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Bleaching of Hardwood Kraft Pulp by Xylanase Pretreatment*1

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ABSTRACT

This study was carried out to investigate the effect of xylanase pretreatment of the unbleached hardwood kraft pulp during the conventional Chlorine-Extraction- Hypochlorite (CEH) bleaching on pulp property. Optimum bleaching condition was evaluated by using Novozym produced from the fungus *Humicola insolens*. Also the effect of chelating agent prior to enzyme treatment was analyzed. The kappa number of enzymatic bleached pulp at the enzyme charge 10 IU/ml was slightly similar to that of bleached pulp without enzyme. By enzyme treatment, the chlorine charge in conventional CEH bleaching process of hardwood KP could be reduced by 17%, while no adverse effect on pulp yield and strength was. The optimum condition for enzyme pretreatment was 10 IU/ml xylanase charge, 3 to 4 hrs treatment, and 2% pulp consistency. In sugar composition in the enzyme pretreated pulp, arabinose and mannose were not much different, but more xylose was retained. This high content of hemicellulose in pulp seems to play an important role in pulp properties. The pulp pretreatment by chelating agent prior to enzyme treatment could improve the enzyme activity and enhance the bleaching effect at 0.2% diethylenetriamine pentaacetic acid (DTPA) charges.

Key words: enzyme charge, xylanase, hardwood kraft pulp, CEH sequence, chelating agent

INTRODUCTION

Conventional bleaching of wood pulp has involved the use of chlorine and chlorine derivatives. It is widely accepted upto now that the effluents from such bleach plants are very harmful to the environment (Tshuchikawa *et al.*, 1995). This concern was driven by the growing alarm over chlorinated organic compounds, collectively termed as adsorbable organic halide (AOX) present in bleach plant effluents(Rennel, 1995). Particularly after dioxins were discovered both of bleach effluents and in some paper products, bleached with molecular chlorine, numerous investigators have devoted to develope more environmentally benign bleaching process (Zabel *et al.*, 1995; Eriksson, 1998).

Enzymatic pretreatment can be utilized to alter

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topochemical variations in delignification. These variations could be partially attributed to the difference in the lignin structure from the secondary wall and middle lamella regions (Suurnakki *et al.*, 1994). In the enzymatic pretreatment for bleaching, the hydrolysis of hemicellulose is held to a minimum by using only small amount of enzymes in order to maintain a high pulp yield and the advantageous properties of hemicellulose in pulp(Viikari *et al.*, 1986). The roles of xylanases in bleaching have recently been reviewed from both fundamental (Suurnakki *et al.*, 1997) and applied (Tolan & Guenette, 1997) aspects. Pretreatment of pulp with enzymes prior to bleaching helps in improving the final brightness of pulp and eliminating the use of chlorine and chlorine compounds(Fruhauf, 1995; Puls & Stork, 1995; Wang *et al.*, 1995). Therefore the pulp pretreatment with enzyme will reduce the consumption of bleaching chemicals in the following bleaching process (Davis, 1997), and expect abating the environmental pollution of bleaching effluent. In recent years the most promisable enzyme is recommending to be utilized at the high temperature and broad pH range. Novozym 342 is active on over a broad pH range 5 to 9, slightly acidic to mildly alkaline conditions, at temperatures up to 65℃.

This study was attempted to investigate the effect of enzyme pretreatment of the unbleached hardwood kraft pulp(KP) during the conventional Chlorine-Extraction-Hypochlorite (CEH) bleaching on pulp property. Optimum bleaching condition and the effect of chelating agent on the biobleaching were evaluated.

MATERIALS AND METHODS

Hardwood KP was obtained from Donghae pulp mill. The kappa number was 27.4, and viscosity was 1,098cc/g. The enzyme, Novozym 342, was purchased from Novo Nordisk. This enzyme is a mixture of cellulases and hemicellulases produced by submerged cultures of the fungus *Humicola insolens*. The enzyme activity exhibited at optimum temperature of 50℃ and pH optimum of 6.5. The xylanase activity was assayed according to the method of Bailey *et al.* (1992). The activities determined in this experiment were xylanase 140 IU/ml and CMCase 0.28 IU/ml.

Unbleached pulps were pretreated with enzyme in plastic bags. The treatment was carried out at 50℃ and pH 6.5 (pH was adjusted with sodium acetate buffer solution and water, and fine adjustment by 0.1N of HCl or NaOH). After enzymatic treatment the pulps were thoroughly washed with water. The reference pulps were treated as described above, but without enzymes. Unbleached pulps were also pretreated with chelating agents, diethylenetriamine pentaacetic acid (DTPA) and ethylenediamine tetraacetic acid (EDTA), at 50℃ for 30min, 5% pulp consistency, and pH 5. After enzyme and chelating-enzyme pretreatments, pulp samples were bleached in a multistage bleaching sequence, Chlorine-Extraction-Hypochlorite(CEH). The sugar analysis in treated pulp was done by Borchardt's gas chromatographic method(Bochardt & Piper, 1970; Bochardt & Easty, 1983) and physical properties of pulp sheets were measured according to K.S. methods. In order to determine bleaching stability, post-color number calculated from the bleached KP sheets kept in an oven at 105℃ for 3 hr.

RESULTS AND DISCUSSION

Optimum conditions of enzyme pretreatment

The main factors affecting on enzymatic pretreatment are enzyme charge, reaction time, pulp consistency, temperature and pH value. The effect of enzyme charge on biobleaching was shown in Fig. 1. Kappa number and viscosity of the pulp gradually were decreased with increasing the enzyme charges. When the enzyme charge exceeded 10 IU/ml, the pulp viscosity was decreased distinctly and kappa number decreased slightly. While enzyme charges were 10 IU/ml, the brightness reached a maximum. When enzyme charges exceeded more than 10 IU/ml, the brightness decreased gradually because of probably the oxidation of impurities in xylanase enzyme.

The effect of treating time on kappa number and viscosity was shown in Fig. 2. Kappa

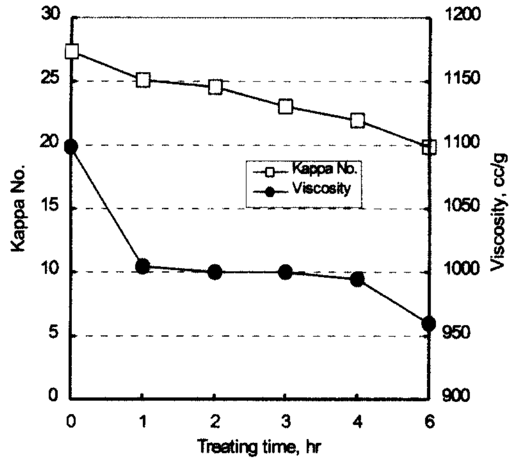

Fig. 1. Effect of enzyme charge on bleaching.

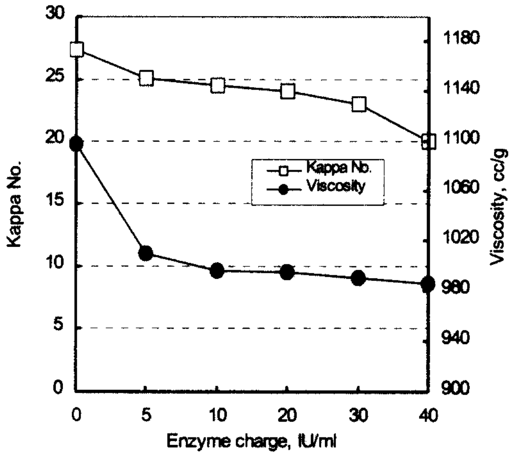

Fig. 2. Effect of treating time on bleaching.

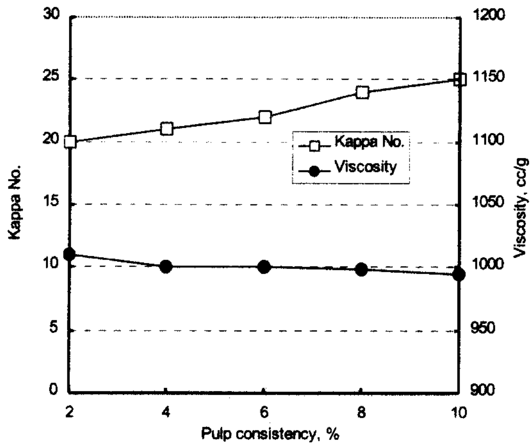

Fig. 3. Effect of pulp consistency on bleaching.

number and viscosity of the pulp were decreased gradually with increasing of treating time. After 4 hrs treatment, kappa number decreased slowly and reached at maximum value, and viscosity also decreased distinctly.

Fig. 3 showed the effect of pulp consistency on kappa number and viscosity of the pulp. The high pulp consistency disturbed delignification during bleaching, and had kappa number increased to some extent. It is attributed to uneven mixing of enzyme and pulp. It could be found that optimum condition for enzyme pre-treatment was 10 IU/ml xylanase charge, 3 ~ 4 hrs treatment, and 2% consistency.

Influence of the Enzyme pretreatment on CEH sequence bleaching

CEH sequence has been widely used in bleaching procedure of kraft pulp. The influence of the enzyme pretreatment on CEH sequence was investigated. The effect of enzyme charge on CEH bleaching was presented in Table 1. At same chlorine charge, kappa number, viscosity and pulp yield decreased with increasing enzyme charge. The brightness of pulp had no obvious improvement by pretreating with enzyme, but a brighter pulp was obtained when enzyme treatment followed by the CEH sequence compared to the treatment without enzyme. At 12% of chlorine charge, the pulps with lower post-color number were obtained with enzyme treatment. On the other hand, enzyme treatment (enzyme charge 10 IU/ml) resulted in 2% weight loss by pulp hydrolysis.

Influence of the enzyme charge on pulp strength was shown in Table 2. The pulp strength slightly was decreased after enzyme treatment. As shown in Table 1 and Table 2, the kappa number of enzymatic bleached pulp with enzyme charge 10 IU/ml(total chlorine charge 10%) was slightly similar to that of bleached pulp(total chlorine charge 12% without enzyme addition), and both pulps were very close in pulp yields and sheet strengths. From the results it can be found that, by enzyme pretreatment, the chlorine charge in conventional CEH bleaching could be saved by 17% at the same brightness levels. Therefore, pollutant loads in the bleaching effluent could be reduced.

Influence of enzyme pretreatment without adjusting pH on pulp properties

The optimum pH for enzyme pretreatment was pH 6.5 in order to simplify the technology and reduce the production cost. Hardwood KP was pretreated by enzyme solutions which are adjusted to pH 6.5, and followed by the conventional CEH bleaching. As shown in Table 3, the main indices of both pulps were very close. Pulp brightness of the pulp bleached at pH adjusted with buffer was 78.7%, while higher brightness of 80.1% at pH adjusted with tap water. Therefore tap water could be directly used to adjust pulp consistency instead of buffer solution(pH 6.5) during enzyme pretreatment.

A cellulase/hemicellulase mixture is capable of increasing the diffusion of NaOH in sycamore sapwood in both the tangential and longitudinal directions(Jacobs-Young *et al.*, 1997). This means that enzyme treatment is believed diffusion improvement by changing the fiber structure. It was also reported that xylanase has been shown to improve the surface of the pulp fiber (Kantelinen *et al.*, 1988). Enzyme pretreatment is capable of lowering the kappa number of the pulp, while maintaining similar viscosity. Bleaching with xylanase pretreatment followed by CEH sequence (X-CEH) resulted in lower pulp viscosity than the control. The main differences in sugar compositions of the pulp were in xylose

Table 1. Effect of the enzyme charge on CEH bleaching

Cl_2 charge, %	10					12				
Enzyme charge, IU/ml	0	3	5	7	10	0	3	5	7	10
Kappa No.	3.8	3.5	3.4	3.3	3.2	3.2	3.1	2.9	2.8	2.7
Viscosity, cc/g	842	836	824	816	801	820	791	781	774	762
Post-color No.	3.46	2.93	2.84	2.6	2.41	2.86	2.32	2.30	2.25	2.06
Yield, %	94.6	94	93.6	93.2	92.8	93.6	93.4	93.1	92.3	91.7

Table 2. Effect of the enzyme charge on sheet strength

Cl_2 charge, %	10					12				
Enzyme charge, IU/ml	0	3	5	7	10	0	3	5	7	10
Breaking length, km	6.76	6.64	6.54	6.41	6.25	6.40	6.10	5.98	5.67	5.53
Burst index, kPa.m^2/g	6.49	6.37	6.20	6.18	6.10	6.31	6.20	6.07	5.98	5.75
Tear index, mN.m^2/g	16.6	15.7	14.6	14.1	13.5	15.6	14.4	13.9	12.7	11.9

Table 3. Effect of pH adjusted with different media on sheet strengths of the enzyme-CEH sequence bleached pulp (pH 6.5)

pH	6.5(Buffer solution)	6.5(Tap water)
Kappa No.	3.16	3.05
Viscosity, cc/g	801	798
Post-color number	2.41	2.36
Yield, %	92.8	92.7
Brightness(GE), %	78.7	80.1
Breaking length, km	6.25	6.20
Burst index, kPa · m^2/g	6.10	6.08
Tear index, mN · m^2/g	13.5	13.9

* Cl_2 charge 10%, enzyme charge 10 IU/ml

Table 4. Sugar analysis of enzyme pretreated hardwood kraft pulp

	Sugar composition, %			
	Xylose	Arabinose	Glucose	Mannose
CEH	11.1	-	88.5	0.35
X-CEH	14.3	-	85.3	0.38

and glucose compositions as in Table 4. Arabinose and mannose were not much different, and more xylose was contained in the enzyme pretreated pulp than that of the control. It is well known that hemicellulose in pulp plays an important role in paper sheet properties. Retention of hemicellulose has increase the pulp yield, improves pulp strength and affects sheet property (Viikari *et al.*, 1986; Lumme *et al.*, 1998). The enzymatic hydrolysis would be changed fiber structure more permeable, and allowed the bleaching reagents to diffuse more easily into the lignin and lignin-carbohydrate complex (LCC) at the next bleaching stages (Kantelinen *et al.*, 1988). This would be attributed to degrading and dissolving of small amount of xylan and LCC in residual lignin. Because of these openings the bleaching chemical permeability was improved, pulp bleachability was enhanced, and consequently the bleaching chemical consumption would be reduced.

Influence of chelating agent pretreatment on enzyme treatment

It is well acknowledged that heavy metal ions restrain enzyme activities. Chelating agents can dispel the restraint of heavy metal ions to enzyme. Unbleached pulps were pretreated with chelating agents before the enzyme treatment. Fig. 4 and Fig. 5 showed the effect of different charges of EDTA and DTPA on pulp properties. Both EDTA and DTPA enhanced the enzyme treatment effectively, and the more the agent charged, the better delignification obtained. Compared to the effect between EDTA and DTPA, DTPA gives a little higher delignification and lower decreasing pulp viscosity. A good result was obtained at 0.2% DTPA charge, the kappa number slightly decreased by 1.57 units and the viscosity increased by 60 cc/g compared to without DTPA pretreatment (Fig 4. and Fig. 5)

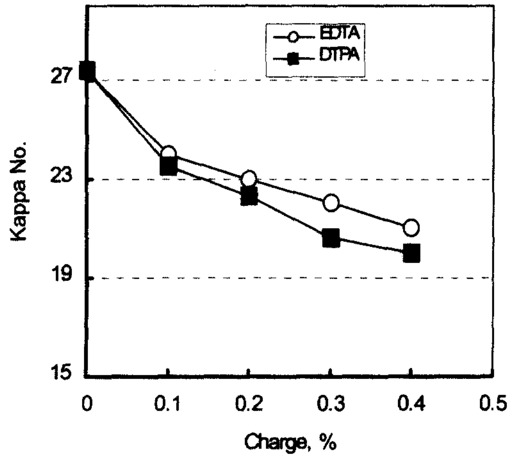

Fig. 4. Effect of chelating agent on kappa number.

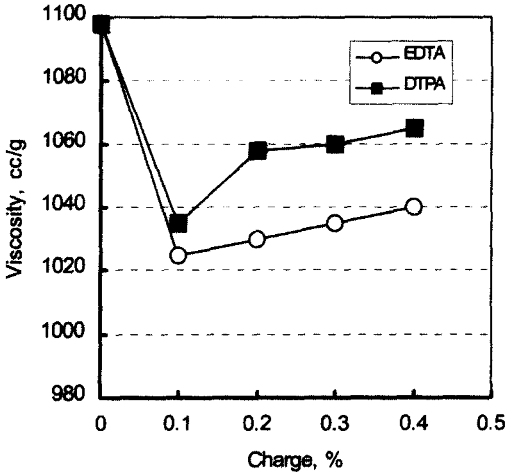

Fig. 5. Effect of chelating agent on pulp viscosity.

Influence of chelating agent pretreatment on CEH sequence bleaching of enzyme treated pulp was shown in Table 5. By addition of DTPA (Q-X-CEH), although pulp yields and kappa no. were almost same, viscosity was a little higher, the brightness increased from 80.1 to 84.3%, and pulp strengths were enhanced, especially tear index increases from 11.9 to 14.4mN · m^2/g.

CONCLUSION

This study was carried out to investigate the effect of enzyme pretreatment of the hardwood unbleached kraft pulp during the conventional Chlorine-Extraction-Hypochlorite (CEH) bleaching on pulp property. Optimum bleaching condition and the effect of chelating agent on the biobleaching were evaluated by using Novozym produced from the fungus *Humicola insolens.* Also the effect of chelating agent prior to enzyme treatment was evaluated. The optimum conditions for enzyme pretreatment is 10 IU/ml xylanase charge, 3 to 4 hr treatment, and 2% consistency.

The kappa number of enzymatic bleached pulp with enzyme charge 10 IU/ml was slightly similar to that of bleached pulp, and both pulps were very close in pulp yields and sheet strengths. By enzyme treatment, the chlorine charge in conventional CEH bleaching process of

Table 5. Effect of chelating agent pretreatment on CEH sequence bleaching of enzyme treated pulp

Bleaching sequence	X-CEH	Q-X-CEH
Kappa No.	2.66	2.47
Viscosity, cc/g	761	770
Yield, %	91.7	91.6
Brightness(GE), %	80.1	84.3
Breaking length, km	5.53	5.77
Burst index, kPa · m^2/g	5.75	5.87
Tear index, mN · m^2/g	11.9	14.4

* Enzyme treatment conditions : Enzyme charge 10 IU/ml, treatment time 4 h, pulp consistency 2%, kappa No. and viscosity of the pulp were measured after alkaline extraction. Q(chelating agent, DTPA) charge 0.2%

hardwood KP could be reduced by 17%, while no adverse effect on pulp yield and strength. In sugar compositions, arabinose and mannose are not much different, but more xylose was retained in the enzyme pretreated pulp. This high hemicellulose in pulp seems to play an important role in fiber properties. Chelating agents, EDTA and DTPA, enhanced the enzyme treatment effectively, and 0.2 % DTPA addition resulted in better paper properties. The another important advantage of using this enzyme was that there is no need to adjust pH by particular buffer solution.

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