraction (E) stages were applied. After the chosen reaction times, pulps were filtered and washed with distilled water. Residual hydrogen peroxide and chlorine dioxide were checked by iodometric titration of the filtrates. Bleaching conditions for the different stages are presented in **Table II**.

Analysis of pulp chemical and physical properties

The chemical and physical properties of the pulps were analyzed according to TAPPI Test Methods: T 205 om-88 (Forming handsheets for physical tests of pulp), T 227 om-85 (Freeness of pulp), T 230 om-89 (Viscosity of pulp), T 236 cm-85 (Kappa number of pulp), T 248 cm-85 (Laboratory beating of pulp), and T 525 om-86 (Defuse brightness of pulp). The physical properties of the bleached kraft pulps were evaluated at the Institute of Paper Science and Technology (IPST), Atlanta, GA.

Brightness reversion

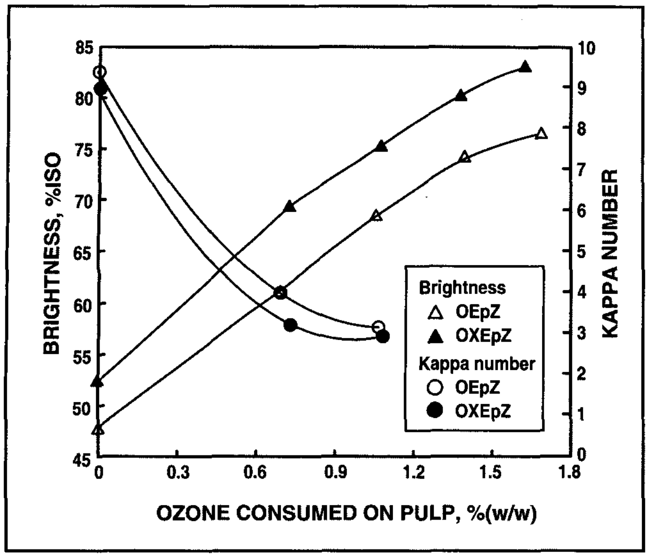
Airdry sheets of bleached kraft pulps were kept in an oven at 105°C for 4 h. Brightness was read after storage of the sheets at room temperature in a dark box for 2 h.

Results

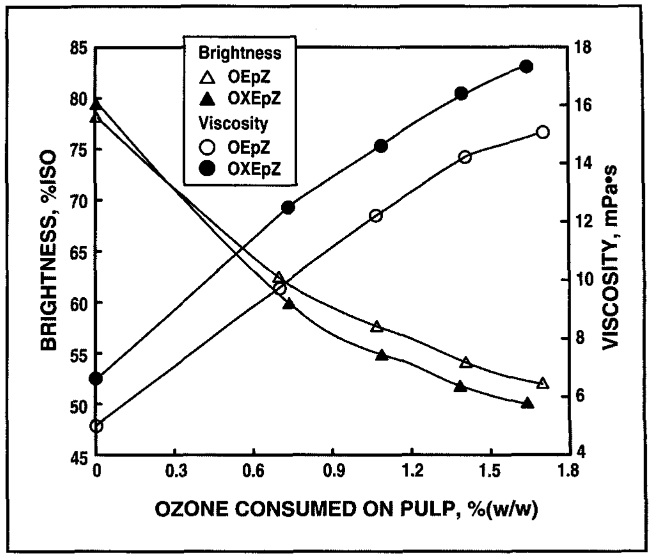
Effect of xylanase treatment on softwood kraft pulp

The effect of xylanase treatment on an unbleached pine kraft pulp having a kappa number of 41.8, viscosity of 50.5 mPa.s and brightness of 23.4% (ISO) was studied. This pulp was delignified with increasing interval of chlorine dioxide charge of 0.25–0.50% up to a total charge of 2.5% to obtain pulp samples within the kappa number range of 10 to 40. The delignified pulps were than treated with a xylanase stage followed by an alkaline peroxide stage as prescribed in Table II.

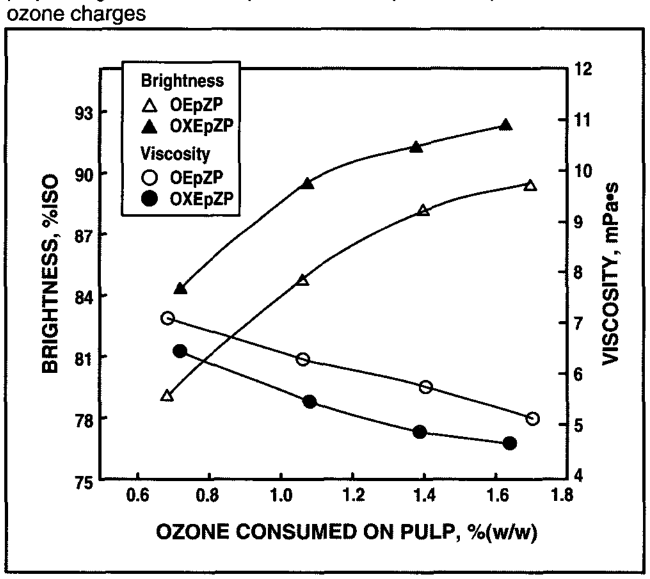
The results obtained in this study are illustrated in **Fig. 1.** Xylanase treatment has a favorable effect on pulp brightness, which increased about 2–3% in the whole kappa number range (Fig. 1A). However, the most pronounced effect on kappa number and viscosity was found to be in the kappa number range of 10 to 30 (Fig. 1B). The effect of the peroxide stage on kappa number, brightness, and viscosity increased with decreased lignin contents.



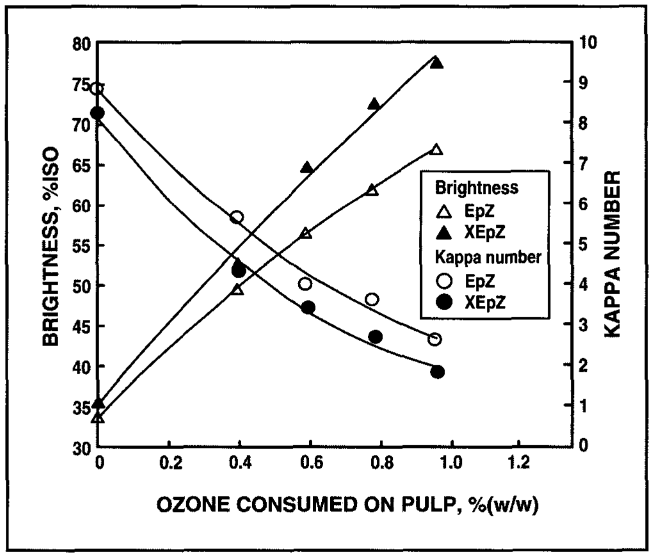
2. Effect of ozone consumption on brightness and kappa number of an oxygen bleached pine kraft pulp treated with or without xylanase



3. Effect of ozone consumption on brightness and viscosity of an oxygen bleached pine kraft pulp treated with or without xylanase



4. Effect of a peroxide stage on brightness and viscosity of pine kraft pulps delignified in the sequences of OXEpZP or OEpZP with various ozone charges



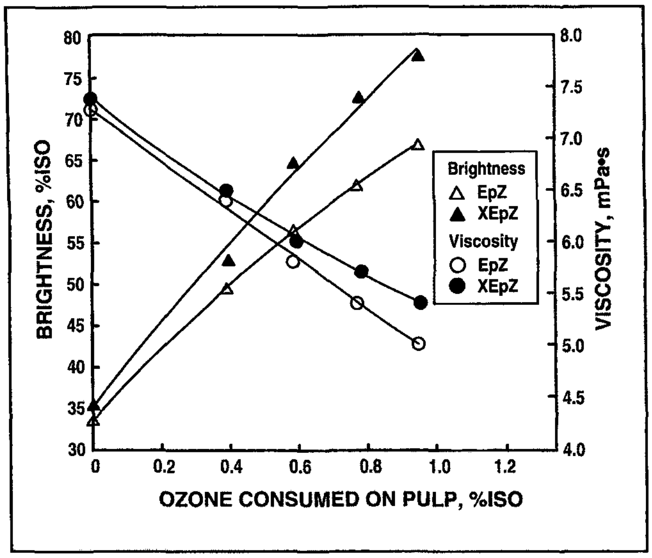
5. Effect of ozone consumption on brightness and kappa number of a pine superbatch kraft pulp treated with or without xylanase

Bleaching of pine kraft and superbatch pulps

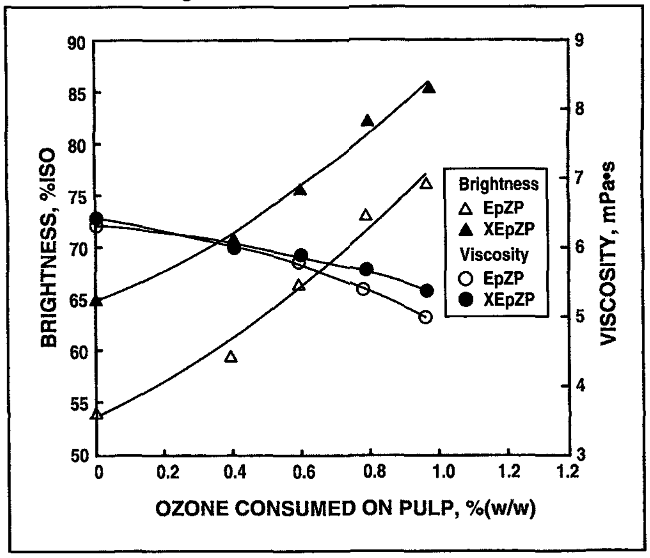
Bleaching of pine kraft pulp. A mill-produced, oxygen-bleached pine kraft pulp was treated with our *Aureobasidium* xylanase. This treatment decreased the kappa number from 12.0 to 11.2, increased viscosity from 18.4 to 18.8 mPa·s and brightness from 33.6 to 37.6% (ISO).

For the softwood pine kraft pulp, a bleaching sequence of OXEpZP was adopted. The Ep stage following the xylanase stage was found to be very beneficial and effective in minimizing the total ozone charge. The effect of ozone charge on oxygen bleached, xylanase, and Ep treated pulp has been studied and the results are depicted in **Figs. 2 and 3**. The kappa number in the ozone stage was reduced from 9.0 to 2.9 for the OXEp treated pulp; when xylanase was not applied, the kappa number decreased from 9.5 to 4.2 with gradually increased ozone charges up to 0.8% (Fig. 2). However, the viscosity of the pulp was also drastically reduced to approximately 10 mPa·s (Fig. 3). The pulp bleached in the OXEpZ sequence has consistently higher brightness than OEpZ bleached pulp at the same levels of ozone consumption. Also, brightness of the xylanase-treated pulp developed much faster and the brightness ceiling was higher compared to the OEpZ pulp.

6. Effect of ozone consumption on brightness and viscosity of a pine superbatch kraft pulp treated with or without xylanase



7. Effect of a peroxide stage on brightness and viscosity of pine superbatch pulps delignified in the sequences of XEpZP or EpZP with various ozone charges



Effect of a peroxide stage on ozone-treated pine kraft pulp

An alkaline peroxide treatment was applied as the final stage. Brightness and viscosity properties after the OXEpZP and OEpZP stages, respectively, are presented in **Fig.** 4. Significantly higher brightness was obtained for the OXEpZP bleached pulp compared to the OEpZP pulp. Also, a brightness ceiling as high as around 92% (ISO) was achieved only when the OXEpZP sequences were used. Viscosities of ozone-treated pulps, using TAPPI Test Method T 230, are generally low. The pulp viscosity at a targeted brightness of 86%, using the OXEpZP sequence, is 6.5 mPa·s. At the same brightness, the OEpZP bleached pulp has a viscosity of 6.0 mPa·s.

Bleaching of pine superbatch pulp

A mill-produced pine superbatch pulp was also treated with our *Aureobasidium* xylanase. Xylanase treatment of this pulp decreased the kappa number from 11.3 to 10.6, increased viscosity from 7.9 mPa·s to 8.6 mPa·s, and brightness from 30.1% to 33.4% (ISO).

The effect of ozone charge on the xylanase-treated pulp was extensively investigated and the results are summarized in **Figs. 5 and 6**. The kappa number of the pulp decreased readily from 8.3 to below 2 with gradually increased ozone charges up to around 1.0% (Fig. 5). However, the viscosity of the pulps was also drastically reduced (Fig. 6). After the XEpZ sequence, the pulp has consistently lower kappa number and higher brightness than the EpZ pulp at the same levels of ozone charges. Brightness of the XEpZ pulp developed much faster and has a higher brightness ceiling compared to the EpZ pulp.

Effect of a peroxide stage on ozone-treated pine superbatch pulp

An alkaline peroxide treatment was applied as the final stage. Pulp properties after the XEpZP and EpZP stages, respectively, are presented in **Fig.** 7. Significantly higher brightness of the XEpZP bleached pulp was obtained compared to the EpZP pulp. However, a brightness ceiling of around 86% (ISO) was achieved with only the XEpZP sequence. Viscosities of ozone treated pulps, using TAPPI Test Method T 230, are generally low. The pulp viscosity at a targeted brightness of 86% using the XEpZP sequence is 5.4 mPa·s. However, at the same brightness the EpZP bleached pulp has a viscosity of only 5.0 mPa·s.

Comparison of some properties of pulps bleached in different sequences

A comparison of some properties of pine kraft and superbatch pulps bleached in different sequences is presented in **Table III**. The pulps were bleached to a brightness range of 82% to 88% (ISO) with different sequences. As a reference the pulps were also bleached using the sequence of (O)DEDED to a brightness of 86%. Pulps bleached in the (O)XEpZP sequences have a much higher brightness compared to the corresponding control sequences of (O)EpPZ at the same level of total ozone consumption. Viscosity of the EnZone-bleached pulps were generally low, only between 5.0 mPa·s and 7.0 mPa·s compared to the reference pulps 19.1 mPa·s for (O)DEDED bleached pine kraft and 8.4 for DEDED bleached superbatch pulp. However, the effect of the xylanase treatment was significant. It boosted the ceiling brightness by 4–5 points while the final viscosities were the same as the control sequences without xylanase.

The brightness stability of the fully bleached pulps was also tested (**Table IV**). Brightness of the EnZone-bleached pulps was very stable when an alkaline peroxide was applied as the final stage as in the sequences (O)XEpZP and (O)EpZP. The (O)XEpZP and (O)EpZP bleached pulps have much higher brightness stability compared to the (O)DEDED and O(X)EpZD bleached pulps using chlorine dioxide as the final stage.

III. Comparison of some properties of pine kraft and superbatch pulps bleached in different sequences

Bleaching sequence	Ozone consumed on pulp, %	Viscosity, mPa•s	Brightness, % ISO
Pine kraft pulp			
OXEpZP	0.76	6.5	86.3
OEpZP	0.76	6.8	82.3
ODEDED	--	19.1	86.2
Pine superbatch pulp			
XEpZP	0.96	5.4	88.1
EpZP	0.95	5.0	82.9
DEDED	--	8.4	86.2

IV. Brightness reversion of bleached kraft pulps (kept at 105°C for 4 h)

Beaching sequence	Brightness, % (ISO)		p.c. no.[a]
	Before aging	After aging	
Pine kraft pulp			
OXEpZP	86.4	84.1	0.40
OEpZP	82.3	80.8	0.39
OXEpZD	88.2	83.9	0.76
OEpZD	86.2	82.3	0.74
ODEDED	86.4	83.4	0.58
Pine superbatch pulp			
XEpZP	88.1	86.7	0.20
EpZP	82.9	81.5	0.35
DEDED	86.7	84.0	0.51

[a]p.c. no. (post color number) used as a measure of color reversion

Comparison of beatability of EnZone bleached and ECF bleached pulps

The beatability of the fully bleached pine kraft and superbatch pulps was evaluated. The results obtained from the beatability tests are presented in **Fig. 8A and 8B**. Pulps bleached with the EnZone, control and reference sequences have very similar initial Canadian Standard Freeness (CSF). However, the pulps bleached in the sequences (O)XEpZP and (O)EpZP were much easier to refine to certain CSF values than the reference pulps bleached in (O)DEDED. This indicates that xylanase treatment seems to have no adverse effect on the beatability. However, the ozone stage is the likely cause of the drastically changed behavior of the freeness development during refining.

Physical properties of the bleached pulps

The physical properties of pulps bleached in different sequences and in the reference sequence (O)DEDED were determined. The results obtained from physical tests of pine pulps bleached in the sequences (O)XEpZP, (O)EpZP and the reference sequence (O)DEDED are presented in **Fig. 9**. Tensile index values of the pulps are very similar; however, the (O)XEpZP bleached pulps show lower tear index values compared to the reference pulps of both pine kraft (Fig. 9A) and pine superbatch (Fig. 9B) types but higher than the control (O)EpZP pulps.

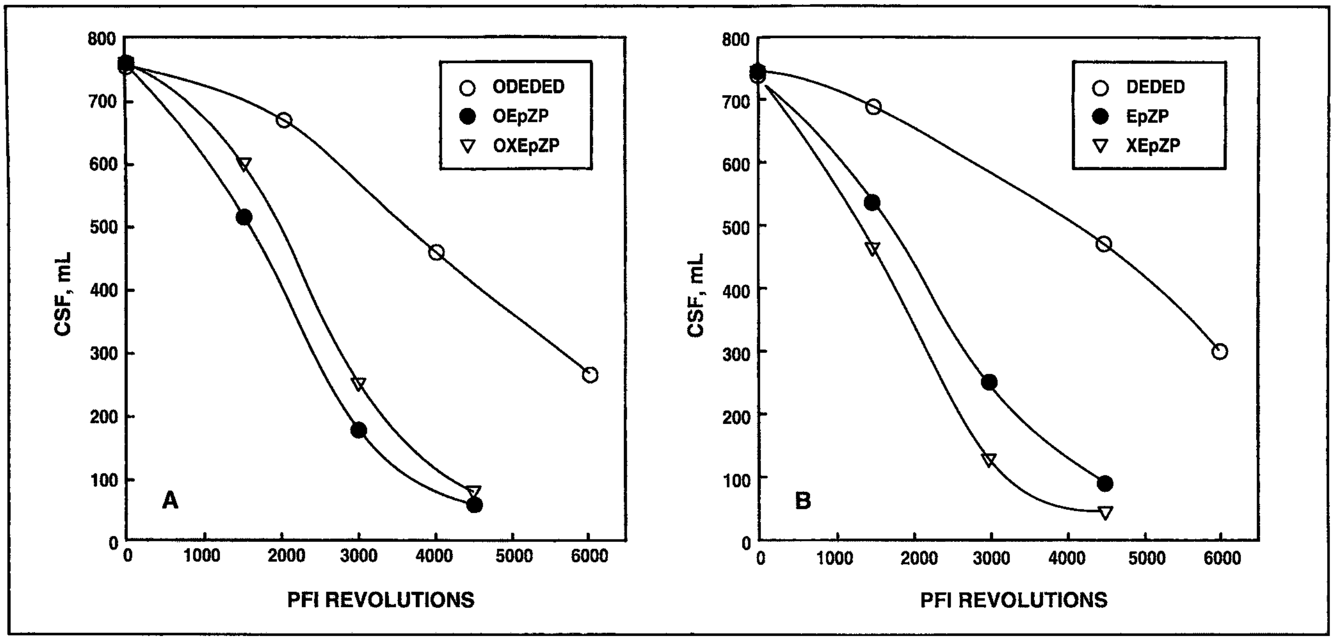
Discussion

The effects of xylanase treatment as one bleaching stage of kraft pulps have been studied in many laboratories and also in mill trials *(11–15)*. Xylanase treatment facilitates bleaching of the treated pulps in the subsequent stages, reduces the need for subsequent bleaching chemicals, is highly selective toward the xylan remaining in the pulp and can maintain, or even improve, pulp physical properties *(11–14)*. The pilot scale and mill trials using commercially available xylanases have also demonstrated these benefits *(15)*.

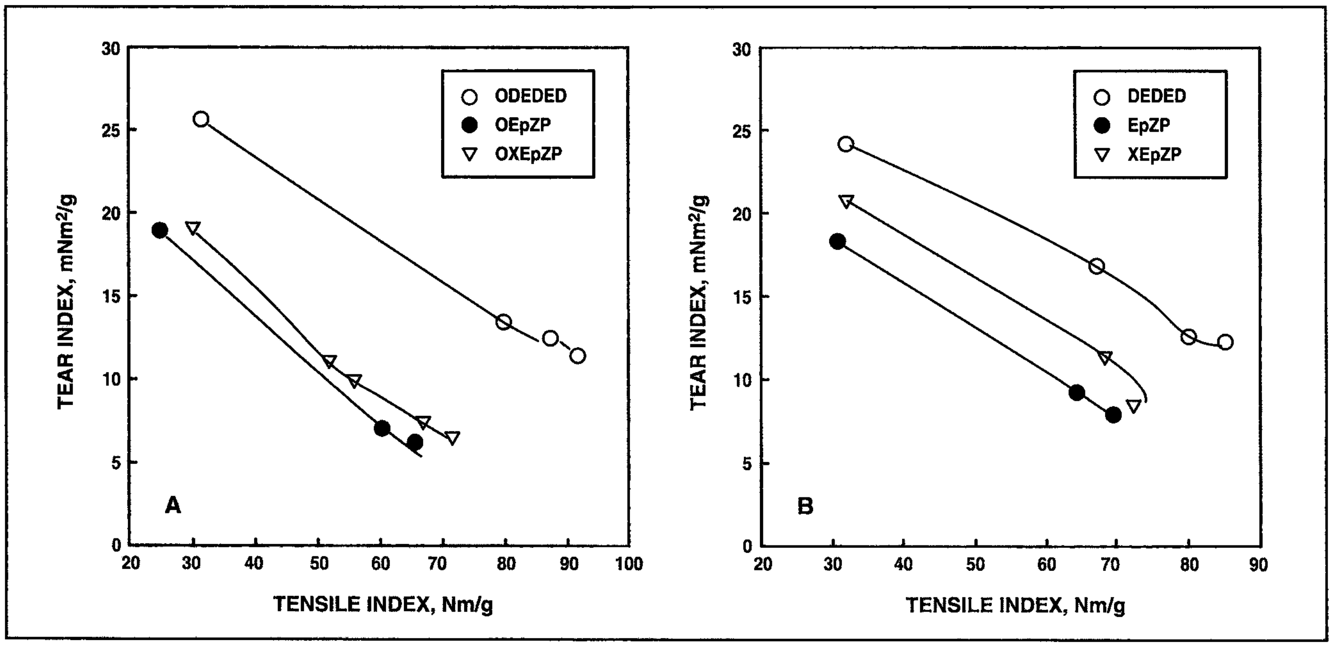
Xylanase treatment is generally more effective on hardwood than on softwood kraft pulps partly because of their different chemical compositions *(10, 13)*. We reported here that xylanase is most effective on a softwood pulp within the kappa number range of 10–30. This finding has also been confirmed using kraft pulps cooked to different lignin contents *(10)*. The kappa number range of 10 to 30 represents most commercially produced softwood kraft pulps. It is therefore demonstrated that xylanase treatment can be used either before or after the oxygen delignification stage.

Viscosities of ozone-delignified pulps are generally lower than con-

8. Comparison of CSF and PFI beating relationship of pine pulps bleached in the sequences (O)XEpZP, (O)EpZP and (O)DEDED. A: Pine kraft pulp. B: Pine superbatch pulp.



9. Tear and tensile relationship of pine pulps bleached in the sequences (O)XEpZP, (O)EpZP and (O)DEDED. A: Bleached pine kraft pulp. B: Bleached superbatch pulp.



ventionally bleached pulps. However, the rapid decrease in pulp viscosity during the ozone bleaching is not accompanied by the expected decrease in pulp physical strength. The possible reasons for this were addressed in our previous paper *(9)*.

We have also reported previously that the beatability characteristic of eucalyptus kraft pulps bleached in the EnZone sequence was similar to pulp bleached in the ODEDED sequence *(9)*.

Pine kraft pulps bleached by the EnZone process and in the control sequences were found to be much easier to refine than the corresponding reference pulps. This finding was verified in multiple tests despite their initially similar CSF values compared to the pulps bleached in the reference (O)DEDED sequence. The exact mechanism of this phenomenon is not clear. One possible explanation could be that the structure and viscosity changes caused by the ozonation stage contribute to an easier beatability.

Biobleaching

We have recently been awarded a grant from the Georgia Research Alliance (GRA) to scale-up the EnZone process to a 1–5-ton/day operation. Pilot studies of bleaching of kraft pulps with the EnZone process are now under way. TJ

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